



**SYNTHESIS AND CHARACTERISATION OF
CHELATING, HEMILABILE *N*-HETEROCYCLIC
CARBENE LIGANDS: APPLICATIONS OF THEIR
COBALT(II) AND NICKEL(II) COMPLEXES AS
CATALYSTS FOR ARYL AMINATION**

2014

HALLIRU IBRAHIM

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CATALYSTS FOR ARYL AMINATION**

HALLIRU IBRAHIM

2014

A thesis submitted to the School of Chemistry & Physics, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Westville Campus, for the degree of Doctor of Philosophy.

In this thesis, the chapters are written as discrete research papers, with an overall *introduction* and final *conclusion* chapters. Where one (or all) of the chapters has already been published, typically these chapters would have been published in internationally-recognised peer-reviewed journals.

As the candidate's supervisor, I have approved this thesis for submission:

Supervisor:

Signed: Name ...M. D. Bala..... Date:

ABSTRACT

The chemistry and applications of *N*-heterocyclic carbenes (NHCs) as ligands for the preparation of transition metal complexes has remained at the forefront of research in organometallic chemistry and homogeneous catalysis worldwide. This is evidenced by the increasing number of research articles on the subject area. Hence, this thesis report on three different ligand frameworks consisting of a symmetric CNC pincer architecture and two non-symmetric *N*-substituted imidazoles bearing a picolyl and a ferrocenylphenyl imidazole functionalities. These were then used to synthesise new ligand precursors (imidazolium salts) which were later on complexed to Ni and Co via transmetalation of corresponding NHC-Ag complexes.

The synthesis of the pincer imidazolium salts via a solvent free method led to the development of a new technique based on the use of a short plug of silica to purify such salts and isolate them in excellent yields. This method has been published and is now adopted in our laboratory and extended to the purification of a wider variety of salts including those based on the related triazolium moiety. All the compounds (salts and metal complexes) have been fully characterised by NMR (^1H , ^{13}C , ^{31}P), IR, HRMS or MS-ES⁺, EA and in some cases single crystal X-ray diffraction analyses. Sharp melting points were also recorded for all air stable, none hygroscopic compounds. The characterisation data have established the chemical composition and purity of all the compounds reported in this thesis.

All the complexes are active as catalysts for the activation of C-N coupling of aryl amines and aryl halides. The catalyst systems showed excellent selectivity to *N*-mono arylation as no trace of *N,N*-diarylated products were observed. The high selectivity and excellent yields to desired products achieved under mild reaction conditions and low catalyst loading of 1 mol% of Ni or Co has made the current catalyst systems competitive in comparison to classical Cu mediated or CuI catalysed Ullman coupling and Pd catalysed systems. A highly active *in situ* generated *NiCl₂/imidazolium salt* catalyst was also developed, hence opening up a simple, robust and functional group tolerant system for C-N coupling reactions that may easily be generated from commercially available imidazolium salts in combination with over the counter metal salts such as NiCl₂.

DECLARATIONS

DECLARATION 1 – PLAGIARISM

I,HALLIRU IBRAHIM....., declare that:

1. The research reported in this thesis, except where otherwise indicated is my original work.
2. This thesis has not been submitted for any degree or examination at any other University.
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DECLARATION 2 – PUBLICATIONS

DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/or include research presented in this thesis (include publications in preparation, submitted, *in press* and published and also give details of the contributions of each author to the experimental work and writing of each publication)

Publication 1

Ibrahim, H.; Bala, M.D.; Omondi, B. **1-[4-(1H -imidazol-1-yl)phenyl]ethanone monohydrate**; *Acta Crystallographica Section E*, **2012**, E68, o2305.

Contributions: I did all the experimental work, wrote the initial draft of the paper and subsequent modifications towards publication of the paper. The other authors are my supervisor (BMD) and crystallographer (OB).

Publication 2

Ibrahim, H.; Bala, M.D. **1-(4-Nitrophenyl)-1H -imidazol-3-ium chloride**; *Acta Crystallographica Section E*, **2013**, E69, o114.

Contributions: I did all the experimental work, wrote the initial draft of the paper and subsequent modifications towards publication of the paper. The other author is my supervisor.

Publication 3

Ibrahim, H.; Bala, M.D. **Improved methods for the synthesis and isolation of imidazolium based ionic salts**; *Tetrahedron Letters*, **2014**, 55, 6351—6353.

Contributions: I did all the experimental work, the synthesis and characterisation of all the compounds and wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. The other author is my supervisor.

Publication 4

Ibrahim, H.; Bala, M.D. **Air stable pincer (CNC) N-heterocyclic carbene-cobalt complexes and their application as catalysts for C-N coupling reactions**. Manuscript in preparation.

Contributions: I did all the experimental: synthesized all the salts, Ag-NHC and the corresponding cobalt complexes, and carried out all the characterisation and subsequent catalytic application of the complexes in activating C-N coupling of aryl halides with aryl amines. I wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. The other author is my supervisor.

Publication 5

Ibrahim, H.; Bala, M.D. **Cobalt and nickel complexes of chelating pyridyl and alkenyl-N-heterocyclic carbene ligands: synthesis, characterization and application as amination catalysts.** Manuscript in preparation.

Contributions: I synthesized and characterised all the compounds, carried out the catalysis and wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. The other author is my supervisor.

Signed:

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This work is dedicated to my wife and children.

LIST OF PUBLICATIONS

1. Ibrahim, H.; Bala, M.D. **Improved methods for the synthesis and isolation of imidazolium based ionic salts**; *Tetrahedron Letters*, **2014**, 55, 6351—6353.
2. Ibrahim, H.; Bala, M.D. **1-(4-Nitrophenyl)-1H-imidazol-3-ium chloride**; *Acta Crystallographica Section E*, **2013**, E69, o114.
3. Ibrahim, H.; Bala, M.D.; Omondi, B. **1-[4-(1H-imidazol-1-yl)phenyl]ethanone monohydrate**; *Acta Crystallographica Section E*, **2012**, E68, o2305.

CONFERENCE PROCEEDINGS

1. Muhammad Dabai Bala, Halliru Ibrahim. **Cobalt and Nickel Complexes with Chelating Pyridyl and Alkenyl-N-Heterocyclic Carbene ligands: Structural Elucidation and Application as Amination Catalysts**. (Oral presentation at the 41st International Conference on Coordination Chemistry, 21st—25th July 2014, Suntec conference and exhibition centre Singapore).
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Chapter one

General introduction

1.1 Background

Wanzlick¹ and Öfele¹⁻² pioneered the field of *N*-heterocyclic carbene (NHC) chemistry. Their work in the study of NHC complexes of early transition metals paved the way to the isolation of the first free carbene by Arduengo in 1991.³ Their pioneering works combined to provide routes of overcoming complications associated with the isolation of free carbenes⁴ to the extent that they are now commercially available.⁵ A carbene is a carbon containing a pair of unshared electrons; an active species which could exist in a singlet or triplet state, and is short lived except under exclusive conditions. Since the 1950's when curiosity in their chemistry was high, carbenes have continuously played important roles in organic and inorganic transformations. The excellent sigma donating ability of *N*-Heterocyclic carbenes make them better options to other ligand forms like ethers, amines, and even phosphines in organometallic and co-ordination chemistry.⁶ Their excellent co-ordination properties have been comprehensively investigated by Nolan and co-workers⁷ through structural and thermochemical studies. Complexes generated from NHC ligands contain metal-carbene bonds which are more stable than in Fisher or Schrock-type complexes, and this is due to pronounced back-bonding.⁸

The intrinsic behaviour of NHC ligands and their transition metal complexes has been studied over the years and findings have been well documented.^{6, 9} NHCs are not replicas of phosphoranes; they are much more versatile with high potential as catalysts on their own, when complexed with a metal or as in-situ generated catalyst systems in homogeneous catalysis. They are found to be tolerant to prevailing functional groups, work at ambient temperatures and strongly co-ordinate to metal centre in catalytic system without ligand dissociation.

NHCs are generally classified into five different forms (Figure 1.1): Imidazolin-2-ylidene, **1.1** was the first type of NHC to be complexed to silver. It consists of an imidazole ring with substituents at the nitrogen atoms (1,3-position) and a singlet carbene located at the 2-position. Benzimidazol-2-ylidenes **1.2** is a derivative of **1.1**; has a benzene ring fused to the

backbone of the imidazole ring. Imidazolidin-2-ylidenes **1.3**, are similar to **1.1** except that the backbone of the ring (4,5-position) is saturated thereby making the NHC more electron-rich. Tetrahydropyrimid-2-ylidenes **1.4**, is based on six-membered saturated ring systems, and are an extension of imidazolyliidenes. 1,2,4-Triazolin-5-ylidenes **1.5**, the triazoles are composed of a five-membered ring with three nitrogen atoms (1,2,4-positions) and the carbenes located at the 3- and/or 5-positions (Figure 1.1).

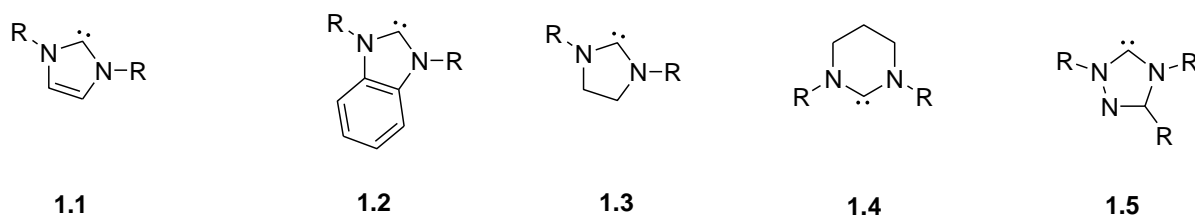


Figure 1.1 : Different forms of NHC.

The diverse structural features of imidazole based NHCs; is such that they could be functionalized, **1.6** immobilized, **1.7** made hydrophilic, **1.8** chiral, **1.9** and or chelating, **1.10a** and **1.10b** (Figure 1.2). The influence of these structural features are more pronounced in the nature of the complexes they generated.²

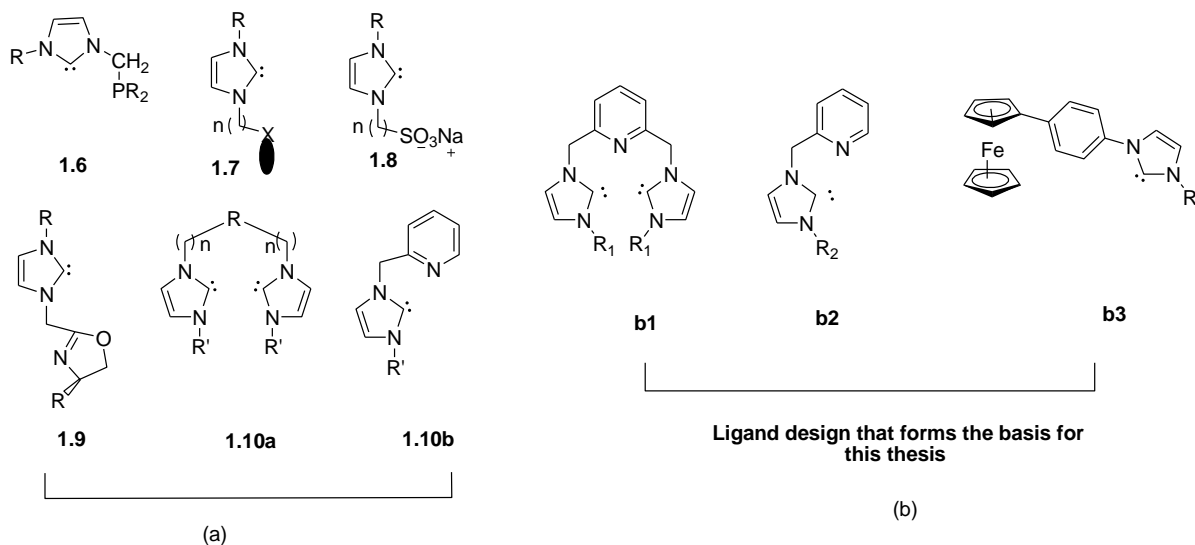


Figure 1.2: (a) Various types of N-heterocyclic carbene and (b) ligand design reported.

With the exception of **1.10a** (pincer NHC), much interest has been given to NHC-metal complexes of the other structural forms of the ligands. Pincer NHCs as they are known; and most especially the chelating type (CNC or CPC) complexed with cheap, affordable, environmentally friendly and non-toxic metals like nickel and cobalt are less explored.¹⁰ We

believe that with the growing interest in green homogeneous catalysis using environmentally benign metals; nickel and cobalt are good candidates to explore. The advantageous characteristic high tunability, improved stability to metal centres and generally high thermal stability of pincer and chelating NHCs¹⁰⁻¹¹ have been explored in their complexes with ruthenium,¹² iridium¹³ and palladium.¹⁴ The development of non-precious metal-NHC complexes is a major area of focus for homogeneous catalysis due to low toxicity and safe disposal to the environment. It is believed that, the high sigma donating ability of pincer, chelating or functionalized NHC ligands can provide desirable properties while still preventing decomposition of the metal centre as commonly encountered in homogeneous catalysis.

1.2 Nature, state and properties carbenes

Carbenes are neutral, divalent carbon species with six-electron valence shell; bearing two (2) unpaired π -electrons and sp^2 hybridization on the carbon. Electronic stability on the carbene is achieved by the nucleophilicity of the electron-rich groups adjacent to the carbene carbon (Figure 1.3; **a**). The influence of the adjacent electron-rich groups on the π -electrons in the carbene makes it exist in either a singlet state (were the electrons remain in the same degenerate orbital) as in the first isolated crystalline free carbene³ or in a triplet state (in unequal energy orbitals). Splitting into either a singlet or triplet state correlates with increasing electronegativity of the π -donor groups and the magnitude of their inductive, mesomeric and steric effects on the carbene carbon.

In metal-carbene complexes; carbenes could be classified as Fischer or Schrock. Non-bonding electrons in Fischer carbenes occupy same orbital and consequently behave like singlet carbenes. Such carbenes easily coordinate with metals via sigma bond formation without any formal charge as divalent 2-electron donor ligands (Figure 1.3; **b**). Schrock carbenes are nucleophilic and usually co-ordinate to metals of high oxidation state when compared to Fischer carbenes. They possess a triplet state in their spin electronic multiplicity, bear a formal charge of -2 when bonded to a metal and are usually called “alkylidenes” (Figure 1.3; **c**). Stability in Schrock carbene-metal complexes is derived by the formation of two covalent bonds between the two un-paired electrons in the carbene and the metal orbital electrons.¹⁵

In addition to the influence of the π -donating adjacent electron-rich groups; stability of a carbene can also be enhanced by the formation of a cyclic system and conjugation therein. Adjacent atoms in such cyclic conjugated structures stabilize the carbene in Fischer-type and contribute in forming a heterocyclic system containing a sextet of delocalized electrons. When the adjacent atoms/group is nitrogen the result is regarded as '*N*-Heterocyclic Carbene' (NHC). The NHCs are formally defined as the extreme form of Fischer heterocyclic carbenes containing at least one nitrogen atom within the ring structure, having no formal charge on the carbene carbon and their stability enhanced by the aromaticity of the ring system (Figure 1.1).¹⁶

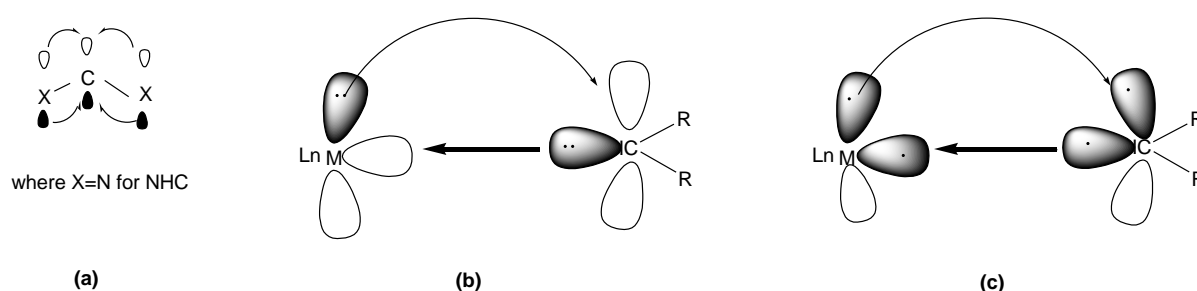


Figure 1.3: (a) Stabilization of a carbene by adjacent hetero atoms, (b) description of electron donation in Fischer carbene and (c) covalent bonding in Schrock carbene.

1.3 Simple and chelating NHC ligands

Simple NHC ligands: As substitutes for phosphines in organometallic chemistry, NHCs share some resemblance with phosphines: both are neutral, good electron donors and have excellent structural tunability. On the other hand, NHCs form stronger sigma bonds with metals due to little or no back donation into the π anti bonding orbitals.⁷ Consequently, the expected back bonding from the filled metal d_{xy} and d_{yz} orbitals in complexes with late transition metals like Pd(0) or Pt(0) into the NHC $p\pi$ -orbital is negligible. This is because orbitals are already occupied by the high electron density of the adjacent nitrogen atom/groups to the carbene.¹⁷ This unique property allows the NHC to also form complexes with metals that have empty d -orbitals as there is no requirement for back donation from the metal.¹⁸ In a strong and robust metal-NHC bond in a complex containing phosphine and NHC ligands the weaker phosphine-metal bond will dissociate in preference to the metal-NHC bond.¹⁹

Due to the intrinsic properties of the NHCs they have been used in a wide range of applications either on their own or complexed with transition metals. In the field of catalysis; efficient and effective systems have been reported for olefin metathesis, Suzuki-Miyaura coupling, aryl amination, transfer hydrogenation and C-H activation to mention but a few.

Chelating NHC ligands: Hemilability allows for added stabilization of metal centres via co-ordination. Hemilabile chelating ligands form vacant coordination sites by undergoing partial dissociation from a metal centre which greatly influences the catalyst life in homogeneous catalysis. In this context the pyridine moiety has been widely studied²⁰ as a second donor group in conjunction to the carbene. The most commonly reported pyridine functionalized NHC ligands include **1.11** (Figure 1.4) which has been complexed to Pd via transmetalation of Ag(NHC) and exhibits an excellent activity in Heck reaction.^{20b} The same ligand precursor was also used to form Ni(NHC)₂Cl₂ complex which is active in the polymerization of norbornane and ethylene.²¹ NHC precursor **1.12**, was directly reacted with basic Pd(OAc)₂ to form a Pd(0) complex^{20a} which showed moderate activity in the co-polymerization of CO and norbornane.

In essence, pyridine as a potential donor group on NHC offers high versatility to the ligand as it is expected to bind weakly to the metal. Variation of substituents on the pyridine moiety also extends the structural tuneability of the NHC ligand.²²

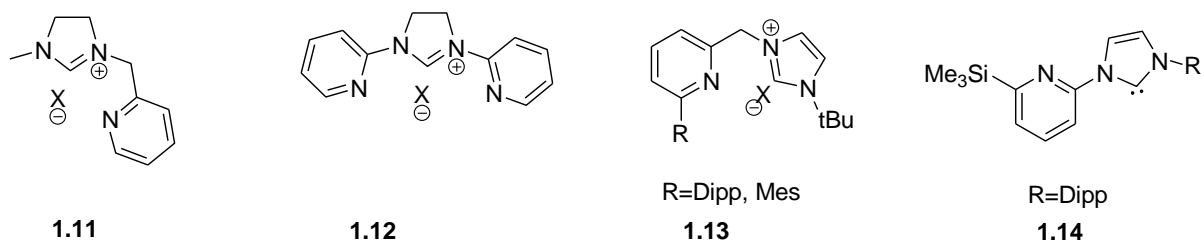
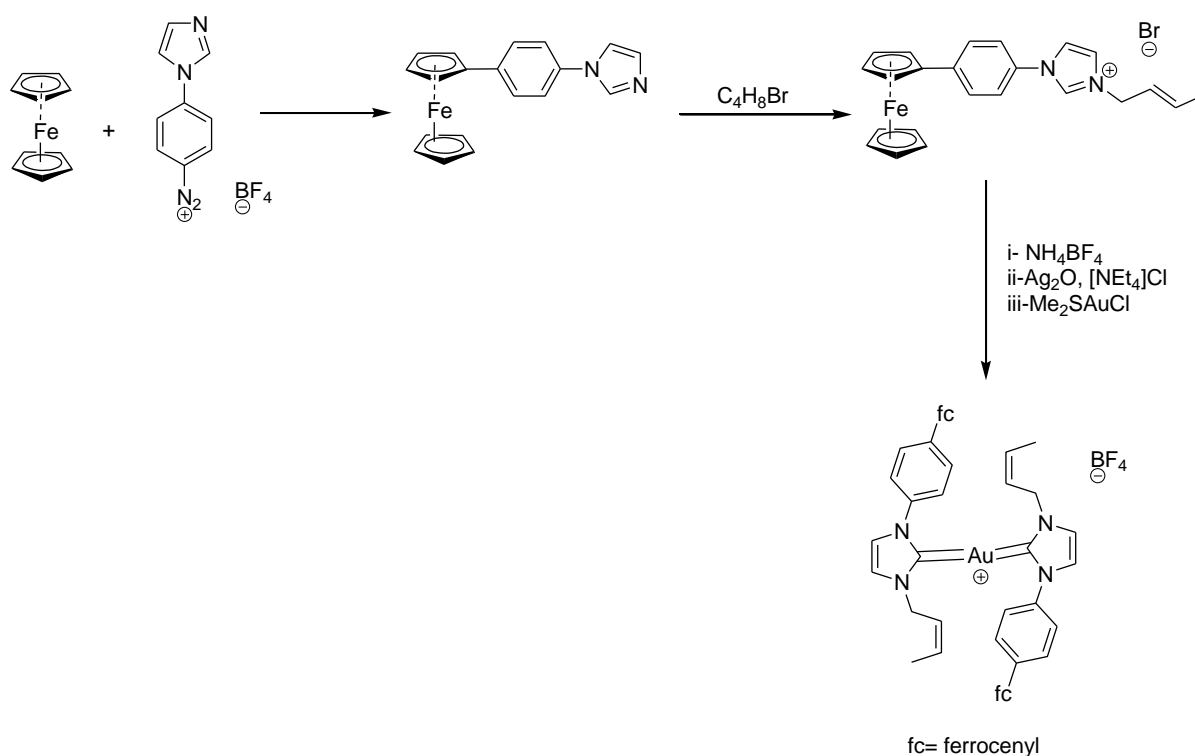


Figure 1.4: Examples of pyridine functionalized NHC precursors and ligand.

Various synthetic routes and forms^{23,14a,24,25} of the pincer (meridentate) NHC ligands have been reported over the years. The basic reason of choice for this kind of NHC ligands (Figure 1.2; b1) is the ‘pincer’ architecture; which provides a pre-organised backbone capable of blocking meridional or pseudo-meridional (site for efficient drainage of electron density) coordination sites of the metal, leaving the remaining sites available for catalysis. It also accounts for the excellent thermal and oxidative stabilities of their complexes; such that they have melting/decomposition temperature above 250 °C.²⁶ The first of such chelating pincer (CNC) NHC-metal complexes was reported by Peris *et al.* in 2001 and they exhibited slightly

distorted square planar geometry,²⁷ although the chelating pyridine lies on a plane coplanar with the plane of the NHC-metal moiety.^{26b} Similarly, when NHC ligands are functionalized by alkenyl moieties,²⁸ they result in metal complexes with hemilabile alkenyl (C=C) arms that impart good catalytic properties in homogeneous catalysis.

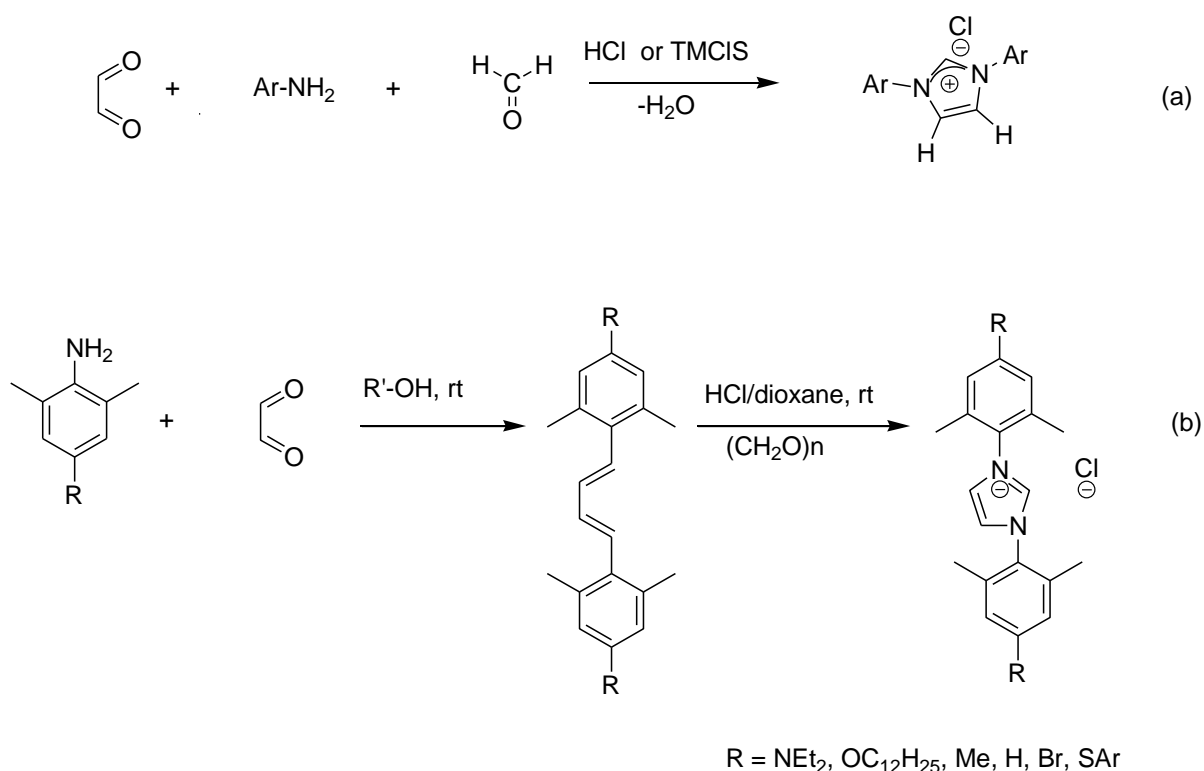
The unique electronic (redox) and geometric properties of ferrocene makes it possible for the moiety to be incorporated into various compounds with applications in medicine, plastics, metallurgy, petroleum and textile industries.²⁹ Its high redox potential confer profound catalytic and electronic activities to such compounds (Figure 1.2; **b3**).³⁰ The stability to air and moisture of both organic and organometallic compounds containing ferrocene moieties accounts for their use in immunoassays,³¹ anti-cancer chemotherapy,³² redox shuttle³⁰ and catalysis.³³ Aromatic spacers are usually introduced into ferrocene moieties to improve their aromatic and electronic character.³⁴ Such reactions (Scheme 1.1) could be applied to the synthesis of *N*-substituted ferrocenylaryl imidazole^{30, 32} and subsequent access to electrophoric NHC-metal complexes. It is noteworthy that bi-metallic complexes of such *N*-substituted ferrocenylaryl imidazolylidene containing environmentally benign metals like cobalt and nickel are very rare.



Scheme 1.1: Route to the synthesis of an electrophoric NHC-metal complex.³²

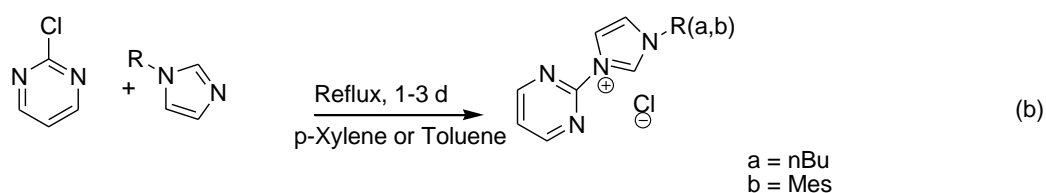
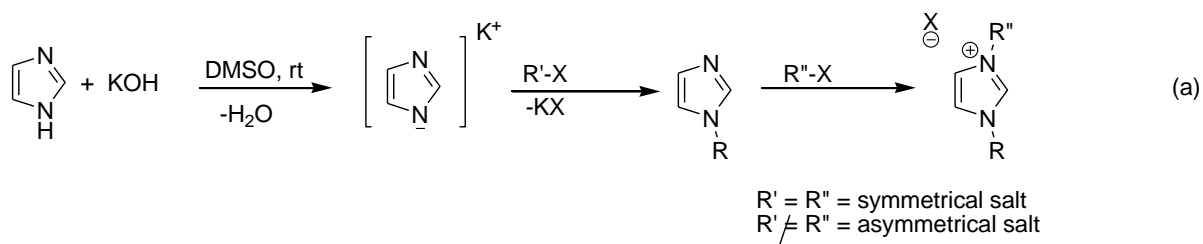
1.4 Synthesis of NHC precursors

The commonest method for the synthesis of monodentate bis-1,3-diarylimidazolium salts is the one pot addition of glyoxal with aryl amine in the presence of a catalytic amount of formic acid to form diimine intermediate. This is followed by a ring forming stage to form the diazole imidazolium salt via the reaction of the diimine with formaldehyde in the presence of a counter ion source usually a mineral acid³⁵ or trimethyl chloro silane (TMCIS)³⁶ [Scheme 1.2 (a)]. We have recently used a solvent-free technique in the synthesis of the diaryldiimine with high yield; and achieved ring closure with paraformaldehyde and HCl as counter ion source to generate bis-1,3-diarylimidazolium salts.³⁷ In a similar vein Leuthaußer *et al.* have modified Arduengo's one-pot synthesis of 1,3-diarylimidazolium salts and were able to sustain the yield of purer salts by alleviating the purification shortcomings of the earlier method [Scheme 1.2 (b)].³⁸



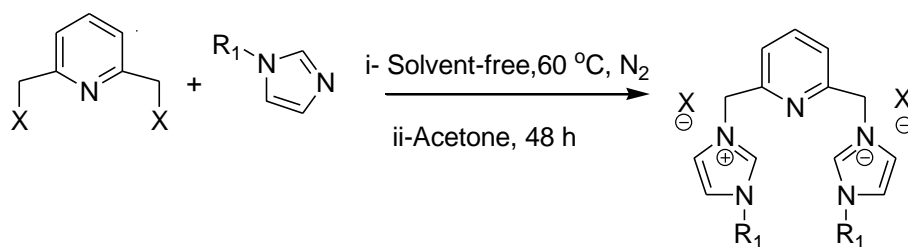
Scheme 1.2: (a) Typical synthesis of symmetrical bis-1,3-diarylimidazolium salts and (b) a modification of Arduengo's one-pot synthesis of 1,3-diarylimidazolium salts.

Symmetrical and asymmetrical alkyl imidazolium salts are generated by first activating the secondary nitrogen on imidazole with an alkyl halide, followed by quaternization of the tertiary nitrogen (Scheme 1.3). The former stage is usually associated with deprotonation of the 2° nitrogen using a base (mostly KOH) followed by the addition of an alkyl halide in an aprotic polar solvent to yield an *N*-substituted imidazole. The later stage is usually achieved by refluxing the *N*-substituted imidazole with an appropriate alkyl halide in an aprotic solvent under inert conditions. This route might take several days under extreme temperatures.



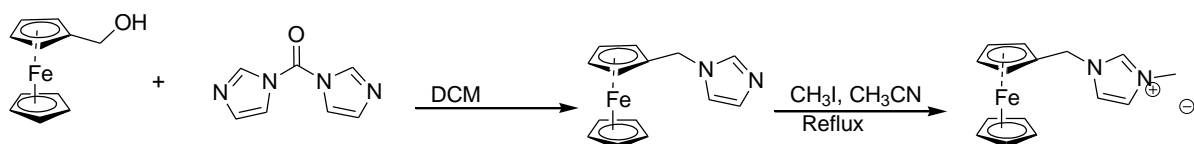
Scheme 1.3: (a) Synthetic route to *N*-alkyl imidazoles and subsequent formation of salts. (b) Quaternization of imidazolium nitrogen to yield the corresponding salt.³⁹

Use of environmentally unfriendly solvent (dioxane)⁴⁰ under extreme temperature conditions and long reaction times are some of the draw backs of using solution techniques to achieve quaternization of imidazolium nitrogen. Although, in permissible situations the quaternization may be conducted under solvent-free reaction conditions (Scheme 1.4) which offer the advantage of avoiding environmentally unfriendly solvents and subsequent precipitation of the salt with acetone as reported by Simons and co-workers.⁴¹



Scheme 1.4: Commonly employed strategy for the synthesis of pincer (CNC) NHC ligand precursors.⁴¹

In a situation where solvent-free technique might not be possible, quaternization is achieved by stirring at room temperature in DCM or refluxing the *N*-substituted imidazole with alkyl halide source in environmentally benign polar aprotic solvents like acetonitrile under inert conditions (Scheme 1.5).^{30, 32} The use of acetonitrile as commonly employed in synthesis of alkenyl/alkyl ferrocenyl phenyl/methyl imidazolium salts gave good to excellent yields, and this could be due to its high dielectric effect and basic nature.³⁰



Scheme 1.5: Synthetic route to alkylferrocenyl imidazolium salts.

1.5 Synthesis of NHC ligands from the precursors

NHC ligands are largely synthesised by the deprotonation of ligand precursors in liquid ammonia,⁴² with amines or polar aprotic solvents. In other words; bases like NaH, KO*t*-Bu or KN(SiMe₃)₂ and even transitional metal amides could be used within permissible temperatures of -78 to 0 °C. Deprotonation with bases occur quickly and quantitatively in a homogeneous phase and allow the procurement of wide varieties of heterogenized, functionalized and even chiral carbenes,⁵ although such bases are not selective on the imidazolium proton and tend to attack other active or acidic protons on the ligand precursor.

The NHC precursors or salts exist as high boiling ionic liquids or solids with melting point as high as 157 °C or higher. The carbenes on the other hand are stable under inert conditions and could be stored for months at -30 °C. They are also stable in solution to 50 °C and

slightly yellow or orange to purple coloured solutions of the carbenes are spectroscopically pure, even though the colour indicates possible decomposition.

1.6 Synthesis of transition metal-NHC complexes

Depending upon structural features, intended application and distinct functionalities on the NHC precursor, different routes to the synthesis of NHC-metal complexes are available. This is also dependant on the kind or nature of the metal precursor to be used.

Most monodentate carbene-metal complexes have been successfully synthesis via the free carbene route,⁴³ although there are also reported successes of this route with chelating pincer-NHC-metal complexes.^{3, 4b, 44} The sensitivity of the bases used like NaH/KH, KO*t*-Bu or KN(SiMe₃)₂ in some instances usually leads to binding not at the expected imidazolyl C2 but at C5 to the metal.^{44b} For NHC ligand precursors with methylene linkers or active proton groups; the free carbene route is not suitable as those bases are not selective and result to decomposed or completely unidentifiable products.⁴⁵ The method is not suitable for air and moisture sensitive conditions.

Basic metal precursors like [HCr(CO)₅]⁻ and those containing acetate groups are directly reacted with the NHC ligand precursor (salt) to generate corresponding metal complexes.^{4b} The method has also been employed for nickel,⁴⁶ cobalt and palladium-NHC complexes⁴⁷ with general formula M(NHC)₂X₂. The use of DMSO, tetrabutylammonium iodide or bromide, and extreme temperatures are among the shortcomings of this method and made it unsuitable for temperature sensitive imidazolium salts. The method is also not selective on the imidazolium C2 proton as deprotonation of unsubstituted C4 or C5 could lead to formation of the metal-NHC bond via those carbons.⁴⁸

Limitations of the above highlighted methods are alleviated with the discovery of silver-NHC complex transmetalation route. NHC ligand precursors containing acidic protons in their linker i.e. lutidyl^{14b, 26b} or picoyl²¹ or active proton functionalities; for instance -OH, -NH₂⁴⁵ and those in which the free carbene is not easily accessible are metalated via a carbene transfer reaction. In situation also where regio-selectivity in the metal bond via C2 or geometry of the resulting metal-NHC complex is of high importance to intended application; silver-NHC transmetalation is the best route. The silver-NHC complexes are prepared by the reaction of basic Ag₂CO₃, Ag₂O or AgOAc with imidazolium salts in polar solvents like DCM, methanol or 1,2-dichloromethane.^{14b, 21, 26, 49} The silver complex is then either isolated

or used *in situ* to transmetalate the carbene to the appropriate metal. Other transition metal complexes have also proven and reported to be transmetalation agents for saturated NHC ligands onto a range of metals in good yield.⁵⁰

1.7 Synthesis of chelating NHC-metal complexes

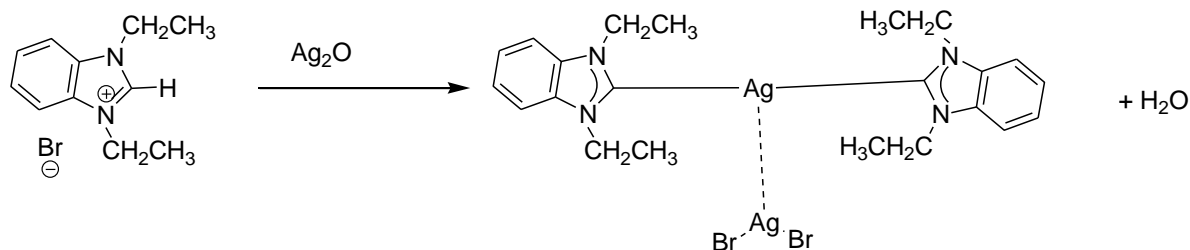
Transmetalation via silver-NHC complexes is usually employed to relieve the highlighted problems associated with the synthesis of chelating NHC-metal complexes with free carbenes. Though, they were first made with monodentate NHC ligands,^{49, 51} Ag-NHC complexes have gained popularity and could be synthesised via the four routes listed below:

- 1- Reaction of silver salt with free carbenes.
- 2- In-situ generation of free carbenes from imidazolium salts using a base in the presence of silver salt.
- 3- Transmetalation of tungsten-NHC complexes with silver complexes; and this is the simplest and more efficient method for chelating or bis NHCs
- 4- Treatment of basic silver reagents like Ag_2O , Ag_2CO_3 or AgOAc with imidazolium salts.

The use of basic silver reagents simultaneously deprotonates the imidazolium proton and coordinates the silver metal to the generated carbene (Scheme 1.6).

Advantages of using intermediate Ag-NHC complex in generating metal-NHC complexes include:

- 1- Eliminate the possible decomposition of the liberated carbene due to their high moisture and air sensitivity.
- 2- Retains active proton functionalities in the framework of the imidazolium salts which could be affected by the base during deprotonation of the imidazolium proton to liberate the free carbenes.
- 3- Ag-NHC complexes are usually stable to atmospheric conditions, and require no protected solvents.
- 4- Transmetalation leads to *cis*-geometry in the metal-NHC complexes rather than the *trans*-geometry, and this allows for greater catalytic potential in the metal-NHC complex generated.



Scheme 1.6: Example of the synthesis of a Ag-NHC complex.

1.8 Characterization of Ag-NHC complexes

Preliminary characterizations like ^1H and ^{13}C NMR are excellent techniques in the detection of Ag-NHC complexes. The spectroscopic observation of Ag-C carbene chemical shift within the range 213 – 163 ppm is a distinct indication that metal-carbene bond is formed.⁵² However, some Ag-NHC complexes have no detectable Ag-carbene coupling or resonance; this was explained to be as a result of ‘fluxional behaviour’ in the Ag-NHC complexes in solution (Figure 1.5).⁴⁹ For such complexes; the absence of far down field imidazolium (C2-H) proton in the ^1H NMR indicates that deprotonation by the basic silver reagent has occurred and the silver metal is bonded via the C2 carbene carbon in the complex.

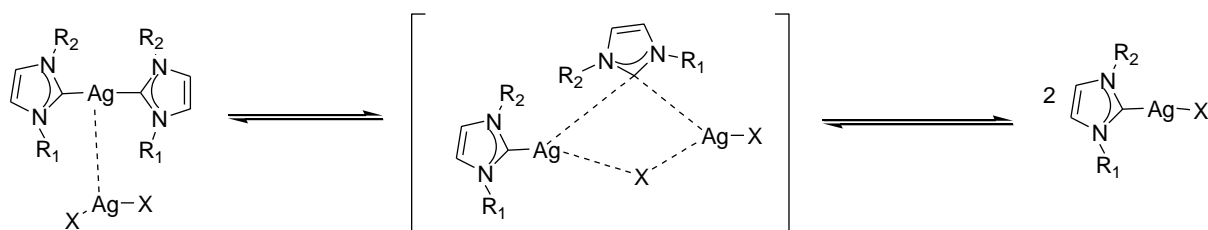


Figure 1.5: Fluxional behaviour in Ag-NHC complex.

The fluxional behaviour of the intermediate Ag-NHC complex is important in carbene transmetalation reactions. So far among all the reported Ag-NHC complexes; those with *bis*(NHC) complexes are still comparatively low.⁵³

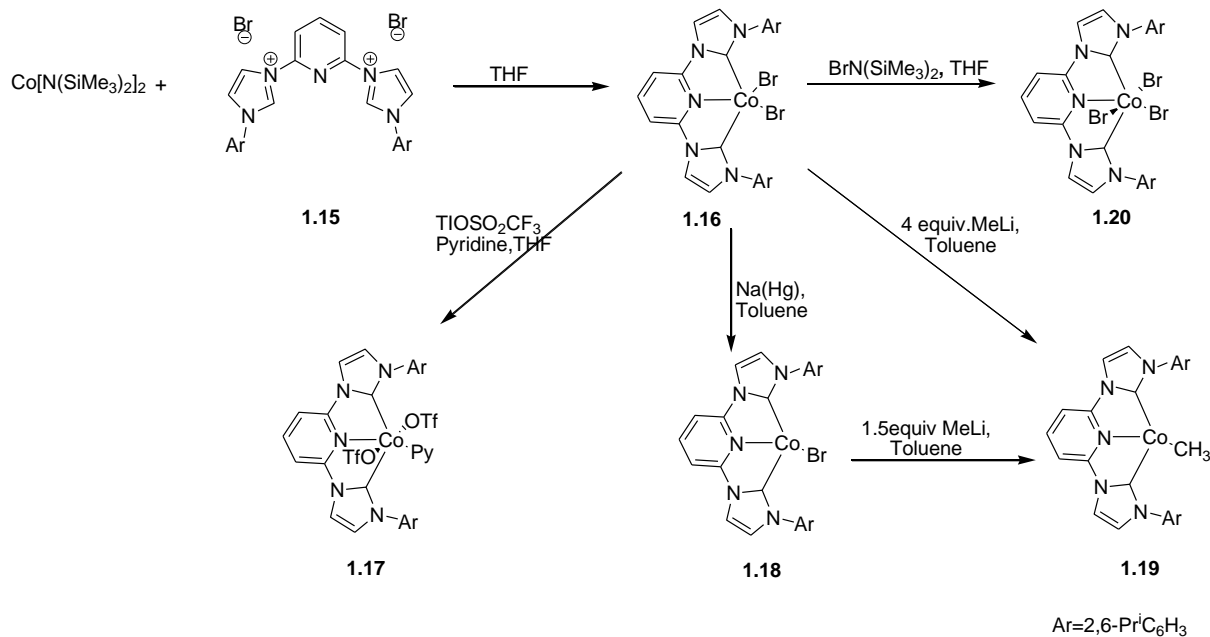
1.9 Synthesis and catalytic activities of chelating NHC complexes of cobalt and nickel

Many reviews have been written on the prevailing synthetic route to NHC ligands, their complexes and catalytic application since the isolation of the first stable carbene by Arduengo. Here we review the most recent and high yielding synthetic routes to chelating NHC complexes of cobalt and nickel and their application in homogeneous catalysis.

1.9.1 Synthesis of chelating NHC-cobalt complexes

Most of the reported organo-cobalt complexes are based on classical donor ligands like Cp, phosphines and CO.⁵⁴ However, the number of cobalt-NHC complexes is limited,^{9b} and only a few examples are available with multidentate NHC ligands having pincer or functionalized architecture.⁵⁵

Aminolysis of cobalt *bis* [*bis*(trimethyl silyl) amide] $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ with pincer imidazolium salt, **1.15** by Danopoulos and co-workers⁵⁵ yielded a range of ‘pincer’ (CNC)NHC-Co complexes (Scheme 1.7). Complex **1.16** was obtained as a reddish-purple, microcrystalline, moderately air sensitive paramagnetic solid ($\mu_{\text{eff}} = 2.00\mu_{\text{B}}$) and characterized only by analytical methods. Transformations of **1.16** by a variety of reagents and conditions yielded complexes with Co exhibiting +1 and +3 oxidation states. In the presence of pyridine; THF solution of **1.16** and $\text{TfOSO}_2\text{CF}_3$ gave yellowish-green, air stable, paramagnetic cobalt complex, **1.17** which adopt a distorted octahedral geometry with the trifluoromethane sulphonate group occupying trans-orientation. The average Co-carbene bond length is the same (1.941Å), while Co-N(pyridine) bond is shorter than expected for pyridine group of a ‘pincer’ group, although, Co-O (triflates) are still within reported range.⁵⁶

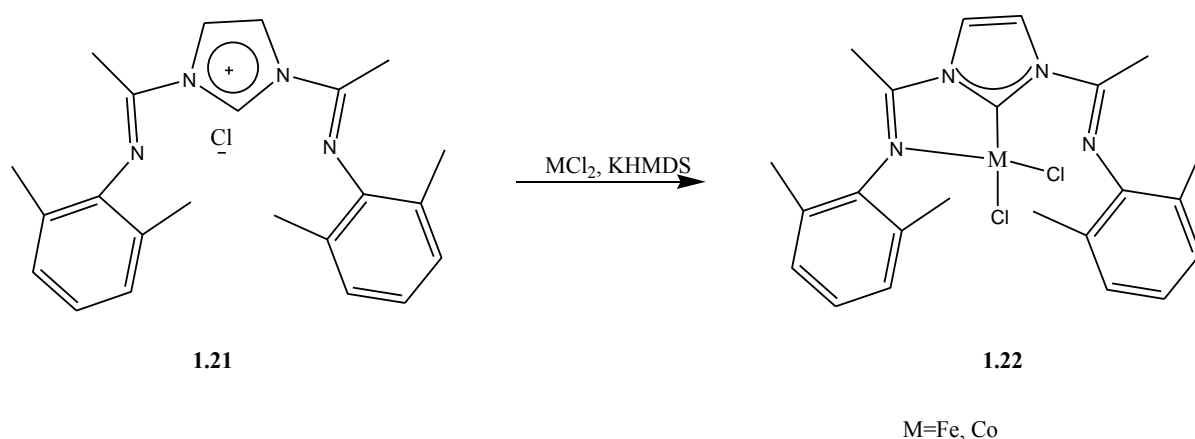


Scheme 1.7: Synthesis of Co(I), (II) and (III)-'pincer' NHC complexes as described by Danopoulos *et al.*⁵⁵

The reduction of **1.16** in toluene with Na(Hg) gave a high yield of a greenish-brown, air sensitive, diamagnetic complex (ⁱPrCNC)CoBr, **1.18** which is unstable in chlorinated and protic solvents. The Co(I) complex gave a ¹H NMR spectrum with the para hydrogen of the pyridine having an unusual downfield shift (9.55ppm); which is even more pronounced after subsequent methylation with MeLi in toluene to give reddish-brown, air and photosensitive crystalline (ⁱPrCNC)CoCH₃, **1.19**. ¹H NMR of **1.19** is similar to that of its precursor with the exception of the methyl resonating at -0.85 ppm and depicted a crystal data of square planar Co(I) centre, with the pyridine and carbene rings coinciding with the coordination plane and the bulky aromatic rings nearly perpendicular to the plane. In a bid to understand the utility of pincer NHC ligands as spectators for higher oxidation state of Co, **1.16** was oxidized with BrN(SiMe₃)₂, which yielded an octahedral, diamagnetic and air stable Co(III)-NHC complex, **1.20** that displayed a broad ¹H NMR spectrum; supporting the C₅-symmetric structure.

The difficulties associated with the synthesis of *bis*[(arylimino)alkyl or aryl]imidazole-2-ylidene complexes of cobalt and other late transition metals have been recently resolved from the work of Thaqfi and Lavoie.⁵⁷ The usual unsuccessful deprotonation of the imidazolium salt and subsequent transmetalation with Ag₂O or Ag₂CO₃ was alleviated by using silver amide as both base and silver source. The silver complex was easily made by the addition of

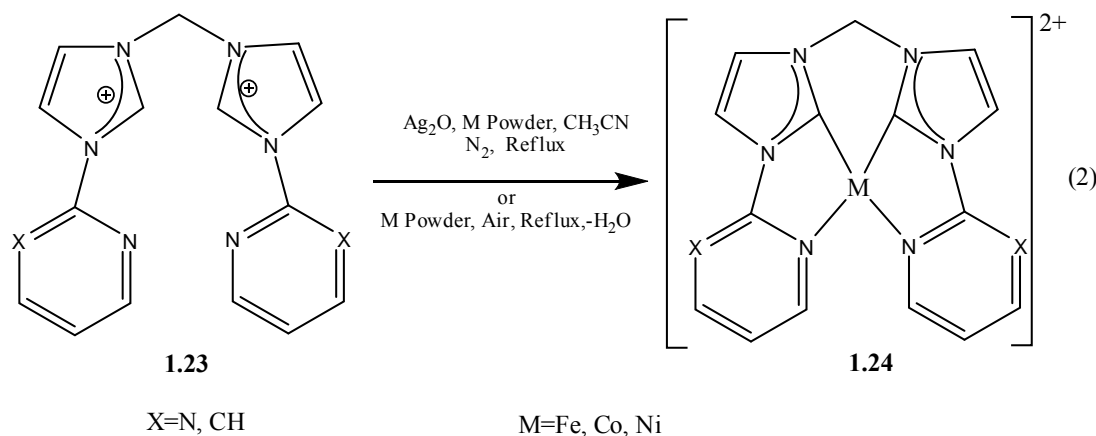
in situ prepared filtrate of $\text{AgN}(\text{SiMe}_3)_2$ to a suspension of **1.21** in toluene at low temperature. The silver complex is thus precipitated out with greater than 67% yield; alongside volatile byproducts. To avoid the problem of transmetalation from the silver adduct, an *in situ* iron or cobalt *bis*[*bis*(trimethyl)silyl]amide was prepared by treating the respective metal salt with potassium hexamethyldisilazide (KHMDS) at low temperature and adding the filtrate directly to the suspension of the imidazolium salt, **1.21** (Scheme 1.8). Hence, metal-NHC complexes, **1.22** were successfully precipitated out as salts with pentane at >85% yields.



Scheme 1.8: Synthesis of *bis*[(arylimino)alkyl or aryl]imidazole-2-ylidene complexes of Fe and Co.

The paramagnetic nature of **1.22** is indicated by their respective magnetic susceptibility as measured using Evans method⁵⁸ and featureless NMR spectra with broad resonance over a wide frequency range. The crystal data showed that both complexes are iso-structural and crystallized in the $P2_1/c$ space group with the metal centre adopting a distorted tetrahedral geometry and the ligand chelating to the metal in a bidentate format via the carbenic carbon and one of the iminic side chains.

Liu *et al.*,⁵⁹ have shown that chelation of NHC could also be easily achieved via simple *in situ* transmetalation from silver-NHC complexes to the desired metals. Most exciting is the fact that even simple metal powder of iron, cobalt or nickel could be used to achieve the transmetalation (Scheme 1.9).

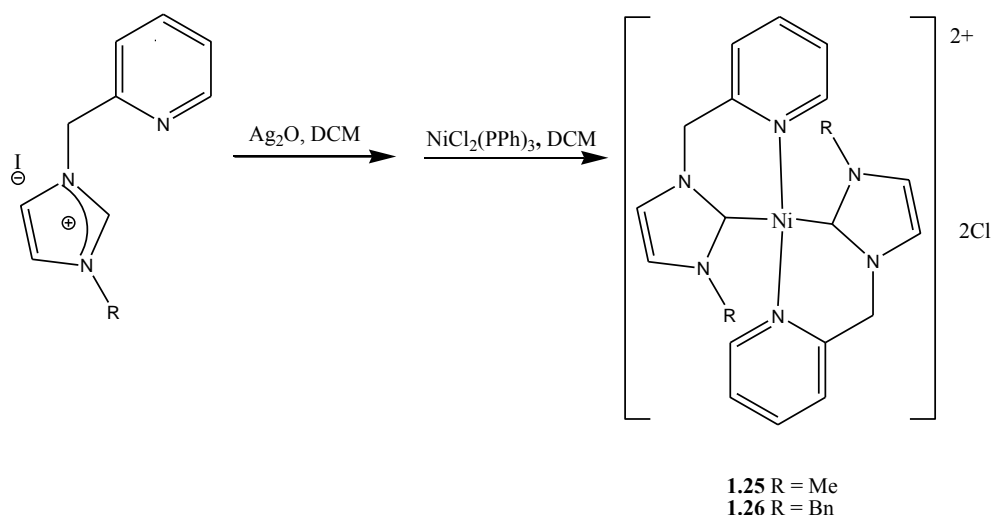


Scheme 1.9: Synthesis of metal-NHC complexes using simple metal powders.

1.9.2 Synthesis of chelating NHC-nickel complexes

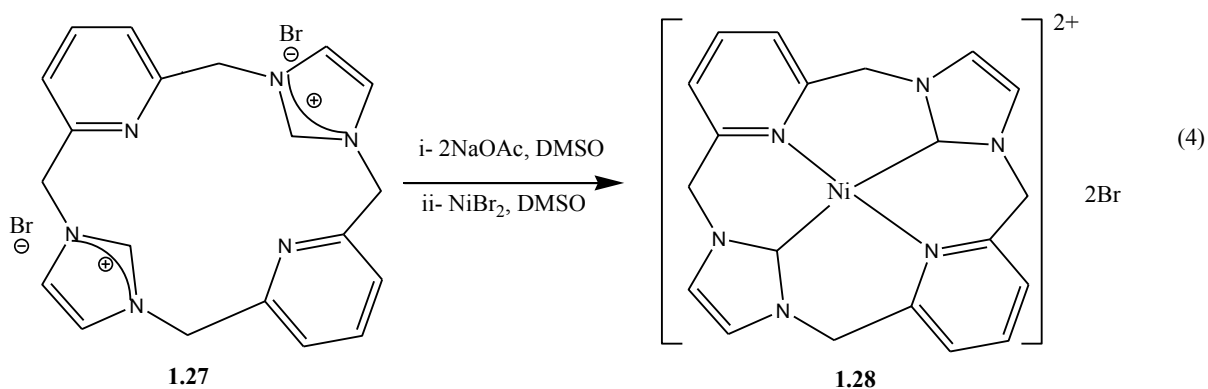
The initial interest in catalyst systems promoted by precious metals has been replaced with recent and versatile systems developed from NHC-Ni(0) and NHC-Ni(II) complexes. Such complexes have proven to be active in C-S coupling,⁶⁰ cyclo addition reactions,⁶¹ addition polymerization of norbornane,⁴⁵ aryl amination,⁶² C-C coupling, styrene polymerization,⁶³ and Suzuki and Kumada coupling reactions.^{26, 64} It is worthy to note that; the stability to air and moisture as exhibited by electron rich NHC-Ni(II) complexes is not observed in the corresponding Ni(0) analogues. Catalytic systems with Ni(II)-NHC complexes are active without the need for a co-catalyst, while Ni(0)-NHC complexes do require the use of co-catalysts for their activity.²¹

Functionalized NHC complexes of nickel containing picoyl moiety have been synthesized via transmetalation from Ag-NHC complexes of the proligands with $\text{NiCl}_2(\text{PPh}_3)_2$. Simple addition of the nickel precursor to an *in situ* generated silver complex in DCM gave the desired complexes, **1.25** and **1.26** (Scheme 1.10).²¹ The yellowish or orange crystals were recrystallized from MeOH/ether and isolated in good yield.



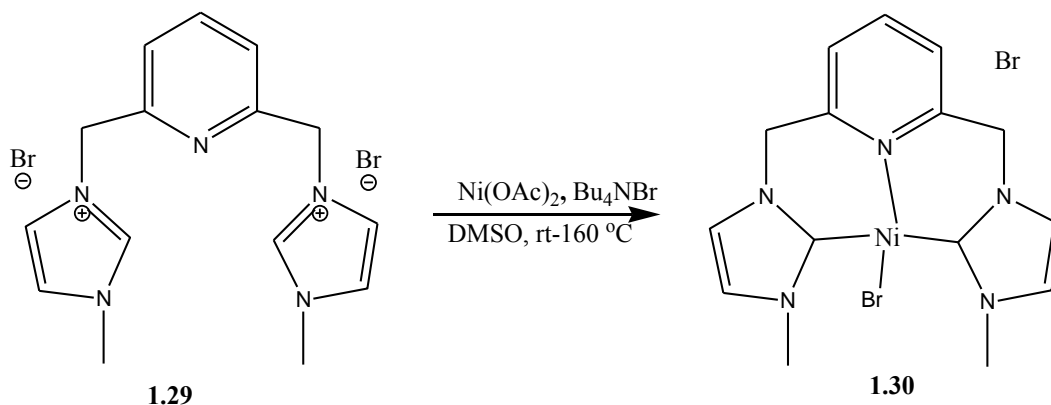
Scheme 1.10: Synthesis of chelating NHC-Ni complex via *in situ* Ag-NHC transmetalation.

Contrary to the accepted norms, the cyclophane–nickel complex **1.28** has been recrystallized from hot water. Its synthesis (Scheme 1.11) involved initial dissolution of the cyclophane salt **1.27**, with NaOAc in DMSO and subsequent removal of the solvent. The resulting dried mixture was then dissolved in dry DMSO together with anhydrous NiBr₂ and then heated under vacuum in inert conditions at 85 °C for three days. The resulting precipitate was filtered and dried under vacuum to yield a yellowish-orange powder and spectroscopically pure, **1.28** in good yield.



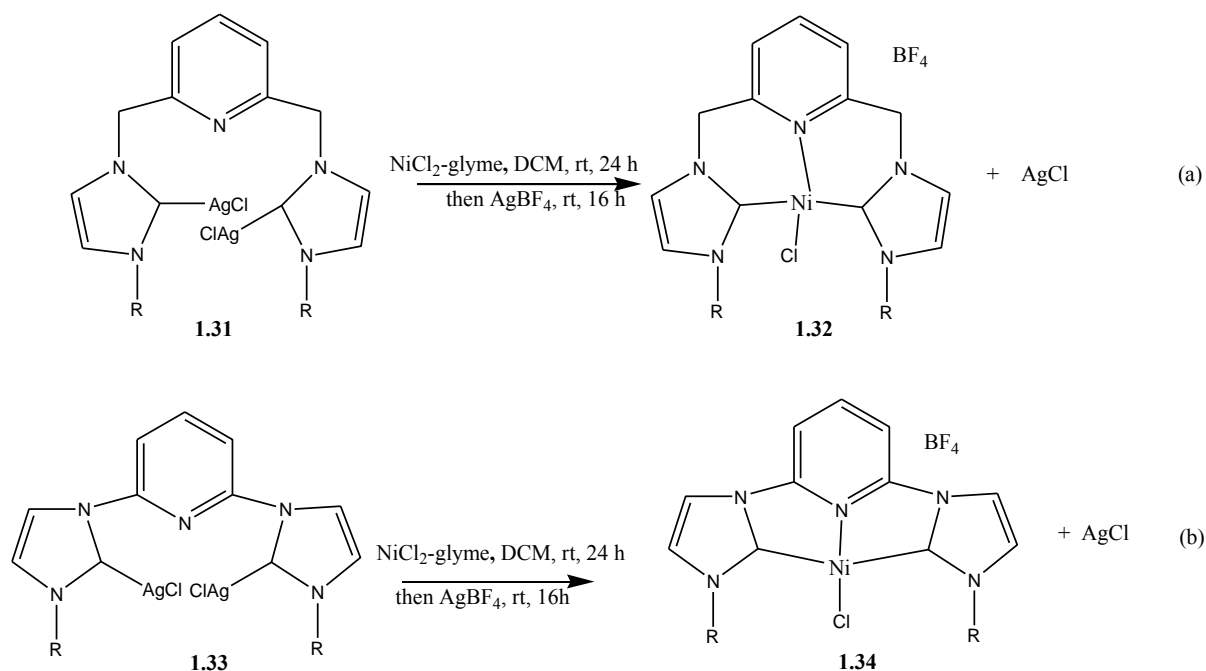
Scheme 1.11: Synthesis of cyclophane nickel complex.

Pincer NHC-Ni complex, **1.30** was readily obtained by *in situ* deprotonation of the imidazolium salt, **1.29** with $\text{Ni}(\text{OAc})_2$ in the presence of Bu_4NBr and DMSO as solvent (Scheme 1.12).^{26a} The thermolysis reaction yielded **1.30** as air and moisture stable yellowish brown solid which readily recrystallized from methanol.



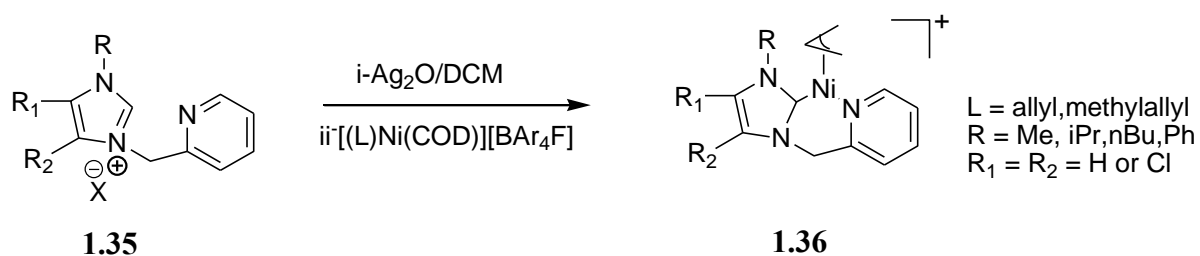
Scheme 1.12: Thermolytic synthesis of pincer NHC-Ni complex using basic metal precursor.

To further harness the efficient catalytic system provided by the thermal and oxidative stabilities of pincer NHC-metal complex frameworks, Inamoto *et al.*^{26b} have synthesized a range of nickel-pincer NHC complexes **1.32** and **1.34** via transmetalation of the Ag complexes of the corresponding imidazolium salts. The anionic metathesis of the intermediate *in situ* generated nickel-NHC complex with AgBF_4 (Scheme 1.13) gave the desired complexes **1.32** and **1.33** as yellow, air stable solids; soluble in most organic solvents and were thus recrystallized from a DCM and petroleum ether solvent mixture. Distinct groups like methyl, mesityl and DIPP proton signals and symmetry are observed in the ^1H NMR spectrum of the complexes. The absence of downfield signal of the imidazolium proton gave clear indication that coordination via the carbene carbon has been achieved.



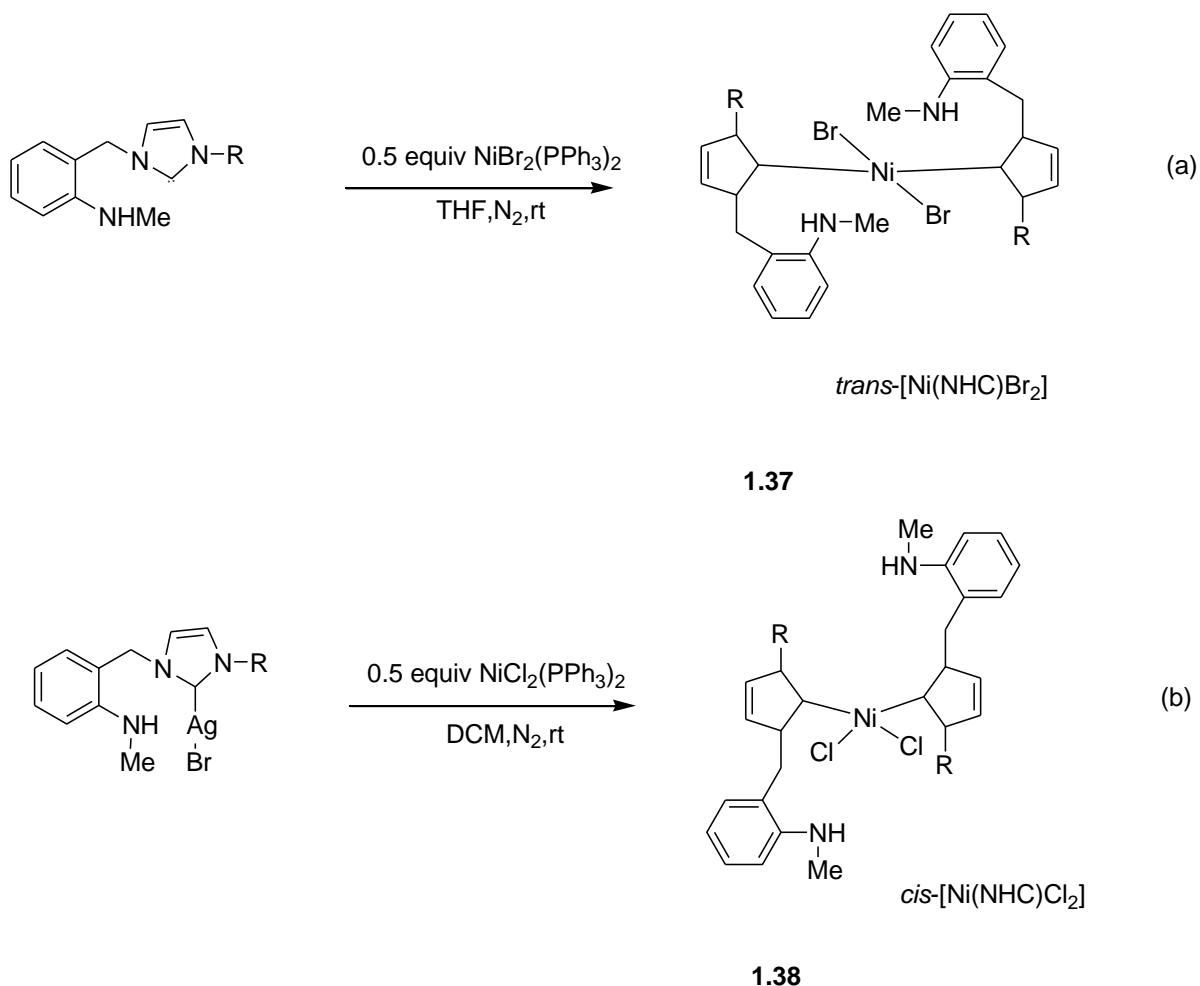
Scheme 1.13: Synthesis via Ag-NHC transmetalation of pincer NHC-Ni complexes with (a) lutidyl and (b) pyridine moieties.

R-allyl-Ni NHC complexes, **1.36** were successfully obtained by transmetalation of the corresponding silver carbene complex with $[(\text{L})\text{Ni}(\text{COD})][\text{BAR}_4\text{F}]$ in DCM (Scheme 1.14).⁶⁵ All the isolated complexes were obtained in good yield and lack a $\text{C}_2\text{-H}$ imidazolium proton signal at 10.12 ppm in **1.35**, confirming the successful co-ordination of the carbene carbon to nickel. The diastereotropic methylene protons in the CH_2 bridge of the bidentate ligand are also observed in the complexes showing expected bond lengths and angles. Complexes **1.36** exist as cationic species which molecules exhibited classic pseudo-square planar geometry characteristic of $d^8\text{M}(\text{II})$ allyl complexes.



Scheme 1.14: Synthesis of R-allyl-Ni-NHC complexes.

Zhang and co-workers⁴⁵ have recently developed a viable olefin-addition catalyst system containing [*bis* (NHC)NiX₂] complexes. The effective deprotonation of the amino containing monodentate carbene or via Ag-transmetalation of the ligand precursor, followed by subsequent addition of NiX₂(PPh₃)₂ (X=Br,Cl,) gave the *trans* and *cis*-halo Ni-NHC complexes **1.37** and **1.38** respectively (Scheme 1.15).



R=2,4,6-Me₃-C₆H₂ or *ter*Bu

Scheme 1.15: Synthesis of (a) *trans* and (b) *cis* nickel-NHC complexes.⁴⁵

Deprotonation was found to be more effective with *n*-butyllithium or sodium *bis*trimethylsilazide [NaN(SiMe₃)₂] as attempted deprotonation with bases like KO^tBu or NaOAc in the presence of the nickel precursors yielded only complex mixtures. Successful metalation was confirmed from the ¹H NMR spectra of **1.37** and **1.38** which lacked the

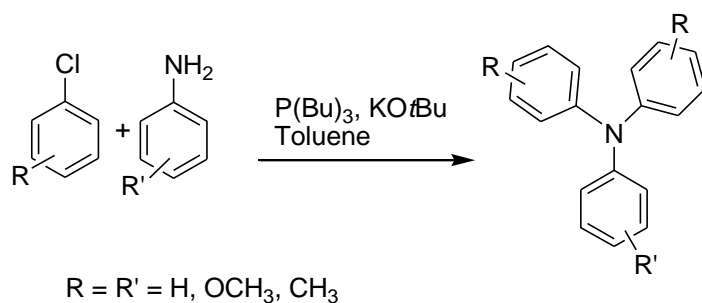
characteristic imidazolium proton signal around 10.7—11.0 ppm, while the ^{13}C NMR spectra indicated a down field shift to 167.3—164.7 ppm of the carbenic carbon.

1.9.3 Catalysis

For more than two decades ^{47a} NHC-metal complexes have opened up the possibility of their application as homogeneous catalysts for olefin polymerization, transfer hydrogenation, C-C and C-N coupling reactions by using simple substrates and reaction conditions to yield products not possible by traditional synthetic methods^{47a}.

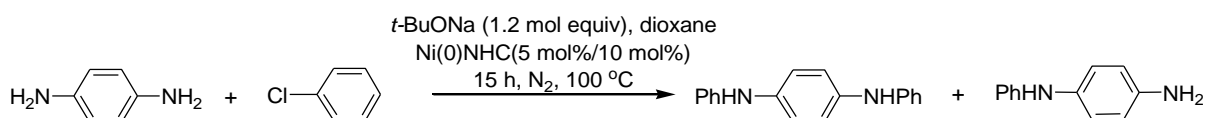
1.9.4 Chelating ‘pincer’ and functionalized NHC-transition metal complex as catalyst for *N*-arylation of aniline

Carbon-carbon and carbon-nitrogen coupling reactions are of great importance in the synthesis of a wide range of organic compounds. Many transition metal-NHC complexes have proven to be efficient catalysts for Suzuki-Miyaura and other known coupling reactions. Although, most Miyaura C-N coupling are catalysed by Pd(0) or copper mediated Ullman reactions, the use of the former is not economical as almost stoichiometric amounts of the catalyst is used⁷⁰ while the latter proceeded under extreme temperatures.⁷¹ The widespread use of Pd catalyzed cross coupling reactions have been impeded in the past by the high cost of the aryl iodides and bromides initially used for such reactions. Recent research has been on the use of cheaper aryl chlorides to replace the iodides and bromides. However, the stability of the aryl chlorides hampers their readiness to undergo oxidative addition to 14e-Pd(0) phosphine complexes.⁷² Similarly, copper, copper complex or copper/ligand mediated cross coupling reactions have also suffered setbacks. In all or most of the reported cases; other than under extreme reaction conditions, successes have been with iodo or bromo aryl derivatives and the chloro derivatives have been considered with little exclusion as unlikely targets. The successes have been with tri-*o*-tolylphosphine and tri-*N*-butyl phosphine (Scheme 1.16); which are highly effective ligands for the *N*-arylation of aniline by aryl halides ranging from iodides to chlorides.⁷⁰



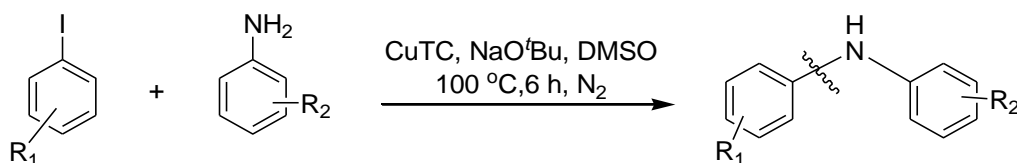
Scheme 1.16: Phosphine catalysed *N*-arylation of aniline.

An efficient and effective Ni(0)NHC *in situ* catalyst system has been developed for C-N coupling of aryl halide with diaryl amines to achieve good to excellent yield of *N*-mono and *N,N'*-diaryl substituted products.^{62b} A wide range of *N*-mono substituted and *N,N'*-substituted arylated products of a variety of aromatic diamines and aryl halides with different electronic groups are successfully obtained with low catalysts loading of 5 mol% (Scheme 1.17). It was understood that such *in situ* catalyst system work best in certain ratio of constituents and increasing the ratio could lead to loss of catalytic activity.



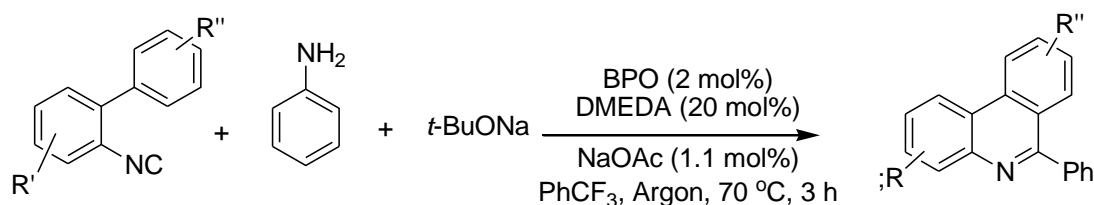
Scheme 1.17: *N*-mono and *N,N'*-diarylation of aryl diamine catalyzed by *in situ* Ni(0)NHC catalyst system.

In a deviation from the common Pd(0) catalyzed arylation of aniline is the recently reported *N*-arylation of aniline alongside other amides and 4-aminopyridines via copper thiophenecarboxylate (CuTC) mediated reaction with aryl iodides (Scheme 1.18).⁷³ The ligand-free catalyst system achieved excellent yields within average of six hours; although the use of high catalyst loading (12.5 mol%), high temperature of 100 °C, extremes in the isolation of the crude product from the solvent and the fact that the process is only applicable to expensive aryl iodides are amongst the shortcomings of the method. It is assumed that the sterically bulky NHC-metal complexes incorporating environmentally benign metals like cobalt and nickel could remedy the limitations associated with the CuTC mediated and other similar catalyst system in achieving *N*-arylation of aniline.



Scheme 1.18: CuTC catalyzed cross-coupling of aniline with aryl iodides.

Cyclic amines with biological importance like the phenanthridines⁷⁴ have recently been synthesized by transition metal-free cyclization arylation of aniline.⁷⁵ The route allow for the one-pot synthesis of C6 phenanthridine derivatives by arylation cyclization of 2-isocyanobiphenyls using aniline as inexpensive arylation agent to afford diversified C6-aryl phenanthridines in good to excellent yields (Scheme 1.19). The reaction proceeds via a key biphenyl imidoyl radical intermediate formed by the addition of aryl radicals to 2-isocyanobiphenyls. The mechanism of the reaction also reveals a pathway involving single electron transfer (SET) of the biphenyl imidoyl radical to the corresponding nitrilium intermediate. This is followed by electrophilic aromatic substitution (S_{EAr}) as a competitive pathway to intramolecular homolytic aromatic substitution (HAS).⁷⁶ Notable fact in this process the great impact of the base in such arylation reactions as it is responsible for the deprotonation of the aniline and subsequent oxidative addition of the isocyanobiphenyl to achieve the synthesis of the polynuclear heterocyclic compounds.

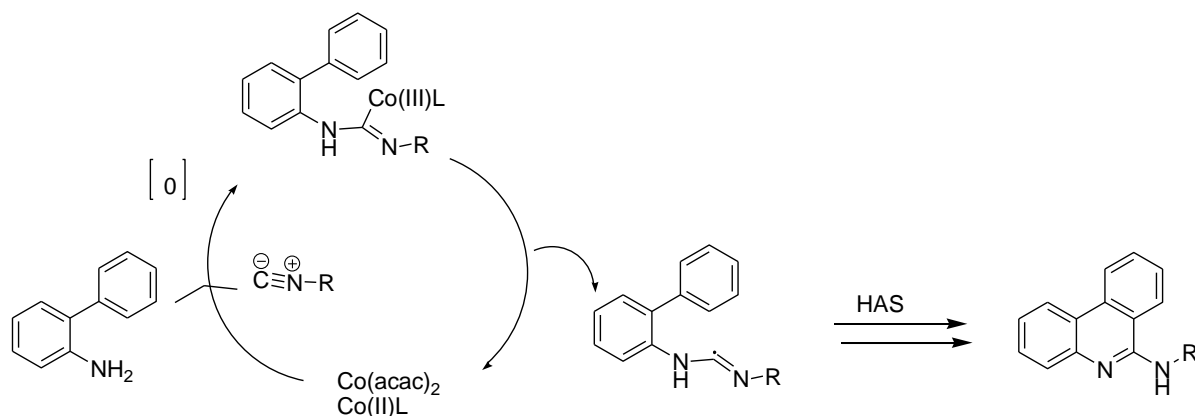


BPO = benzoyl peroxide
DMEDA = N,N'-dimethyl ethylene diamine

Scheme 1.19: Formation of phenanthridines by isocyanobiaryl insertion.

HAS mechanism is believed to also prevail in the work of Zhu and co-workers⁷⁷ which was published almost simultaneously as the above. In contrast to the inert conditions and metal-free catalytic system employed by the latter, the former efficiently achieved the formation with oxygen as the oxidant and provided a new approach to synthesis of phenanthridine

derivatives by utilizing readily available 2-aryl anilines with isocyanides. Notable observation is the effect of a cobalt-catalysed system to facilitate an alternative use of isocyanides instead of 2-isocyanobiaryl with different radical precursors (Scheme 1.20).



Scheme 1.20: Mechanism for the formation of Phenanthridines by isocyanide insertion

1.10 Summary, perspectives and conclusion

The chemistry of chelating *N*-heterocyclic carbene ligands and their complexes with late transition metals: cobalt and nickel has been reviewed. The basic interest is in understanding of the chemistry behind their high sigma donating ability, tunability and greater stability associated with metal complexes with such ligands in homogeneous catalysis.

Various synthetic routes used for the formation of the complexes, ranging from simple deprotonation of the azolium proton of the NHC salt precursors by simple bases to transmetalation of Ag-NHC complexes of the desired ligand and direct metalation with metal acetates, alkoxides or transition metal bis-(trimethylsilyl) amides has been presented. Choice of base for deprotonation is important and best result is obtained with butyl lithium or alkali metal bistrimethylsilazides. Harsh bases like *t*-BuOK and *t*-BuONa have been reported to in some cases attack other acidic protons on the ligand precursor thereby given rise to unidentifiable products. Where the geometry of the complex is important in directing catalytic activity, transmetalation via initial Ag-NHC complex is best suited for obtaining *cis*-geometry round the metal centre.

Most of these complexes of Ni and Co are paramagnetic, such that obtaining resolved NMR spectra is in most cases difficult. The poor solubility in most solvents exhibited by the

complexes and/or longer relaxation times gave rise to poor or broad NMR spectra. Solid state structures of the complexes usually gave distorted geometrical structures of the chelating ligand around metal centres. This greatly influences stability of the complexes towards decomposition in catalytic reactions and on the other hand, hemi-labile ligands allow the creation of a vacant coordination site for the oxidative addition of the substrate within the catalytic cycle.

Structural versatility, ease of functionalization, chirality, water solubility and chelating effect of the NHC ligands have made them not only viable substitutes but better alternatives to phosphines. The wide use of the ligands on their own, complexed with transition metals or in *in situ* generated catalyst systems has been documented in many applications of homogeneous catalysis. But despite all the excellent catalytic advantages, to the best of our knowledge there is no reported case where chelating ‘pincer’ and functionalized NHC have been used as catalysts in *N*-arylation of aniline with aryl halides. It is expected that since Ni(0)NHC catalyzed *N*-mono arylation of aryl diamine with aryl halides is facile at 65 °C in THF,^{62b} similar or better results could be obtained by using the excellent tuneable property of the NHC ligand in their pincer or functionalized NHC-Metal complexes, or *in situ* generated catalyst system with cobalt or nickel to achieve *N*-arylation of aniline with a wide range of aryl chlorides or iodides under milder conditions and low catalyst loading.

We believe that with the trend in making catalyst systems based on environmentally benign metals like cobalt or nickel, much use and opportunities are still yet to be explored with chelating NHC complexes of such metals.

1.11 Aims of this project

The main aims of this work include the synthesis of novel chelating and functionalized *N*-heterocyclic carbene complexes of cobalt and nickel and an investigation of their catalytic abilities. The ligands were designed with the aim of combining structural features that could lend advantages in catalysis. These include abilities of chelation, tunability and hemilability.

In summary, the aims of this project include:

- Synthesis of NHC ligands with pyridine backbone and *N*-substituted imidazole as the source of carbene and fully characterise the new ligands and complexes.

-Exploration of the potential for steric and electronic tunability property of the NHC ligands for supporting organic catalysis in amination reactions.

-Investigation of the possible hemilability of the substituted functionalized NHC ligands in metal complexes which is useful during catalysis of organic substrate.

-Whenever possible, to incorporate and explore advantages of green chemistry.

1.12 References

1. Wanzlick, H. W.; Schönherr, H. J., *Angew. Chem.* **1968**, *80* (4), 154-154.
2. Öfele, K., *J. Organomet. Chem.* **1968**, *12* (3), 42-P43.
3. Arduengo, A. J.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1991**, *113* (1), 361-363.
4. (a) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G., *Angew. Chem. Int. Ed.* **2005**, *44* (11), 1700-1703; (b) Herrmann, W. A.; Köcher, C., *Angew. Chem. Int. Ed. Eng.* **1997**, *36* (20), 2162-2187; (c) Alder, R. W.; Butts, C. P.; Orpen, A. G., *J. Am. Chem. Soc.* **1998**, *120* (44), 11526-11527; (d) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadiou, B.; Bertrand, G., *Angew. Chem. Int. Ed.* **2005**, *44* (35), 5705-5709; (e) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadiou, B.; Schoeller, W. W.; Bertrand, G., *J. Am. Chem. Soc.* **2004**, *126* (28), 8670-8671.
5. Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002**, *41* (8), 1290-1309.
6. Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R., *Organometallics* **1997**, *16* (4), 682-688.
7. Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P., *Organometallics* **1999**, *18* (12), 2370-2375.
8. Fischer, E. O.; Maasböl, A., *Angew. Chem.* **1964**, *76* (14), 645-645.
9. (a) Merce, L.; Albrecht, M., *Chem. Soc. Rev.* **2010**, *39* (6), 1903-1912; (b) Dí z-González, S.; Marion, N.; Nolan, S. P., *Chem. Rev.* **2009**, *109* (8), 3612-3676.
10. Pugh, D.; Danopoulos, A. A., *Coord. Chem. Rev.* **2007**, *251* (5-6), 610-641.
11. David Morales-Morales; Jensen, C. G. M., *The Chemistry of Pincer Compounds*. Elsevier: Amsterdam, 2007.
12. del Rí o, I.; Robert A. Gossage, R. A.; Lutz, M.; Spek, A. L. a.; van Koten, G., *Inorg. Chim. Acta* **1999**, *287*, 113-116.
13. (a) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H., *Organometallics* **2002**, *21* (17), 3596-3604; (b) Chianese, A. R.; Mo, A.; Datta, D., *Organometallics* **2008**, *28* (2), 465-472.
14. (a) Stephan Gru ndemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W. a.; Crabtree, R. H., *Organometallics* **2001**, *20*, 5485-5488; (b) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B., *Dalton Trans.* **2003**, (5), 1009-1015.
15. Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*. Yale University, N. H., Connecticut, Ed. John Wiley & Sons, Inc.: Hoboken, New Jersey., 2005; pp 1-552.
16. Cheng, Y.; Goon, S.; Meth-Cohn, O., *Chem. Commun.* **1996**, (11), 1395- 1396.

17. Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G., *Chem. Eur. J.* **2000**, *6* (10), 1773-1780.
18. (a) Arnold, P. L.; Mungur, S. A.; Blake, A. J.; Wilson, C., *Angew. Chem. Int. Ed.* **2003**, *42* (48), 5981-5984; (b) Arduengo, A. J.; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J., *J. Am. Chem. Soc.* **1994**, *116* (17), 7927-7928.
19. Crudden, C. M.; Allen, D. P., *Coord. Chem. Rev.* **2004**, *248*, 2247- 2273.
20. (a) Chen, J. C. C.; Lin, I. J. B., *Organometallics* **2000**, *19* (24), 5113-5121; (b) McGuinness, D. S.; Cavell, K. J., *Organometallics* **2000**, *19* (5), 741-748.
21. Wang, X.; Liu, S.; Jin, G.-X., *Organometallics* **2004**, *23* (25), 6002-6007.
22. Andreas A. Danopoulos; Nikolaos Tsoureas; Stuart A. Macgregor; Smith, C., *Organometallics* **2007**, *26*, 253-263.
23. (a) del Río, I.; Robert A. Gossage, R. A.; Lutz, M.; Spek, A. L. a.; van Koten, G., *Inorg. Chim. Acta* **1999**, *287*, 113-116; (b) Chuchuryukin, A. V.; Huang, R.; Lutz, M.; Chadwick, J. C.; Spek, A. L.; van Koten, G., *Organometallics* **2011**, *30* (10), 2819-2830.
24. Serra, D.; Cao, P.; Cabrera, J.; Padilla, R.; Rominger, F.; Limbach, M., *Organometallics* **2011**, *30* (7), 1885-1895.
25. Helgert, T. R.; Hollis, T. K.; Valente, E. J., *Organometallics* **2012**, *31* (8), 3002-3009.
26. (a) Inamoto, K.; Kuroda, J.-i.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T., *Organometallics* **2006**, *25* (12), 3095-3098; (b) Inamoto, K.; Kuroda, J.-i.; Kwon, E.; Hiroya, K.; Doi, T., *J. Organomet. Chem.* **2009**, *694* (3), 389-396.
27. Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H., *Chem. Commun.* **2001**, (2), 201-202.
28. (a) Bala, M. D.; Huang, J.; Zhang, H.; Qian, Y.; Sun, J.; Liang, C., *J. Organomet. Chem.* **2002**, *647*, 105-113; (b) Corberán, R.; Sanaú, M.; Peris, E., *Organometallics* **2007**, *26* (14), 3492-3498.
29. Ferreira, C. L.; Ewart, C. B.; Barta, C. A.; Little, S.; Yardley, V.; Martins, C.; Polishchuk, E.; Smith, P. J.; Moss, J. R.; Merkel, M.; Adam, M. J.; Orvig, C., *Inorg. Chem.* **2006**, *45* (20), 8414-8422.
30. Forgie, J. C.; El Khakani, S.; MacNeil, D. D.; Rochefort, D., *P C C P.* **2013**, *15* (20), 7713-7721.
31. Willner, I.; Katz, E., *Angew. Chem. Int. Ed.* **2000**, *39* (7), 1180-1218.
32. Horvath, U. E. I.; Bentivoglio, G.; Hummel, M.; Schottenberger, H.; Wurst, K.; Nell, M. J.; van Rensburg, C. E. J.; Cronje, S.; Raubenheimer, H. G., *New J. Chem.* **2008**, *32* (3), 533-539.
33. Nazarov, A. A.; Hartinger, C. G.; Arion, V. B.; Giester, G.; Keppler, B. K., *Tetrahedron* **2002**, *58* (42), 8489-8492.
34. (a) Zhao, K.-Q.; Hu, P.; Xu, H.-B., *Surf. Sci.* **2003**, *522*, 105-111.
35. Bantreil, X.; Nolan, S. P., *Nature Protocols/Protocol* **2010**, *6*, 69-77
36. Hintermann, L., *Beilstein Journal of Organic Chemistry* **2007**, *3*, 22.
37. Ikhile, M. I.; Bala, M. D.; Nyamori, V. O. *S. Afr. J. Chem.* **2011**, *64*, 101-104.
38. Leuthäuber, S.; Schwarz, D.; Plenio, H., *Chem. Eur. J.* **2007**, *13* (25), 7195-7203.
39. Gnanamgari, D.; Sauer, L. O. E.; Schley, D. N.; Butler, C.; Incarvito, C. D.; Crabtree, R. H., *Organometallics* **2009**, *28*, 321-325.

40. (a) Health, C. D.o. P. What You Need To Know About 1,4-Dioxane in Well Water. Downloaded on 2012/02/28.
http://www.ct.gov/dph/lib/dph/environmental_health/eoha/pdf/1_4_dioxane.pdf;
(b) Portier, C. J. Toxicological Profile For 1,4-Dioxane. Downloaded on 2012/04/18.
<http://www.atsdr.cdc.gov/toxprofiles/tp187.pdf>.
41. Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J., *Organometallics* **2003**, *22* (9), 1979-1982.
42. Herrmann, W. A.; Köcher, C.; Gooßen, L. J.; Artus, G. R. J., *Chem. Eur.J.* **1996**, *2* (12), 1627-1636.
43. Bala, M. D.; Ikhile, M. I., *J. Mol. Catal. A: Chem.* **2014**, *385* (0), 98-105.
44. (a) Wu, J.; Dai, W.; Farnaby, J. H.; Hazari, N.; Le Roy, J. J.; Mereacre, V.; Murugesu, M.; Powell, A. K.; Takase, M. K., *Dalton Trans.* **2013**, *42* (20), 7404-7413; (b) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E., *Organometallics* **2003**, *23* (2), 166-168; (c) Arduengo, A. J., *Acc. Chem. Res.* **1999**, *32* (11), 913-921.
45. Zhang, D.; Zhou, S.; Li, Z.; Wang, Q.; Weng, L., *Dalton Trans.* **2013**, *42* (33), 12020-12030.
46. (a) Berding, J.; Lutz, M.; Spek, A. L.; Bouwman, E., *Organometallics* **2009**, *28* (6), 1845-1854; (b) Jothibasur, R.; Huang, K.-W.; Huynh, H. V., *Organometallics* **2010**, *29* (17), 3746-3752.
47. (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J., *Angew. Chem. Int. Ed. Eng.* **1995**, *34* (21), 2371-2374; (b) Herrmann, W. A.; Fischer, J.; Elison, M.; Köcher, C.; Artus, G. R. J., *Chem. Eur. J.* **1996**, *2*, 772; (c) Huynh, H. V.; Ho, J. H. H.; Neo, T. C.; Koh, L. L., *J. Organomet. Chem.* **2005**, *690* (16), 3854-3860.
48. Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P., *J. Am. Chem. Soc.* **2004**, *126* (16), 5046-5047.
49. Wang, H. M. J.; Lin, I. J. B., *Organometallics* **1998**, *17* (5), 972-975.
50. (a) Liu, S.-T.; Hsieh, T.-Y.; Lee, G.-H.; Peng, S.-M., *Organometallics* **1998**, *17* (6), 993-995; (b) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T., *Organometallics* **1999**, *18* (11), 2145-2154.
51. Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F., *Organometallics* **1993**, *12* (9), 3405-3409.
52. Garrison, J. C. a.; Youngs, W. J., *Chem. Rev.* **2005**, *105*, 3978-4008.
53. Lin, I. J. B.; Vasam, C. S., *Comments Inorg. Chem.* **2004**, *25* (3-4), 75-129.
54. (a) Llewellyn, S. A.; Green, M. L. H.; Cowley, A. R., *Dalton Trans.* **2006**, (34), 4164-4168; (b) Fooladi, E.; Dalhus, B.; Tilset, M., *Dalton Trans.* **2004**, (22), 3909-3917; (c) Simms, R. W.; Drewitt, M. J.; Baird, M. C., *Organometallics* **2002**, *21* (14), 2958-2963.
55. Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S., *Organometallics* **2004**, *23* (21), 4807-4810.
56. Mizoguchi, T. J.; Kuzelka, J.; Spingler, B.; DuBois, J. L.; Davydov, R. M.; Hedman, B.; Hodgson, K. O.; Lippard, S. J., *Inorg. Chem.* **2001**, *40* (18), 4662-4673.
57. Thagfi, J. A.; Lavoie, G. G., *Organometallics* **2012**, *31* (21), 7351-7358.
58. Bain, G. A.; Berry, J. F., *J. Chem. Educ.* **2008**, *85* (4), 532.
59. Bin Liu; Qin Qin Xia; Chen, W., *Angew. Chem.* **2009**, *121*, 5621-5624.
60. Zhang, Y.; Ngeow, K. C.; Ying, J. Y., *Org. Lett.* **2007**, *9* (18), 3495-3498.
61. Duong, H. A.; Cross, M. J.; Louie, J., *J. Am. Chem. Soc.* **2004**, *126* (37), 11438-11439.

62. (a) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y., *Org Lett.* **2003**, *5* (13), 2311-2314; (b) Kuhl, S.; Fort, Y.; Schneider, R., *J. Organomet.Chem.* **2005**, *690* (24–25), 6169-6177; (c) Brenner, E.; Schneider, R.; Fort, Y., *Tetrahedron* **2002**, *58* (34), 6913-6924; (d) Gradel, B. t.; Brenner, E.; Schneider, R.; Fort, Y., *Tetrahedron Lett.* **2001**, *42* (33), 5689-5692; (e) Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K., *J. Org. Chem.* **2007**, *72* (14), 5069-5076.
63. Buchowicz, W.; Koziół, A.; Jerzykiewicz, L. B.; Lis, T.; Pasynekiewicz, S.; Pęcherzewska, A.; Pietrzykowski, A., *J.Mol. Catal. A: Chem.* **2006**, *257* (1–2), 118-123.
64. Zhou, Y.; Xi, Z.; Chen, W.; Wang, D., *Organometallics* **2008**, *27* (22), 5911-5920.
65. Benítez Junquera, L.; Puerta, M. C.; Valerga, P., *Organometallics* **2012**, *31* (6), 2175-2183.
66. (a) Song, H.; Fan, D.; Liu, Y.; Hou, G.; Zi, G., *J. Organomet. Chem.* **2013**, *729* (0), 40-45; (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A., *Angew. Chem. Int. Ed.* **2001**, *40* (18), 3387- 3389; (c) Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A., *Angew. Chem. Int. Ed.* **2000**, *39* (9), 1602-1604; (d) Danopoulos, A. A.; Braunstein, P., *Dalton Trans.* **2013**, *42* (20), 7276-7280; (e) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. J., *Organometallics* **2012**, *32* (3), 723-732.
67. (a) Ye, J.; Chen, W.; Wang, D., *Dalton Trans.* **2008**, (30), 4015-4022; (b) Jennifer, A. L.; Robert, H. C., *ChemInform* **2001**, *32* (38).
68. Yu, R. P.; Darmon, J. M.; Milsman, C.; Margulieux, G. W.; Stieber, S. C. E.; DeBeer, S.; Chirik, P. J., *J. Am. Chem. Soc.* **2013**, *135* (35), 13168-13184.
69. (a) Sheldrick, G., *Acta Crystallogr. Sect. A* **1990**, *46* (6), 467-473; (b) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J., *J. Am. Chem. Soc.* **2001**, *123* (17), 4029-4040.
70. Patil, N. M.; Kelkar, A. A.; Nabi, Z.; Chaudhari, R. V., *Chem. Commun.* **2003**, *0* (19), 2460-2461.
71. Chen, J.; Yuan, T.; Hao, W.; Cai, M., *Tetrahedron Lett.* **2011**, *52* (29), 3710-3713.
72. (a) Gossage, R.; Koten, G., In *Activation of Unreactive Bonds and Organic Synthesis*, Murai, S.; Alper, H.; Gossage, R. A.; Grushin, V. V.; Hidai, M.; Ito, Y.; Jones, W. D.; Kakiuchi, F.; Koten, G.; Lin, Y. S.; Mizobe, Y.; Murai, S.; Murakami, M.; Richmond, T. G.; Sen, A.; Suginome, M.; Yamamoto, A., Eds. Springer Berlin Heidelberg: 1999; Vol. 3, pp 1-8; (b) Fu, G. C., *Acc.Chem. Res.* **2008**, *41* (11), 1555- 1564.
73. Quan, Z.-J.; Xia, H.-D.; Zhang, Z.; Da, Y.-X.; Wang, X.-C., *Appl. Organomet. Chem.* **2014**, *28* (2), 81-85.
74. (a) Abdel-Halim, O. B.; Morikawa, T.; Ando, S.; Matsuda, H.; Yoshikawa, M., *J.Nat. Prod.* **2004**, *67* (7), 1119-1124; (b) Sripada, L.; Teske, J. A.; Deiters, A., *Organic & Biomolecular Chemistry* **2008**, *6* (2), 263-265; (c) Park, G. Y.; Wilson, J. J.; Song, Y.; Lippard, S. J., *Proceedings of the National Academy of Sciences* **2012**, *109* (30), 11987-11992.
75. Xia, Z.; Huang, J.; He, Y.; Zhao, J.; Lei, J.; Zhu, Q., *Org. Lett.* **2014**, *16* (9), 2546-2549.
76. Studer, A.; Curran, D. P., *Angew.Chem. Int. Ed.* **2011**, *50* (22), 5018-5022.
77. Zhu, T.-H.; Wang, S.-Y.; Tao, Y.-Q.; Wei, T.-Q.; Ji, S.-J., *Org. Lett.* **2014**, *16* (4),1260-1263.

Chapter two

Improved methods for the synthesis and isolation of imidazolium based ionic salts¹

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Abstract

Solvent-free reactions were used for the synthesis of a series of imidazolium-based ionic salts: 3,3'-[pyridine-2,6-diylbis(methylene)]bis(1-R-1*H*-imidazol-3-ium)chloride; (R=methyl, ethyl, butyl, isobutyl, hexyl, and benzyl). A simple and effective filtration process was used to isolate all the products in high purity and with yields >93% within a 24 h period. The highly pure ionic compounds which are precursors to *N*-heterocyclic carbene ligands used in catalysis were fully characterized as gray-white hygroscopic salts.

Keywords:

Green chemistry, Silica gel filtration, Ionic salt, *N*-Heterocyclic carbene

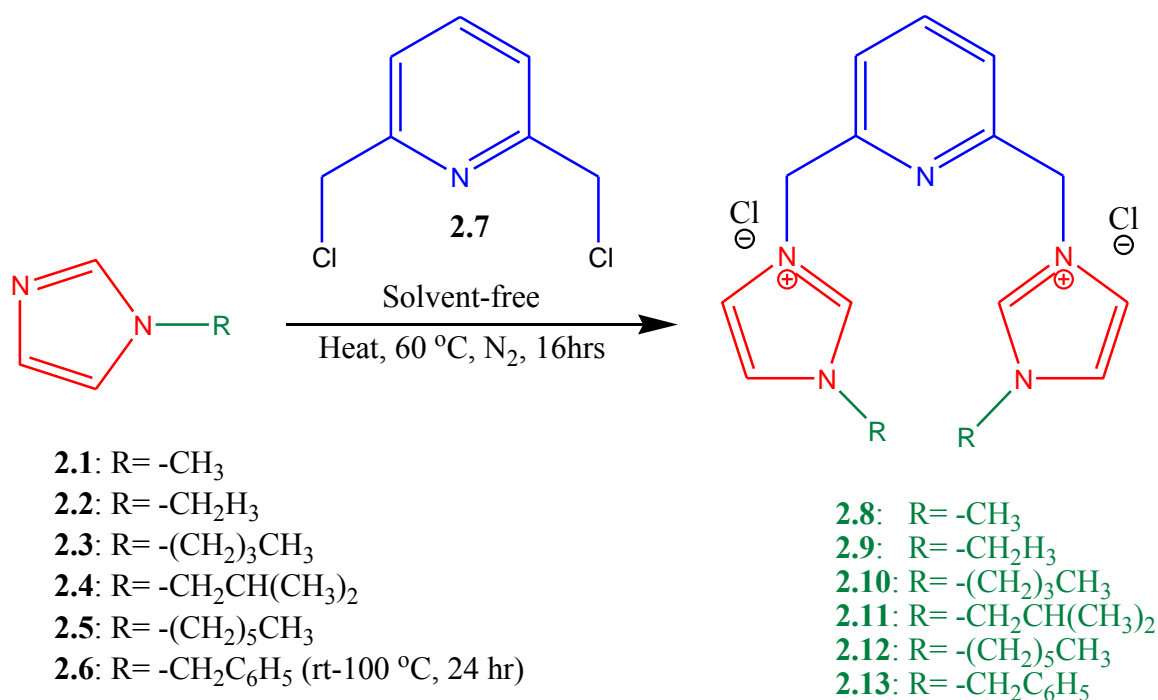
The isolation of the first stable carbene by Arduengo¹ paved the way to the use of ionic imidazolium salts as cheap and affordable sources of *N*-heterocyclic carbene (NHC) ligands, and when appropriately constituted, they also serve as convenient sources of ionic liquid (IL) solvents. On the one hand, the detailed spectroscopic and structural studies of NHC ligands supported by their excellent coordinating ability² have made them credible alternatives to phosphines in organometallic chemistry and catalysis³ while on the other hand, the unique physical and chemical properties of IL solvents, which include low melting points (usually below 100 °C) accompanied by high thermal stability, wide electrochemical windows, negligible vapour pressures, high viscosity, non-volatility and non-flammability distinguish them from traditional organic solvents.⁴ In metal-free catalysis,⁵ imidazolium salts have created a niche as highly effective catalysts and initiators in the synthesis of quinoxaline derivatives⁶ and in the hydrogenation of ketones to alcohols,⁷ while they also effect C-

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metalation of nicotinamide groups on hydride ion uptake.⁸ In addition, they exhibit biological and antimicrobial activities.⁹ More importantly, when coupled to metal ions, their complexes have found use as catalysts in a wide range of applications such as C–S coupling,¹⁰ hydrovinylation,¹¹ olefin metathesis,¹² hydrogenation of ketones to alcohols,¹³ oxidation of alcohols to ketones,¹⁴ hydrosilation of amides to amines and nitriles,¹⁵ and in Heck reactions.¹⁶ This wide diversity of features which includes their ability to be functionalized, immobilized, made hydrophilic, chiral, or chelating has influenced their applications and those of the metal complexes generated from them.¹⁷ Of particular interest to catalysis is the pincer form of the NHC ligand characterized by multiple binding to metal centres and the ability to stabilize various stages of active species in a catalytic cycle. In this study, various pincer imidazolium salts with potential to serve as sources of pincer NHC ligands are reported. The novelty of our study is not in the nature of the salts (a few variants of which are known), but in the simple and effective technique used for their synthesis and isolation in excellent yields. We report herein a simple and quick throughput technique for the isolation of high purity NHC precursors that will be, we suggest, universally applicable to a wide variety of salt formulations.

Typically, the synthesis of pincer CNC ligands (Scheme 2.1) has been achieved through the use of organic solvents such as *N*-methyl-2-pyrrolidone, 1,4-dioxane or tetrahydrofuran (THF),¹¹ which are highly detrimental to the environment. In addition, it has been well established¹⁸ that with such synthetic routes the reactions progress rather slowly, often over several days and at high temperatures. There is also the potential for side reactions that often result in diminished yields and contaminated products requiring even more post-reaction treatment for their purification. The common practice still employed by many researchers today for the synthesis of NHC ligand salt precursors is the quaternization (functionalization) of an imidazole *N*-position with suitable alkyl/aryl halides in an appropriate solvent; usually an aprotic solvent. A reaction conducted by this route usually takes several days and only proceeds under high temperatures (solvent reflux). Examples include reports by Nielsen,¹⁶ Serra¹¹ and Crabtree.¹⁸ Essentially, there are two main issues that we addressed:

- i. Using a high yielding and efficient synthetic procedure as an improvement over currently available methods.
- ii. Developing a simple, non-complicated means of isolating the products in pure form.



Scheme 2.1: Synthetic route to compounds 2.8–2.13.

In this Letter, we have addressed the points raised above by using a solvent-free technique for the synthesis of several pincer NHC salts and utilizing the acidic nature of silica to temporarily adsorb the salts **2.8–2.13**, thereby resulting in a simple but effective purification protocol. The method allows for the synthesis (and high isolated yields) of NHC ligand precursor salts with a chelating CNC donor architecture built around a lutidine backbone. It must be noted at this stage that ours is not the first attempt at utilizing solvent-free techniques for the synthesis of ionic liquids and salts. In fact, Youngs and co-workers¹⁹ have applied this method to obtain pincer NHC ligands, which were later complexed to silver and transmetalated to rhodium and palladium. However, our approach is a significant improvement over previously reported methods in terms of quick throughput, isolated yields, and the purity of products. The major point of divergence is that most previous methods eventually relied on slow precipitation of the final product from an organic solvent which can often take days to achieve; an example is acetone over 48 h in Youngs' method. This methodology leads to lower yields as compared to the modified strategy we have developed which reduced significantly the total reaction time to just 16–24 h. Table 2.1 shows a comparison with reported procedures, where compounds **2.9**, **2.11**, **2.12**, and **2.13** have not been previously reported.

Table 2.1: Comparison of isolated yields for compounds 2.8—2.13

Compound	Our work		Other studies for comparison	
	Conditions	Yield (%)	Conditions	Yield (%)
2.8	SF	95	RD ¹¹	85
2.9	SF	94	NC	-
2.10	SF	94	SFY ¹⁹	85
2.11	SF	94	NC	-
2.12	SF	80 ^a	NC	-
2.13	SF	94	NC	-

NC = New compound, not previously reported.

RD = 1,4-dioxane as solvent; 100 °C, 12 h, precipitated from MeOH/Et₂O, 0 – 5 days.

SF = Solvent-free, 60 °C, 16 h, purified via trapping with silica, obtained as MeOH eluent.

SFY = Solvent-free, 60 °C, precipitated from acetone, 2 d.

^a Reactants **2.5** & **2.7** are in a 3:1 mole ratio.

The starting materials, *N*-substituted imidazoles **2.1–2.5** were synthesized at room temperature by adaptation of the method of Starikova *et al.*,²⁰ while benzyl imidazole **2.6** was synthesized by a modification of the method of Corberán *et al.*²¹ In the synthesis of the imidazolium pincer compound, all the salts were isolated within 24 h as pure, hygroscopic materials. The pure ionic salts were characterized by NMR, IR, and high resolution MS. As the salts are highly hygroscopic and quickly absorbed varying amounts of water, it was impossible to obtain consistent CHN analysis data, but the neat NMR spectra and HRMS analyses confirmed isolation of high purity compounds.

The reactants [*N*-substituted imidazoles **2.1–2.6** and 2,6-bis(chloromethyl) pyridine (**2.7**), in 2:1 mole ratio] were mixed neat at room temperature.²² With gentle stirring, the reaction flask was gradually brought to 60 °C over about 20 min, and by this time the contents of the reaction flask had melted to a colourless liquid which was kept at the same temperature for a further 16 h. With the exception of **2.13**, a change in color from colorless to gray or the formation of a very viscous crude product indicated completion of the reaction. In the synthesis of **2.13** however, progress and reaction completion was observed as a gradual change in color from light yellow to gray. It is important at this stage to emphasize that if not for the continued sublimation of **2.7**, up to 100% conversion and yield was possible via this method. This could have meant no further purification was necessary, but as shown in Table 2.1 yield of 95% was the highest isolated in this study. After analysis of the crude product

using thin-layer chromatography (TLC) with 100% ethyl acetate as the mobile phase, we observed the unreacted *N*-substituted imidazole **2.1–2.6** with R_f values that varied from 0.48 to 0.75, while traces of unreacted **2.7** moved with the solvent front. Most importantly, the salt products **2.8–2.13** were immobilized onto the TLC plate and only became mobile (R_f value = 0.20) when the solvent system was switched to 100% methanol. Based on this observation, we attempted separating the residual unreacted starting materials from the product by direct extraction with the ethyl acetate, but realized that some of the salt products were also extracted along with the starting materials, which led to diminished isolated yields. Hence we used a short plug (about 3 cm thick) of silica in a glass column to temporarily immobilize the product, thereby enabling removal of unreacted starting materials with ethyl acetate. We believe the basic salts were immobilized on to the acidic silica via the imidazolium nitrogen in products **2.8–2.13** and depending on the solvent system, the temporary immobilization can be weakened and eventually the salts were obtained in pure form as methanol eluents. Essentially this is a quick throughput column filtration system based on solvents that are environmentally friendlier than in any system used prior to this. The salts so obtained needed no further purification (confirmed by NMR) before further applications such as use as an IL or as a source of an NHC ligand. However when required, recrystallization from a dichloromethane/hexane mixed solvent system yielded hygroscopic crystals of **2.8–2.13**. After several attempts at adopting published methods, it is worth noting that this new isolation method is now standard in our laboratories and has been adapted to the synthesis of a wide variety of substituted imidazolium salts, including those based on the triazole moiety, with appreciable success.

Characteristic signals of the imidazolium salts were observed in the NMR spectra of the salts,^{2b,21} within the ranges 9–9.9 and 153–160 ppm for ^1H and ^{13}C NMR data, respectively. The downfield singlet in the ^1H NMR and the far downfield imidazolium NCHN (C2) carbon peaks suggest formation of the salts. The ATR-FTIR spectra identified all the expected functional groups, that is, aryl C=C, C-N and C-H sp^3 stretching vibrations,²¹ while further analysis by high-resolution MS confirmed formation of the salts in pure form. The HRMS (TOF-MS ES^+) of all the salts exhibited peaks due to the molecular ion with the loss of one chloride ion. The found values are all within the acceptable limits (0.003 m/z units) of the calculated values of the parent-derived ion peak. All the solid salts showed narrow melting point ranges within expected limits of their molecular composition and were comparable to related published data.

Salt **2.8** was obtained as a white hygroscopic powder, while **2.9**, **2.10**, **2.11**, and **2.13** were hygroscopic gray-white solids and **2.12** was a colorless, hygroscopic, jelly-like substance. With the exception of **2.12**, all the other salts were obtained in excellent yields higher than 92%. The lower yield of **2.12** could be associated with the flexibility of the longer alkyl side chain, which reduced the rate of coupling of the *N*-imidazole **2.5** with 2,6-bis(chloromethyl)pyridine (**2.7**). Many attempts at the synthesis of **2.12** based on the default molar ratio and conditions used for the other salts resulted in low yields being recorded, but when the ratio of **2.5** was trebled, the yield almost doubled to 80%.

In conclusion, we have developed a generic strategy applicable to the synthesis of a wide variety of imidazolium-based ionic salts in a safe and controlled manner that is easy to adapt.²² The method is high yielding and environmentally benign because it is based on a solvent-free technique. The acidity of silica gel was employed for trapping the salts and aiding their isolation in high purity within reasonable time frames. The method reported here significantly reduces the reaction time, decreases the severity of the reaction conditions, eliminates the use of eco-unfriendly solvents and makes viable the preparation of ionic salts in a rapid and reproducible manner. The synthetic route is not only suitable for the aryl and alkyl substituted compounds reported herein, but is robust enough to tolerate a wide variety of functional groups and is important because the system improves on all the limitations highlighted in previously employed strategies for the synthesis of, especially, pincer NHC ligand precursors.

2.1 Acknowledgements

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2.2 Supplementary data

Supplementary data (experimental procedures and spectroscopic characterization) associated with this article can be found, in the online version, at:

<http://dx.doi.org/10.1016/j.tetlet.2014.09.116>.

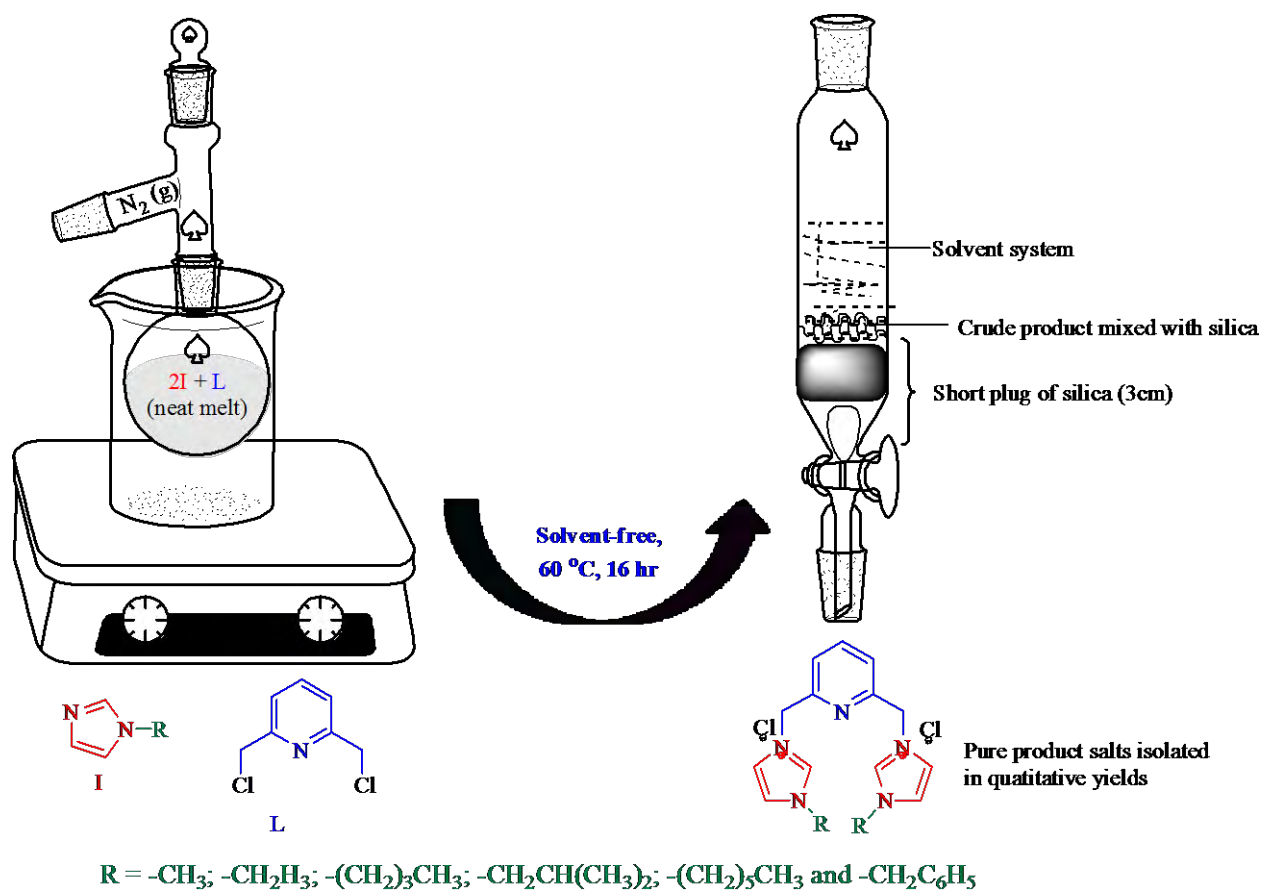
2.3 References and notes

1. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361–363.
2. Syska, H.; Wolfgang, A. H.; Kuhn, F. E. *J. Organomet. Chem.* **2012**, 703, 56–62.
3. Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics*. **1997**, 16, 682–688.
4. Zhao, D. *École Polytechnique Fédérale De Lausanne; EPFL: Lausanne*, **2007**.
5. Di'ez-Gonza'lez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, 109, 3612–3676.
6. Gao, L.; Liu, R.; Yu, C.; Yao, C.; Li, T.; Xiao, Z. *Res. Chem. Intermed.* **2014**, 40, 2131.
7. Ikhile, M. I.; Nyamori, V. O.; Bala, M. D. *Tetrahedron Lett.* **2012**, 53, 4925–4928.
8. McSkimming, A.; Ball, G. E.; Bhadbhade, M. M.; Colbran, S. B. *Inorg. Chem.* **2012**, 51, 2191–2203.
9. Melaiye, A.; Simons, R. S.; Milsted, A.; Pingitore, F.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *J. Med. Chem.* **2004**, 47, 973–977.
10. Zhang, Y.; Ngeow, K. C.; Ying, J. Y. *Org. Lett.* **2007**, 9, 3495–3498.
11. Serra, D.; Cao, P.; Cabrera, J.; Padilla, R.; Rominger, F.; Limbach, M. *Organometallics* **2011**, 30, 1885–1895.
12. Sanford, M. S.; Love, J. A. A.; Grubbs, R. H. *Organometallics* **2001**, 20, 5314–5318.
13. (a) Bala, M. D.; Ikhile, M. I. *J. Mol. Catal. A: Chem.* **2014**, 385, 98–105; (b) Wylie, O. W. N.; Lough, A. J.; Morris, R. H. *Organometallics* **2012**, 31, 2137–2151.
14. Kopylovich, M. N.; Karabach, Y. Y.; Guedes da Silva, M. F. C.; Figiel, P. J.; Lasri, J.; Pombeiro, A. J. L. *Chem. Eur. J.* **2012**, 18, 899–914.
15. Bezier, D.; Venkanna, G. T.; Sortais, J.-B.; Darcel, C. *ChemCatChem*. **2011**, 3, 1747–1750.
16. Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, 327, 116–125.
17. Öfele, K. J. *Organomet. Chem.* **1968**, 12, 42–43.
18. Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, 20, 5485–5488.
19. Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, 22, 1979–1982.
20. Starikova, O. V.; Dolgushin, G. V.; Larina, L. I.; Komarova, T. N.; Lopyrev, V. A. *Arkivoc* **2003**, xiii, 119–124.
21. (a) Corberán, R.; Sanaú, M.; Peris, E. *Organometallics* **2007**, 26, 3492–3498; (b) Imidazole (0.010 mol, 0.680 g) was stirred at room temperature with KOH (0.015 mol) in DMSO (25 ml) for 2 h. Benzyl bromide (Aldrich, 98% assay, 1.436 g cm⁻³, 0.010 mol, 1.2 ml) was then added dropwise at 100 °C and the mixture heated at reflux temperature for 24 h. Chilled distilled H₂O was used to wash and dilute the mixture until neutral. The organic components were extracted with CH₂Cl₂/CHCl₃ (50/50, 6 x 10 ml), dried over anhydrous MgSO₄, and concentrated under reduced pressure to yield orange-brown crude products. Pure *N*-benzyl imidazole (R_f = 0.48 in EtOAc) was obtained as the CH₂Cl₂ (100%) eluent. Yield: yellow viscous oil that dried to give a white solid; 0.948 g, 60%; mp 67–69 °C; δ_H (400 MHz, DMSO-d₆): 5.19 (2H, s, CH₂), 6.96 (1H, s), 7.19 (1H, s), 7.27 (2H, d, *J* = 14.9 Hz), 7.29 (1H, d, *J* = 1.3 Hz), 7.34 (2H, d, *J* = 7.6 Hz), 7.79 ppm (1H, s); δ_C (400 MHz, DMSO-d₆): 49.5, 119.5, 127.4, 127.7, 128.6, 128.7, 137.4, 137.7 ppm; IR (ATR cm⁻¹): 3348 (broad, residual moisture), 3031 (=C-H), 2929 (sp³ C-H), 1672 (C=N), 1454 (aryl C=C), 1075 (C-N medium) and 708 (phenyl moiety); HRMS (TOF MS ES⁺): C₁₀H₁₁N₂⁺ calculated 159.0922, found 159.0925.

22. A typical experimental procedure is described: *N*-substituted imidazole **2.1–2.6** (1 mmol equiv) and 2,6-bis(chloromethyl)pyridine (**2.7**) (0.5 mmol equiv for each compound, mp 73–78 °C; Aldrich) were mixed with gentle stirring under inert conditions in a 50 ml round-bottom flask. The temperature was gently raised to 60 °C giving a molten substance that was allowed to continue stirring for 16 h at 60 °C. The resultant gray or light brown crude solid was allowed to cool to room temperature and loaded onto a short plug of silica gel. Unreacted starting materials were eluted with EtOAc while the product salts were obtained ($R_f = 0.20$) as MeOH (100%) eluents. The solvent was removed under reduced pressure to yield the pure imidazolium salt **2.8–2.13**.

Supplementary data

Graphical Abstract



2.4 EXPERIMENTAL SECTION

2.4.1 General

All reactions except the synthesis of the *N*-substituted imidazole **2.1-2.6** are done under inert conditions (nitrogen atmosphere) using standard Schlenk techniques. Reaction solvent for **2.1-2.6** is DMSO (Aldrich) used as obtained and all glassware were oven dried at 110 °C. While other solvents like dichloromethane, hexane, methanol, ethyl acetate are analytical grade; properly distilled and dried using standard techniques prior to use. Imidazole, 2, 6-dichloro lutidine **2.7**, deuterated solvents and KOH were purchased in reagent grade purity from Aldrich or Fluka and are used as obtained. Infrared spectra were recorded by a PerkinElmer universal ATR Spectrum 100 FT-IR spectrometer. ¹H and ¹³C spectra were recorded on NMR 400 MHz Bruker Ultra shield spectrometer and samples were dissolved in deuterated methanol (CD₃OD) or DMSO-d₆. All chemical shift values (in ppm) are recorded and reported relative to solvent peak in both the ¹H and ¹³C spectra. High resolution mass spectrometry was recorded on Waters Micromass LCT Premier TOF MS (ES+ or ES-).

***N*-benzyl imidazole (2.6).** Imidazole (0.010 mol, 0.680 g) was stirred at room temperature with KOH (0.015 mol) in DMSO (25 ml) for 2 h. Benzyl bromide (Aldrich, 98% assay, 1.436 g cm⁻³, 0.010 mol, and 1.2 ml) was then added drop wise at 100 °C and refluxed for 24 h while maintaining the temperature. Chilled distilled water was used to wash and dilute to neutral and organic component extracted with DCM/CHCl₃ (6 x 10 ml). The organic layer was then dried with anhydrous MgSO₄ and concentrated under vacuum yielding orange-brown crude purified via column chromatography. Pure *N*-benzyl imidazole; (R_f value 0.48 in ethyl acetate) was obtained as DCM (100%) eluent. Yield: yellow viscous oil that dried to give white solid; 0.948 g, 60%; m.p. 67-69 °C (68-70 °C lit); δ_H (400 MHz, DMSO-d₆): 5.19

(2H, s, CH₂), 6.96 (1H, s), 7.19 (1H, s), 7.27 (2H, d, $J = 14.9$ Hz), 7.29 (1H, d, $J = 1.3$), 7.34 (2H, d, $J = 7.6$) and 7.79 ppm (1H; s); δ_c (400 MHz, DMSO-d₆): 49.5, 119.5, 127.4, 127.7, 128.6, 128.7, 137.4 and 137.7 ppm; IR (ATR cm⁻¹): 3348 (broad, residual moisture), 3031 (=C-H), 2929 (SP³ C-H), 1672 (C=N), 1454 (aryl C=C), 1075 (C-N medium) and 708 (phenyl moiety); HRMS (TOF MS ES⁺): C₁₀H₁₁N₂⁺ calculated 159.0922, found 159.0925.

2.4.2 *Bis alkyl imidazolium salts 2.8-2.13*

A generic experimental procedure is described: *N*-substituted imidazoles **2.1-2.6** (1 mmol equivalent) and 2,6-bis(chloromethyl)pyridine **2.7** (0.5 mmol equivalent for each compound, m.p 73-78 °C; ALDRICH) were mixed together under inert condition in a 50ml round bottom flask with gentle stirring. The temperature was then gently raised to 60 °C; giving a molten substance that was allowed to continue stirring for 16 h at 60 °C. The resultant grey or light brown crude solid was allowed to cool to room temperature and loaded onto a short plug of silica. Unreacted starting materials are rinsed-out with ethyl acetate while the salts were obtained (R_f value 0.01) as methanol (100%) eluents. Solvent is then removed under reduced pressure to yield pure imidazolium salts **2.8-2.13**.

For practical purpose; a column (3 cm diameter) is packed with a short plug of silica (about 3 cm high from the tap) using dry hexane. A mixture of the crude salt with dry silica (1:1 ratio) was then loaded into the column so that it lay on the short plug of silica already in the column. The set-up is then eluted first with dry ethyl acetate to remove any starting material (TLC was used to monitor progress). The salt product was then obtained in pure form by elution with dry methanol and concentrated. Recrystallization of the salts was carried out with DCM/hexane. Characterization data are presented below.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-methyl-1*H*-imidazol-3-ium) chloride (2.8).

N-methyl imidazole **2.1** (0.21 g, 2.50 mmol) and 2,6-*bis*(chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH) were used. Yield: grey-white hygroscopic powder; 0.41g, 95%; δ_{H} (400 MHz, MeOD): 4.04 (2x3H, s, CH₃), 5.62 (2x2H_{lutidine}, s, CH₂), 7.58 (2x1H_{lutidine}, d, $J = 7.7$ Hz), 7.69 (2x2H, s, -CH=CH_{imidaz}), 7.92 (1H, t, $J = 7.7$ Hz, CH_{lutidine}) and 9.43 ppm (2x1H, s, N-CH-N_{imidaz}); δ_{C} (400 MHz, MeOD): 36.8 (CH₃), 54.4 (CH₂), 123.8, 124.6, 138.8, 140.4 and 154.9 ppm (NCN); IR (ATR cm⁻¹): 3381 (broad, residual moisture), 2996 (=C-H), 3017(SP³ C-H), 1570 (C=N), 1441 (aryl C=C), 1170 (C-N medium) and 621(aryl). HRMS (TOF MS ES⁺): C₁₅H₁₉ClN₅⁺ calculated 304.1329, found 304.1321. Further analytical data match available literature data.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-ethyl-1*H*-imidazol-3-ium) chloride (2.9).

N-ethyl imidazole **2.2** (0.24 g, 2.50 mmol) and 2,6-*bis*(chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH). Yield: milky-white hygroscopic solid; 0.43 g, 93.5.7%; m.p. 268-270 °C; δ_{H} (400MHz, MeOD): 1.46 (2x3H, t, $J = 7.3$ Hz, CH₃), 4.23 (2x2H, q, $J = 7.2$ Hz, CH₂), 5.47 (2x2H, s, CH₂_{lutidine}), 7.39 (2x1H_{lutidine}, d-d, $J = 7.7$ Hz), 7.60 (2x2H_{imidaz}, s, -CH=CH), 7.79 (1H_{lutidine}, t, $J = 7.7$ Hz) and 9.13 ppm (2x1H_{imidaz}, s, N-CH-N); δ_{C} (400 MHz, MeOD): 15.7 (CH₃), 46.2 (CH₂), 54.7 (CH₂ lutidine), 123.4, 124.4, 140.2, 154.2, 155.4 and 158.8 ppm (NCN); IR (ATR cm⁻¹): 3327 (broad, residual moisture), 3131(-NR-), 3061(SP³ C-H), 1593 (C=N), 1458 (aryl C=C) and 1160 (C-N medium). HRMS (TOF MS ES⁺): C₁₇H₂₃ClN₅⁺ calculated 332.1642, found 332.1645.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-butyl-1*H*-imidazol-3-ium) chloride (2.10).

N-butyl imidazole **2.3** (0.31 g, 2.5 mmol) and 2,6-*bis*(chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH) were mixed together. Yield: whitish-grey highly hygroscopic solid; 0.4986 g, 93.01%; m.p. 219-221 °C (220 °C lit); δ_{H} (400 MHz, MeOD): 1.01 (2x3H, t, $J = 1.3$, CH₃), 1.40 (2x2H, m, CH₂), 1.93 (2x2H, q, $J = 8.2$ Hz), 4.31 (2x2H, t,

$J = 3.5$ Hz), 5.59 (2x2H_{lutidine}, s), 7.55 (2x1H_{lutidine}, d, $J = 6.6$ Hz), 7.68 (2x1H, imidaz –CH=, d, $J = 1.9$ Hz), 7.74 (2x1H imidaz =CH-; $J = 1.9$ Hz), 7.92(1H_{lutidine}, t, $J = 7.9$ Hz) and 9.25ppm (2x1H_{imidaz}, s, N-CH-N); δ_C (400 MHz, DMSO-d₆): 13.2 (CH₃), 18.7 (CH₂), 31.3 (CH₂), 48.5 (CH₂), 52.6 (CH₂ lutidine), 122.1, 123.2, 136.8, 137.9, 138.9 and 153.6 ppm (NCN); IR (ATR cm⁻¹): 3360 (broad, residual moisture), 3060 (-NR-), 2958 (SP³ C-H), 1594 (C=N), 1458 (aryl C=C) and 1159 (C-N medium). HRMS (TOF MS ES⁺) C₂₁H₃₁CIN₅⁺ calculated 388.2268, found 388.2265. Further analytical data match reported literature data.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-isobutyl-1H-imidazol-3-ium) chloride (2.11).

Isobutyl imidazole **2.4** (0.31 g, 2.50 mmol) and 2,6-bis(chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH) were mixed together. Yield: grey-white waxy hygroscopic solid, 0.499 g, 93.6%; m.p. 197-199 °C; δ_H (400 MHz, MeOD): 0.89 (2x3H, d, $J = 6.6$ Hz), 2.11 (2x1H, m,), 4.01 (2x2H, d, $J = 7.3$ Hz), 5.49 (2x2H_{lutidine}, s), 7.41 (2x1H_{lutidine}, d-d, $J = 12.7$ Hz), 7.61(2x2H imidaz , =CH-CH, d, $J = 1.8$ Hz), 7.81 (1H_{lutidine}, t, $J = 7.8$ Hz) and 9.14 ppm (2x1H_{imidaz}, s, N-CH-N); δ_C (400 MHz, MeOD): 19.7 (CH₃), 20.6 (CH), 54.5 (CH₂), 57.8 (CH₂ lutidine), 121.3, 122.6, 123.1, 123.5, 138.9 and 152.5 ppm (NCN); IR (ATR cm⁻¹) 3304 (broad, residual moisture), 3071(-NR₂), 2996 (=C-H), 2874(SP³ C-H), 1594 (C=N), 1452 (aryl C=C) and 1159 (C-N medium). HRMS (TOF MS ES⁺): C₂₁H₃₁CIN₅⁺ calculated 388.2268, found 388.2260.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-hexyl-1H-imidazol-3-ium) chloride (2.12). *N*-

hexyl imidazole **2.5** (0.38 g, 2.50mmol) and 2,6-bis (chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH) were mixed. Yield: colourless jelly salt, 0.325 g, 54%; δ_H (400 MHz, MeOD): 0.82 (2x3H, t, $J = 6.4$ Hz, CH₃), 1.26 (2x3x2H, m), 1.81 (2x2H, q, $J = 13.1$ Hz, CH₂), 4.16 (2x2H, t, $J = 6.2$ Hz, CH₂), 5.47 (2x2H_{lutidine}, s, CH₂), 7.39 (2x1H_{lutidine}, d, $J = 6.0$ Hz), 7.45 (2x2H_{imidaz} s, =CH-CH), 7.80 (1H_{lutidine}, t, $J = 19.5$ Hz), and 9.11 ppm (2x1H_{imidaz}, s, N-CH-N); δ_C (400 MHz, MeOD): 14.3 (CH₃), 23.5 (CH₂), 26.9

(CH₂), 31.1 (CH₂), 32.3 (CH₂), 54.6 (CH₂), 65.7(CH₂), 123.7, 139.7, 153.5, 154.2, 155.0 and 158.8 ppm (NCN); IR (ATR cm⁻¹): 3354 (broad, residual moisture), 3147(-NR-), 2929 (SP³ C-H), 1595 (C=N), 1458 (aryl C=C) and 1093 (C-N medium). HRMS (TOF MS ES⁺): C₂₅H₃₉ClN₅⁺ calculated 444.2894, found 444.2886.

3,3'-(pyridine-2,6-diylbis(methylene))bis(1-benzyl-1*H*-imidazol-3-ium) chloride (2.13).

N-benzyl imidazole imidazole **2.6** (0.39 g, 2.50 mmol) and 2,6-*bis*(chloromethyl)pyridine **2.7** (0.22 g, 1.25 mmol; m.p. 73-78 °C; ALDRICH) were mixed together in an inert condition in a 50ml round bottom flask with gentle stirring. The temperature was slowly raised to 65 °C; yielding a light yellow molten substance which was allowed to continue stirring for a further 16 h at 60 °C. The resultant light brown crude solid was loaded onto the short plug of silica to remove any unreacted starting materials with methanol/ethyl acetate (1:9) while the salt **2.13** was obtained as methanol eluent. The eluent was concentrated under reduced pressure to yield a milky-white hygroscopic solid. Yield: 0.584 g, 94.2%; m.p. 295-297 °C; δ_H (400 MHz, DMSO-d₆): 5.61 (2x2x2H, s, CH₂ benzyl & lutidine), 7.40 (2x3H, m, aryl protons,), 7.52 (2x3H, m, aryl protons, 7.82 (2x2H_{imidaz}, d, *J* = 1.8 Hz, -CH=CH), , 7.94 (1H_{lutidine} , t, *J* = 7.8 Hz) and 9.89 ppm (2x1H_{imidaz}, s, N-CH-N); δ_C (400 MHz, DMSO-d₆): 51.7 (CH₂ benzyl), 52.6 (CH₂ lutidine), 122.1, 122.2, 123.5, 128.1, 128.4, 128.7, 135.1, 137.1, 138.8 and 153.6 ppm (NCHN); IR (ATR cm⁻¹): 3364 (broad, residual moisture), 3051(tertiary amine), 2996 (=C-H), 1559 (C=N), 1456 (aryl C=C), 1025 (C-N medium) and 711 (phenyl). HRMS (TOF MS ES⁺): C₂₇H₂₇ClN₅⁺ calculated 456.1955, found 456.1946.

Chapter three

Air stable pincer (CNC) *N*-heterocyclic carbene-cobalt complexes and their application as catalysts for C-N coupling reactions*

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Abstract

Two new pincer (CNC) NHC-Co complexes: 3,3'-(dimethylimidazolin-2-ylidene)lutidine chlorocobalt(II) hexafluorophosphate, **3.3a** and 3,3'-(dibenzylimidazolin-2-ylidene)lutidine chlorocobalt(II) hexafluorophosphate, **3.3b** were synthesised in good yields via transmetalation of the corresponding Ag-NHC complexes. Spectroscopic analyses (¹H, ¹³C, ³¹P, FT-IR) and analytical techniques (melting point, MS-ES⁺) were used to characterize the complexes. **3.3b** showed distinct paramagnetic properties as observed from its ¹H NMR data. Magnetic measurements indicated it has a susceptibility of 4.12 μ_B, consistent with three unpaired electrons for high spin paramagnetic species. Both complexes showed excellent activity in catalysing the C-N coupling of aryl halides with primary aryl amines to yield desired secondary aryl amines in good to excellent isolated yields.

Keywords

Pincer NHC, Paramagnetic, arylation, C-N coupling, Isolated yield.

3.1 Introduction

Isolation of the first stable carbene¹ paved the way to growing the interest on synthetic and catalytic importance attached to the combination of heterocyclic compounds and pincer architecture.² Although they come in various ligand frame works;³ the excellent thermal stability of pincer NHCs and their profound ability to stabilize metal centres make them credible alternatives to traditional ligands such as phosphines and amines in complexes that are used as catalysts in homogeneous catalysis.⁴ Such pincer NHC-metal complexes activate the formation of a variety of carbon-element bonds of wide synthetic and catalytic importance via mechanisms characterised by conventional two-electron oxidative addition-reductive elimination pathways.⁵ Many reports have been published on pincer phosphines

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and amines in the forms of PNP, CNN and NPN donor atoms.⁶ Although, those containing pincer carbene in the form of CCC or CNC are quite rare,⁷ they do offer greater advantage than N- or P- donors and are more tightly bounded to the metal.^{7a} These unique properties and consequent excellent catalytic activities of pincer carbenes have been reported in books² and a number of reviews,⁸ although most have been in their complexes with exotic metals like palladium, ruthenium platinum, iridium etc. A recent development in the field of homogeneous catalysis is the desire to develop catalytic system based on cheap, earth abundant, affordable and environmentally benign metals like cobalt, nickel and iron; which could still offer high activities in organic transformations comparable to those of platinum group metals.⁹

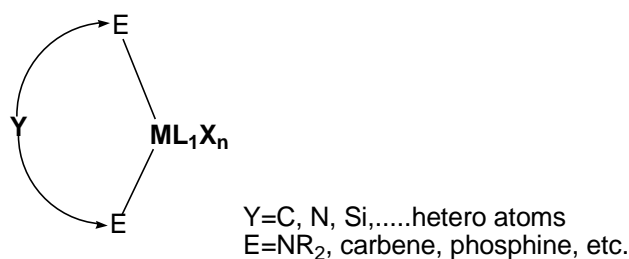
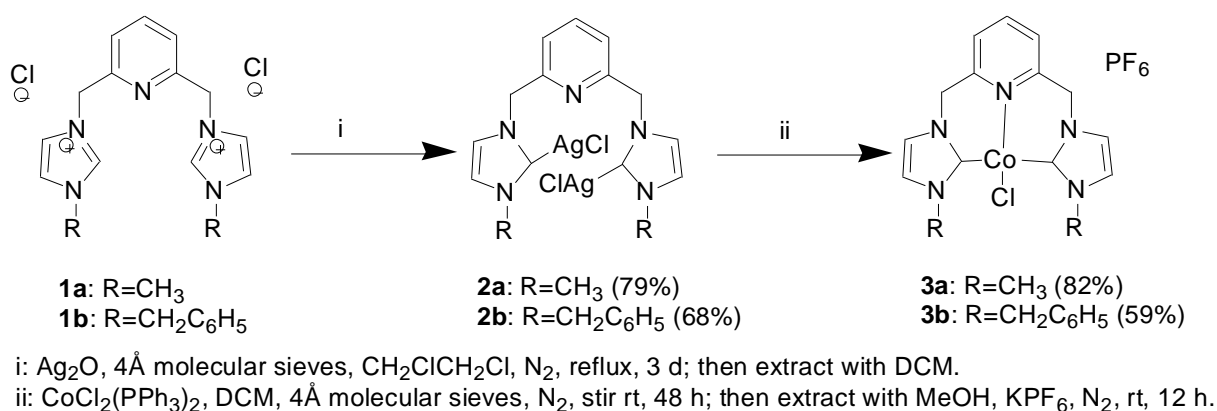


Figure 3.1: Generalized pincer architecture.

In recent time, few Co-NHC complexes with pincer architecture and their catalytic activity studies are reported.¹⁰ Such complexes have proven to be excellent catalysts in novel intra and intermolecular C-H bond activation¹¹ and the polymerization of ethylene.¹² Similarly, NHC complexes containing nickel has proven to activate Heck, Suzuki and Kumada-Tamao-Corriu coupling reactions. In this paper we report the synthesis of two new pincer (CNC) NHC-cobalt complexes; their *mer* or tridentate configuration is aimed at promoting excellent thermal stability and provide a desired steric property in the catalytic application of the complexes. It is known that C-N coupling reactions especially, aryl C-N are very important as they are routes to the synthesis of important organic compounds with biological, industrial and pharmaceutical applications.^{5b, 13} This has prompted the development of many synthetic strategies for the formation of aryl carbon-aryl nitrogen bonds.¹⁴ Typical and pioneering strategies are those developed by Buchwald and Hartwig involving the use of NHC-Pd complexes or palladium(0) catalyst systems^{14a, 15} and copper mediated or copper catalyzed classical Ullman coupling reactions.¹⁶ The latter method proceeded under harsh conditions, long reaction times and required stoichiometric amounts of the copper catalyst.¹⁷ The desire

to go green and to alleviate all the shortcomings of these earlier coupling strategies have prompted chemists to seek alternatives for example using NHC-metal complexes of cheaper and environmentally benign metals like iron,¹⁸ and nickel¹⁹ in activating aryl C-N coupling. Despite the environmentally benign nature of cobalt and its salts and the rapid progress made in its use as catalysts for activating C-C coupling reaction,²⁰ systems containing Co as the central metal in aryl amination catalysis are quite rare,²¹ and to the best of our knowledge those containing pincer NHC-Co complexes have not been reported. Very recent works by Tan and co-worker^{21b} have shown how facile it is to achieve amide nitrogen-aryl carbon bond coupling with simple cobalt oxalate; a strategy so green that it could be done in water. Unfortunately the method couldn't activate direct aryl carbon-aryl nitrogen bond and when possible it was only with expensive aryl iodide. Other similar reported cases involved the use of combinations of CoCl_2 /phosphine to achieve cross coupling²² or $\text{Co}(\text{acac})_2$ /1,10-phenanthroline to achieve intermolecular C-N and C-O coupling in the synthesis of benzimidazoles and benzoxazoles.²³

In this work, we assumed that the combination of steric bulkiness and high thermal stability of the pincer NHC ligand with cheaper and environmentally benign cobalt metal in NHC-metal complexes could offer desirable catalytic advantages in homogeneous catalysis²⁴ and greener alternatives to the use of PGMs. We therefore report the synthesis of two new pincer (CNC) NHC-Co complexes **3.3a** and **3.3b** alongside a preliminary report on their application as catalysts in activating aryl C-N coupling reaction of aryl amines with aryl halides with low catalyst loading of 1 mol%.



Scheme 3.1: Synthesis of pincer (CNC) N-heterocyclic carbene-cobalt complexes 3.3a and 3.3b

3.2 Results and discussion

3.2.1 Synthesis and characterization of NHC-Co complexes

The ligand precursor (**3.1a**: R=Me) was first reported by Hermann *et al.*²⁵ and later by others.^{7a, 26} We recently reported a viable solvent free synthesis of both **3.1a** and **3.1b** alongside other imidazolium salts; incorporating an excellent filtration technique that use silica gel to purify the imidazolium salts as precursors of NHC ligands.²⁷ The procedure alleviated all the limitations associated with purification and isolation of imidazolium salts in previously reported methods.^{26a, 28} Figure 3.2 presents the ortep diagram of 3,3'-(pyridine-2,6-diylbis(methylene))bis(1-methyl-1H-imidazol-3-ium) hexafluorophosphate, **C1a** which is an analogue of imidazolium salt **3.1a** bearing a PF_6^- , which confer the effect of counter ion on the stability of imidazolium salts to air. Hence, stirring the methanol solution of **3.1a** with 2 mole equivalents of KPF_6 , led to anion metathesis of the chloride counter ions to yield air stable pale brown microcrystals of **C1a** as previously reported for similar moisture sensitive imidazolium salts.²⁹ The crystals for **C1a** were obtained by slow diffusion of DCM into methanol solution of the salt (selected bond lengths and angles were presented in Table 3.1).³⁰

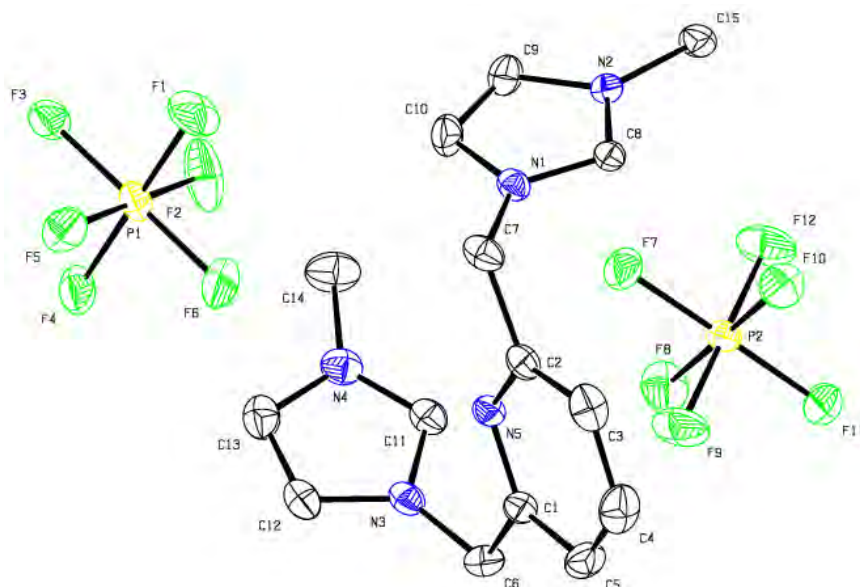


Figure 3.2: Molecular structure of **C1a** with thermal ellipsoids drawn at the 50% probability level with hydrogen atoms omitted for clarity.

Initial attempts to metalate **3.1** via the free carbene route as employed for similar pincer NHC ligands failed.³¹ This could be associated with the relative acidity of the methylene protons on the lutidyl moiety which could be deprotonated in the presence of strong bases leading to decomposition or unidentifiable products.³² Basic metal oxide deprotonation of the imidazolium proton by Ag_2O at room temperature followed by stirring with anhydrous cobalt salts as employed in a similar situation reported by Simons *et al.*;²⁸ resulted in isolation of the ligand precursors as observed with similar complexes based on PtCl_2 .^{26a} We were also able to isolate a metal anion complex 3,3'-(pyridine-2,6-diylbis(methylene))bis(1-benzyl-1H-imidazol-3-ium) tetrachloridocobaltate(II) **C1b** (as presented in Figure 3.3, with selected bond lengths and angles in Table 3.1);³⁰ alongside the ligand precursor **3.1b** while attempting the *in situ* transmetalation of Ag-NHC to Co using anhydrous CoCl_2 ,³³ a situation similar to the isolation of a co-crystal of the ligand and FeCl_4 anion in an effort to metalate bulky imidazolium salts with FeCl_2 via the free carbene route.³⁴

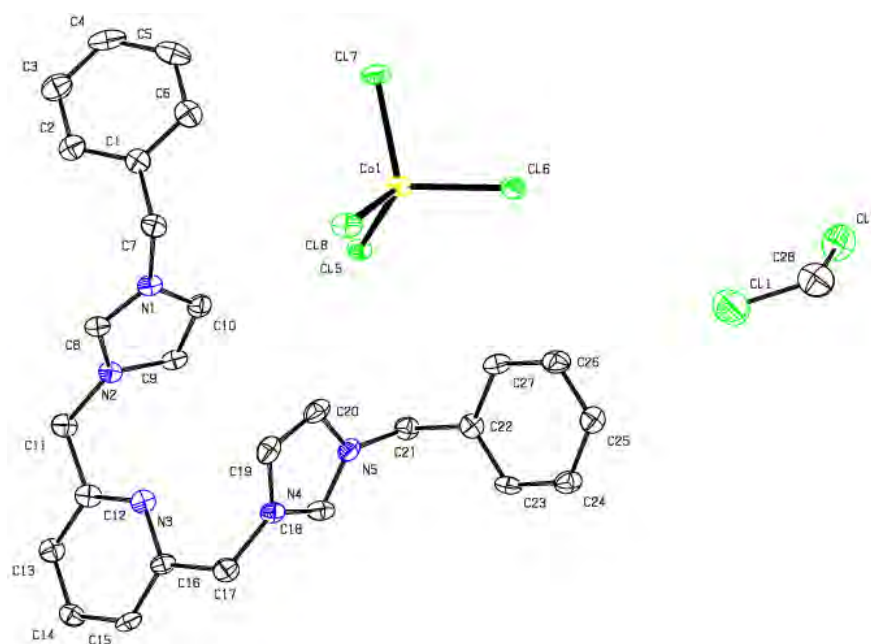


Figure 3.3: Crystal structure of C1b with thermal ellipsoids drawn at the 50% probability level with hydrogen atoms omitted for clarity.

It is assumed that the steric bulk of the imidazolium salts in both cases hindered effective deprotonation of the imidazolium proton by basic Ag_2O .^{32b} Our attempt to also achieve metalation via thermochemical metalation with basic $\text{Co}(\text{OAc})_2$ ³⁵ resulted only in decomposition products due to the high temperatures used and the thermal sensitivity of the lutidyl methylene protons.

Table 3.1: Selected bond lengths (Å) and angles (°) for C1a and C1b

C1a		C1b	
	Bond lengths		Bond lengths
C(1)-N(5)	1.3297(18)	C(9)-C(10)	1.341(9)
C(2)-N(5)	1.3417(18)	C(11)-N(2)	1.459(8)
C(6)-N(3)	1.4573(19)	C(12)-N(3)	1.332(8)
C(7)-N(1)	1.4721(18)	C(16)-N(3)	1.342(8)
C(12)-C(13)	1.347(2)	C(19)-C(20)	1.348(9)
	Bond angles		Bond angles
N(5)-C(1)-C(5)	123.30(14)	N(2)-C(8)-H(8)	125.1
N(3)-C(6)-C(1)	111.06(12)	N(3)-C(12)-C(13)	123.7(6)
N(1)-C(7)-C(2)	112.15(12)	N(4)-C(17)-C(16)	112.1(5)

Eventually, selective metalation^{32b} of the imidazolium C2 carbon with Ag was achieved by thermolytic basic deprotonation of the C2-bond proton with Ag₂O in refluxing 1,2-dichloroethane under an atmosphere of nitrogen and some 4Å molecular sieves; a method that has shown success with similar NHC ligand precursors.^{24, 36} The resulting pincer NHC-Ag complexes (**3.2a** and **3.2b**) were obtained in good yields. They were subsequently transmetalated to cobalt to afford desired pincer NHC-Co complexes **3.3a** and **3.3b** in excellent yields. Because of our previous failed attempts at metalating with Ag at room temperature; the success obtained in this case has confirmed that the reaction is temperature dependant. The added molecular sieves absorbed any trace of moisture associated with the imidazolium salts which might likely hinder the formation of the complexes. Furthermore, as the reaction is partially akin to a condensation reaction; the liberated water (which might reduce the yield by product hydrolysis) was absorbed onto activated 4Å molecular sieves to circumvent any side reactions. We believe that the failure of the previous attempt at metalation via the free-carbene route might be partly due to the solvation of the base by the moisture associated with the imidazolium salts. The refluxing condition also enhanced the absorptive ability of the molecular sieves and increased the rate of the reaction as compared to other reported cases. Solvent plays an important role in chemical reactions by affecting the rate, yield and even the path of the reaction. Some solvents act beyond solvation only but may also act as reagents, reactants or lead to alteration in the molecular structure of the product. The use of solvents like DMSO, dioxane, methanol and DCM has not been successful in our quest to synthesize the chelating Ag-NHC complexes even when the reaction was conducted at reflux temperatures. We do relate this failure to possible

selectivity associated with the pre-ligand and strength of the solvents to promote the reaction. The use of 1,2-dichloroethane as reported by Inamoto²⁴ and Danopoulos³⁶ has both led to the formation of the silver complex and the subsequent metathesis of the counter ion from bromide to chloride in both cases. This property is attributed to the polar nature of the halogenated solvent.

Addition of a mixture of either **3.1a** or **3.1b** and 2 molar equivalents of silver(I)oxide to an oven dried Schlenk flask (cooled under nitrogen) charged with analytically grade 1,2-dichloroethane afforded a mixture which was refluxed for 3 d in the absence of light. At the end of the reaction time; the dark colour of silver oxide has faded and the resulting light yellowish brown or orange suspension was concentrated under reduced pressure. The residue in either case was then extracted with DCM for 1 h, filtered through a bed of celite and concentrated to afford yellowish white microcrystals of **3.2a** (79% yield) and an orange-yellow air sensitive solid of **3.2b** (68% yield). Both Ag-NHC complexes have sharp melting points, 119—122 °C for **3.2a** similar to reported literature,^{7b, 26b} and 70—72 °C for **3.2b**. The absence of a distinct singlet peak of C2-H imidazolium proton at 9.43 and 9.80 ppm in the ¹H NMR spectra of **3.2a** and **3.2b** respectively indicated successful deprotonation and formation of a Ag-NHC bond.³⁷ The far down field signal at 179 ppm and 180 ppm in the ¹³C NMR spectrum of **3.2a** and **3.2b** respectively, which is characteristic of carbene (C2) carbon further confirmed metalation with silver. The slight up-field shift of the methyl proton in **3.2a** from 3.8 to 3.7 ppm and the methylene in the lutidyl moiety from 5.6 in the salt to 5.4 ppm as previously reported for similar NHC-Ag complexes²⁹ was another evidence that the NHC-silver complex was obtained. Contrary to reported cases of similar complexes^{8a, 24, 36} the up-field shift could be attributed to the electron releasing effect due to the electron rich methyl group. While on the other hand the almost coalesced methylene protons in both the lutidyl and benzyl moieties in **3.1b** at 5.59 and 5.57 ppm²⁷ distinctly split up in **3.2b** and shifted slightly up-field to 5.31 and 5.20 ppm respectively. Also, aromatic protons in the lutidyl, imidazolyl and the phenyl moieties have split into multiplet peaks when compared to the distinct signals observed in **3.1b**. In both **3.2a** and **3.2b**; the coupling splitting pattern of all the protons and their integration counts agree to that of the expected target silver-NHC complex. Further characterization of the Ag-NHC complexes **3.2a** and **3.2b** confirmed the structural morphology of the complexes. Both complexes showed similar TOF MS ES⁺ fragmentation patterns with distinct molecular ions [M⁺: M-AgCl], [M⁺: M-2AgCl] and [M⁺: M-2AgCl-R] respectively.

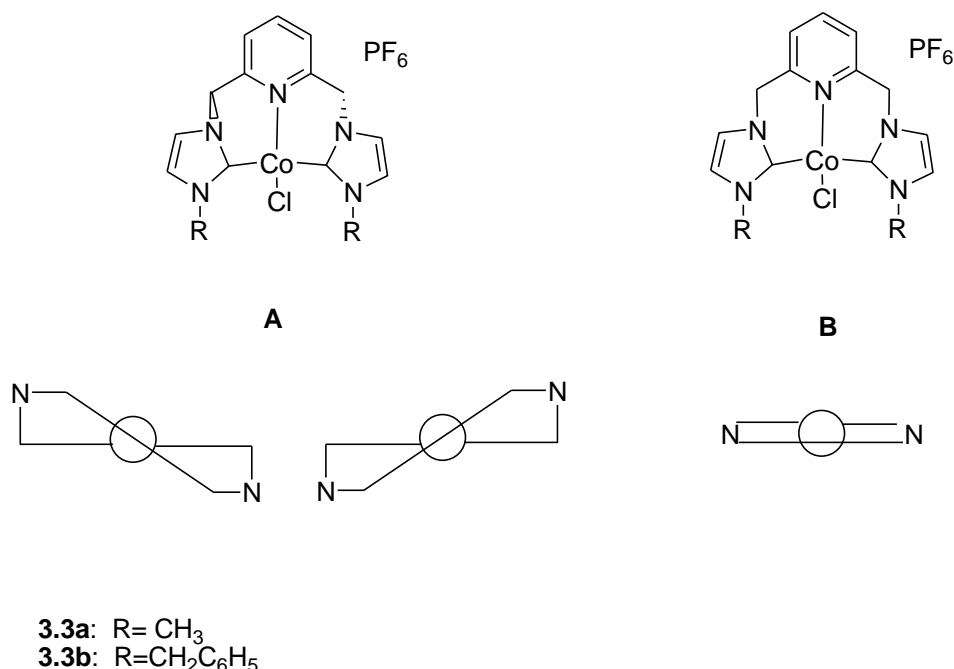
Transmetalation to the desired cobalt was achieved via a slight modification of reported literature methods.^{24, 36} Hence to a clear sky-blue DCM solution of $\text{CoCl}_2(\text{PPh}_3)_2$ (metal precursor) was drop-wise added the DCM solution of either **3.2a** or **3.2b**. This prompted the formation of dark green precipitates within light blue solutions. The mixture was stirred at room temperature for 48 h. This observation led us to assume that the cobalt-NHC complex was the precipitate that formed. At the end of the reaction, the blue supernatant changed colour to slightly blue-brown while the green precipitate remained intact. Filtration and washing of the residue with more DCM (till it became clear) and subsequent extraction with dry methanol afforded a brown suspension which was then filtered over a bed of celite to give an orange-brown methanol solution. All volatiles were then removed under vacuum to afford air sensitive green microcrystals. Preliminary observation and broad peaks in the ^1H NMR data of the green microcrystals suggested formation of the cobalt complexes, which were distinct as compared to the intermediate Ag-NHC complexes. Although, there is not much significant downfield shift in the two spectra; the two doublets representing the backbone protons in the imidazole moiety coalesced to a singlet in the cobalt complexes due to the higher symmetry of the molecules. Free rotation of the sp^3 methylene carbon in the lutidine moiety enhanced by the need to minimize bond-pair repulsion of the chloride ions in both **3.2a** and **3.2b** is alleviated by the chelation of the dicarbene donors onto cobalt. This mode of binding increased the symmetry of the expected distorted square planar geometry of the molecules, resulting in a singlet for the back-bone protons in the imidazolium moieties.

In order to improve solubility and lower the oxophilicity of the complexes, anion exchange was conducted for the chloride counter ion with a bulkier group which also enabled easier characterization of the complexes. To achieve this, into a methanol solution of the afforded air sensitive green microcrystals was added KPF_6 and the mixture stirred at room temperature for 12 h. The milky orange-brown suspension gradually turned into a clear orange-brown suspension which was filtered through a bed of celite and concentrated to give fine dark-green, air stable cobalt complexes **3.3a** (97% yield) and **3.3b** (59% yield). The ^1H NMR spectra of these complexes are similar to their intermediates bearing the Cl^- counter ion although much better resolved. The peaks in **3.3b** were broad; indicative of the paramagnetic nature of the complex, but all expected protons were accounted for. The coupling multiplicity also confirmed the argument for increased symmetry in the molecule as depicted by the coalescing of the imidazole back-bone proton signals in both complexes. The apex proton signal in the lutidyl moieties of both complexes splits into triplets, while the adjacent

proton in the lutidyl moiety of **3.3a** gave a distinct doublet. With the exception of the apex proton in **3.3b**; all the aromatic proton signals have coalesced into a single multiplet. Integration did confirm the single triplet peak as the apex proton (1H) on the lutidyl moiety; while the coalesced multiplet accounted for 2x8H i.e. 2x5H (phenyl), 2x2H (imidazolyl C4 and C5 protons) and 2x1H (lutidyl protons). The two methylene groups in the benzyl and lutidyl moieties also appeared as singlet peaks at 5.26 and 5.36 ppm respectively; without much significant shift from the positions in the ^1H NMR spectrum of the Ag-NHC intermediate (complex **3.2b**). The ^{13}C NMR spectrum of **3.3a** is quite resolved with a sharp peak at 184 ppm accounting for the C2 carbene-cobalt. However, the ^{13}C NMR spectrum of **3.3b** was obtained with all carbons except the C2 (carbene-metal) fully accounted for. This is usually related to the paramagnetic nature of such complexes and their longer relaxation times.^{31-32, 38} Measurement of saturation magnetization (Ms) was used to determine the magnetic susceptibility³⁹ of **3.3b** which confirmed the complex as a paramagnetic, high spin compound with magnetic susceptibility of $4.12 \mu_B$. The value is consistent with three unpaired electrons for cobalt complexes in agreement with reported data for similar complexes.^{38, 40} All the displaced PPh_3 were removed as DCM soluble components with the purity of the complexes confirmed by ^1H and ^{31}P NMR. The absence of a distinct peak at -6 ppm in the spectra confirmed the complete removal of the PPh_3 and presence of the PF_6^- counter ion was also confirmed by the characteristic multiplet peak at -154 ppm in the ^{31}P NMR spectra of the complexes.⁴¹

A common feature in the ^1H NMR spectrum of similar NHC-transition metal complexes with lutidyl moiety is the appearance of the methylene protons in the lutidyl backbone as a doublet of doublets (at 5.43 and 5.53 ppm) due to the diastereotopicity that results from the twisted conformation of such complexes. This feature has been reported for analogous pincer palladium,^{7, 36} platinum^{26b} and nickel-NHC complexes.²⁴ Although, we couldn't report the crystal structural data of **3.3a** and **3.3b**; their ^1H NMR spectra clearly indicated that the complexes are among a few exceptional cases whereby a characteristic twisted conformation is not observed. Instead of appearing as doublet of doublets; the methylene protons of the lutidyl backbone in **3.3a** and **3.3b** appeared as broad singlets at 5.49 and 5.36 ppm respectively. This phenomenon is similar to what was reported and fully explained by Gründemann *et al.*,^{7b} using variable temperature studies. It was proposed that the methylene protons were involved in a dynamic atropisomerization process in all the three rings that generate the pincer architecture. As described below (Scheme 3.2), the twisted conformation

usually adopted could be interconverted between the left and right hand twisted forms with corresponding chirality change in the complexes (structure A). Only at a fast-rate exchange limit of inter-conversion is structure B (as in **3.3a** and **3.3b**) which has a C_{2v} symmetry with equivalent lutidyl (methylene) protons observed.



Scheme 3.2: Limiting structures of the atropisomerization for 3a and 3b in solution and their corresponding Newman-projection formula along Co-N bond as adapted from Gründemann *et al.*^{7b}

Both **3.3a** and **3.3b** showed very high melting point/decomposition temperatures ≥ 230 °C, typical of pincer NHC-metal complexes. Their TOF MS-ES⁺ fragmentation spectra gave similar fragmentation patterns with molecular ions characterized by a Co²⁺ centre with the loss of (Cl⁻ and PF₆⁻ counter ion) [M²⁺: M-Cl-PF₆]. This is followed by the loss of the Co²⁺ ion to generate an ionic dimer of the resulting carbene [M⁺: M-CoCIPF₆]. For **3.3b**, the subsequent loss of one of the benzyl groups generated the parent molecular ion with > 80 % abundance. Both complexes showed typical FTIR stretching vibrations at 1374 and 1356 cm⁻¹ for **3.3a** and **3.3b** respectively; corresponding to a typical C-N stretch in aromatic amines.^{38, 42}

3.2.2 Catalytic *N*-arylation of aniline

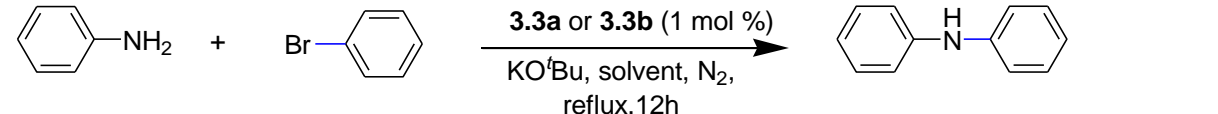
Buchwald^{13a, 43} and Hartwig^{14, 15b} are pioneers in transition metal catalyzed aryl C-N coupling reactions.^{15a} For about two decades, synthetic chemists around the world have employed

their palladium catalyst systems until in the late 90's that the first non-precious metal i.e. nickel catalysed amination reaction was reported.^{19a, b} Transition metal catalytic systems containing cobalt are quite rare¹⁰ and except for a few systems involving cobalt salts,^{21b, 44} their application for activating C-N coupling reactions is scarce and to the best of our knowledge those containing pincer NHC-Co complexes have not been reported.

Optimization of reaction parameters including determination of the best base and solvent for the process was initially conducted in a systematic manner to establish the optimum combinations of reaction conditions for the coupling reaction. C-N coupling reactions have been conducted at high temperatures using a variety of solvents that include THF, dioxane, DMSO, DMF, toluene, and acetonitrile.^{15a, 16b, c, 19a-c, 21b} Most of these are high boiling solvents which is a major shortcoming in their use for this process. Except in some rare cases;^{21b} little or no success was reported for aryl C-N coupling with water as the solvent.^{16c} Much reported success has been with the use of THF, dioxane, acetonitrile and toluene. Based on these analysis; we decided to use the first three solvents in studying the catalyst reaction conditions.

Kuhl *et al.*,^{19b} reported that the function of the base in transition metal NHC complex catalyzed C-N coupling reactions is twofold: (1) to reduce the oxidation state of the metal to the desired active state and (2) to either deprotonate the imidazolium salt and generate in-situ NHC-metal complex or act as a deprotonating agent to the amino substrate. In our preliminary selection of bases; the use of NaH was avoided (even though it has a high potential of easily reducing both Ni and Co ions) due to the risk of attack to the methylene protons in the lutidyl moiety which will trigger a collapse of the pincer architecture and invariably destroying the catalyst.^{32a} KOH was also avoided due to the fact that it could yield phenolic products with the substrate.^{16c} Most reported cases of successful aryl C-N coupling have been achieved with the use of either NaO^tBu or KO^tBu as the base. Both are efficient and easily removed at the end of the reaction as precipitates on a bed of celite. Inorganic bases like K₂CO₃ and Na₂PO₄ have also been reported to be suitable in Cu-catalyzed aryl C-N coupling.^{16c, 45} In this study, the established solvents (THF, dioxane and acetonitrile) and bases (KO^tBu, K₂CO₃ and Na₂PO₄) were utilised and results of the preliminary investigations are presented in Table 3.2.

Table 3.2: Preliminary investigation of the C-N coupling reaction conditions

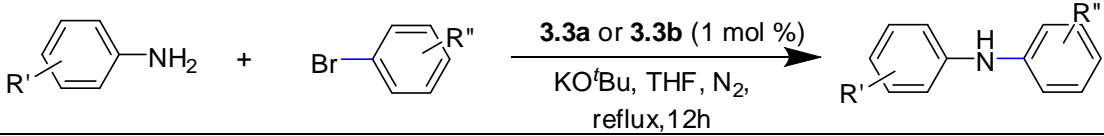
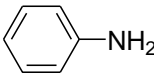
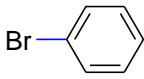
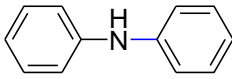
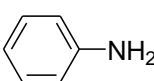
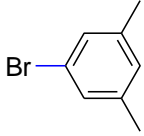
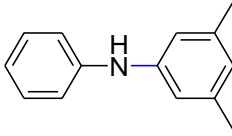
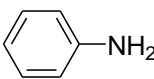
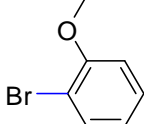
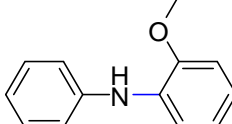
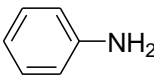
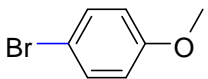
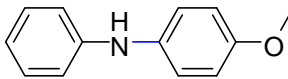
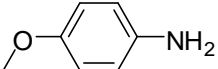
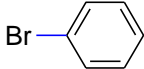
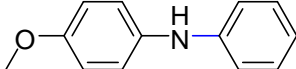
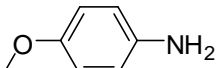
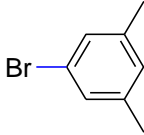
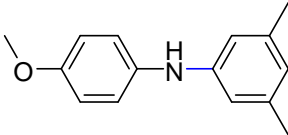
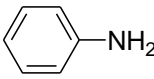
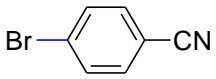
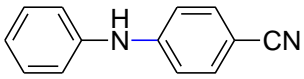
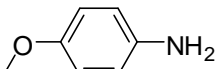
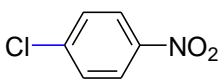
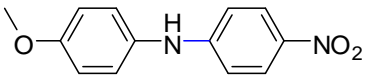
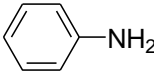
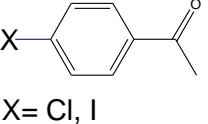
			
Entry	Solvent	Yield per catalyst (%) ^g	
		3.3a	3.3b
1 ^a	THF	12 ^{bPh}	08 ^{bPh}
2 ^b	“	-	-
3 ^c	“	-	-
4	“	57	63
5 ^d	“	58	63
6	Acetonitrile	43	50
7	Dioxane	56	60
8 ^e	THF	Trace	Trace
9 ^f	THF	35	39

Except where mentioned; reactions were conducted using aniline (1.0 mole equivalent), phenyl bromide (1.2 mole equivalent), KO^tBu (1.2 mole equivalent), catalyst (1 mol% of **3.3a** or **3.3b**), N₂ atmosphere in refluxing dry THF (20 ml) for 12 h. Reaction progress was monitored by TLC. ^{bPh} Isolated yield of biphenyl. ^a No catalyst used. ^b No catalyst used and reaction done at room temperature. ^c No base used. ^d Aniline (1.2 mole equivalent) and phenyl bromide (1.0 mole equivalent) used. ^e K₂CO₃ (1.2 mole equivalent) used as base. ^f Na₂PO₄ (1.2 mole equivalent) used as base. ^g Isolated yield from column chromatography, average of two runs.

The preliminary study on the reaction conditions began under anaerobic conditions in refluxing THF with aniline and phenyl bromide substrates. Results from entry 1 (absence of any catalyst) only confirmed the isolation of biphenyl as the major product. This homo-coupled dimerized product has been reported to be a by-product in variants of the Hiyama coupling reaction⁴⁶ and is temperature enhanced since entry 2 showed that at room temperature no trace of the biphenyl was observed with only the substrates recovered. Entry 3 conducted in the absence of a base gave neither of the desired C-N coupled product nor the biphenyl. This indicated that the base plays a vital role in the catalytic reaction as we discuss later in the mechanism. Introduction of 1 mol% of either **3.3a** or **3.3b** as catalysts resulted in good isolated yields (57 and 63% respectively) of the *N*-mono arylated product without any trace of the biphenyl (entry 4). This implies that both catalysts were able to activate C-N coupling and at the same time suppress the thermally-driven self-dimerization of phenyl bromide. The relatively higher yield with catalyst **3.3b** is due to the advantage of its steric bulk which is desired during the reductive elimination of the product in the catalytic cycle.^{19b} Swapping around the mole ratio of amine to aryl halide (1.2:1 instead of 1:1.2) as employed by Yang and co-workers^{15a} in their NHC-Pd catalyst system did not yield much significant

increase in the desired diphenyl amine product (entry 5; 58 and 63% for **3.3a** and **3.3b** respectively). Therefore, all further reactions were conducted based on the original mole ratio of 1:1.2 as employed by Kuhl *et al*^{19b} and others.^{16c} Entries 6 and 7 indicated that THF was the more suited solvent for this reaction as both acetonitrile and dioxane led to reduced isolated yields. Krzyminski *et al.*,⁴⁵ have reported the CuI catalyzed aryl C-N coupling of *p*-anisidine with phenyl bromide using K₂CO₃ as base. Based on this, and having established that THF is the best solvent for the current catalyst system, K₂CO₃ was used as the base (entry 8) resulting in only traces of the desired product. A possible explanation is that K₂CO₃ works best at the higher temperature of refluxing DMSO as compared to refluxing THF. Comparatively lower yields were also obtained with the use of Na₂PO₄ (entry 9; 35 and 39% for **3.3a** and **3.3b** respectively) which led to the conclusion that both bases only work better at elevated refluxing temperatures as previously reported.⁴⁵ Hence, under the reaction conditions: aryl amine (1 mole equivalent); aryl halide (mostly bromide; 1.2 mole equivalent); KO^tBu as base (1.2 mole equivalent); N₂; refluxing THF (20 ml); reaction time of 12 h; 1.0 mol% of catalysts; this study was extended to the arylation of a variety of aryl halides (mostly bromide) with the results presented in Table 3.3.

Table 3.3: Amination of aryl halides catalyzed by pincer NHC-Co complexes (3.3a and 3.3b)

					
Entry	Substrate	Product	Yield per catalyst (%) ^a		
			3.3a	3.3b	
1				57	63
2				68	71
3				71	72
4				69	72
5				75	77
6				77	80
7				82	79
8				82	82
9			Aldol product		

In all entries except otherwise mentioned; aryl amine (1.0 mole equivalent), aryl halide (1.2 mole equivalent), KO^tBu (1.2 mole equivalent), NHC-Co complex (1.0 mol %), dry N₂ atmosphere in refluxing THF for 12 h; progress of the reaction monitored by TLC. ^aIsolated yield from column chromatography, average of two runs.

The use of various electronic and steric inducing groups on the aryl halide was to study the scope and limitations of the catalyst systems reported herein. Entry 1 presents results of the coupling of aniline and phenyl bromide as the reference substrates to which other substrates are later compared. Modest yields of 57 and 63% of the product diphenylamine were respectively isolated for **3.3a** and **3.3b** which still compares favourably to a similar study based on a NHC-Pd catalyst system.^{15a}

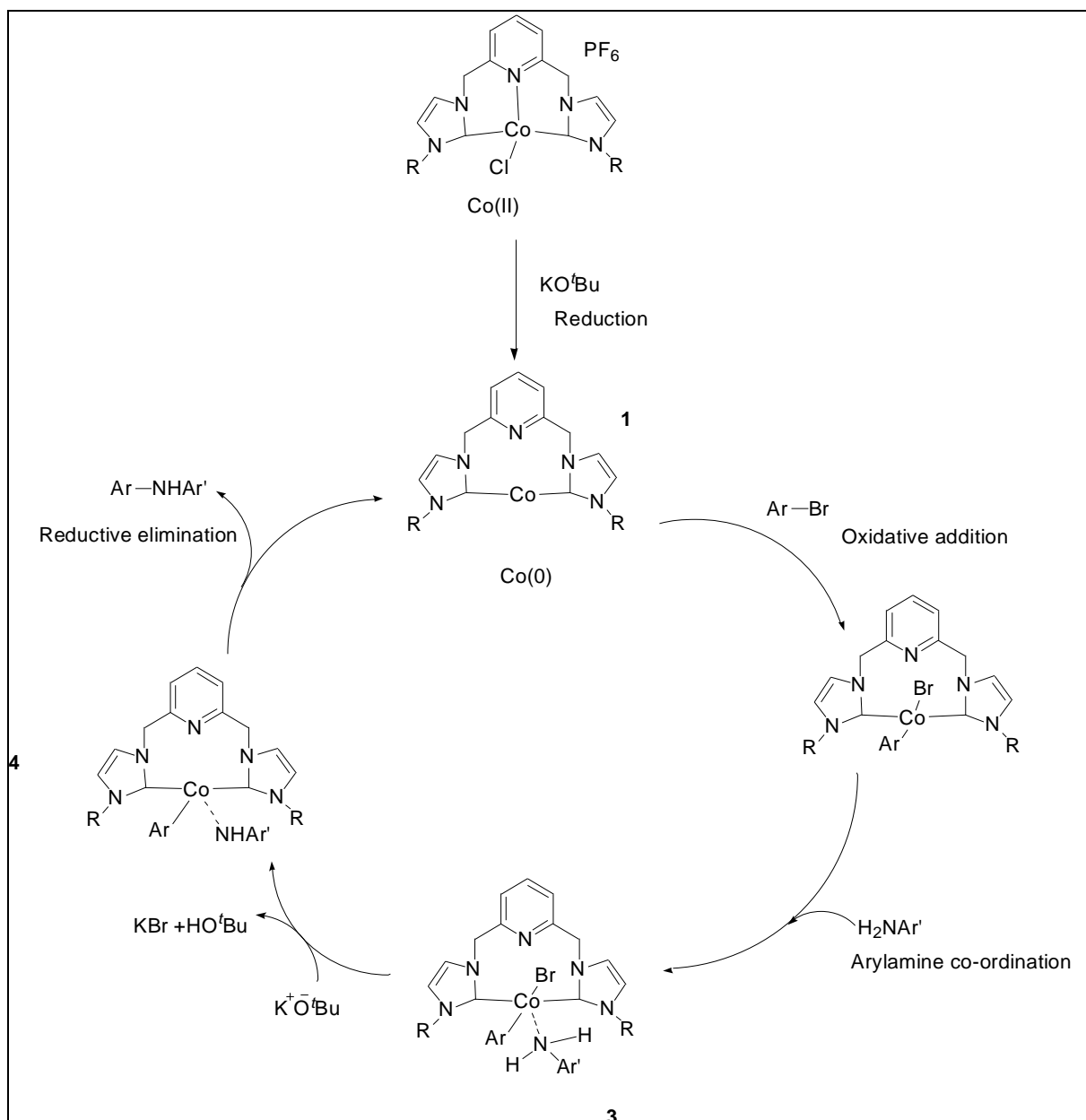
A close examination of the result shows that under similar conditions both catalysts **3.3a** and **3.3b** yielded comparable quantities of products, hence the main determinant of catalytic activity is the electronic property of the substrates. It is very clear that varying the position of the substituent(s) around the phenyl ring of either substrate has little impact on the catalytic activity, as for example relatively similar isolated yields were recorded for 2-bromoanisole (entry 3) and 4-bromoanisole (entry 4). These findings clearly indicate that substrates' steric size has very little impact on the present catalytic systems; therefore differences in catalytic performance are best attributed to electronic properties of the substituents on either or both substrates. Studies by Hartwig *et al.*,^{5b, 15b} and Matsubara *et al.*,^{19c} have indicated that the presence of electron releasing groups on aryl amines enhances their chances of catalytic amination with aryl halides, this is also observed in this study where higher yields were recorded for entries 5 and 6 bearing electron releasing methoxy substituted aryl amines. On the other hand, electron withdrawing *para* substituents deactivate the ring system in aryl halides thereby weakening the bond to the halide leaving group which becomes susceptible to oxidative attack by the catalyst (see step 2, Scheme 3.3). Hence, the ca. 80 % yield recorded for entry 7 is due to the influence of the electron withdrawing CN group on the aryl bromide ring, similar observations have previously been recorded elsewhere.^{19c} This also explains the high isolated yields obtained for entry 8, which is a result of an activated aryl amine (due to the methoxy substituent) and an equally activated *para*-nitro substituted aryl halide. However, the failure of both **3.3a** and **3.3b** to activate the arylation of aniline with either *p*-chloro or *p*-iodo acetophenone (entry 9) is worth noting, because after several attempts only the aldol products were isolated in high yields. Coincidentally, attempted arylation of acetophenone by Matsubara *et al.*,^{19c} also yielded only aldol products. The base used as a promoter preferentially attacks acetophenone leading to the formation of aldol products with little activation of the catalyst for the desired arylated product.

In conclusion, the reported catalyst systems are very selective for secondary amine arylated products only and no biphenyls (products of reduction of aryl bromide) were isolated. Also

no traces of *N,N*-diarylated (3° amine) products which have been observed in palladium^{5b} and CuI/tributyl phosphine^{16a} catalyst systems for C-N coupling reactions were isolated in the current systems.

3.2.3 Mechanism of the Co-NHC complexes catalysed *N*-arylation of aniline

Hao and co-workers recently proposed that Co-salts containing a Co(II) centre activate C-N coupling of benzamide with an aryl iodide by generating an active Co(IV) specie after initial coordination of the benzamide before it underwent oxidative addition with the aryl iodide. However, successful C-N coupling reactions of aryl amines activated by transition metal-NHC catalyst systems have been reported with the use of Pd,^{5b, 13a, 15b} Ni^{19c} and in situ generated Ni complexes with oxidation state zero active metal centres. In this study, the ligand frame work containing a pincer CNC architecture was designed to provide thermal and structural stability and for the Co-N bond to act as a hemilabile arm that provides a temporary coordination site for the aryl halide substrate in the oxidative addition stage of the catalytic cycle. This is only feasible after elimination of the PF₆⁻ counter ion and bonded chloride in the presence of the KO^tBu base. As shown in the proposed mechanism adapted from Matsubara *et al.*,^{19c} (Scheme 3.3) the generated Co(II) specie (observed by mass fragmentation of the complexes) was subsequently reduced by the base to form the active Co(0) specie (**1**) which then oxidatively added the aryl bromide (**2**). The base also promoted the coordinative addition of the aryl amine to form a five membered specie (**3**) which after reductive elimination yielded the desired *N*-mono arylated aniline.



Scheme 3.3: Proposed mechanism for pincer NHC-Co complexes (3.3a and 3.3b) catalysed N-mono arylation of aniline.

3.3 Conclusions

Two new pincer NHC-Co complexes bearing a CNC donor architecture were synthesized from the transmetalation of corresponding Ag-NHC complexes; which further demonstrate the vast application of Ag as a transmetalation agent. Both thermally and air stable complexes were obtained in excellent yields. The paramagnetic nature of one of the complexes (**3.3b**) was observed from the broad ¹H NMR peaks and the magnitude of the magnetic moment

determined by its hysteresis loop measurement. Both complexes have shown high activity in catalysing *N*-mono arylation of aniline with cheap aryl bromides in good to excellent yield under mild conditions and low catalyst loading of 1 mol%. The results are comparable to those obtained for palladium catalysts or harsher conditions of Cu mediated (or CuI catalysed) Ullman type coupling reactions.

3.4 Experimental section

All experiments were performed under a dinitrogen atmosphere using standard Schlenk techniques. All solvents used were analytically pure and dried prior to use using standard drying techniques: THF and hexane in benzophenone distilled over sodium wire, methanol in iodine distilled twice over magnesium ribbons, DCM distilled over calcium hydride or P₂O₅.⁴⁷ 1,2-dichloroethane is ACS reagent grade distilled over CaCl₂ and stored with molecular sieves. 4Å molecular sieves were activated by washing with methanol, dried for 24 h in an oven at 150 °C, then further heated in a furnace at 500 °C for 2 d and cooled in a desiccator. Deuterated solvents were obtained from Merck and are used without further purification. CoCl₂(PPh₃)₂ was prepared using a standard procedure.⁴⁸ Ag₂O, KPF₆, KO^tBu and all aryl halide substrates used were analytically pure obtained from Sigma-Aldrich and used without further purification. The aryl amine substrates were also obtained from Sigma-Aldrich, distilled prior to use and stored under molecular sieves in a desiccator. NMR spectra were recorded on Bruker Ultra shield Avance (400 or 600 MHz) spectrometer operating at room temperature unless stated otherwise and samples were dissolved in deuterated CDCl₃, CD₃OD or DMSO-d₆. The spectra were internally referenced relative to solvent peak and chemical shift values recorded (in delta δ ppm) with respect to δ = 0 for tetramethylsilane in both ¹H and ¹³C NMR spectra.⁴⁹ Hysteresis loop measurement for determination of saturated magnetization was conducted on Vibrating Sample Magnetometer (VSM) Lakeshore 735. Infrared spectra were recorded on a PerkinElmer universal ATR Spectrum 100 FT-IR spectrometer. Mass spectroscopy and elemental analysis (where applicable) data were recorded on Waters Micromass LCT Premier TOF MS (ES⁺ or ES⁻) and ThermoScientific Flash2000 Elemental Analyser respectively. Pincer imidazolium salts **3.1a** and **3.1b**; were synthesised and isolated in excellent yield using improved solvent free technique.²⁷

3,3'-(dimethylimidazolin-2-ylidene)lutidine disilver dichloride (3.2a). An oven dried Schlenk flask with activated molecular sieves (5.0 g) was cooled under nitrogen, degassed twice and charged with a mixture of 3,3'-(pyridine-2,6-diylbis(methylene))bis(1-methyl-1H-

imidazol-3-ium) chloride **3.1a** (0.24 g, 0.71 mmol) and silver (I) oxide (0.33 g; 1.42 mmol). The flask was then wrapped in aluminium foil and its contents refluxed in 1,2-dichloroethane (30 ml) under nitrogen for 36 h. With the disappearance of dark colour of the silver oxide, the resulting yellowish brown mixture was concentrated under reduced pressure and the residue extracted with dry DCM and filtered through a tick pad of celite. All volatiles in the filtrate were removed under reduced pressure and the off-white solid obtained was washed with hexane and dried under vacuum to give the silver complex **3.2a** as a faint yellowish-white powder, stable in air and unstable in chloroform and highly soluble in DCM and DMSO. Yield: 0.31 g, 0.56 mmol, 79%. mp. 119—122 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 7.82 (t, *J*=7.7 Hz, 1H, apex proton_(lutidyl)), 7.54 (d, *J*=1.8 Hz, 2x1H_(lutidyl)), 7.42 (d, *J*=1.7 Hz, 2x1H, =CH-(imidazolyl), 7.28 (d, *J*=7.7 Hz, 2x1H, -CH=(imidazolyl), 5.40 (s, 2x2H, CH₂_(lutidyl)), 3.75 (s, 2x3H, methyl). ¹³C NMR (400 MHz, DMSO-d₆): δ 179.8 (NCN), 155.9, 138.8, 122.7, 122.6, 121.8, 55.2 (NCH₂), 38.3 (CH₃). FTIR (neat) ν_{C-N} 1349, 1336 cm⁻¹. Anal. Calcd for C₁₅H₁₇Ag₂Cl₂N₅·0.3CH₂Cl₂: C, 31.71; H, 3.06; N, 12.09. Found: C, 31.69; H, 2.82; N, 11.71. MS-ES⁺: m/z(%) 551(4) [(M + H)]⁺, 409(20) [(M - AgCl)]⁺, 375(5) [(M - AgCl₂ + H)]²⁺, 360(90) [(M - AgCl₂ - CH₃)]⁺, 255(100) [(M - 2AgCl - CH₃ + 2H)]⁺. All other analytical data matched those previously reported.^{7a, 26}

3,3'-(dibenzylimidazolin-2-ylidene)lutidine disilver dichloride (3.2b). A mixture of imidazolium salt 3,3'-(pyridine-2,6-diylbis(methylene))bis(1-benzyl-1H-imidazol-3-ium) chloride **3.1b** (0.5 g; 1.02 mmol) and Ag₂O (0.47 g; 2.04 mmol) were charged into an oven dried Schlenk tube cooled under nitrogen. The mixture was then refluxed with 1,2-dichloroethane (40 ml) in the dark for 36 h. All volatiles were then removed and the off-brown residue extracted with DCM (40 ml) for 12 h. The orange-yellow extract was then filtered via celite and concentrated under reduced pressure to give an orange-yellow air sensitive solid. Yield: 0.49 g, 0.69 mmol, 68%. mp 70—72 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (t, *J*=7.7 Hz, 1H, apex proton_(lutidyl)), 7.28—7.26 (m, 2x5H_(phenyl)), 7.18 (d, *J*=5.8 Hz, 2x1H, -CH=(imidazolyl), 7.16 (s, 2x1H, =CH-(imidazolyl), 6.99 (d, *J*=1.6 Hz, 2x1H_(lutidyl)), 5.31 (s, 2x2H, CH₂_(lutidyl)), 5.20 (s, 2x2H, CH₂_(benzyl)). ¹³C NMR (400 MHz, CDCl₃): δ. 180.5 (NCN), 155.5, 138.8, 135.4, 129.3, 129.1, 127.9, 122.8, 122.1, 121.3, 56.7 (NCH₂), 55.9 (CH₂). FTIR (neat) ν_{C-N} 1350, 1336 cm⁻¹. MS-ES⁺: m/z(%) 526(50) [(M - AgCl₂)]⁺, 420(100) [(M - 2AgCl + H)]⁺, 330(98) [(M - 2AgCl - CH₂C₆H₅ + H)]⁺.

3,3'-(dimethylimidazolin-2-ylidene)lutidinechlorocobalt(II) hexafluorophosphate (3.3a). To a clear sky-blue DCM (20 ml) solution of cobalt precursor CoCl₂(PPh₃)₂ (0.18 g, 0.27 mmol) was added orange-yellow DCM solution (20 ml) of 3,3'-(dimethylimidazolin-2-

ylidene)lutidine disilver dichloride **3.2a** (0.10 g, 0.18 mmol, 553.97 g mol^{-1}). This prompted the immediate formation of a dark green precipitate and the reaction mixture stirred in the dark for 48 h. At the end of the reaction time; the DCM supernatant was filtered via cannula, and the residue washed with more DCM (2 x 20 ml) till the washing becomes colourless. The resulting dark green crude was then extracted with dry methanol (40 ml) and filtered over a bed of celite. The orange-brown filtrate obtained was then concentrated to yield green, highly air sensitive microcrystals which were then re-dissolved in dry methanol (20 ml) and were stirred at room temperature with KPF_6 (0.05 g, 0.27 mmol) for 12 h. The resulting suspension was allowed to settle down and the clear orange-brown supernatant filtered via a bed of celite. The solvent was removed under reduced pressure to yield dark green air stable microcrystals of 3,3'-(dimethylimidazolin-2-ylidene)lutidine chlorocobalt(II) hexafluorophosphate **3.3a**; highly soluble in methanol and insoluble in chlorinated solvents and ether. Yield: 0.08 g, 0.15 mmol, 82%. mp/dec 250—253 °C. ^1H NMR (600 MHz, CD_3OD): δ 7.91 (t, $J=7.7$ Hz, 1H, apex proton_(lutidyl)), 7.55 (s, 2 x(1H,1H), $\text{CH}=\text{CH}$ _(imidazolyl)), 7.48 (d, $J=7.8$ Hz, 2x1H, $-\text{CH}=\text{}$ _(lutidyl)), 5.48 (s, 2x2H, CH_2 _(lutidyl)), 3.93 (s, 2x3H, methyl). ^{13}C NMR (600 MHz, CD_3OD): δ 184.6 (NCN), 153.5, 138.9, 123.4, 123.1, 122.3, 53.0 (NCH_2), 35.2 (CH_3). ^{31}P NMR (600 MHz, CD_3OD): δ 135.8—153.3 (m, PF_6^-). FTIR (neat) $\nu_{\text{C-N}}$ 1374 cm^{-1} , ν_{Ar} 811 cm^{-1} . MS-ES⁺: m/z(%) 326(3) [(M - Cl - PF_6)]²⁺, 268(90) [(M - CoCIPF₆ + H)]⁺.

3,3'-(dibenzylimidazolin-2-ylidene)lutidinechlorocobalt(II) hexafluorophosphate (3.3b).

To a clear sky-blue DCM (20 ml) solution of cobalt precursor $\text{CoCl}_2(\text{PPh}_3)_2$ (0.29 g; 0.44 mmol) was added orange-yellow DCM solution (20 ml) of Ag-NHC complex 3,3'-(dibenzylimidazolin-2-ylidene)lutidine disilver dichloride **3.2b** (0.20 g, 0.29 mmol). This prompted the immediate formation of a dark green precipitate and the reaction mixture stirred in the dark for 48 h. At the end of the reaction time; the DCM soluble expected to contain unreacted metal source and the liberated phosphines was filtered via cannula, and the residue washed with more DCM (2 x 20 ml) and filtered. The resulting dark green crude was then extracted with dry methanol (40 ml) and filtered over a bed of celite. The orange-brown filtrate was then concentrated to yield green, air sensitive paste which was immediately dissolved in fresh dry methanol (40 ml) for anionic metathesis. To the resulting methanol solution was added KPF_6 (0.06 g, 0.31 mmol) and the suspension stirred at room temperature for 12 h. The mixture was allowed to settle down and the clear orange-brown supernatant filtered via a bed of celite. The solvent was removed under reduced pressure to yield dark

green air stable microcrystals of 3,3'-(dibenzylimidazolin-2-ylidene)lutidine chlorocobalt(II) hexafluorophosphate **3.3b**, highly soluble in methanol and insoluble in DCM. Yield: 0.11g, 0.17 mmol, 59%. mp 236—238°C. ¹H NMR (400 MHz, CD₃OD): δ 7.77 (t, *J*=1.8 Hz, 1H, apex proton(lutidyl)), 7.36-7.28 [m, 2x8H: 5H(phenyl), 2H(imidazolyl), 1H(lutidyl)], 5.36 (bs, 2x2H, CH₂(lutidyl)), 5.26 (s, 2x2H, CH₂(benzyl)). ¹³C NMR (400 MHz, CD₃OD): δ 154.6, 140.2, 135.1, 130.4, 130.3, 129.8, 124.8, 1230.7, 123.3, 54.5 (NCH₂), 54.1 (CH₂). ³¹P NMR (400 MHz, CD₃OD): δ 135.8-153.3 (m, PF₆⁻). FTIR (neat) ν_{C-N} 1356 cm⁻¹, ν_{Ar} 801 cm⁻¹. $\mu_{eff} = 4.12 \mu_B$. MS-ES⁺: m/z(%) 478(3) [(M - Cl - PF₆)²⁺], 420(15) [(M - CoClPF₆ + H)]⁺, 330(80) [(M - CoClPF₆ - CH₂C₆H₅ + H)]⁺.

Typical procedure for catalysed arylation of aniline. To an oven dried Schlenk tube cooled under nitrogen was added KO^tBu (1.46 g, 0.013 mol), **3.3a** (0.051 g, 0.0001 mol, 506.02 gmol⁻¹), phenyl bromide (2.0 g, 1.34 ml, 0.013 mol) and aniline (1.0 g, 1 ml, 0.01 mol). The mixture was then stirred and refluxed in THF (20 ml) under nitrogen for 12 h, with the reaction progress monitored by TLC. The reaction mixture was then filtered over a bed of celite and the residue washed with DCM. All volatiles in the filtrate were removed under reduced pressure and the resulting crude paste mixed with silica. The desired diphenyl amine product was isolated by column chromatography as an eluent of hexane:DCM (9:1) solvent system. Yield: 0.96 g, 0.006 mol, 57%. Mp 49—51 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 8.12 (bs, 1H, NH), 7.21 (d, *J*=7.4 Hz, 2x2H), 7.06 (d, *J*=7.6 Hz, 2x2H), 6.81 (t, *J*=7.3 Hz, 2x1H). ¹³C NMR (400 MHz, DMSO-d₆): δ 143.4, 129.1, 119.6, 116.7. FTIR (neat) ν_{N-H} 3380 (bs, 2° amine), ν_{C-H} 3041, ν_{C-N} 1307, ν_{Ar} 741 cm⁻¹.

3.5 References:

1. Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J., *Liebigs Ann.Chem.* **1997**, 1997 (2), 365-374.
2. Morales-Morales, D.; Craig, G. M. J., *The Chemistry of Pincer Compounds*. Publisher: Elsevier Science; 1 edition (August 2, 2007): 2007; p Hardcover: 466 pages.
3. (a) Chuchuryukin, A. V.; Huang, R.; Lutz, M.; Chadwick, J. C.; Spek, A. L.; van Koten, G., *Organometallics* **2011**, 30 (10), 2819-2830; (b) del Río, I.; Robert A. Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G., *Inorganica Chimica Acta* **1999**, 287, 113-116.
4. (a) Jennifer, A. L.; Robert, H. C., *ChemInform* **2001**, 32 (38); (b) Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*. Yale University, N. H., Connecticut, Ed. John Wiley & Sons, Inc.: Hoboken, New Jersey., 2005; pp 1-552.

5. (a) Vastine, B. A.; Hall, M. B., *Coord. Chem. Rev.* **2009**, *253* (7–8), 1202-1218; (b) Hartwig, J. F., *Angew. Chem. Int. Ed.* **1998**, *37*(15), 2046-2067.
6. (a) Vuzman, D.; Poverenov, E.; Shimon, L. J. W.; Diskin-Posner, Y.; Milstein, D., *Organometallics* **2008**, *27* (11), 2627-2634; (b) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Ben-Ari, E.; Milstein, D., *Organometallics* **2011**, *30* (10), 2721-2729; (c) Hahn, C., *Chem. Eur. J.* **2004**, *10*, 5888 – 5899; (d) Fan, L.; Foxman, B. M.; Ozerov, O. V., *Organometallics* **2004**, *23* (3), 326-328.
7. (a) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H., *Chem. Commun.* **2001**, (2), 201-202; (b) Stephan Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H., *Organometallics* **2001**, *20*, 5485-5488.
8. (a) Pugh, D.; Danopoulos, A. A., *Coord. Chem. Rev.* **2007**, *251* (5–6), 610-641; (b) Gladysz, J. A., *Chem. Rev.* **2011**, *111* (3), 1167-1169; (c) Selander, N.; J. Szabó, K., *Chem. Rev.* **2010**, *111* (3), 2048-2076.
9. (a) Blaser, H.-U., *ChemCatChem* **2011**, *3* (4), 780-780; (b) Kulkarni, A. A.; Daugulis, O., *Synthesis* **2009**, *2009* (24), 4087-4109; (c) Chakraborty, S.; Guan, H., *Dalton Trans.* **2010**, *39* (32), 7427-7436.
10. Dí z-González, S.; Marion, N.; Nolan, S. P., *Chem. Rev.* **2009**, *109* (8), 3612-3676.
11. Danopoulos, A. A.; Braunstein, P., *Dalton Trans.* **2013**, *42* (20), 7276-7280.
12. (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A., *J. Am. Chem. Soc.* **1998**, *120* (16), 4049-4050; (b) J. P. Britovsek, G.; C. Gibson, V.; J. McTavish, S.; A. Solan, G.; J. P. White, A.; J. Williams, D.; S. Kimberley, B.; J. Maddox, P., *Chem. Commun.* **1998**, (7), 849-850.
13. (a) Wolfe, J. P.; Buchwald, S. L., *J. Org. Chem.* **1996**, *61* (3), 1133-1135; (b) Beller, M.; Breindl, C.; Riermeier, T. H.; Tillack, A., *J. Org. Chem.* **2001**, *66* (4), 1403-1412.
14. (a) Driver, M. S.; Hartwig, J. F., *J. Am. Chem. Soc.* **1997**, *119* (35), 8232-8245; (b) Driver, M. S.; Hartwig, J. F., *J. Am. Chem. Soc.* **1996**, *118* (30), 7217-7218.
15. (a) Yang, J.; Li, P.; Zhang, Y.; Wang, L., *J. Organomet. Chem.* **2014**, *766* (0), 73-78; (b) Hartwig, J. F., *Nature* **2008**, *455* (7211), 314-322.
16. (a) Patil, N. M.; Kelkar, A. A.; Nabi, Z.; Chaudhari, R. V., *Chem. Commun* **2003**, *0* (19), 2460-2461; (b) Quan, Z.-J.; Xia, H.-D.; Zhang, Z.; Da, Y.-X.; Wang, X.-C., *Appl. Organomet. Chem.* **2014**, *28* (2), 81-85; (c) Chen, J.; Yuan, T.; Hao, W.; Cai, M., *Tetrahedron Lett.* **2011**, *52* (29), 3710-3713; (d) Haider, J.; Kunz, K.; Scholz, U., *Advanced Synthesis & Catalysis* **2004**, *346* (7), 717-722.
17. Lindley, J., *Tetrahedron* **1984**, *40* (9), 1433-1456.
18. (a) Correa, A.; Bolm, C., *Angew. Chem. Int. Ed.* **2007**, *46* (46), 8862-8865; (b) Correa, A.; Carril, M.; Bolm, C., *Chem. Eur. J.* **2008**, *14* (35), 10919-10922.
19. (a) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y., *Organometallics* **2002**, *21* (8), 1554-1559; (b) Kuhl, S.; Fort, Y.; Schneider, R., *J. Organomet. Chem.* **2005**, *690* (24–25), 6169-6177; (c) Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K., *J. Org. Chem.* **2007**, *72* (14), 5069-5076; (d) Allen, C. L.; Williams, J. M. J., *Chem. Soc. Rev.* **2011**, *40* (7), 3405-3415.
20. (a) Amouri, H.; Bégué, J.-P.; Chennoufi, A.; Bonnet-Delpon, D.; Gruselle, M.; Malézieux, B., *Org. Lett.* **2000**, *2* (6), 807-809; (b) Nicholas, K. M., *Acc. Chem. Res.* **1987**, *20* (6), 207-214.
21. (a) Qian, X. Cobalt-Catalyzed C-C and C-N Coupling reactions. *Ecole Polytechnique X*, 2013; (b) Tan, B. Y.-H.; Teo, Y.-C., *Organic & Biomolecular Chemistry* **2014**, *12* (38), 7478-7481.
22. Toma, G.; Yamaguchi, R., *Eur. J. Org. Chem.* **2010**, *2010* (33), 6404-6408.

23. Saha, P.; Ali, M. A.; Ghosh, P.; Punniyamurthy, T., *Organic & Biomolecular Chemistry* **2010**, *8* (24), 5692-5699.
24. Inamoto, K.; Kuroda, J.-i.; Kwon, E.; Hiroya, K.; Doi, T., *J. Organomet.Chem.* **2009**, *694* (3), 389-396.
25. (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J., *Angew. Chem. Int. Ed. Eng.* **1995**, *34* (21), 2371-2374; (b) Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002**, *41* (8), 1290-1309.
26. (a) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; *Inorg. Chim. Acta* **2002**, *327*(1), 116-125; (b) Serra, D.; Cao, P.; Cabrera, J.; Padilla, R.; Rominger, F.; Limbach, M., *Organometallics* **2011**, *30* (7), 1885-1895.
27. Ibrahim, H.; Bala, M. D., *Tetrahedron Lett.* **2014**, *55* (46), 6351-6353.
28. Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J., *Organometallics* **2003**, *22* (9), 1979-1982.
29. Melaiye, A.; Simons, R. S.; Milsted, A.; Pingitore, F.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J., *J. Med. Chem.* **2004**, *47* (4), 973-977.
30. Crystal data: **C1a**: C₁₅ H₁₉ F₁₂ N₅ P₂, (0.26x0.19x0.16 mm), M = 559.29, Orthorhombic, space group P b c a, a = 9.4039(4) Å, b = 18.1969(8) Å, c = 25.6999(12) Å, V = 4397.8(3) Å³, Z = 4, D_c = 1.689 mg/m³, T = 173(2) K, i(Mo KR) = 0.313 mm⁻¹, λ = 0.71073 Å, GOF = 1.037. **C2a**: C₂₈ H₂₉ Cl₆ Co N₅, (0.16x0.14x0.10 mm), M = 707.19, Monoclinic, space group P 1/n, a = 9.1770(17) Å, b = 17.129(3) Å, c = 19.886(3) Å, β = 94.182(10)°, V = 3117.6(9) Å³, Z = 4, D_c = 1.507 mg/m³, T = 173(2) K, i(Mo KR) = 1.093 mm⁻¹, λ = 0.71073 Å, GOF = 1.008.
31. Wu, J.; Dai, W.; Farnaby, J. H.; Hazari, N.; Le Roy, J. J.; Mereacre, V.; Murugesu, M.; Powell, A. K.; Takase, M. K., *Dalton Trans.* **2013**, *42* (20), 7404-7413.
32. (a) Zhang, D.; Zhou, S.; Li, Z.; Wang, Q.; Weng, L., *Dalton Trans.* **2013**, *42* (33), 12020-12030; (b) Garrison, J. C. a.; Youngs, W. J., *Chem. Rev.* **2005**, *105*, 3978-4008.
33. For practical purposes: A mixture of imidazolium salt with 2 molar equivalent of Ag₂O in anhydrous DCM was stirred at room temperature for 24 h and filtered via bed of celite. To the filtrate obtained was then added anhydrous CoCl₂ (0.5 mole equivalent) and the resulting precipitate stirred at room temperature for 12 h. Removal of the supernatant via cannula and drying the residue under vacuum gave a blue solid which was recrystallized from a mixture of methanol/DCM to give blue crystals of C1b.
34. Ikhile, M. I.; Bala, M. D., *Acta Crystallogr. Sect. E* **2010**, *66* (11), m1493.
35. Li, F.; Hu, J. J.; Koh, L. L.; Hor, T. S. A., *Dalton Trans.* **2010**, *39* (22), 5231-5241.
36. Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B., *Dalton Trans.* **2003**, (5), 1009-1015.
37. Gnanamgari, D.; Sauer, L. O. E.; Schley, D. N.; Butler, C.; Incarvito, C. D.; Crabtree, R. H., *Organometallics* **2009**, *28*, 321-325.
38. Thagfi, J. A.; Lavoie, G. G., *Organometallics* **2012**, *31* (21), 7351-7358.
39. (a) For practical purpose on magnetic susceptibility measurement: Data from hysteresis loop measurement using Vibrating Sample Magnetometer VSM gave an initial magnetization curve as a plot of magnetic moment/mass (emu/g) against field (Oes) which qualitatively confirmed the paramagnetic nature of the complexes. The determined saturated magnetization M_s values which are function of the number of moles n used per atom (0.025—0.031g) are used to determine the magnetic

- susceptibility (μ_{eff}) of the complexes in μB and compared with the calculated magnetic moments consistent with the number of unpaired electrons. In essence, the quotient M_s/n divided by a constant 5584.9 gives the magnetic susceptibility of the complexes. The constant 5584.9 is derived from the equation: $\mu_B \cdot N_A = 5584.9$ emu/mole; where N_A is Avogadro's number; (b) Cullity, B. D.; Graham, C. D., *Introduction to Magnetic Materials*. 2nd Edition ed.; John Wiley and Sons: 2008; p. 568. Downloaded on 2014/11/02. http://www2.fisica.unlp.edu.ar/magnet/Cullity_Graham.pdf; (c) Bain, G. A.; Berry, J. F., Diamagnetic corrections and Pascal's constants. *J.Chem. Educ.* **2008**, *85* (4), 532.
40. Evans, D. F., *J. Chem. Soc.* **1959**, (0), 2003-2005.
 41. Twyman, R. M. NMR spectroscopy-applicable elements/ Phosphorus-31 2005. Downloaded on 2013/03/17. <http://www.writescience.com/RMT%20PDFs/Elsevier/eans%20NMR-P31.pdf>.
 42. <http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html>. Downloaded on 2014/06/06.
 43. Wolfe, J. P.; Wagaw, S.; Buchwald, S. L., *Journal of the American Chemical Society* **1996**, *118* (30), 7215-7216.
 44. Zhu, T.-H.; Wang, S.-Y.; Tao, Y.-Q.; Wei, T.-Q.; Ji, S.-J., *Org. Lett.* **2014**, *16* (4), 1260-1263.
 45. Krzyminski, K.; Wera, M.; Sikorski, A.; Blazejowski, J., *Acta Crystallogr. Sect. E* **2009**, *65* (1), o152.
 46. (a) Denmark, S. E.; Wu, Z., *Org. Lett.* **1999**, *1* (9), 1495-1498; (b) Hatanaka, Y.; Goda, K.-i.; Okahara, Y.; Hiyama, T., *Tetrahedron* **1994**, *50* (28), 8301-8316.
 47. Standard solvent drying techniques. Downloaded on 2012/11/27. <http://delloyd.50megs.com/moreinfo/drying.html>.
 48. Venanzi, L. M., *J.Chem. Soc.* **1958**, 0 (0), 719-724.
 49. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010**, *29*, 2176-2179.

Chapter four

Cobalt and nickel complexes of chelating pyridyl and alkenyl-*N*-heterocyclic carbene ligands: synthesis, characterization and application as amination catalysts*

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Abstract

Six new imidazolium salts of the form 3-*R*-1-picolylimidazolium bromide (**4.1a**: *R*= 4-nitrophenyl, **4.1b**: *R*= 4-acetylphenyl, **4.1c**: *R*= 4-cyanophenyl, **4.1d**: *R*= allyl, **4.1e**: *R*= butenyl, **4.1f**: *R*= pentenyl) and three new salts bearing 1-(1-alkenyl)-3-(4-ferrocenylphenyl)imidazolium bromide (**4.4a**: alkenyl = allyl, **4.4b**: alkenyl = butenyl, **4.4c**: alkenyl = pentenyl); were synthesized and isolated in high yields. Four of the salts (**4.1a**, **4.1d**, **4.1e**, and **4.4a**) were used as NHC ligand precursors in reaction with excess Ag₂O affording Ag-NHC complexes (isolated air stable **4.2a**, **4.5a** and *in situ* utilised **4.2d**, **4.2e**) which were transmetalated to desired Co and Ni to yield corresponding complexes of the form M(NHC)₂Cl₂ in good to excellent yields. The afforded three Ni-NHC complexes (**4.3a'**, **4.3d'**, **4.3e'**) and the four Co-NHC complexes (**4.3a**, **4.3d**, **4.3e**, **4.6a**) were relatively stable in air and with the only exception of **4.6a** were insoluble in chlorinated solvents but very soluble in methanol and DMSO. Both **4.3d** and **4.3e**; showed paramagnetic properties as observed from their ¹H NMR spectra, with magnetic susceptibility of 2.53 and 2.73 μ_B respectively; consistent with one unpaired electron for high spin paramagnetic cobalt complexes. All the imidazolium salts, isolated Ag-NHC complexes and the corresponding Co and Ni-NHC complexes were characterized spectroscopically and by analytical techniques. The seven complexes were active in catalysing C-N coupling of aniline with phenyl bromide based on a low catalyst loading of 1 mol% under mild reaction conditions. Good to excellent yields of the desired diaryl amine products were obtained with either the *in situ* generated complex obtained from a mixture of NiCl₂/**4.1a** (1:2 mole ratio), or isolated **4.3a'** when either was used as a catalyst in the activation of C-N coupling of aryl amines with substituted aryl bromides bearing a variety of functional groups. The yields are comparable to those obtained with platinum group metals or harsher temperature conditions of CuI or Cu mediated Ullman reactions.

Keywords

Pyridyl, Imidazolium salts, Transmetalation, C-N coupling, Diarylamine, Isolated yield.

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4.1 Introduction

Since the pioneering works of Öfele, Wanzlick and Arduengo,¹ *N*-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands in organometallic catalysis, organic and inorganic synthetic transformations.² The excellent sigma donating ability of *N*-heterocyclic carbenes (NHCs) make them better options to other ligand forms like ethers, amines, and even phosphines in organometallic and co-ordination chemistry.³ Most NHC-metal complexes are with heavy metals like rhodium, iridium, ruthenium & palladium (PGMs). Comparatively fewer complexes of NHC-nickel or cobalt are known.^{1a, 3-4} Additional advantages in favour of NHCs include the fact that they proffer high catalytic activity either in their metal complexes or as *in situ* generated catalyst systems with a wide scope of applications and efficiencies in homogeneous catalysis. They were also found to be tolerant to many functional groups, work at ambient temperatures and strongly coordinate to metal centres in catalytic systems without ligand dissociation.⁵

Bidentate or polydentate ligands containing both strong and weak donor groups (hemilabile ligands) have found widespread applications in homogeneous catalysis.⁶ Tridentate, asymmetric ligands containing donor groups like NO₂, CN, COR and alkenyl functionalities are very rare⁷ and their complexes with environmentally benign metals like nickel and especially cobalt are scarce.^{4b} Except for a few examples that are stabilised by classical donor ligands like Cp, phosphines, heterocyclic system and CO,⁸ few examples are available with multidentate functionalised NHC ligands.⁹ In multidentate ligands with donor atoms of varying binding strengths to the metal centre, the presence of weak donors help generate the hemilabile character of such ligands, imparting the ability of reversible dissociation from the metal centre and providing a vacant coordination site for the complexation of substrates during a catalytic cycle without ligand decomposition.¹⁰ The presence of nitrogen as one of the hemilabile donor atoms in conjunction with the classic carbene donor in the series of NHC precursors discussed herein has made them suitable for the generation of hemilabile ligands.

Initial interest in NHC catalyst systems promoted by the PGMs has been replaced by recent and versatile systems developed from NHC-Co(II),¹¹ NHC-Ni(0)^{2j, 12} and NHC-Ni(II)¹³ due to their cost effectiveness and distinct catalytic abilities. Such complexes have proven to be

active in C-S coupling,¹⁴ cyclo addition,¹⁵ addition polymerization of norbornane,¹⁶ aryl amination,^{2j, 13, 17} C-C coupling, styrene polymerization¹⁸ Suzuki and Kumada coupling reactions.¹⁹ It is worthy to note that the stability to air and moisture exhibited by electron rich NHC-M(II) complexes is not observed in their M(0) analogues. Catalytic systems based on Ni(II)-NHC complexes are active without the need for a co-catalyst, while those based on Ni(0)-NHC complexes do require the use of co-catalysts for their activity.⁷

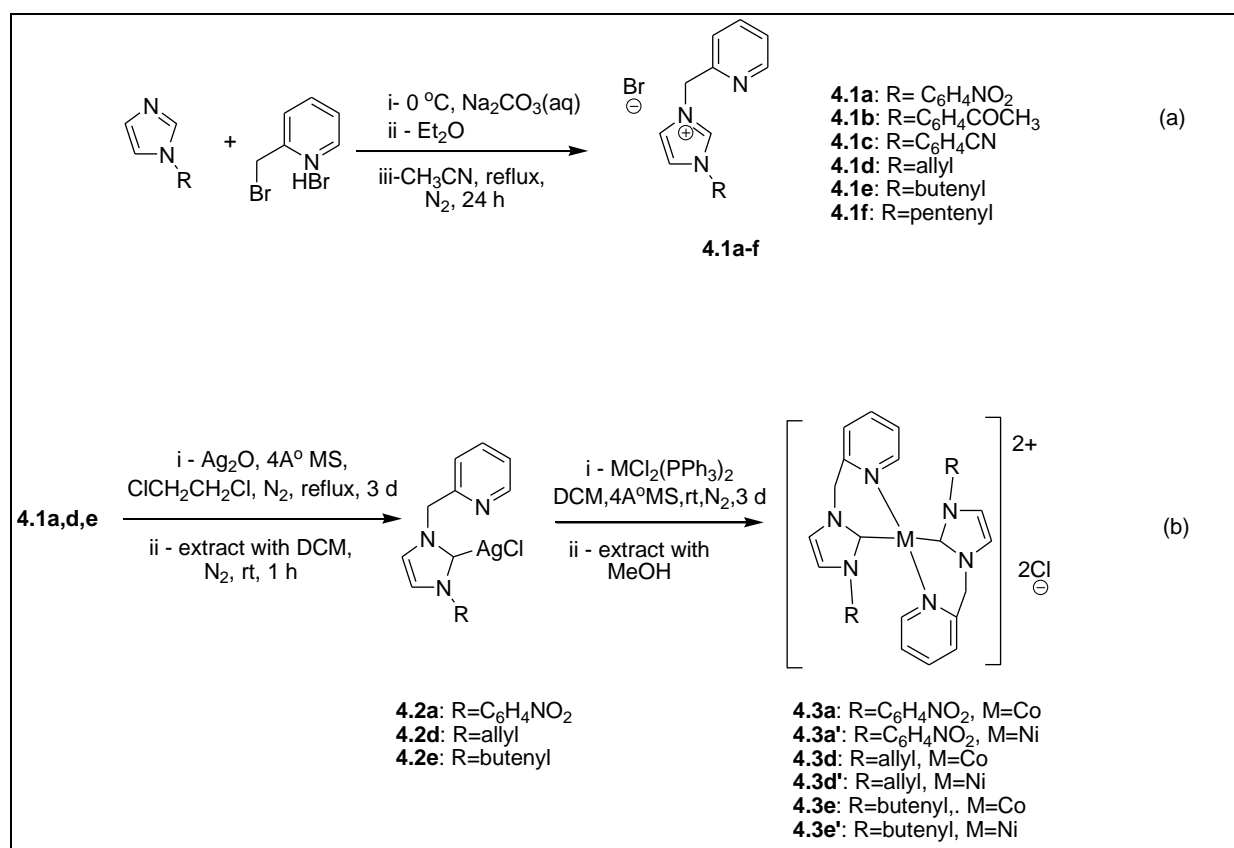
Coupling reactions like C-N coupling are very important in organic synthesis as routes to important groups of chemicals for pharmaceutical, industrial and synthetic applications. Although, most aryl C-N coupling reactions were catalysed by Pd(0) or copper mediated Ullman reactions; the use of the former is not economical and employed the application of phosphonated ligands²⁰ while the latter proceeded via harsh conditions, high temperatures or requires stoichiometric amounts of a copper catalyst.²¹ Such catalyst systems do often work in the absence of an organic ligand, however excess amounts of the substrates which are organic are used to fill up for the deficiency.²² Except for the use of Ni(0)/bisarylimidazolium salts by Kuhl *et al.*^{2j} and recent work by Matsubara and co-workers where they used a nickel(II) halide complex bearing a mixed PPh₃/NHC ligand as a catalyst precursor¹³, efficient catalyst systems containing nickel as the central metal for arylation of aromatic amines are still rare. To the best of our knowledge the use of functionalised, tridentate and sterically demanding NHC-metal complexes incorporating environmentally benign metals like cobalt and nickel as catalysts for the arylation of aniline is still novel. Herein, we report the synthesis of new tridentate functionalised imidazolium salts and their Ag, Co and Ni complexes. Findings on the application of the complexes as catalysts for the coupling of aryl amines with aryl halides to selectively yield diaryl amines products are also reported.

4.2 Results and discussions

4.2.1 Synthesis:- picolyl functionalised salts

In the synthesis of the *N*-substituted imidazoles; conventional synthetic strategy applicable to the type of *N*-substituent were applied.²³ The picolyl functionalised ligand precursors (**4.1a-f**) were synthesised using modification of established procedures [Scheme 4.1 (a)]²⁴ and purified in an almost similar strategy to their corresponding *N*-substituted imidazoles. All the imidazolium salts were obtained in excellent yields via a purification technique described for

similar salts.²⁵ The effect of reaction solvent on product yield and reaction rate was studied in the synthesis of the imidazolium salts. Acetonitrile tend to give higher yields with great ease of purification when compared to DCM, methanol or toluene as reaction solvent.^{24a, 26} Both 3-(4-nitrophenyl)-1-picolylimidazolium bromide **4.1a**, and 3-(4-cyanophenyl)-1-picolylimidazolium bromide **4.1c**, precipitated out from the reaction solution after about 12 h of reaction time; and eventually obtained by a simple filtration of the salt under nitrogen followed by washing with dry acetonitrile. Alternatively, the crude product may be concentrated and the salt isolated as methanol eluent via column chromatography.²⁵ Both **4.1b** and the alkenyl picolyl imidazolium salts **4.1d-f**, were purified in a similar fashion as methanol eluents which were then isolated as either grey-brown highly hygroscopic solids (**4.1b**), brown waxy substance (**4.1d**) or light brown oils (**4.1e & f**).



Scheme 4.1: Synthesis of (a) functionalized imidazolium salts with picolyl moiety and (b) picolyl functionalised imidazol-2-ylidene(NHC)-Ni(II) and Co(II) complexes.

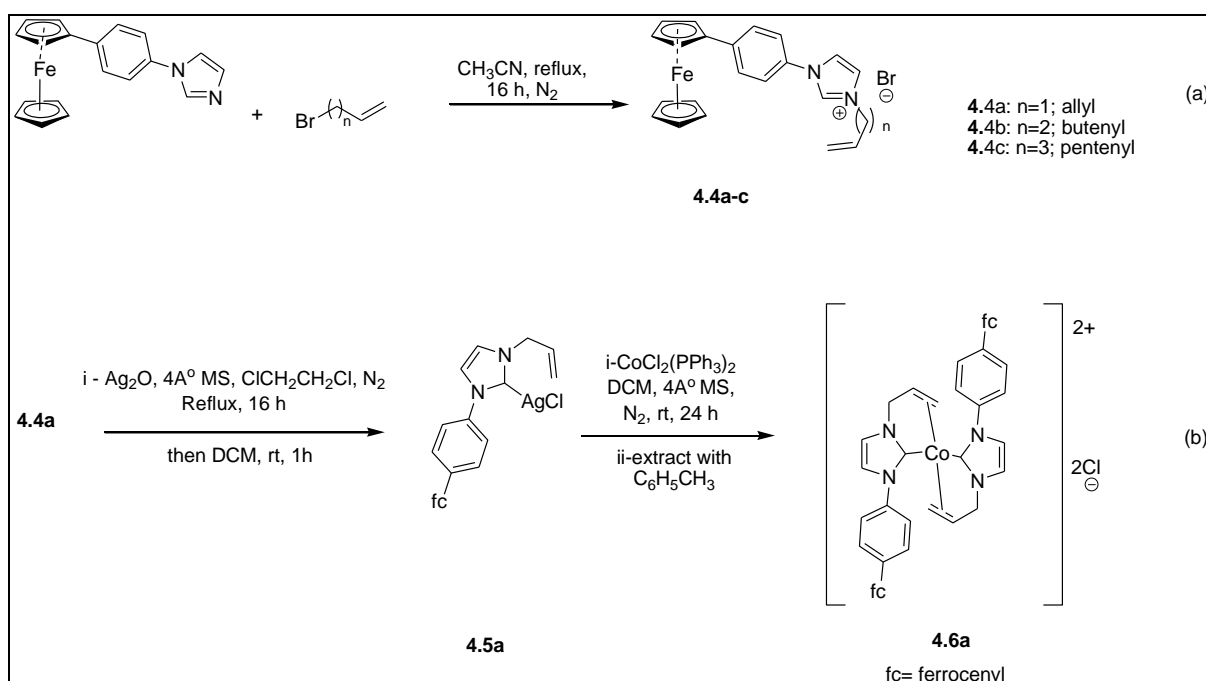
4.2.2 Characterization

Each of the salts (**4.1a-f**) showed a distinct singlet peak at between 9-11 ppm in their ^1H NMR spectra; which is typical of a C-2 imidazolium proton.^{6a, 27} Coupling of the imidazole with the picolyl moiety in all the salts **4.1a-f** was confirmed with the appearance of a distinct singlet characteristic of the methylene (NCH_2) that always appeared at around 5.5-5.7 ppm;^{7, 24a} integrating for 2H. The alkenyl C2 protons ($\text{CH}_2=\text{CH}$) appeared as a multiplet in **4.1d-f**, while the distinct singlet at 2.60 ppm corresponded to the methyl group on the acetyl functional group in **4.1b**. The rest of the protons in the ^1H NMR spectra of all the salts were within the aromatic region and conformed to the expected integration and coupling multiplicity. The corresponding ^{13}C NMR spectra of the salts gave the methylene carbon peak (NCH_2) at the range 53.5-54.9 ppm with the characteristic down field peak of the imidazolium carbon at 152-154 ppm.^{24a, 27a} The carbonyl $\text{C}=\text{O}$ appeared at 1675 cm^{-1} in the FTIR spectrum of **4.1b**, while corresponding methyl carbon from the acetyl functional side and the characteristic carbonyl carbon peak appeared at 65.8 and 196.4 ppm respectively in the ^{13}C NMR spectrum. The CN peak in **4.1c** appeared at 117 ppm in its ^{13}C NMR with its stretching vibration peak (FT-IR) at 1597 cm^{-1} . All the salts **4.1a-f** are extremely hygroscopic and quickly imbibed varying quantities of moisture (FTIR broad peaks at $3349\text{--}3355\text{ cm}^{-1}$). Unfortunately, this property made it difficult to obtain exact and accurate CHN analysis results. This is a common problem that has been reported for similar imidazolium salts.²⁵ However, the purity of the salts has been established from their NMR and corresponding HRMS analysis results. HRMS data for all the salts gave peaks that corresponded to the molecular ion with the loss of the bromide counter ion. All the found values are within acceptable limits of calculated values. The three solid microcrystalline salts **4.1a-c** showed sharp melting temperatures of $220\text{--}222\text{ }^\circ\text{C}$, $199\text{--}202\text{ }^\circ\text{C}$ and $265\text{--}267\text{ }^\circ\text{C}$ respectively, indicative of pure solids.

4.2.3 Synthesis:- ferrocenyl functionalised imidazolium salts

N-substituted 4-ferrocenylphenyl imidazole and the subsequent alkenyl-4-ferrocenylphenyl imidazolium salts **4.4a-c** were prepared by modification of reported literature methods [Scheme 4.2 (a)].^{24b, 28} With the exception of the butenyl functionalised salt; the rest of salts were obtained in good to excellent yields. It is assumed that the high sensitivity of the adduct (butenyl bromide) to light and air was responsible for the low yield of **4.4b** which was also

extremely sensitive to light and air as it decomposed immediately upon exposure. On the other hand, the allyl functionalised **4.4a** and the pentenyl functionalised **4.4c** salts are relatively stable in air. Another distinctive feature of the alkenyl salts is that; while the allyl version was easily purified by precipitation out of the crude product mixture with diethyl ether; the two other members were trapped on a short plug of silica in a column. Then the unreacted starting materials were removed with ethyl acetate while the salts were obtained as eluents of methanol and concentrated under reduced pressure. For example, the addition of dry ether to a concentrated methanol fraction gave **4.4c** as orange-brown microcrystals partially stable in air and very stable in DCM, chloroform and methanol.



Scheme 4.2: Synthesis of (a) alkenyl-4-ferrocenylphenyl imidazolium salts and (b) allyl-4-ferrocenylphenyl imidazol-2-ylidene(NHC)-Co(II) complex.

4.2.4 Characterization

¹H NMR analysis of **4.4a-c** in CDCl₃ gave peaks that corresponded to substituted Cp at 4.6 and 4.3 ppm which accounted for 2x2H and the unsubstituted Cp at 4.0 ppm which integrated to 5H; while in the corresponding ¹³C NMR spectra the corresponding peaks were observed at 69 and 66 ppm respectively. Like in all other imidazolium salts, a down field singlet peak observed in the region >9.5 ppm accounted for the imidazolium proton, while the

corresponding imidazolium C-2 carbon appeared as a peak at far down field >142 ppm in the ^{13}C NMR. The two complementing characteristic peaks that accounted for salt formation were similar to reported values for similar compounds.^{27b, 28 24b} Both **4.4a** and **4.4c** gave acceptable EA results when augmented with imbibed water (moisture) molecules. All HRMS data were consistent with proposed molecular structures within acceptable limits.

4.2.5 Synthesis and characterization of metal-NHC complexes

All the nickel and cobalt complexes reported herein were synthesized via transmetalation from corresponding Ag-NHC complexes [Schemes 4.1 (b) and 4.2 (b)]. It is worthy to note that difficulties encountered in the formation of Ag-NHC of bulky ligand precursors by conventional methods could be alleviated with the use of Ag_2O in refluxing 1,2-dichloroethane.^{7, 10b, 24a, 29} The incorporation of molecular sieves was to improve the yields and eliminate moisture and other impurities. Hence, Ag-NHC complexes of **4.1a**, **4.1d**, **4.1e** and **4.4a** were prepared by refluxing the corresponding mixtures of the salts and excess Ag_2O in 1,2 dichloroethane for 3 d, within which the dark colour of Ag_2O disappeared. The complete formation of the Ag-NHC complexes was qualitatively determined by monitoring the disappearance of the C2 imidazolium proton (9—11 ppm) in the ^1H NMR spectra of the crude products. Concentration of the crude and extraction with DCM afforded the Ag-NHC complexes **4.2a**, **4.2d**, **4.2e** and **4.5a**; with exchange of the halide ion from the original bromide of the salt to chloride.^{19a} Complexes **4.2a** and **4.5a** are stable to air and light and were isolated and fully characterized. **4.2a** (88% yield) was obtained as dark brown air stable microcrystals, melting point 173—176 °C, while **4.5a** (85% yield) was obtained as air stable orange microcrystals, melting point 63—66 °C. The lower melting temperatures of the Ag-NHC complexes as compared to the ligand precursors is an indicator of the relative low thermal stability of the Ag-NHCs as compared to the imidazolium salts.³⁰ The two other Ag-NHC complexes derived from salts **4.1d** and **4.1e** were used *in situ* for transmetalation to Co and Ni without further characterization due to their high sensitivity to air, moisture and light. The absence of a distinct singlet peak at 10.2 or 10.9 ppm initially observed respectively in the ^1H -NMR data of the ligand precursors **4.1a** and **4.4a** indicated successful deprotonation of the imidazolium proton by the basic Ag_2O . ^{13}C NMR data of **4.2a** confirmed the formation of a NHC-Ag complex with a downfield shift of the C2 carbon from 152 ppm in the corresponding imidazolium salt **4.1a** to 180.4 ppm in **4.2a**; typical of a carbene-metal bond.³¹ The methylene protons in the picolyl moiety also shifted up-field (5.70 to 5.58 ppm)

in the ^1H NMR data of **4.2a** with a corresponding downfield shift of the methylene carbon peak (53.5 to 56.4 ppm) as reported for similar Ag-NHC complexes.^{24a} The elemental analysis (CHN) data obtained for both **4.2a** and **4.5a** agreed with the formation of Ag(ligand)Cl rather than Ag(ligand)Br complexes; thereby confirming that metathesis of the halide did occur with the use of refluxing 1,2-dichloroethane. The MS-ES⁺ results of **4.2a** and **4.5a** gave molecular ions corresponding to the [(ligand+H)]⁺ and [Ag(ligand)₂]⁺ characteristic of Ag-NHC complexes of the form Ag(ligand)halide.^{24a}

Transmetalation of the Ag-NHC complexes **4.2a**, **4.2d**, **4.2e** and **4.5a** to the desired cobalt or nickel with either $\text{CoCl}_2(\text{PPh}_3)_2$ or $\text{NiCl}_2(\text{PPh}_3)_2$ as the metal precursors was achieved by a slight modification of established transmetalation procedure.⁷ A distinct colour change in each of the reactions was an early indicator of successful transmetalation. For example, the blue colour of the DCM solution of $\text{NiCl}_2(\text{PPh}_3)_3$ was observed to gradually fade and develop a yellow/orange precipitate of the product $\text{Ni}(\text{NHC})_2\text{Cl}_2$. Unreacted Ag-NHC, the metal precursor and displaced PPh_3 were removed as DCM soluble components by washing and cannula filtration. Extraction of the residue with methanol followed by filtration through a bed of celite and final evaporation of the solvent under reduced pressure afforded the respective orange lemon-green fairly air stable powders of $\text{Ni}(\text{NHC})_2\text{Cl}_2$ (**4.3a'**, **4.3d'**, **4.3e'**) or equally air stable dark green powders of the $\text{Co}(\text{NHC})_2\text{Cl}_2$ (**4.3a**, **4.3d**, **4.3e**) complexes. The cobalt complexes turned into dark orange solutions when dissolved in methanol while the nickel complexes maintained their colour in methanol solutions. None of the complexes showed a peak around 9-11 ppm in their respective ^1H NMR spectra, a confirmation of successful deprotonation of the imidazolium proton and formation of a carbene-metal bond. Purity of the complexes was confirmed by their ^{31}P NMR data which gave no peak around -6 ppm characteristic of PPh_3 .³² The complexes were further characterized by melting point, FTIR, MS-ES⁺ and HRMS.

The ^1H NMR data of **4.3a** accounted for all the expected protons, although the expected doublet and singlet peaks that account for the diastereotropic methylene protons in each ligand moiety as observed in similar complexes,^{7, 9a} appeared as a singlet with a slight up-field-shift from 5.58 ppm in **4.2a** to 5.47 ppm in **4.3a**. This was attributed to possible dynamic atropisomerization that might exist in the three aromatic rings that generated the ligand moieties as observed in related NHC-metal complexes bearing pincer CNC architecture.³³ In such systems, only at fast rate of inter-conversion would the two methylene (NCH_2) protons be observed on the same plane and generate a singlet peak as observed in this

case. The yellow microcrystalline Ni-NHC complex **4.3a'** gave a ^1H NMR data similar to that obtained for the Co-NHC analogue. Although the peaks are not as sharp, they accounted for all the protons. Similarly, the expected diastereotropic protons representing NCH_2 methylene protons appeared as singlet peak with slight up-field as observed in the Co-NHC complex **4.3a**.

Cobalt complexes **4.3d** and **4.3e** gave identical broad ^1H NMR spectra, although distinct peaks corresponding to the expected protons were fully accounted for in the spectrum of **4.3d**. A broad multiplet peak in **4.3e** at 8.81—7.89 ppm integrated to $2 \times 6\text{H}$, accounting 4H (pyridyl) and 2H ($\text{CH}=\text{CH}$ imidazolyl). The methylene protons from the picolyl moieties of individual ligands appeared as a distinct singlet and a doublet around 5.9 and 5.3 ppm in both **4.3d** and **4.3e** due to diastereotropic relationship existing in the protons. Both **4.3d** and **4.3e** are paramagnetic, high-spin species as observed from the respective magnetic susceptibility (2.53 and $2.73 \mu_{\text{B}}$) measurements.³⁴ These values are in agreement with data reported for related cobalt complexes and are consistent with one unpaired electron.^{11b} However, fully resolved ^1H NMR spectra were obtained for the corresponding nickel complexes **4.3d'** and **4.3e'**, with all the expected proton peaks accounted for. The characteristic doublet and singlet peaks accounting for the diastereotropic protons of each methylene bridge in each of the ligand moieties appeared in **4.3d'** at δ 5.81 and 5.97 and for **4.3e'** at δ 5.90 and 5.65 a confirmation of complexation to the dicarbene nickel complexes.

Finally, the addition of orange DCM solution of **4.5a** to a green DCM solution of $\text{CoCl}_2(\text{PPh}_3)_2$ gave a green solution that was continuously stirred for 24 h in the dark, after which all volatiles were removed. Unlike what was previously observed in the formation of cobalt complexes **4.3a**, **4.3d** and **4.3e** no distinct green solid or precipitate was formed in this case. However, the resulting crude solid obtained was washed with hexane to remove liberated phosphines and the cobalt complex extracted with dry toluene and filtered through a bed of celite. Removal of all volatiles followed by several ether rinses afforded a yellowish-green gelatinous precipitate which was filtered and dried to give a lemon green air stable powder (72% yield). The powder has a high melting point (196—198 °C) and its ^1H NMR data strongly suggested it to be the desired Co-NHC complex **4.6a**, because all the expected protons were fully accounted for in the NMR spectrum. The imidazolyl and phenyl protons coalesced around the peaks of the CDCl_3 solvent with a significant down-field shift of the protons in the allyl moiety when compared with the chemical shift in the intermediate (**4.5a**);

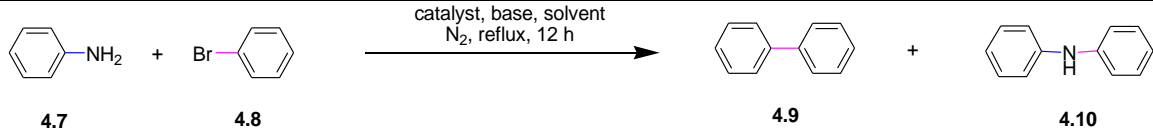
i.e. allyl C3(2H): shifted from 4.38 to 5.28; C1(2H): from 5.30 to 5.53 and C2(1H): from 6.00 to 6.11 ppm.

4.2.6 Catalytic arylation of aniline

The pioneering works of Migata and co-workers in 1983 paved the way to transition metal catalysed arylation of amines with aryl halides,³⁵ although, credit for C-N coupling is attributed to Stephen L. Buchwald and John F. Hartwig after whom the well-known Buchwald–Hartwig amination was named.^{20a, 36} Most C-N coupling reactions are initiated by bases which function to reduce and activate the catalytic metal centers. Alkali metal salts KO^tBu and NaO^tBu are the most effective bases in catalytic reactions involving C-C coupling of α -ketones with aryl halide,¹³ metal-NHC catalysed arylation of aromatic amines,^{2j, 13, 20b} CuTC catalysed arylation of amines and amides^{22d}, etc. The organic nature of the bases and the fact that their precipitates could easily be isolated and removed are some of the advantages associated with their use in such coupling reactions. More common bases like KOH are known to react and give phenolic products while K₃PO₄ usually gave lower yields in C-N coupling reactions.³⁷ However, inorganic bases like K₂CO₃ and Na₂PO₄ are specifically preferred in Cu-catalysed aryl C-N coupling.³⁷⁻³⁸

With the aforementioned information in mind, preliminary investigation of the C-N coupling reaction of aniline (**4.7**) and phenyl bromide (**4.8**) was conducted in THF, acetonitrile and dioxane promoted by KO^tBu as the base to yield the desired arylated amine (**4.10**). Results of the preliminary study are presented in Table 4.1 and further discussed below.

Table 4.1: Optimization of reaction conditions for arylation of aniline (4.7) with phenyl bromide (4.8)

						
Entry	Catalyst	Substrates' mole equivalents		Solvent	Yield (%) ^a	
		4.7	4.8		4.9	4.10
1	-	1.2	1	THF	13	Trace
2 ^b	-	1.2	1	THF	-	-
3	-	-	1.2	THF	-	-
4 ^c	-	1	1.2	THF	-	-
5	4.3d	1.2	1	THF	28	32
6	4.3d	1	1.2	THF	27	40
7	4.3d'	1	1.2	THF	21	60
8	4.3d'	1	1.2	Acetonitrile	Trace	Trace
9	4.3d'	1	1.2	Dioxane	29	41
10	4.3a'	1	1.2	THF	28	67
11	4.3a	1	1.2	THF	30	15
12	4.3e'	1	1.2	THF	21	40
13	4.3e	1	1.2	THF	13	20
14	4.6a	1	1.2	THF	15	70
15 ^d	4.3a'	1	1.2	THF	12	Trace
16 ^e	4.3a'	1	1.2	THF	18	20
17 ^f	4.3a'	1	1.2	THF	31	68
18 ^g	4.3a'	1	1.2	THF	38	28
19 ^h	4.3a'	1	1.2	THF	23	69
20 ^f	NiCl ₂	1	1.2	THF	Trace	Trace
21 ^f	NiCl ₂ / 4.1a (1:1)	1	1.2	THF	25	60
22 ^f	NiCl ₂ / 4.1a (1:2)	1	1.2	THF	28	65
23	NiCl ₂ / 4.1a (1:2)	1	1.2	THF	24	63

Except otherwise mentioned, all reactions were done with 1 mol% of catalyst, 1.2 mole equivalent KO^tBu, under an atmosphere of nitrogen and refluxing solvent for 12 h. Progress of reaction monitored by TLC. ^a Isolated yield from column chromatography, average of two runs. ^b Reaction done at room temperature. ^c Reaction done in the absence of a base. ^d 1.2 mole equivalent of K₂CO₃ used as the base. ^e 1.2 mole equivalent of Na₂PO₄ used as the base. ^f Reaction done for 18 h. ^g 0.5 mol% of catalyst used. ^h 2.0 mol% of catalyst used.

As a control reaction, the two substrates were reacted together in the absence of any catalyst (entry 1) and as expected no trace of the desired diphenyl amine was recorded. However, 13% of biphenyl (confirmed by NMR and IR) as a yellowish-white solid, mp 70—72 °C was isolated as a by-product in what is believed to be a variant of the Hiyama (C-C) coupling reaction.³⁹ Further studies were conducted on the blank control reaction (entries 2, 3 and 4) by first lowering the reaction temperature to room and conducting the reaction in the absence of a base or the aryl amine. The results indicate an interesting trend that heat, base and both substrates are all required for the reduction and dimerization of the aryl halide.

The application of 1 mol% of $\text{Co}(\text{allylNHC})_2\text{Cl}_2$, **4.3d** with a slight molar excess of the aryl amine yielded a modest quantity of the desired diphenyl amine (32%, entry 5) along with a corresponding increase in the quantity of the biphenyl product. By changing the relative mole ratios of the substrates such that a slight excess of the aryl halide was used and maintaining the same catalyst as in entry 5, an increase in the isolated yield of the 2° amine and a slight decrease in that of the side product was observed (entry 6). This implies that; the aniline itself is promoting the unwanted aryl halide reduction and the catalyst selectivity plays the dual role of promoting aryl amination while suppressing biphenyl formation. While maintaining the solvent and the mole ratio of the substrate and the base; and using the corresponding Ni analogue **4.3d'** (entry 7), an improvement in the yield of the desired 2° amine (60%) was observed. This was expected as most non-precious metal catalyst systems reported to be active in C-N coupling reactions are based on nickel metal and its complexes.²ⁱ

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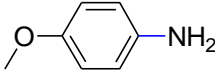
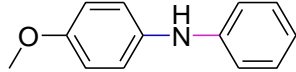
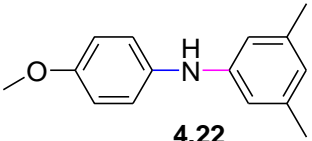
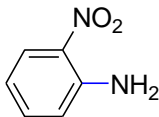
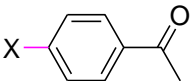
The role of solvents is important in aryl coupling reactions as entries 8 and 9 indicate that THF is the best solvent suited for the current catalyst systems, as both acetonitrile and dioxane negatively affected catalyst productivity. This observation implies that despite the fact that both THF and dioxane are ethereal solvents, mono *N*-arylation of aromatic amines is more facile in THF. In a related work by Kuhl *et al* selective mono *N*-arylation of aromatic diamines was achieved in THF, while *N,N'*-diarylation of the aromatic diamines was the result when refluxing dioxane was used.^{2j} Based on the results of entries 7—9; THF was henceforth, used as the reaction solvent to study the influence of other catalyst parameters (entries 10—23). Parameters investigated include the influence of various bases, steric and electronic nature of the NHC ligand and the availability of two electroactive metal centres.

Hence, entries 12 and 13 illustrate the influence of ligand sterics on the catalysis with bulkier butenyl functionalised catalysts **4.3e** and **4.3e'** yielding lower conversions of the desired product when compared to the allyl variants (entries 5 and 6). Entry 14 based on the ferrocenyl functionalised catalyst **4.6a** yielded the highest conversion to the desired product (70%). This is an indication of cooperative effect of two electroactive (ferrocenyl and Co^{2+}) centres. Further studies were conducted with **4.3a'** and *in situ* generated catalyst systems obtained from the mixture of imidazolium salt **4.1a** and anhydrous NiCl_2 (entries 15–22). Only traces or low yield (20%) of the desired diphenyl amine were obtained with the use of K_2CO_3 and Na_2PO_4 as bases (entries 15 and 16 respectively). After increasing the reaction time to 18 h (entry 17), not much increase in yield of the desired diarylamine (68%) was observed as compared to the standard 12 h (entry 10, 67%). Entries 18 and 19 indicate that the optimum catalyst loading for the current system is 1 mol% as the productivity was significantly diminished at 0.5 mol% loading and showed negligible increase when 2 mol% loading was used.

Finally, the study was extended to investigate *in situ* generated catalyst systems. The work of Kuhl *et al.*,^{2j} has shown that; bulky imidazolium salts could generate *in situ* catalysts from their mixture with appropriate metal sources,^{2j} and also one of our works has shown that *in situ* generated NHC-Fe complexes are efficient systems for the transfer hydrogenation of ketones.⁴⁰ Therefore, entries 21–23 report on the efficiency of *in situ* generated catalysts in this study. A mixture of NiCl_2 /**4.1a** yielded 63% of the desired product after 12 h reaction time which is comparable to the most active catalyst (**4.6a**) tested thus far. This is a very important finding given the difficulty and laborious synthetic strategies required for the preparation and isolation of the metal complexes. Hence, in order to study the extent and limitations of the *in situ* generated catalysts, the study was extended to a series of aryl amine/aryl halide combinations bearing a variety of functional groups. The results of this study are presented in Table 4.2 and following discussion and for the purpose of comparison, complex **4.3a'** was run alongside the *in situ* ones under the same reaction conditions.

Table 4.2: NHC-metal complexes catalysed *N*-mono arylation of aryl amines with aryl bromides.

Entry	Substrate	Product	Catalyst	Yield(%) ^b
1			4.3a'	67
	4.7	4.8		
1a			NiCl ₂ / 4.1a	65
2			4.3a'	69
	4.7	4.11		
2a			NiCl ₂ / 4.1a	66
3			4.3a'	71
	4.7	4.13		
3a			NiCl ₂ / 4.1a	69
4			4.3a'	81
	4.7	4.15		
4a			NiCl ₂ / 4.1a	79
5			4.3a'	73
	4.7	4.17		
5a			NiCl ₂ / 4.1a	70
6			4.3a'	70
	4.7	4.19		
6a			NiCl ₂ / 4.1a	70
		4.20		

7		4.8		4.3a'	75
	4.21		4.20		
7a				NiCl ₂ /4.1a	73
8	4.21	4.13		4.3a'	76
			4.22		
8a				NiCl ₂ /4.1a	78
9		4.8		4.3a'	0
	4.23				
9a				NiCl ₂ /4.1a	0
10	4.7			4.3a'	Aldol
		4.24			
		X=Cl, I			
10a				NiCl ₂ /4.1a	Aldol

All reactions were conducted with either **4.3a'** (1.0 mol%) or a mixture of NiCl₂/**4.1a** (1:2 molar ratio), KO^tBu (1.2 mole equivalent), aryl amine (1.0 mole equivalent), aryl bromide (1.2 mole equivalent), under an atmosphere of nitrogen and refluxing THF (20 ml) for 12 h. Progress of the reaction was monitored by TLC. ^bIsolated yield from column chromatography on average of two runs.

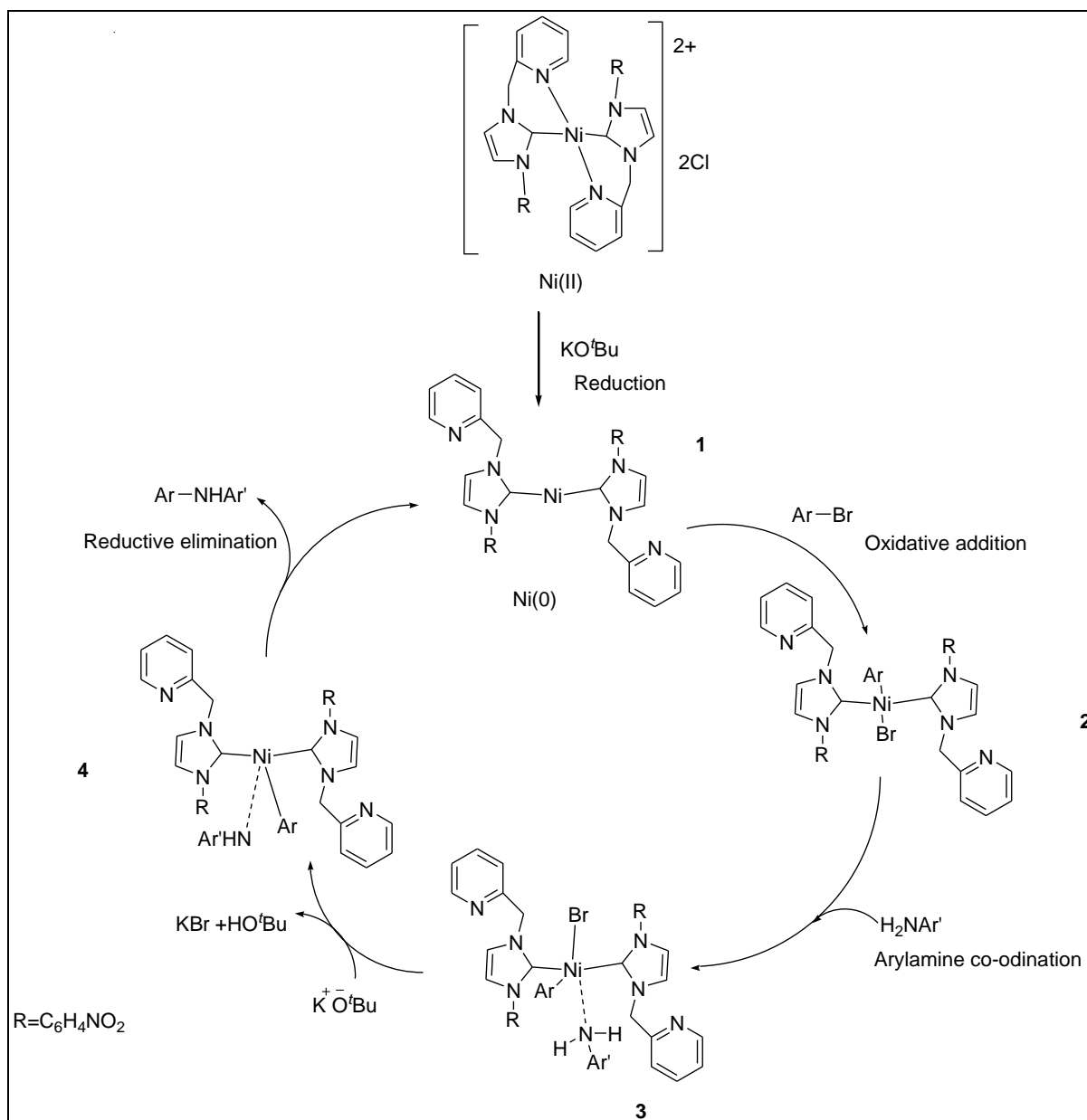
A recent microwave assisted Pd-NHC catalysed C-N coupling reaction was reported^{20b} with an average yield of 84% which is comparatively higher than values reported here. However, what this study has demonstrated is that appreciably good yields of the diphenyl amine could be obtained under milder conditions with a cheap and environmentally benign nickel catalyst. Hence, an examination of the variety of substrates in Table 4.2 reveals that the steric position or electronic nature of the substituent on the aryl halide had very little overall influence on the coupling reaction as most substrate combinations returned comparable isolated yields of the desired product of circa 70%. A noticeable improvement was observed with *para*-substituted aryl bromide bearing the electron withdrawing CN group (entry 4, circa 80% yield) which has been established to render the aryl halide more reactive and easily susceptible to oxidative attack by the nickel centre.

Under the present reaction conditions with either catalyst system, no products were isolated in the attempted arylation of 2-nitro aniline, which is similar to reports for related substrates

under more harsher reaction conditions and CuI as catalyst.⁴¹ Both catalysts (**4.3a'** and NiCl₂/**4.1a**) also failed to activate the formation of the desired diarylamine with the mixture of aniline and *p*-chloro or iodoacetophenone. In both cases, aldol product from the self-condensation of acetophenone was isolated in excellent yields which has also been reported by Matsubara *et al.* to be more facile in such base promoted competitive reactions.¹³ Finally, it is interesting to note that in all the combinations studied, comparable catalytic efficiencies were recorded for the isolated metal complex **4.3a'** and the *in situ* generated NiCl₂/**4.1a** catalyst, hence opening up a simple, robust and functional group tolerant system for C-N coupling reactions.

4.2.7 Proposed mechanism

Recent and past studies on Ni and Pd-NHC complex catalysed aryl C-N coupling reactions have been achieved with the metal in the zero (0) oxidation state. In such studies, the choice of the base was mostly associated with the ease to which it was able to initiate reduction of the metal centre and thereby create the active specie with an oxidation state capable of activating the coupling reaction. On this basis a mechanistic pathway (Scheme 4.3) is proposed for the Ni-NHC activated C-N coupling reported in this study. As mentioned earlier, the design of the ligands and complexes was such that stable nickel or cobalt(II)-NHC complexes were obtained and based on their morphology and *cis*-geometry such complexes could be easily reduced to the desired Ni(0) or Co(0) species (**1**; Scheme 4.3). It is assumed that; available electrons from the base will reduce the metal centre, and at the same time result in the detachment of the pyridyl *N*-Metal bond, thereby creating a coordination site for the aryl halide substrate (**2**; Scheme 4.3). The nucleophilic addition of the aryl amine will generate a five membered metal centre (**3**; Scheme 4.3) and the subsequent release of the diarylamine product via reductive elimination (**4**; Scheme 4.3) completes the catalytic cycle regenerating the active Ni(0) specie.



Scheme 4.3: Proposed mechanism for the Ni(II)-NHC complex catalysed C-N coupling of aryl bromides with aryl amines.

4.3 Conclusions

Here in we have reported the successful synthesis in excellent yields of six new imidazolium salts bearing a picolyl moiety and three new salts with *N*-substituted 4-ferrocenylphenyl imidazole. The salts were conveniently characterized and their purity established. As precursors of NHC ligands; four of these salts were metalated with silver, affording Ag-NHC complexes in good yields. Transmetalation of both the isolated and *in situ* utilized Ag-NHC

complexes afforded the desired Co or Ni-NHC complexes in good to excellent yields based on $\text{CoCl}_2(\text{PPh}_3)_2$ or $\text{NiCl}_2(\text{PPh}_3)_2$ as metal precursors respectively.

All the seven complexes are active in catalysing *N*-mono arylation of aniline with phenyl bromide, with the highest yield obtained with the bimetallic complex **4.6a**. The catalyst systems showed excellent selectivity to *N*-mono arylation as no trace of *N,N*-diarylated products were observed. The excellent yields of the products, mild reaction conditions and the use of green, environmentally benign and cheap metals made the current catalyst systems competitive in comparison to classical Cu mediated or CuI catalysed Ullman coupling and Pd catalysed systems in the activation of aryl C-N coupling reactions.

4.4 Experimental

All experiments except mentioned otherwise were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were analytical grade and dried prior to use using standard techniques: THF and hexane in benzophenone distilled over sodium wire; methanol in iodine distilled twice over magnesium ribbons; 1,2-dichloroethane distilled over CaCl_2 and stored with molecular sieves and DCM distilled over calcium hydride or P_2O_5 .⁴² Methanol washed 4Å molecular sieves were activated by drying in an oven at 150 °C for 24 h followed by heating in a furnace at 500 °C for 2 d and cooled in a desiccator. Deuterated solvents were obtained from Merck and are used without further purification. Both $\text{CoCl}_2(\text{PPh}_3)_2$ and $\text{NiCl}_2(\text{PPh}_3)_2$ were prepared using a standard procedure.⁴³ *N*-substituted imidazoles and ferrocenyl phenyl imidazole were prepared by the modification of established procedures,²³ while the corresponding salts were purified and isolated using a recently reported technique.²⁵ The aryl amines used were analytically pure; obtained from Sigma-Aldrich and distilled prior to use and stored with molecular sieves. Potassium tertiary butoxide, 2-bromomethyl pyridine hydrobromide, allyl bromide, butenyl bromide, pentenyl bromide and all aryl halide substrates used were analytically pure; obtained from Sigma-Aldrich and used without further purification. NMR spectra were recorded on a Bruker ultra-shield Avance (400 or 600 MHz) spectrometer operating at room temperature unless stated otherwise and samples were dissolved in deuterated CDCl_3 , CD_3OD or DMSO-d_6 . The spectra were internally referenced relative to solvent peak(s) and chemical shift values recorded (δ ppm) with respect to $\delta = 0$ ppm for tetramethylsilane in both ^1H and ^{13}C NMR spectra.⁴⁴ Hysteresis loop measurement for determination of saturated magnetization was conducted on Vibrating Sample Magnetometer (VSM) Lakeshore 735.

Infrared spectra were recorded on a PerkinElmer universal ATR Spectrum 100 FT-IR spectrometer. Mass spectrometry and elemental analysis (where applicable) were recorded on Waters Micromass LCT Premier TOF MS-ES⁺ and ThermoScientific Flash2000 Elemental Analyser respectively.

4.4.1 General synthetic procedure for the ligand precursors 4.1a-f and 4.4a-c

The imidazolium salts which are NHC ligand precursors were synthesised by the modification of literature procedures.^{24-25, 28} Spectroscopic and analytical data obtained are presented. A typical and generic procedure for the synthesis of the imidazolium salts 3-*R*-1-(2-pyridylmethyl)imidazolium bromide (**4.1a-f**) is described:

A saturated solution of Na₂CO₃ was first used to neutralize 2-bromomethyl pyridine hydrobromide at 0 °C. The neutral pink solution obtained was then extracted with diethyl ether (3 x 10 ml) at 0 °C and the clear solution of liberated bromomethylpyridine dried over anhydrous MgSO₄ and filtered. The colourless filtrate was then reduced to 1/3 of the initial volume under reduced pressure and added to a solution of *N*-substituted imidazole (1 mole equivalent) in dry acetonitrile (40 ml) at 0 °C. The remaining ether was removed at reduced pressure and the content of the flask subjected to gentle reflux for 18 h. Progress of the reaction was monitored by TLC. The solvent was then removed under reduced pressure and the TLC of the crude obtained in methanol:ethyl acetate (1:4) solvent system gave unreacted starting materials with R_f values 0.7—1.0 while the salt remained unmoved at the spot. Purification was thus obtained with column chromatography. The starting materials were eluted out with ethylacetate and the salt obtained as methanol eluent. All volatiles were then removed at reduced pressure to give the salts in excellent yield.

3-(4-nitrophenyl)-1-(2-pyridylmethyl)imidazolium bromide (4.1a). Prepared from 2-(bromomethyl)pyridine (1.6 mmol) and equimolar para nitrophenyl imidazole in acetonitrile. Product obtained as redish-orange solid, yield: 0.52 g, 90%; mp 220—222 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.3 (s, 1H, NCHN), 8.58—8.50 (m, 4x1H, phenyl), 8.15—8.13 (m, 3x1H, pyridyl), 7.92—9.91 (m, 1H, pyridyl), 7.60 (d, *J*=7.8 Hz, 1H, CH=CH_{imidazolyl}), 7.43 (d, *J*=6.1 Hz, 1H, CH=CH_{imidazolyl}), 5.70 (s, 2H, NCH₂). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 152.9 (NCHN), 149.6, 147.6, 139.2, 137.5, 136.9, 125.5, 124.4, 123.8, 122.9, 122.7, 121.2, 53.6. FTIR (neat): ν_{moisture} 3404, ν_{C-H aromatic} 3017, ν_{C=C} 1625, ν_{NO} 1538, ν_{C=N} 1349,

ν_{Ar} 744 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{BrN}_4\text{O}_2$: C, 49.88; H, 3.63; N, 15.51. Found: C, 49.38; H, 4.11; N, 16.82. HRMS (m/z) for $\text{C}_{15}\text{H}_{13}\text{N}_4\text{O}_2$: calcd 281.1039, found 281.1030.

3-(4-acetylphenyl)-1-(2-pyridylmethyl)imidazolium bromide (4.1b). Prepared from 2-(bromomethyl)pyridine (0.31 g, 1.21 mmol) and 1-(4-(1H-imidazol-1-yl)phenyl)ethanone (0.23 g, 1.21 mmol) in acetonitrile. Product obtained as air sensitive shiny orange-brown microcrystal, yield 0.39 g; 91%; mp 199—202 °C. ^1H NMR (400 MHz, CDCl_3): δ 11.1 (s, 1H, NCHN), 8.51 (d, $J=4.4$ Hz, 1H, imidazolyl), 8.19 (s, 1H, imidazolyl), 8.07 (dd, $J=16.5$ Hz, 2x2H, phenyl), 7.97 (s, 1H, pyridyl), 7.83 (d, $J=7.7$ Hz, 1H, pyridyl), 7.74—7.71 (m, 1H, pyridyl), 7.35—7.26 (m, 1H, pyridyl), 5.96 (s, 2H, NCH_2 pyridine), 2.60 (s, 3H, CH_3 acetyl). ^{13}C NMR (400 MHz, CDCl_3): δ 196.4 (C=O), 152.1 (NCHN), 149.8, 137.8, 137.7, 137.5, 136.0, 130.5, 124.2, 124.1, 124.0, 121.8, 120.6, 54.2, 26.8. FTIR (neat): ν_{moisture} 3381, $\nu_{\text{C-H}}$ 3061, 2955, $\nu_{\text{C=O}}$ 1675, $\nu_{\text{C-N}}$ 1237, ν_{Ar} 836 cm^{-1} . HRMS (m/z) for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}$: calcd 278.1289, found 278.1293.

3-(4-cyanophenyl)-1-(2-pyridylmethyl)imidazolium bromide (4.1c). Dry acetonitrile solution of liberated bromomethylene pyridine (0.30 g, 1.18 mmol) was refluxed with acetonitrile solution of 4-imidazolylbenzotrile (0.20 g, 1.18 mmol). Crude product was obtained as distinct off-white precipitate within reddish-pink solution. Precipitate of the salt was filtered out of the mixture under atmosphere of nitrogen using vacuum filtration, rinsed with dried acetonitrile and dried in a desiccator. Yield: 0.37 g; 93%; mp 265—267 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 10.2 (s, 1H, NCHN), 8.57 (d, $J=4.4$ Hz, 1H pyridyl), 8.49 (d, $J=1.4$ Hz, 1H, pyridyl), 8.23 (dd 2x1H, $\text{CH}=\text{CH}$ imidazolyl), 8.12—7.61 (m, 3H+1H, phenyl), 7.59 (d, $J=7.8$ Hz, 1H, pyridyl), 7.42 (dd, $J=5.1$ Hz, 1H, pyridyl), 5.69 (s, 2H, NCH_2). ^{13}C NMR (400 MHz, DMSO-d_6): δ 153.0 (NCHN), 149.5, 137.9, 137.5, 136.8, 134.4, 124.4, 123.8, 122.7, 122.6, 121.0, 117.8 (CN), 112.3, 53.6. FTIR (neat): ν_{moisture} 3345, ν_{CH} 3050, $\nu_{\text{CN(nitrile)}}$ 1597, ν_{Ar} 748. Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{BrN}_4\cdot\text{CH}_3\text{OCH}_3$: C, 55.82; H, 4.95; N, 14.47. Found: C, 55.76; H, 5.00; N, 19.03. HRMS (m/z) for $\text{C}_{16}\text{H}_{13}\text{N}_4$: calcd 261.1140, found 261.1131.

3-allyl-1-(2-pyridylmethyl)imidazolium bromide (4.1d). Acetonitrile solution of 2-bromomethyl pyridine (1.34 g, 5.3 mmol) was added drop wise to allyl imidazole (0.57 g, 5.3 mmol) in acetonitrile at 0 °C and the mixture subjected to reflux for 24 h. The salt was obtained as methanol eluent from column chromatography of the crude. All volatiles were then removed under reduced pressure to yield the pure salt as a brownish-grey waxy solid.

Yield: 1.29 g, 87.0%. ^1H NMR (400 MHz, DMSO- d_6): δ 9.78 (s, 1H, NCHN), 8.51 (s, 1H, pyridyl), 8.23 (s, 1H, pyridyl), 7.98 (d, 2H, CH=CH_{imidazolyl}), 7.36 (s, 1H, pyridyl), 7.22 (d, $J=12.9$ Hz, 1H, pyridyl), 6.51 (m, 1H, CH=CH_{allyl}), 5.69 (s, 2H, NCH₂), 3.44 (s, 2H, CH₂=CH_{allyl}), 1.78 (s, 2H, CH₂-N_{allyl}). ^{13}C NMR (400 MHz, DMSO- d_6): δ 153.2 (NCHN), 149.9, 137.5, 135.3, 123.7, 123.6, 122.9, 122.6, 121.7, 119.5, 53.0, 14.4. FTIR (neat): ν_{moisture} 3401, $\nu_{\text{C-H}}$ 3050, $\nu_{\text{C=C}}$ 1551, $\nu_{\text{C=N}}$ 1497, ν_{Ar} 759 cm^{-1} . HRMS (m/s) for C₁₂H₁₄N₃: calcd 200.1188, found 200.1183.

3-butenyl-1-(2-pyridylmethyl)imidazolium bromide (4.1e). Liberated 2-bromomethyl pyridine (1.34 g, 5.3 mmol,) in acetonitrile was added at 0 °C to acetonitrile solution of butenyl imidazole (0.65 g, 5.3 mmol) and refluxed. Isolated yield from column: 1.23 g, 79%; brown waxy solid. ^1H NMR (400 MHz, CD₃OD): δ 9.20 (s, 1H, NCHN), 8.57 (d, $J=4.6$ Hz, 1H, pyridyl), 7.90 (t, $J=1.6$ Hz, 1H, pyridyl), 7.69 (d, $J=2.0$ Hz, 2x1H, CH=CH_{imidazolyl}), 7.55 (d, $J=7.9$ Hz, 1H, pyridyl), 7.43—7.41 (m, 1H, pyridyl), 5.84—5.79 (m, 1H, CH=CH_{alkenyl}), 5.58 (s, 2H, NCH₂), 5.10—5.06 (m, 2H, CH₂=CH_{alkenyl}), 4.37—4.33 (m, 2H, CH₂ alkenyl), 2.68—2.66 (m, 2H, CH₂ alkenyl). ^{13}C NMR (400 MHz, CD₃OD): δ 154.4 (NCHN), 151.0, 139.2, 134.2, 125.3, 124.2, 123.6, 122.9, 119.6, 54.8, 50.2, 47.1, 35.3. FTIR (neat): ν_{moisture} 3358, $\nu_{\text{C-H}}$ 3050, 2973, $\nu_{\text{C=C}}$ 1628, $\nu_{\text{C=N}}$ 1450, ν_{Ar} 785 cm^{-1} . Anal. Calcd for C₁₃H₁₆BrN₃·2H₂O: C, 47.28; H, 6.10; N, 12.72. Found: C, 47.16; H, 6.40; N, 14.44. HRMS (m/s) for C₁₃H₁₆N₃: calcd 214.1344, found 214.1337.

3-pentenyl-1-(2-pyridylmethyl)imidazolium bromide (4.1f). Liberated 2-bromomethyl pyridine (1.34 g, 5.3 mmol) in acetonitrile was added to acetonitrile solution of pentenyl imidazole (0.72 g, 5.3 mmol) and refluxed. Isolated yield from column: 1.31 g, 81%; brown waxy solid. ^1H NMR (400 MHz, DMSO- d_6): δ 9.42 (s, 1H, NCHN), 8.54 (d, $J=4.8$ Hz, 1H, CH=CH_{imidazolyl}), 7.90—7.87 (m, 2x1H, pyridyl), 7.84 (s, 1H, CH=CH_{imidazolyl}), 7.52 (d, $J=7.7$ Hz, 1H, pyridyl), 7.40—7.38 (m, 1H, pyridyl), 5.85—5.81 (m, 1H, CH=CH_{alkenyl}), 5.60 (s, 2H, NCH₂), 5.05—4.95 (m, 2H, CH₂-N_{alkenyl}), 4.29 (t, $J=7.1$ Hz, 2H, CH₂=CH_{alkenyl}), 2.03—1.99 (m, 2H, CH₂ alkenyl), 1.94—1.89 (m, 2H, CH₂ alkenyl). ^{13}C NMR (400 MHz, DMSO- d_6): δ 153.5 (NCHN), 149.5, 137.5, 136.9, 127.8, 125.9, 123.6, 123.1, 115.7, 52.9, 48.5, 29.6, 28.3, 12.4. FTIR(neat): $\nu_{(\text{moisture})}$ 3402, $\nu_{\text{C-H}}$ 3072, $\nu_{\text{C=N}}$ 1437, 1158, and ν_{Ar} 756 cm^{-1} . Anal. Calcd for C₁₄H₁₈BrN₃·2H₂O: C, 48.85; H, 6.44; N, 12.20. Found: C, 49.24; H, 6.81; N, 13.97. HRMS (m/s) for C₁₄H₁₈N₃: calcd 228.1501, found 228.1495.

1-[1-allyl]-3-(4-ferrocenylphenyl)imidazolium bromide (4.4a). 4-Ferrocenylphenyl imidazole (0.271 g, 0.82 mmol) and allyl bromide (4.4 mmol, 0.38 ml) were refluxed together in acetonitrile (20 ml) under inert condition of argon for 24 h. The solvent was reduced to almost 3ml followed by addition of dry ether which prompted the precipitation of an orange microcrystalline substance which was further washed with dry ether (3x10ml) and then dried in vacuum. Yield: brown microcrystals, 0.25 g, 68%, mp 183—185 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.8 (s, 1H, NCHN), 7.75—7.55 (m, 5x1H: 4H; phenyl, 1H; CH=CH), 7.31 (d, *J*=8.2 Hz, 1H, CH=CH), 6.12—6.11 (m, 2H, CH=CH₂ alkenyl), 5.59—5.46 (m, 2H, CH₂=CH alkenyl), 5.26 (s, 2H, CH₂-N alkenyl), 4.66 (m, 2H, substituted Cp), 4.39 (m, 2H, substituted Cp), 4.06 (s, 5H, unsubstituted Cp). ¹³C NMR (400 MHz, CDCl₃): δ 142.7 (NCHN), 135.7, 131.7, 129.9, 127.6, 123.0, 122.6, 121.8, 82.7, 69.9, 66.8, 52.5, 40.9. FTIR (neat): ν_{moisture} 3337, ν_{CH} 3057, $\nu_{\text{C=C}}$ 1549, ν_{CN} 1418, ν_{Ar} 833 cm⁻¹. Anal. Calcd. for C₂₂H₂₁BrFeN₂·2H₂O·CH₃CN: C, 54.78; H, 5.36; N, 7.98. Found: C, 54.80; H, 4.84; N, 6.66. HRMS (m/s) for C₂₂H₂₁BrFeN₂: calcd 369.1054, found 369.1044.

1-[1-butenyl]-3-(4-ferrocenylphenyl)imidazolium bromide (4.4b). 4-Ferrocenylphenyl imidazole (0.19 g, 0.59 mmol) and excess of butenyl bromide (1ml, density 1.33 gml⁻¹) were mixed together in a Schlenk tube containing dry acetonitrile (30 ml). The mixture was refluxed under inert condition for 18 h with the progress of reaction monitored by TLC. The solvent was removed under reduced pressure and the crude purified by column chromatography. Unreacted starting materials were removed as eluents of ethyl acetate while the salt (that remained at the spot on TLC with ethyl acetate 100% solvent system) was obtained as methanol eluent. Concentration of the methanol fraction followed by subsequent addition of dry ether gave the salt as a yellow powder; unstable in air, but stable dissolved in DCM or chloroform. Isolated yield: 0.16 g; 60%. ¹H NMR (400 MHz, CDCl₃): δ 10.89 (s, 1H, NCHN), 7.63 (m, 4x1H, phenyl), 7.51 (s, 1H, CH=CH imidazolyl), 7.38 (s, 1H, CH=CH imidazolyl), 5.85 (m, 1H, alkenyl), 5.16—5.10 (m, 2H, CH₂ alkenyl), 4.68—4.60 (m, 4x1H, substituted Cp), 4.39 (s, 2H, CH₂=CH alkenyl), 4.06 (s, 5x1H, un-substituted Cp), 1.25 (m, 2H, CH₂-N alkenyl). ¹³C NMR (400 MHz, CDCl₃): δ 142.6, 132.7, 127.6, 122.2, 121.8, 119.8, 119.5, 82.1, 69.8, 66.8, 34.4, 29.7.

1-[1-pentenyl]-3-(4-ferrocenylphenyl)imidazolium bromide (4.4c). 4-Ferrocenylphenyl imidazole (0.20 g, 0.61 mmol) and excess of pentenyl bromide (1 ml) were mixed together in a Schlenk tube containing dry acetonitrile (30 ml). The mixture was refluxed for 18 h with progress monitored by TLC. Removal of the solvent under reduced pressure and purification

of the crude by trapping it on a short plug of silica in a column afforded the salt as eluent of methanol while the unreacted starting materials were initially removed as eluents of ethyl acetate. Concentration of the methanol fraction followed by subsequent addition of dry ether gave the salt as brownish-orange microcrystals relatively stable in air, DCM and chloroform. Isolated yield: 0.25 g, 86%. mp 185—188 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.9 (s, 1H, NCHN), 7.75 (d, *J*=12.9 Hz, 1H, CH=CH_{imidazolyl}), 7.70—7.61 (m, 4x1H, phenyl), 7.28 (s, 1H, imidazolyl), 5.83—5.74 (m, 1H, CH=CH_{alkenyl}), 5.09—5.01 (m, 2H, CH₂_{alkenyl}), 4.66 (d, *J*=1.7 Hz, 2H, Cp), 4.57 (t, *J*=1.3 Hz, 2H, CH₂-N_{alkenyl}), 4.39 (d, *J*=1.7 Hz, 2H, Cp), 4.04 (s, 5H, un-substituted Cp), 2.21 (m, 2H, CH₂_{alkenyl}), 2.17 (m, 2H, CH₂_{alkenyl}). ¹³C NMR (400 MHz, CDCl₃): δ 142.7, 136.1, 135.8, 131.7, 127.6, 123.9, 121.7, 120.4, 116.5, 82.5, 69.8, 66.8, 30.2, 29.7, 29.3. FTIR (neat): ν_{moisture} 3408, ν_{CH} 3039, 2941, ν_{C=C} 1549, ν_{C-N} 1411, ν_{Ar} 818 cm⁻¹. Anal. Calcd. for C₂₄H₂₅BrFeN₂·3H₂O: C, 54.26; H, 5.88; N, 5.27. Found: C, 54.69; H, 6.19; N, 7.05. HRMS (m/s) for C₂₄H₂₅N₂Fe: calcd 397.1367, found 397.1366.

4.4.2 Generic synthesis of Ag-NHC complexes **4.2a**, **4.2d**, **4.2e** and **4.5a**

Equimolar quantities of the required imidazolium salt (**4.1a**, **4.1d**, **4.1e** and **4.4a**) and Ag₂O were loaded into oven dried Schlenk tube containing 4 Å molecular sieves initially cooled under nitrogen. To this was then added 1,2-dichloroethane (30 ml) and the mixture subjected to vigorous stirring and refluxed in the absence of light for 3 d. By then, the dark colour of the silver(I)oxide had faded. The solvent was then removed under reduced pressure and the resulting residue extracted with DCM and filtered through a bed of celite. Compounds **4.2d** and **4.2e** were generated *in situ* (the absence of imidazolium C2-H at δ >9 in the ¹H NMR spectrum of the crude confirmed formation of Ag-NHC), and used immediately for transmetalation to the desired Co or Ni. Complexes **4.2a** and **4.5a**; were isolated from the DCM soluble filtrate which was first concentrated and the resulting residue stirred with hexane or toluene. Removal of solvents to dryness afforded the Ag-NHC complexes in excellent yields. The complexes were characterized by spectroscopic and analytical methods.

[1-(4-nitrophenyl)-3-(2-pyridyl)imidazol-2-ylidene]silver(I)chloride (4.2a). Both 1-(4-nitrophenyl)-3-(pyridine-2-ylmethyl)-1H-imidazol-3-ium bromide **4.1a**, (0.50 g; 1.38 mmol) and silver(I)oxide (0.32 g; 1.38 mmol) were added into a Schlenk tube and refluxed in 1,2-dichloroethane (30 ml) in the dark for 3 d. Yield: brown microcrystalline powder, stable in air and unstable in chloroform but soluble in DCM and DMSO; 0.510 g, 88%, mp. 173—176 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 8.50 (d, *J*=4.4 Hz, 1H, pyridyl), 8.29 (d, *J*=9.0 Hz,

2x1H, phenyl), 8.04—8.02 (m, 1H, pyridyl), 8.02 (d, $J=1.9$ Hz, 2x1H, phenyl), 7.85 (d, $J=1.9$ Hz, 1H, CH=CH_{imidazolyl}), 7.81—7.80 (m, 1H, pyridyl), 7.39 (d, $J=7.9$ Hz, 1H, CH=CH_{imidazolyl}), 7.34 (t, $J=2.2$ Hz, 1H, pyridyl), 5.58 (s, 2H, NCH₂). ¹³C NMR (400 MHz, DMSO-d₆): δ 180.4 (NCN; C-Ag), 155.3, 149.5, 146.8, 144.4, 137.4, 125.7, 124.9, 124.4, 123.3, 122.4, 120.4, 56.4 (NCH₂). FTIR (neat): ν_{C-H} 3084, 2946 ν_{C-N} 1515, ν_{N-O} 1336, ν_{Ar} 844, 750 cm^{-1} . Anal. Calcd. for C₁₅H₁₂AgClN₄O₂. 0.1CH₃C₆H₅: C, 43.57; H, 2.98; N, 12.94. Found: C, 44.21; H, 2.66; N, 13.78. MS-ES⁺: $m/z(\%)$ 667(10) [Ag(ligand)₂]⁺, 281(100) [(ligand + H)]⁺.

[1-(allyl)-3-(4-ferrocenylphenyl)imidazol-2-ylidene]silver(I)chloride (4.5a). Oven dried Schlenk flask equipped with molecular sieves and cooled under nitrogen was loaded with a mixture of Ag₂O (0.06 g, 0.26 mmol) and allyl-4-ferrocenylphenyl imidazolium bromide salt **4.4a** (0.096 g, 0.22 mmol). The mixture was refluxed with 1,2-dichloroethane (40 ml) in the dark for 24 h. Removal of the solvent at reduced pressure and subsequent extraction of the crude with DCM gave an orange supernatant which was filtered over a bed of celite and concentrated to yield the Ag-NHC complex **4.5a** as bright orange air stable microcrystals. Yield: 0.10 g; 85%, mp 63–66 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.55—7.53 (m, 2H, phenyl), 7.45—7.43 (m, 2H, phenyl), 7.32 (d, $J=1.6$ Hz, 1H, CH=CH_{imidazolyl}), 7.21 (s, 1H, CH=CH_{imidazolyl}), 6.06—5.96 (m, 1H, CH=CH₂), 5.35—5.26 (m, 2H, CH₂=CH), 4.82—4.66 (m, 2H, CH₂-N), 4.64 (d, $J=3.4$ Hz, 2H, substituted Cp), 4.38 (d, $J=1.7$ Hz, 2H, substituted Cp), 4.07 (s, 5H, unsubstituted Cp). ¹³C NMR (400 MHz, CDCl₃): δ 140.9, 137.4, 132.6, 127.2, 123.9, 121.9, 120.0, 83.5, 71.7, 69.7, 69.5, 66.6, 54.8. FTIR (neat): ν_{C-H} 3084, 2919, ν_{C-C} 1528, ν_{CN} 1341, ν_{Ar} 838 cm^{-1} . Anal. Calcd. for C₂₂H₂₀AgClFeN₂: C 51.48; H 3.94; N 5.48. Found C 53.38; H 3.93; N 5.94. MS-ES⁺: $m/z(\%)$ 843(55) [Ag(ligand)₂]⁺, 369(100) [(ligand + H)]⁺.

Co[3-(4-nitrophenyl)-1-picolyimidazolin-2-ylidene]₂Cl₂ (4.3a). To a solution of CoCl₂(PPh₃)₂ (0.15 g; 0.24 mmol) in DCM (20 ml) was added drop-wise a DCM (20 ml) solution of silver-NHC complex **4.2a** (0.10 g, 0.24 mmol). The green precipitate that formed was continuously stirred at room temperature in the dark for 2 d. At the expiration of the reaction time the supernatant liquid was filtered via cannula and the solid green residue washed with more DCM till the washing became clear. Dry methanol (40 ml) was then used to extract the solid and the orange-brown extract filtered through a bed of celite. The clear orange-brown filtrate was then concentrated under reduced pressure to afford green, air stable microcrystals of the cobalt-NHC complex: **4.3a**. Yield: 0.114 g, 69%; mp 275—278 °C. ¹H

NMR (400 MHz, CD₃OD): δ 8.42 (s, 2x1H, pyridyl), 8.25 (s, 2x(1H, 1H), pyridyl), 8.02 (s, 2x1H, pyridyl), 7.80—7.70 (m, 2x(4H), phenyl), 7.42 (s, $J=4.6$ Hz, 2x1H, CH=CH imidazolyl), 7.20 (s, 2x1H, CH=CH imidazolyl), 5.46 (s, 2x2H, NCH₂). ¹³C NMR (400 MHz, CD₃OD): δ 153.7, 150.8, 149.6, 140.5, 139.1, 137.7, 126.6, 125.5, 124.6, 124.4, 122.9, 55.5. FTIR (neat): ν_{moisture} 3364, $\nu_{\text{C-H}}$ 3092, ν_{NO} 1522, ν_{CN} 1300, ν_{Ar} 852, 748 cm⁻¹. MS-ES⁺: m/z(%) 690(5) [M + H]⁺, 619(10) [M - 2Cl⁻], 562(10) [(M - CoCl₂ + 2H)]²⁺, 282(18) [(ligand + 2H)]²⁺, 281(100) [(ligand + H)]⁺.

Ni[3-(4-nitrophenyl)-1-picolyimidazolin-2-ylidene]₂Cl₂ (4.3a'). To a dark blue solution of NiCl₂(PPh₃)₂ (0.15 g; 0.23 mmol) in DCM (20 ml) was added an equimolar DCM solution (20 ml) of **4.2a**. This prompted a yellow precipitate to be formed and the mixture stirred in the absence of light at room temperature for 2 d. The DCM soluble extract was filtered via cannula and the residue washed with more DCM (2 x 20 ml). The resulting yellow residue was then extracted with dry methanol (40 ml) and filtered through celite. Removal of all volatiles under reduced pressure yielded **4.3a'** as orange-yellow microcrystals that became moist when exposed for a while in air. Yield: 0.153 g; 96%; mp 283—285 °C. ¹H NMR (400 MHz, CD₃OD): δ 8.84 (bs, 2x1H, pyridyl), 8.42 (d, $J=8.8$ Hz, 2x2H, phenyl), 8.14 (s, 2x1H, CH=CH imidazolyl), 7.95 (d, $J=8.7$ Hz, 2x1H, CH=CH imidazolyl), 7.89—7.73 (m, 2x(1H, 1H), pyridyl), 7.54 (d, $J=7.9$ Hz, 2x1H, pyridyl), 7.34 (d, $J=6.2$ Hz, 2x2H, phenyl), 5.59 (s, 2x2H, NCH₂). No ¹³C NMR spectrum was available due possible decomposition during the accumulation of FID. FTIR (neat): $\nu_{\text{broad moisture}}$ 3289, $\nu_{\text{C=C}}$ 1523, $\nu_{\text{C-N}}$ 1340, ν_{Ar} 680 cm⁻¹. HRMS (m/s) for C₃₀H₂₄N₈O₄ClNi: calcd 653.0963, found 653.0983.

4.4.3 Generic procedure for synthesis of 4.3d, 4.3d', 4.3e and 4.3e'

Equimolar amounts of the imidazolium salt and Ag₂O were mixed together in a Schlenk tube containing molecular sieves and refluxed in 1,2-dichloroethane (30 ml) in the dark for 3 d. All volatiles were removed and the dark grey solid extracted with DCM (40 ml) and filtered through a bed of celite. The dark brown filtrate was then reduced to about 1/3 of the initial volume and added drop wise to a Schlenk tube containing a DCM solution of 1 mole equivalent of the metal precursor. The resulting suspension was then stirred in the dark at room temperature for 2 d. The coloured suspension was filtered via cannula and the precipitate washed with more DCM and filtered till the washing became colourless, and then extracted with dry methanol (40 ml). Filtration through a bed of celite and subsequent removal of all volatiles afforded the complex in high yield.

Co(3-allyl-1-picolyimidazolin-2-ylidene)₂Cl₂ (4.3d). Imidazolium salt **4.1d** (0.67 g, 2.39 mmol), Ag₂O (0.55 g, 2.40 mmol) and CoCl₂(PPh₃)₂ (1.57 g, 2.40 mmol) were reacted accordingly. Yield: dark green powder that decompose on long exposure to air; 1.20 g, 93%; mp 185—188 °C. ¹H NMR (400 MHz, CD₃OD): δ 8.32 (s, 2x1H, pyridyl), 7.59 (s, 2x1H, pyridyl), 7.51 (s, 2x1H, CH=CH), 7.47—7.40 (m, 2x1H, pyridyl), 7.29 (d, *J*=7.9 Hz, 2x1H, CH=CH), 7.13 (d, *J*=5.2 Hz, 2x1H, pyridyl), 6.59—6.57 (m, 2x1H, CH=CH₂), 5.82 (d, *J*=7.6 Hz, 2H, NCH₂), 5.31 (s, 2H, NCH₂), 5.26 (s, 2x2H, CH₂=CH), 1.56 (d, *J*=6.9 Hz, 2H, CH₂-N allyl). FTIR (neat): $\nu_{(\text{broad moisture})}$ 3378, $\nu_{\text{C-H}}$ 3105, $\nu_{\text{C=C}}$ 1596, $\nu_{\text{C=N}}$ 1438, and ν_{Ar} 718 cm⁻¹. $\mu_{\text{eff}} = 2.53 \mu_{\text{B}}$. MS-ES⁺: *m/z*(%) 492(60) [(M - Cl)]⁺, 457(20) [(M - 2Cl)]²⁺, 200(100) [(ligand + H)]⁺.

Ni(3-allyl-1-picolyimidazolin-2-ylidene)₂Cl₂ (4.3d'). Imidazolium salt **4.1d** (0.67 g, 2.39 mmol), Ag₂O (0.55 g, 2.40 mmol) and NiCl₂(PPh₃)₂ (1.57 g, 2.40 mmol) were reacted accordingly. Yield: lemon-green microcrystals relatively stable in air, 1.19 g, 93%; mp 243—245 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.16 (s, 2x1H, pyridyl), 8.05 (s, 2x1H, pyridyl), 7.83 (s, 2x1H, CH=CH), 7.69 (s, 2x1H, pyridyl), 7.37 (s, 2x1H, CH=CH), 7.16 (d, *J*=12.1 Hz, 2x1H, pyridyl), 6.57 (d, *J*=13.5 Hz, 2x1H, CH=CH₂ allyl), 5.97 (s, 2H, NCH₂), 5.81 (d, *J*=13.6 Hz, 2H, NCH₂), 4.09 (s, 2x2H, CH₂=CH allyl), 1.48 (s, 2x2H, CH₂-N allyl). FTIR (neat): $\nu_{(\text{broad moisture})}$ 3323, $\nu_{\text{C=C}}$ 1610, $\nu_{\text{C-N}}$ 1437, ν_{Ar} 743 cm⁻¹. MS-ES⁺: *m/z*(%) 491(100) [(M - Cl)]⁺, 455(10) [(M - 2Cl)]²⁺.

Co(3-butenyl-1-picolyimidazolin-2-ylidene)₂Cl₂ (4.3e). Imidazolium salt **4.1e** (0.56 g, 2.0 mmol), Ag₂O (0.44 g, 2.0 mmol) and CoCl₂(PPh₃)₂ (1.25 g, 2.0 mmol) were reacted accordingly. Yield: dark green air sensitive powder, 0.79 g, 71%; mp 120—123 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.81—7.80 (bm, 2x6H: 4H, pyridyl; 2H, CH=CH), 7.57—7.49 (bm, 2x1H, CH=CH₂), 5.93 (d, *J*=5.8 Hz, 2H, NCH₂), 5.75 (s, 2H, NCH₂), 5.05 (t, *J*=12.2 Hz, 2x2H, CH₂=CH), 4.11—4.01 (m, 2x2H, CH₂-N alkenyl), 2.23 (s, 2x2H, CH₂). FTIR (neat): $\nu_{(\text{broad moisture})}$ 3365, $\nu_{\text{C=C}}$ 1596, $\nu_{\text{C-N}}$ 1437, ν_{Ar} 762 cm⁻¹. $\mu_{\text{eff}} = 2.73 \mu_{\text{B}}$. MS-ES⁺: *m/z*(%) 557(7) [(M + 2H)]²⁺, 520(22) [(M - Cl)]⁺, 485(20) [(M - 2Cl)]²⁺, 214(100) [(ligand + H)]⁺.

Ni(3-butenyl-1-picolyimidazolin-2-ylidene)₂Cl₂ (4.3e'). Imidazolium salt **4.1e** (0.56 g, 2.0 mmol), Ag₂O (0.44 g, 2.0 mmol) and NiCl₂(PPh₃)₂ (1.25 g, 2.0 mmol) were reacted accordingly. Yield: yellowish green air sensitive powder, 0.92 g, 83%; mp 108—110 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.25 (s, 2x1H, pyridyl), 8.06 (s, 2x1H, pyridyl), 7.84 (s,

2x1H, CH=CH), 7.44 (d, $J=18.3$, 2x2H, pyridyl), 6.93 (m, 2x1H, CH=CH₂), 5.90 (d, $J=14.9$ Hz, 2H, NCH₂), 5.65 (s, 2H, NCH₂), 4.81—4.77 (m, 2x2H, CH₂=CH), 4.11—3.70 (m, 2x2H, CH₂-N_{alkenyl}), 2.32 (s, 2x2H, CH₂_{alkenyl}). FTIR (neat): $\nu_{\text{(broad moisture)}}$ 3329, $\nu_{\text{C=C}}$ 1610, $\nu_{\text{C-N}}$ 1438, ν_{Ar} 769 cm⁻¹. MS-ES⁺: m/z(%) 519(50) [(M - Cl)]⁺, 484(10) [(M - 2Cl)]²⁺, 214(100) [(ligand + H)]⁺.

Co[3-(allyl)-1-(4-ferrocenylphenyl)imidazolin-2-ylidene]₂Cl₂ (4.6a). Orange coloured DCM solution of Ag-NHC complex **4.5a** (0.092 g; 0.18 mmol) was added to equimolar DCM solution of the cobalt precursor CoCl₂(PPh₃)₂ (0.12 g; 0.18 mmol). The clear sky-blue solution of the metal precursor immediately changed colour and the resulting green solution was stirred at room temperature in the dark for 24 h. All volatiles were removed and the dark green residue was washed with hexane (2 x 20 ml) and filtered via cannula. The residue obtained was then extracted with toluene (40 ml) and filtered over a bed of celite. The clear bluish-green filtrate was concentrated at reduced pressure to about 5 ml of the volume and dry diethyl ether was added. This spurred up a lemon green gelatinous precipitate and the suspension was allowed to stir for 1 h. The supernatant was filtered via cannula and the lemon green solid dried under vacuum to afford a lemon green air stable powder of the cobalt-NHC complex **4.6a**. Yield: 0.116 g; 72%, mp 196—198 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, $J=7.1$ Hz, 2x4x1H, phenyl), 7.53 (s, 2x2x1H, CH=CH imidazolyl), 6.13—6.09 (m, 2x1H, CH=CH₂ allyl), 5.57—5.49 (m, 2x2H, CH₂=CH allyl), 5.29—5.27 (m, 2x2H, CH₂-N allyl), 4.67 (d, $J=3.5$ Hz, 2x2H, substituted Cp), 4.40 (d, $J=1.6$ Hz, 2x2H, substituted Cp), 4.06 (s, 2x5H, un-substituted Cp). FTIR (neat): $\nu_{\text{C-H}}$ 3050, $\nu_{\text{C-N}}$ 1434, ν_{Ar} 740, 730 cm⁻¹. MS-ES⁺: m/z(%) 866(30) [(M + H)]⁺, 369(60) [(M - CoCl₂)/2].

4.4.4 Typical procedure for 4.3a' activated arylation of aniline with phenyl bromide

To an oven dried Schlenk tube initially cooled under nitrogen was added aniline (1.0 g, 1 ml, 0.010 mol), phenyl bromide (2.0 g, 1.4 ml, 0.013 mol), KO^tBu (1.46 g, 0.013 mol) and **4.3a'** (0.069 g, 0.0001 mol). The mixture was vigorously stirred in refluxing THF (20 ml) under an atmosphere of nitrogen for 12 h with reaction progress monitored by TLC. The contents of the Schlenk tube were then allowed to cool to room temperature and DCM (30 ml) was added into the flask, stirred for an hour and filtered through a bed of celite. All volatiles in the filtrate were removed under reduced pressure and the crude residue obtained mixed with silica and loaded onto a column. The desired product (diphenyl amine) was obtained as an eluent of hexane:DCM (4:1). Removal of all volatiles gave isolated yield of a low melting

yellowish-brown solid, 1.13 g, 67%. ^1H NMR (400 MHz, DMSO- d_6): δ 8.12 (bs, 1H, NH), 7.21 (d, $J=7.4$ Hz, 2x2H), 7.06 (d, $J=7.6$ Hz, 2x2H), 6.81 (t, $J=7.3$ Hz, 2x1H). ^{13}C NMR (400 MHz, DMSO- d_6): δ 143.4, 129.1, 119.6, 116.7. FTIR (neat) $\nu_{\text{N-H}}$ 3380 (bs, 2° amine), $\nu_{\text{C-H}}$ 3041, $\nu_{\text{C-N}}$ 1307, ν_{Ar} 741 cm^{-1} .

4.4.5 Typical procedure for NiCl₂/4.1a *in situ* activated arylation of aniline with phenyl bromide

Anhydrous NiCl₂ (0.013 g, 0.0001 mol), imidazolium salt **4.1a** (0.072 g, 0.0002 mol) and 4Å molecular sieves were loaded into a Schlenk tube under an atmosphere of nitrogen and stirred together in THF for 1 h at room temperature. To the resulting suspension was then added KO^tBu (1.46 g, 0.013 mol), aniline (1.0 g, 0.010 mol) and phenyl bromide (2.0 g, 0.013 mol). The Schlenk tube was then equipped with a condenser and subjected to reflux for 12 h. After cooling to room temperature, DCM (30 ml) was added and the contents filtered through a bed of celite. The resulting filtrate was then concentrated and the crude obtained was mixed with silica and loaded onto a column. The diarylamine product was isolated as an eluent of hexane:DCM (4:1) after removal of all volatiles.

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4.6 References

- Herrmann, W. A.; Kühn, Fritz E., *J.Organomet. Chem.* **2015**, 775 (0), 101-102;
 - Öfele, K., *J.Organomet. Chem.* **1968**, 12 (3), P42-P43;
 - Wanzlick, H. W.; Schönherr, H. J., *Angew. Chem.* **1968**, 80 (4), 154-154;
 - Arduengo, A. J.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1991**, 113 (1), 361-363.
- Katari, M.; Rajaraman, G.; Ghosh, P., *J.Organomet. Chem.* **2015**, 75 (0), 109-116;
 - Cardoso, J. M. S.; Lopes, R.; Royo, B., *J.Organomet. Chem.* **2015**, 775 (0), 173-177;
 - Ratanasak, M.; Parasuk, V., *J.Organomet. Chem.* **2015**, 775 (0), 6-11;
 - Huang, W.-L.; Hung, G.-J.; He, S.-T.; Chiang, G.-R.; Lo, Y.-H., *J. Organomet. Chem.* **2015**, 775 (0), 1-5;
 - Wang, Z.; Li, S.; Teo, W. J.; Poh, Y. T.; Zhao, J.; Hor, T. S. A., *J. Organomet. Chem.* **2015**, 775 (0), 188-194;
 - Tsoureas, N.; Danopoulos, A. A., *J.Organomet.Chem.* **2015**, 775 (0), 178-187;
 - Berding, J.; Lutz, M.; Spek, A. L.; Bouwman, E., *Organometallics* **2009**, 28 (6), 1845-1854;
 - Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A., *Angew. Chem. Int. Ed.* **2001**, 40 (18), 3387-3389;
 - Gu, S.; Chen, W., *Organometallics* **2009**, 28 (3), 909-914;
 -

- Kuhl, S.; Fort, Y.; Schneider, R., *J. Organomet. Chem.* **2005**, *690* (24–25), 6169–6177; (k) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. J., *Organometallics* **2012**, *32* (3), 723–732; (l) Xia, Z.; Huang, J.; He, Y.; Zhao, J.; Lei, J.; Zhu, Q., *Org. Lett.* **2014**, *16* (9), 2546–2549.
3. Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R., *Organometallics* **1997**, *16* (4), 682–688.
 4. (a) Merce, L.; Albrecht, M., *Chem.Soc.Rev.* **2010**, *39* (6), 1903–1912; (b) Dí z-González, S.; Marion, N.; Nolan, S. P., *Chem. Rev.* **2009**, *109* (8), 3612–3676.
 5. (a) Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002**, *41* (8), 1290–1309; (b) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J., *Angew. Chem. Int. Ed. Eng.* **1995**, *34* (21), 2371–2374.
 6. (a) Gnanamgari, D.; Sauer, L. O. E.; Schley, D. N.; Butler, C.; Incarvito, C. D.; Crabtree, R. H., *Organometallics* **2009**, *28*, 321–325; (b) Song, H.; Fan, D.; Liu, Y.; Hou, G.; Zi, G., *J. Organomet. Chem.* **2013**, *729* (0), 40–45.
 7. Wang, X.; Liu, S.; Jin, G.-X., *Organometallics* **2004**, *23* (25), 6002–6007.
 8. (a) Llewellyn, S. A.; Green, M. L. H.; Cowley, A. R., *Dalton Trans.* **2006**, (34), 4164–4168; (b) Fooladi, E.; Dalhus, B.; Tilset, M., *Dalton Trans.* **2004**, (22), 3909–3917; (c) Simms, R. W.; Drewitt, M. J.; Baird, M. C., *Organometallics* **2002**, *21* (14), 2958–2963.
 9. (a) Douthwaite, R. E.; Haüssinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A., *Organometallics* **1999**, *18* (22), 4584–4590; (b) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S., *Organometallics* **2004**, *23* (21), 4807–4810.
 10. (a) Andreas A. Danopoulos; Nikolaos Tsoureas; Stuart A. Macgregor; Smith, C., *Organometallics* **2007**, *26*, 253–263; (b) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B., *Dalton Trans.* **2003**, (5), 1009–1015.
 11. (a) Beck, R.; Flörke, U.; Klein, H.-F., *Inorg. Chim. Acta* **2009**, *362* (6), 1984–1990; (b) Al Thagfi, J.; Lavoie, G. G., *Organometallics* **2012**, *31* (6), 2463–2469; (c) Danopoulos, A. A.; Braunstein, P., *Dalton Trans.* **2013**, *42* (20), 7276–7280.
 12. (a) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y., *Organometallics* **2002**, *21* (8), 1554–1559; (b) Shanmuganathan, S.; Kühl, O.; Jones, P.; Heinicke, J., *Cent. Eur. J. Chem.* **2010**, *8* (5), 992–998.
 13. Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K., *J. Org. Chem.* **2007**, *72* (14), 5069–5076.
 14. Zhang, Y.; Ngeow, K. C.; Ying, J. Y., *Org. Lett.* **2007**, *9* (18), 3495–3498.
 15. Duong, H. A.; Cross, M. J.; Louie, J., *J. Am. Chem. Soc.* **2004**, *126* (37), 11438–11439.
 16. Zhang, D.; Zhou, S.; Li, Z.; Wang, Q.; Weng, L., *Dalton Trans.* **2013**, *42* (33), 12020–12030.
 17. (a) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y., *Org. Lett.* **2003**, *5* (13), 2311–2314; (b) Brenner, E.; Schneider, R.; Fort, Y., *Tetrahedron* **2002**, *58* (34), 6913–6924; (c) Gradel, B. t.; Brenner, E.; Schneider, R.; Fort, Y., *Tetrahedron Lett.* **2001**, *42* (33), 5689–5692.
 18. Buchowicz, W.; Koziół, A.; Jerzykiewicz, L. B.; Lis, T.; Pasynkiewicz, S.; Pęcherzewska, A.; Pietrzykowski, A., *J.Mol. Catal. A: Chem.* **2006**, *257* (1–2), 118–123.

19. (a) Inamoto, K.; Kuroda, J.-i.; Kwon, E.; Hiroya, K.; Doi, T., *J. Organometallic Chem.* **2009**, *694* (3), 389-396; (b) Zhou, Y.; Xi, Z.; Chen, W.; Wang, D., *Organometallics* **2008**, *27* (22), 5911-5920; (c) Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T., *Organometallics* **2006**, *25* (12), 3095-3098.
20. (a) Wolfe, J. P.; Buchwald, S. L., *J. Org. Chem.* **1996**, *61* (3), 1133-1135; (b) Yang, J.; Li, P.; Zhang, Y.; Wang, L., *J. Organomet. Chem.* **2014**, *766* (0), 73-78.
21. (a) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T., *Tetrahedron Lett.* **2001**, *42*, 4791-4793; (b) Lindley, J., *Tetrahedron* **1984**, *40* (9), 1433-1456.
22. (a) Xu, Z.-L.; Li, H.-X.; Ren, Z.-G.; Du, W.-Y.; Xu, W.-C.; Lang, J.-P., *Tetrahedron* **2011**, *67* (29), 5282-5288; (b) Okano, K.; Tokuyama, H.; Fukuyama, T., *Org. Lett.* **2003**, *5* (26), 4987-4990; (c) Cho, G. Y.; Rémy, P.; Jansson, J.; Moessner, C.; Bolm, C., *Org. Lett.* **2004**, *6* (19), 3293-3296; (d) Quan, Z.-J.; Xia, H.; Zhang, Z.; Da, Y.; Wang, X.-C., *Appl. Organomet. Chem.* **2014**, *28* (2), 81-85.
23. (a) Ibrahim, H.; Bala, M. D.; Omondi, B., *Acta Crystallogr. Sect. E* **2012**, *68* (7), o2305; (b) Corberán, R.; Sanaú, M.; Peris, E., *Organometallics* **2007**, *26* (14), 3492-3498; (c) Ibrahim, H.; Bala, M. D., *Acta Crystallogr. Sect. E* **2013**, *69* (1), o114.
24. (a) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G., *Dalton Trans.* **2000**, *0* (24), 4499-4506; (b) Forgie, J. C.; El Khakani, S.; MacNeil, D. D.; Rochefort, D., *P C C P.* **2013**, *15* (20), 7713-7721.
25. Ibrahim, H.; Bala, M. D., *Tetrahedron Lett.* **2014**, *55* (46), 6351-6353.
26. Zhao, D. Design, Synthesis And Applications Of Functionalized Ionic Liquids. École Polytechnique Fédérale De Lausanne, Lausanne, Epfl, 2007.
27. (A) Ikhile, M. I. N-Heterocyclic Carbene-Iron(II)Complexes: Chemistry And Application As Transfer Hydrogenation Catalysts. University of Kwazulu Natal, Westville campus, Durban, 2011; (b) Nyamori, V. O.; Gumede, M.; Bala, M. D., *J. Organomet. Chem.* **2010**, *695* (8), 1126-1132.
28. Horvath, U. E. I.; Bentivoglio, G.; Hummel, M.; Schottenberger, H.; Wurst, K.; Nell, M. J.; van Rensburg, C. E. J.; Cronje, S.; Raubenheimer, H. G., *New J. Chem.* **2008**, *32* (3), 533-539.
29. Wang, H. M. J.; Lin, I. J. B., *Organometallics* **1998**, *17* (5), 972-975.
30. Lin, I. J. B.; Vasam, C. S., *Comments Inorg. Chem.* **2004**, *25* (3-4), 75-129.
31. (a) Budagumpi, S.; Haque, R. A.; Salman, A. W.; Ghdayeb, M. Z., *Inorg. Chim. Acta* **2012**, *392*, 61-72; (b) Liu, B.; Zhang, Y.; Xu, D.; Chen, W., *Chem. Commun.* **2011**, *47* (10), 2883-2885.
32. Twyman, R. M. NMR spectroscopy-applicable elements/ Phosphorus-31 2005. Downloaded on 2013/03/17.
<http://www.writescience.com/RMT%20PDFs/Elsevier/eans%20NMR-P31.pdf>
33. Stephan Grundemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W. a.; Crabtree, R. H., *Organometallics* **2001**, *20*, 5485-5488.
34. (a) For practical purpose on magnetic susceptibility measurement: Data from hysteresis loop measurement using Vibrating Sample Magnetometer VSM gave an initial magnetization curve as a plot of magnetic moment/mass (emu/g) against field (Oes) which qualitatively confirmed the paramagnetic nature of the complexes. The determined saturated magnetization M_s values which are function of the number of moles n used per atom (0.025—0.031g) are used to determine the magnetic susceptibility (μ_{eff}) of the complexes in μB and compared with the calculated magnetic moments consistent with the number of un-paired electrons. In essence, the

quotient M_s/n divided by a constant 5584.9 gives the magnetic susceptibility of the complexes. The constant 5584.9 is derived from the equation:

$\mu_B \cdot N_A = 5584.9 \text{ emu/mole}$; where N_A is Avogadro's number; (b) Cullity, B. D.; Graham, C. D., *Introduction to Magnetic Materials*. 2nd Edition ed.; John Wiley and Sons: 2008; p. 568. Downloaded on 2014/11/02.

http://www2.fisica.unlp.edu.ar/magnet/Cullity_Graham.pdf.

35. Kosugi, M.; Kameyama, M.; Migita, T., *Chem. Lett.* **1983**, 12 (6), 927-928.
36. (a) Driver, M. S.; Hartwig, J. F., *J. Am. Chem. Soc.* **1996**, 118 (30), 7217-7218; (b) Hartwig, J. F., *Angew. Chem. Int. Ed.* **1998**, 37 (15), 2046-2067.
37. Chen, J.; Yuan, T.; Hao, W.; Cai, M., *Tetrahedron Lett.* **2011**, 52 (29), 3710-3713.
38. Krzyminski, K.; Wera, M.; Sikorski, A.; Blazejowski, J., *Acta Crystallogr. Sect. E* **2009**, 65 (1), o152.
39. (a) Denmark, S. E.; Wu, Z., *Organic Lett.* **1999**, 1 (9), 1495-1498; (b) Hatanaka, Y.; Goda, K.-i.; Okahara, Y.; Hiyama, T., *Tetrahedron* **1994**, 50 (28), 8301-8316.
40. Bala, M. D.; Ikhile, M. I., *J. Mol. Catal. A: Chem.* **2014**, 385 (0), 98-105.
41. Patil, N. M.; Kelkar, A. A.; Nabi, Z.; Chaudhari, R. V., *Chem. Commun.* **2003**, 0 (19), 2460-2461.
42. Standard solvent drying techniques. Downloaded on 2012/11/27
<http://delloyd.50megs.com/moreinfo/drying.html>.
43. Venanzi, L. M., *J. Chem. Soc.* **1958**, 0 (0), 719-724.
44. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010**, 29, 2176-2179.

Chapter five

1-[4-(1H-imidazol-1-yl)phenyl]ethanone monohydrate²

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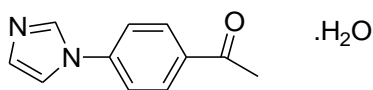
Key indicators: single-crystal X-ray study; T = 173 K; mean (C–C) = 0.002 Å ;
R factor = 0.036; wR factor = 0.098; data-to-parameter ratio = 11.2.

Abstract

In the crystal structure of the title compound, C₁₁H₁₀N₂O.H₂O, the solvent water molecule links the organic molecules through O—H····O and O—H····N hydrogen bonds, forming chains that run diagonally across the bc face. These chains are connected to adjacent chains through weak C—H····O interactions, resulting in hydrogen-bonded sheets extending along the b and c axes. The sheets are connected along the a axis through π - π interactions, with centroid-centroid distances of 3.7571 (9) and 3.7231 (9) Å

5.1 Related literature

For the synthesis of the title compound, see: Corberan & Peris (2008). For the structure of imidazole analogues with bonds to the phenyl group via carbon, see: Gayathri *et al.* (2010). For the structure of imidazole analogues N-bonded to a phenyl group, see: Zheng *et al.* (2011). For structures of other related compounds, see: Ishihara *et al.* (1992).



5.2 Comment

The title compound is an intermediate product in the synthetic route to an N-heterocyclic carbene (NHC) chelating ligand bearing a pyridine backbone. The anhydrous form of the compound is available in chemical book database with CAS No. 10041-06-2. Neither structure of the hydrated nor the anhydrous forms of the title compound have been reported.

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doi:10.1107/S1600536812029157

Our synthetic route and the synthons used are different from those reported in the synthesis of the anhydrous form of the title compound. Absolute configuration of the title compound obtained in pure form from column chromatography using hexane:chloroform (6:4) solvent system was assigned by NMR and IR spectroscopy. Monohydrate block crystals of (**5.1**) were recrystallized from the same solvent system. The imidazole N(2) – phenyl carbon bond [C(9)—N(2)] is 1.3107 (16)Å. The one molecule of water binds as water of crystallization to the organic molecule, and is a constituent of the asymmetric unit cell. Molecules of (**5.1**) are stabilized through an extensive chain of hydrogen bonded network involving neighbouring methoxy (O—H···O) and imidazolium (N—H···O) moieties linked by the water of crystallization. Imidazole analogues of (**5.1**) with bonds to the phenyl group via carbon have been reported by Gayathri *et al.* (2010); while Zheng *et al.* (2011) have reported imidazole bonded to a phenyl group via nitrogen. Other related compounds have been reported by Ishihara *et al.* (1992).

5.3 Experimental

The compound was synthesized by the modification of the method of Corberan *et al.* (2008). A 150 ml round bottom flask containing imidazole (0.01 mol, 0.68 g, Fluka AG) with KOH (0.015 mol, 0.84 g, Merck) was stirred at room temperature in DMSO (30 ml, Merck) for 2 h. Thereafter, *para*-chloroacetophenone (0.01 mol, 1.34 ml, Aldrich) was added dropwise, and then refluxed at 100 °C for 24 h. The reaction mixture was then allowed to cool down to room temperature, washed and diluted with chilled distilled water till it became neutral. Addition of distilled water to the contents of the reaction flask gave a muddy emulsion which took 24 h to partition when extracted with chloroform (6x10 ml). The resulting organic components were dried in anhydrous MgSO₄ and concentrated *in vacuo* yielding crude dark brown oily liquid (1.694 g). Thin layer chromatography of the crude product showed that it contained the expected product (*R_f* value 0.45 in ethyl acetate:methanol 4:6 solvent system) contaminated with unreacted imidazole and *parachloroacetophenone*. Column chromatography of the crude product using hexane:chloroform solvent system afforded the title compound as block-shaped light green crystals (0.987 g, 48% yield), m.p. = 119–122 °C. ¹H NMR (400 MHz, CDCl₃): 8.09(*d*), 7.95(*s*), 7.51(*d*), 7.35(*s*), 7.25(*s*), and 1.62(*s*). ¹³C NMR (400 MHz, CDCl₃): 196.5 (carbonyl CO), 140.8, 135.8, 135.4, 131.2, 130.4, 120.7, 117.7, 26.61(CH₃). IR (ATR, cm⁻¹): 1665(C=O), 1606(C=N), 1530(N-C), 956(C=C), 2222(C-H), 814(*para* substituted benzene), 3202 (water of crystallization absorbance band).

5.3.1 Data collection

APEX2 (Bruker, 2008); cell refinement: SAINTPlus (Bruker, 2008); data reduction: SAINT-Plus and XPREP (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

5.3.2 Crystal data

$C_{11}H_{10}N_2O \cdot H_2O$

$M_r = 204.23$

Triclinic, $P1$

Hall symbol: $-P 1$

$a = 6.7599$ (6) Å

$b = 8.0885$ (8) Å

$c = 9.7168$ (9) Å

$\alpha = 90.350$ (3)°

$\beta = 106.731$ (3)°

$\gamma = 99.486$ (3)°

$V = 501.03$ (8) Å³

Data collection

Bruker SMART APEXII CCD
diffractometer

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.947$, $T_{\max} = 0.987$

6609 measured reflections

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.098$

$S = 1.07$

1711 reflections

153 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

$Z = 2$

$F(000) = 216$

$D_x = 1.354$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7553 reflections

$\theta = 2.2$ – 25.0 °

$\mu = 0.10$ mm⁻¹

$T = 173$ K

Block, colourless

$0.58 \times 0.39 \times 0.14$ mm

1711 independent reflections

1568 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 2.2$ °

$h = -7 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -11 \rightarrow 11$

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.1639P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.15$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ e Å⁻³

5.3.3 Refinement

Carbon-bound H-atoms were placed in calculated positions [$C-H = 0.96 \text{ \AA}$ for Me H atoms and 0.93 \AA for aromatic H atoms; $U_{iso}(H) = 1.2U_{eq}(C)$ (1.5 for Me groups)] and were included in the refinement in the riding model approximation. The O—H H-atom was located in a difference map and freely refined with $O-H = 0.87 - 0.91 \text{ \AA}$ ($U_{iso}(H) = 1.2U_{eq}(O)$).

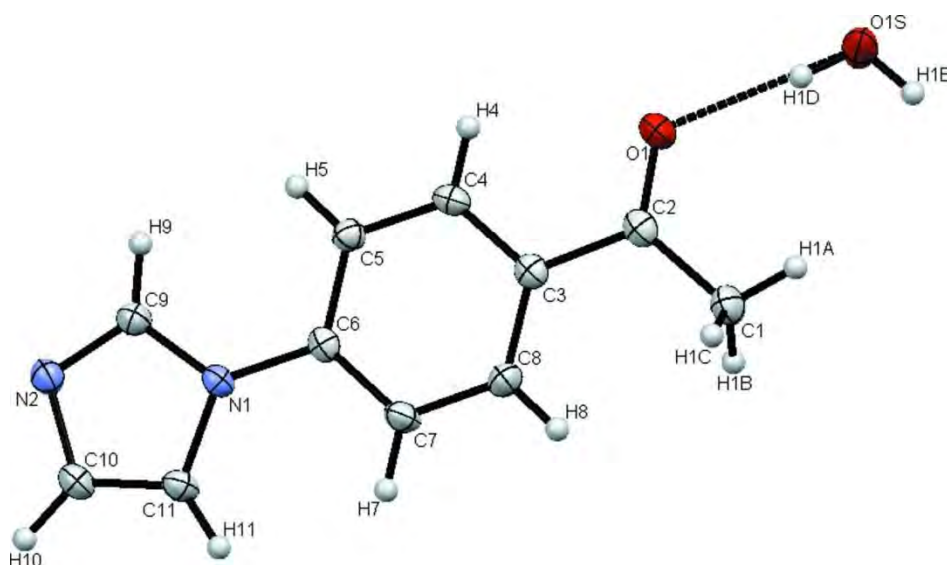


Figure 5.1: ORTEP diagram of compound (5.I). Thermal ellipsoids are represented at the 50% probability level.

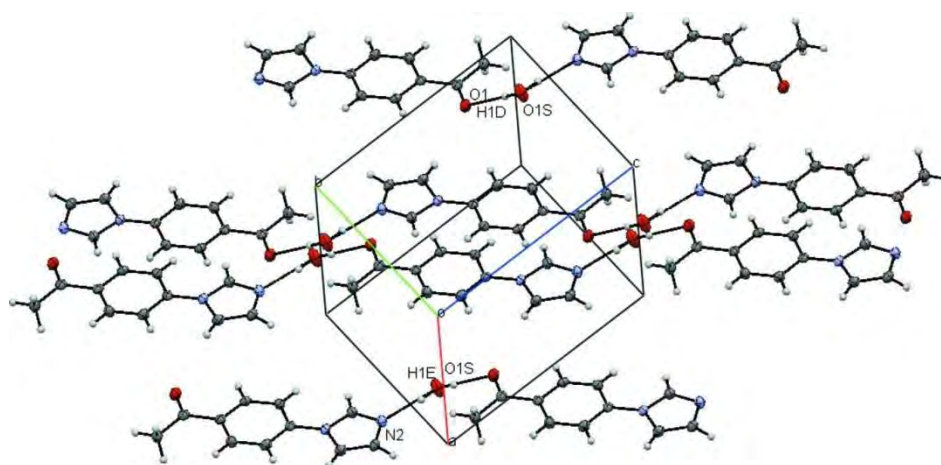


Figure 5.2: Packing diagram showing the O—H...O and N—H...O hydrogen bonds.

5.3.4 Geometry

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes. The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level. Alert level C PLAT029_ALERT_3_C _diffn_measured_fraction_theta_full Low 0.971 PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.594 51 PLAT154_ALERT_1_G The su's on the Cell Angles are Equal0.00300 Deg. PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) 1.20 Ratio PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. #2 H2 O PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) still 84 Perc. NOTED:

5.3.5 Refinement

Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R - factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3585 (2)	0.18679 (16)	0.96056 (14)	0.0245 (3)
H1A	0.3397	0.0859	1.0103	0.037*
H1B	0.2732	0.2621	0.9808	0.037*
H1C	0.5033	0.2395	0.9923	0.037*
C2	0.29495 (19)	0.14436 (15)	0.80160 (14)	0.0195 (3)
C3	0.28326 (18)	0.28277 (15)	0.70069 (13)	0.0174 (3)
C4	0.21354 (19)	0.24258 (15)	0.55292 (14)	0.0184 (3)
H4	0.1746	0.1304	0.5199	0.022*
C5	0.20107 (19)	0.36543 (15)	0.45475 (13)	0.0182 (3)
H5	0.1554	0.3361	0.3566	0.022*
C6	0.25730 (17)	0.53395 (14)	0.50336 (13)	0.0160 (3)
C7	0.32455 (19)	0.57689 (15)	0.65011 (14)	0.0204 (3)

H7	0.3611	0.6892	0.6829	0.024*
C8	0.3369 (2)	0.45188 (16)	0.74724 (14)	0.0208 (3)
H8	0.3818	0.4813	0.8454	0.025*
C9	0.17884 (19)	0.63657 (15)	0.25569 (14)	0.0195 (3)
C10	0.24881 (19)	0.90217 (15)	0.30220 (14)	0.0206 (3)
C11	0.28704 (19)	0.83293 (15)	0.43105 (14)	0.0197 (3)
H11	0.3339	0.8894	0.5213	0.024*
N1	0.24241 (15)	0.66069 (12)	0.40191 (11)	0.0165 (3)
N2	0.18116 (16)	0.77885 (13)	0.19181 (11)	0.0210 (3)
O1	0.25470 (14)	-0.00186 (10)	0.75446 (10)	0.0248 (3)
O1S	0.04729 (17)	0.73832 (13)	-0.11171 (11)	0.0353 (3)
H1D	0.115 (3)	0.820 (3)	-0.147 (2)	0.053 (5)*
H1E	0.093 (3)	0.762 (2)	-0.015 (2)	0.047 (5)*
H9	0.137 (2)	0.5281 (19)	0.2087 (16)	0.024 (4)*
H10	0.262 (2)	1.0191 (17)	0.2805 (14)	0.017 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0292 (7)	0.0211 (6)	0.0227 (7)	0.0052 (5)	0.0064 (6)	0.0051 (5)
C2	0.0160 (6)	0.0193 (6)	0.0237 (7)	0.0030 (5)	0.0067 (5)	0.0031 (5)
C3	0.0146 (6)	0.0177 (6)	0.0208 (7)	0.0032 (5)	0.0061 (5)	0.0020 (5)
C4	0.0180 (6)	0.0135 (6)	0.0233 (7)	0.0021 (5)	0.0058 (5)	-0.0010 (5)
C5	0.0186 (6)	0.0180 (6)	0.0169 (6)	0.0027 (5)	0.0039 (5)	-0.0004 (5)
C6	0.0122 (6)	0.0169 (6)	0.0193 (7)	0.0025 (5)	0.0054 (5)	0.0029 (5)
C7	0.0229 (6)	0.0132 (6)	0.0233 (7)	0.0010 (5)	0.0053 (5)	-0.0007 (5)
C8	0.0233 (7)	0.0206 (6)	0.0163 (6)	0.0020 (5)	0.0036 (5)	-0.0005 (5)
C9	0.0208 (7)	0.0177 (6)	0.0193 (7)	0.0014 (5)	0.0057 (5)	0.0006 (5)
C10	0.0217 (6)	0.0152 (6)	0.0246 (7)	0.0020 (5)	0.0069 (5)	0.0032 (5)
C11	0.0202 (6)	0.0145 (6)	0.0224 (7)	0.0007 (5)	0.0043 (5)	-0.0010 (5)
N1	0.0161 (5)	0.0138 (5)	0.0187 (6)	0.0014 (4)	0.0047 (4)	0.0015 (4)
N2	0.0228 (6)	0.0189 (5)	0.0207 (6)	0.0016 (4)	0.0063 (4)	0.0031 (4)
O1	0.0330 (5)	0.0163 (5)	0.0251 (5)	0.0027 (4)	0.0094 (4)	0.0030 (4)
O1S	0.0489 (7)	0.0281 (5)	0.0209 (6)	-0.0152 (5)	0.0102 (5)	-0.0023 (4)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.5003 (18)	C7—H7	0.93
C1—H1A	0.96	C8—H8	0.93
C1—H1B	0.96	C9—N2	1.3109 (16)
C1—H1C	0.96	C9—N2	1.3109 (16)
C2—O1	1.2240 (15)	C9—N1	1.3634 (17)
C2—C3	1.4896 (17)	C9—H9	0.948 (15)
C3—C8	1.3935 (17)	C10—C11	1.3483 (19)
C3—C4	1.3941 (18)	C10—N2	1.3816 (17)
C4—C5	1.3775 (17)	C10—N2	1.3816 (17)
C4—H4	0.93	C10—H10	0.966 (14)
C5—C6	1.3941 (17)	C11—N1	1.3855 (15)
C5—H5	0.93	C11—H11	0.93
C6—C7	1.3890 (18)	O1S—H1D	0.87 (2)
C6—N1	1.4220 (15)	O1S—H1E	0.91 (2)

C7—C8	1.3835 (18)		
C2—C1—H1A	109.5	C6—C7—H7	120.1
C2—C1—H1B	109.5	C7—C8—C3	121.20 (12)
H1A—C1—H1B	109.5	C7—C8—H8	119.4
C2—C1—H1C	109.5	C3—C8—H8	119.4
H1A—C1—H1C	109.5	N2—C9—N1	112.07 (11)
H1B—C1—H1C	109.5	N2—C9—N1	112.07 (11)
O1—C2—C3	119.93 (11)	N2—C9—H9	125.6 (9)
O1—C2—C1	120.84 (11)	N2—C9—H9	125.6 (9)
C3—C2—C1	119.23 (11)	N1—C9—H9	122.3 (9)
C8—C3—C4	118.11 (11)	C11—C10—N2	110.55 (11)
C8—C3—C2	122.91 (11)	C11—C10—N2	110.55 (11)
C4—C3—C2	118.98 (11)	C11—C10—H10	129.4 (8)
C5—C4—C3	121.44 (11)	N2—C10—H10	120.0 (8)
C5—C4—H4	119.3	N2—C10—H10	120.0 (8)
C3—C4—H4	119.3	C10—C11—N1	106.12 (11)
C4—C5—C6	119.63 (11)	C10—C11—H11	126.9
C4—C5—H5	120.2	N1—C11—H11	126.9
C6—C5—H5	120.2	C9—N1—C11	106.12 (10)
C7—C6—C5	119.90 (11)	C9—N1—C6	126.67 (10)
C7—C6—N1	120.52 (11)	C11—N1—C6	127.20 (10)
C5—C6—N1	119.58 (11)	C9—N2—C10	105.14 (10)
C8—C7—C6	119.72 (11)	H1D—O1S—H1E	104.5 (17)
C8—C7—H7	120.1		
O1—C2—C3—C8	-176.76 (11)	N2—C9—N1—C11	0.29 (14)
C1—C2—C3—C8	2.59 (18)	N2—C9—N1—C11	0.29 (14)
C1—C2—C3—C4	-176.67 (11)	N2—C9—N1—C6	79.67 (10)
C8—C3—C4—C5	1.18 (18)	C10—C11—N1—C9	-0.15 (13)
C2—C3—C4—C5	-179.52 (10)	C10—C11—N1—C6	-179.53 (11)
C3—C4—C5—C6	-0.60 (18)	C7—C6—N1—C9	-179.88 (11)
C4—C5—C6—C7	-0.27 (18)	C5—C6—N1—C9	-0.77 (18)
C4—C5—C6—N1	-179.39 (10)	C7—C6—N1—C11	-0.63 (18)
C5—C6—C7—C8	0.51 (18)	C5—C6—N1—C11	178.48 (11)
N1—C6—C7—C8	179.62 (11)	N1—C9—N2—N2	0.0 (3)
C6—C7—C8—C3	0.10 (19)	N2—C9—N2—C10	0E1 (10)
C4—C3—C8—C7	-0.93 (19)	N1—C9—N2—C10	-0.30 (14)
C2—C3—C8—C7	179.80 (11)	C11—C10—N2—N2	0.00 (19)
N2—C10—C11—N1	-0.02 (14)	C11—C10—N2—C9	0.20 (14)
N2—C10—C11—N1	-0.02 (14)	N2—C10—N2—C9	0E1 (8)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> — \cdots <i>A</i> 1 <i>S</i> —
H1D \cdots O1 ⁱ	0.87 (2)	2.00 (2)	2.8610 (14)	174.6 (19)
O1S—H1E \cdots N2	0.91 (2)	1.92 (2)	2.8246 (15)	172.1 (16)
C5—H5 \cdots O1S ⁱⁱ	0.93	2.39	3.3034 (16)	166
C9—H9 \cdots O1S ⁱⁱ	0.948 (15)	2.345 (15)	3.2677 (16)	164.5 (12)

Symmetry codes: (i) $x, y+1, z-1$;
(ii) $-x, -y+1, -z$.

5.4 Acknowledgement

We wish to thank the University KwaZulu-Natal and the NRF for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2569).

5.5 References

- Bruker (2008). APEX2, SAINT-Plus, XPREP and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Corberan, R. & Peris, E. (2008). *Organometallics*, 27, 1954–1958.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* 30, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* 32, 837–838.
- Gayathri, P., Thiruvalluvar, A., Srinivasan, N., Jayabharathi, J. & Butcher, R. J. (2010). *Acta Cryst.* E66, o2519.
- Ishihara, M., Tonogaki, M., Ohba, S., Saito, Y., Okazaki, M., Katoh, T. & Kamiyama, K. (1992). *Acta Cryst.* C48, 184–188.
- Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
- Zheng, Z., Geng, W.-Q., Wu, Z.-C. & Zhou, H.-P. (2011). *Acta Cryst.* E67, o524

Chapter six

1-(4-Nitrophenyl)-1H-imidazol-3-ium chloride³

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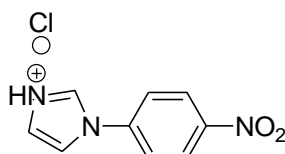
Key indicators: single-crystal X-ray study; T = 173 K; mean (C–C) = 0.002 Å ;
R factor = 0.029; wR factor = 0.076; data-to-parameter ratio = 15.8.

Abstract

In the title salt, C₉H₈N₃O₂⁺Cl⁻, the least-squares planes of the imidazolium and benzene rings are almost coplanar, making a dihedral angle of 4.59 (1)°. In the crystal, the chloride anion links the organic molecules through N—H---Cl hydrogen bonds, forming chains that run diagonally across the bc face, which compliment strong C—H---O hydrogen bonds between neighbouring molecules. These chains are connected to adjacent chains through two weak C—H---Cl interactions, resulting in hydrogen-bonded sheets extending along the b and c axes. The absolute structure of the title compound was determined using a Flack x parameter of 0.00 (6) and a Hooft y parameter of 0.03 (2).

6.1 Related literature

For the synthesis of the title compound, see: Gnanamgari *et al.*, (2009); Coberan & Peris (2008); Singh *et al.*, (2011). For the structure of imidazole with a bond to phenyl via carbon, see: Gayathri *et al.* (2010). For structure of imidazole with a bond to phenyl via nitrogen, see: Zheng *et al.* (2011). For the structure of nitrophenyl imidazole as a ligand in a complex, see: Singh *et al.* (2010, 2011). For related structures, see: Ishihara *et al.* (1992); Scheele *et al.*, (2007). For our related work in this area, see: Ibrahim *et al.* (2012).



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6.2 Comment

Since the isolation of the first stable free carbene, imidazolium based *N*-heterocyclic carbene ligands (NHC) ligands have received wide interest from researchers because substituted imidazolium salts are major precursors to the NHCs commonly employed in organometallic chemistry and catalysis for the stabilization of metal centers. Recently Gayathri *et al.*, (2010) have reported structural analogues of the title compound with imidazole bond to phenyl *via* carbon, while Zheng *et al.*, (2011) have reported the structure with imidazole bond to phenyl *via* nitrogen. For the structure of nitro-phenyl imidazole as a ligand in a metal complex, see: (Singh *et al.*, 2010 and 2011). Structures of related compounds were reported by Ishihara *et al.*, (1992), Scheele *et al.*, (2007) and Ibrahim *et al.*, (2012). Hence, the title compound was obtained in an attempt to synthesize an imidazolium salt by the coupling of 2-chloromethylpyridine hydrochloride with *p*-nitrophenyl imidazole using the method reported by Gnanamgari *et al.*, (2009). Coberan & Peris (2008) and Singh *et al.*, (2011) have also reported synthesis of similar compounds. The grey solid obtained was recrystallized from methanol:ethyl acetate (1:1) solvent system. The planes of the imidazolium and phenyl rings in (6.1) are almost coplanar. Analysis of the absolute structure using likelihood methods (Hooft *et al.*, 2010) was performed using *PLATON* (Spek, 2009). The Hooft γ -parameter was determined to be 0.03 (2) which corroborated the Flack parameter $x = 0.00$ (6). These results in conjunction with a correlation coefficient of 0.997 for the Bijvoet normal probability plot indicate that the absolute structure is correctly assigned. In the title compound, C₉H₈N₃O₂.Cl, the L.S. planes of the imidazolium (N1—C4) and phenyl (C5—C10) rings are almost coplanar with a dihedral angle of 4.59 (1)°. In the crystal, the chloride atom links the organic molecules through N—H⋯Cl hydrogen bonds forming chains that run diagonally across the *bc* face which compliment strong intermolecular C—H⋯O hydrogen bonds between neighbouring molecules. These chains are connected to adjacent chains through two weak C—H⋯Cl interactions resulting in hydrogen bonded sheets extending along the *b* and *c* axes.

6.3 Experimental

To a 150 ml round bottom flask containing DMSO (30 ml, MERCK) was added imidazole (0.01 mol, 0.68 g, Fluka AG) and KOH (0.015 mol, 0.84 g, MERCK) then stirred at room temperature for 2 h. This was followed by the drop wise addition of a solution of 1-chloro-4-nitrobenzene (Fluka, 0.01 mol, 1.57 g) in DMSO (5 ml), and refluxed at 100 °C for 24 h. The resulting solution was first chilled and then diluted with distilled water until neutral.

The organic component was extracted using $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ (1:1, 3 x 20 ml) and then dried with anhydrous MgSO_4 and concentrated under vacuum yielding 2.081 g of pure *N*-paranitrophenylimidazole; ^1H NMR (400 MHz, CDCl_3): 8.36(d; 2H) 7.96(s; 1H), 7.57(d; 2H) and 7.25(1H) ppm. ^{13}C NMR (400 MHz, CDCl_3): 146.6, 142.3, 135.7, 132.04, 126.1, 121.4 and 117.9 ppm. IR (ATR): 3112(=C—H), 2924 ($sp^3\text{C}$ —H), 1596(C=N), 1503 and 1370(aromatic NO_2), 1049 (C—N medium) and 845 (*p*-substituted benzene) cm^{-1} . Aqueous solution of Na_2CO_3 was used to neutralize 2-chloromethyl pyridine hydrochloride (0.82 g, 5.0 mmol) at 0 °C. The liberated 2-chloromethyl pyridine were then extracted with diethyl ether (4x10 ml) and dried over anhydrous MgSO_4 , filtered and the volume reduced to 1/3 of the initial volume at reduced pressure. The afforded volume was then added to a Schlenk tube containing an equimolar amount of *N*-paranitrophenylimidazole initially dissolved in dry toluene (25 ml) and the remaining diethyl ether removed under reduced pressure. The contents of the Schlenk tube were then refluxed at 110 °C for 36 h. The resulting grey solid obtained was filtered, washed with dry ether and dried under vacuum to afford **6.1**; 0.89 g, 79%. ^1H NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1H, NCHN), 8.48 (d, $J=9.1$ Hz, 2x1H, phenyl), 8.42 (s, 1H, CH=CH imidazolyl), 8.15 (d, $J=9.1$ Hz, 2x1H, phenyl), 7.92 (s, 1H, CH=CH imidazolyl). ^{13}C NMR (400 MHz, DMSO-d_6): δ 147.2 (NCHN), 139.7, 135.4, 125.4, 122.8, 121.9, 120.5. Anal. Calcd. for $\text{C}_9\text{H}_8\text{ClN}_3\text{O}_2 \cdot 0.15\text{C}_6\text{H}_5\text{CH}_3$: C; 50.41, H; 3.87, N; 17.55. Found: C; 50.59, H; 3.26, N; 18.36.

6.3.1 Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

6.3.2 Refinement

Carbon-bound H-atoms were placed in calculated positions [$\text{C—H} = 0.93 \text{ \AA}$ for aromatic H atoms; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and were included in the refinement in the riding model. The nitrogen-bound H atom was located on a difference Fourier map and refined freely with isotropic parameters.

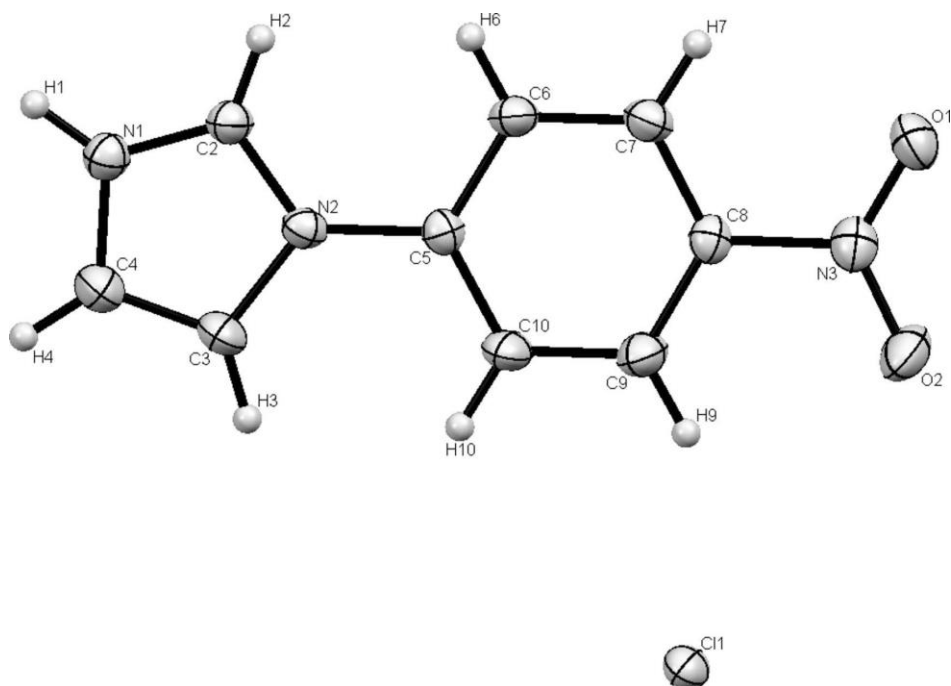


Figure 6.1: *ORTEP* diagram of compound (6.1). Thermal ellipsoids are represented at the 50% probability level.

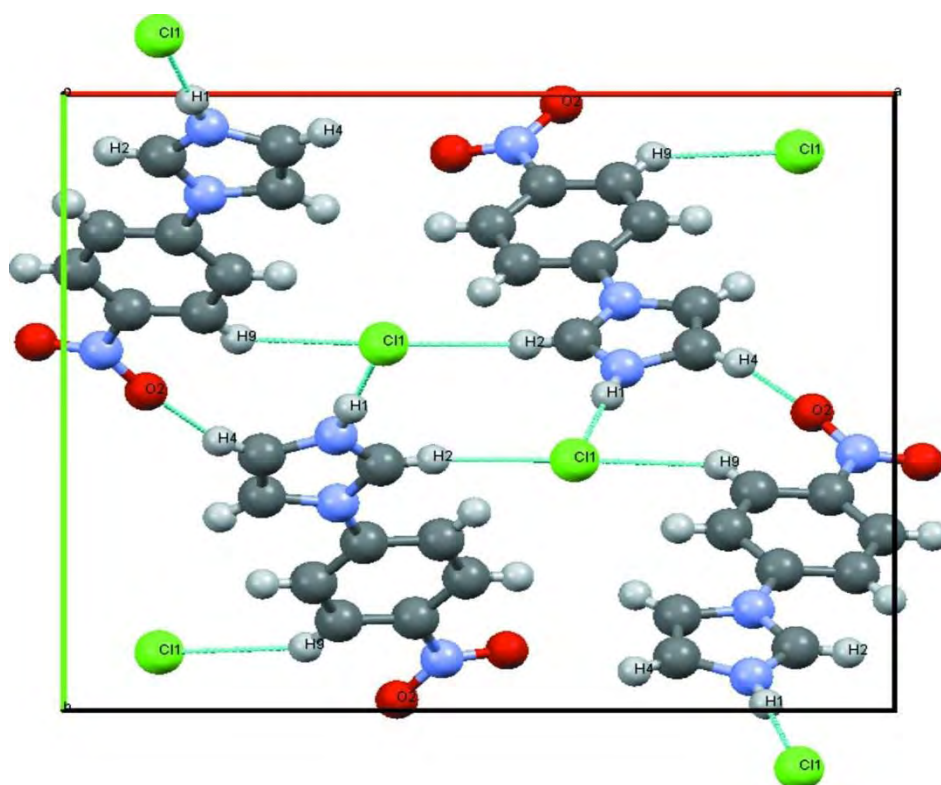


Figure 6.2: Packing diagram showing hydrogen bonding interactions in a crystal of the title salt viewed along crystallographic *c* axis.

6.3.3 Crystal data

$C_9H_8N_3O_2$

Mr = 225.64

Orthorhombic, Pna2₁

Hall symbol: P 2c -2n

a = 14.6042 (8) Å

b = 12.1781 (7) Å

c = 5.6070 (3) Å

V = 997.21 (10) Å³

Z = 4

F(000) = 464

Dx = 1.503 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9896 reflections

θ = 2.2–28.3°

μ = 0.37 mm⁻¹

T = 173 K

Block, colourless

0.54 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

Tmin = 0.524, Tmax = 0.746

20153 measured reflections

2217 independent reflections

2120 reflections with I > 2σ(I)

Rint = 0.060

θmax = 28.3°, θmin = 2.2°

h = -17→19

k = -16→16

l = -7→6

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.029

wR(F²) = 0.076

S = 1.09

2217 reflections

140 parameters

8 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(Fo²) + (0.0354P) + 0.3302P]

where P = (Fo² + 2Fc²)/3

Δρmax = 0.30 e Å⁻³

Δρmin = -0.22 e Å⁻³

Absolute structure: Flack (1983), Hooft et al.
(2010) and Spek (2009); Hooft parameter =
0.03(2), 856 Bijvoet pairs

6.3.4 Special details

Experimental. Carbon-bound H-atoms were placed in calculated positions [$C-H = 0.93 \text{ \AA}$ for aromatic H atoms; $U_{iso}(H) = 1.2U_{eq}(C)$] and were included in the refinement in the riding model. The nitrogen-bound H atom was located on a difference Fourier map and refined freely with isotropic parameters.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C2	0.61881 (11)	0.39839 (13)	-0.1020 (3)	0.0241 (5)
H2	0.5556	0.4068	-0.0918	0.029*
C4	0.76184 (13)	0.41464 (15)	-0.2179 (4)	0.0308 (5)
H4	0.8131	0.4368	-0.3039	0.037*
C3	0.76136 (12)	0.34674 (15)	-0.0291 (4)	0.0303 (4)
H3	0.8120	0.3132	0.0402	0.036*
N3	0.54484 (10)	0.08365 (11)	0.8199 (3)	0.0274 (3)
N2	0.67050 (9)	0.33611 (11)	0.0429 (3)	0.0210 (3)
N1	0.67229 (10)	0.44554 (12)	-0.2608 (3)	0.0251 (3)
O1	0.46671 (9)	0.09724 (10)	0.8910 (3)	0.0323 (4)
O2	0.59895 (10)	0.01721 (12)	0.9069 (3)	0.0406 (4)
H1	0.6548 (14)	0.4898 (17)	-0.386 (4)	0.030 (5)*
Cl1	0.88518 (2)	0.09410 (3)	0.84010 (10)	0.02647 (12)
C8	0.57713 (11)	0.14961 (13)	0.6161 (3)	0.0217 (3)

C9	0.66889 (12)	0.14545 (14)	0.5571 (4)	0.0303 (4)
H9	0.7093	0.1022	0.6443	0.036*
C10	0.69939 (11)	0.20704 (13)	0.3655 (4)	0.0300 (4)
H10	0.7608	0.2048	0.3216	0.036*
C5	0.63843 (11)	0.27213 (12)	0.2387 (3)	0.0204 (3)
C6	0.54623 (11)	0.27679 (13)	0.3038 (4)	0.0264 (4)
H6	0.5058	0.3212	0.2196	0.032*
C7	0.51553 (11)	0.21484 (13)	0.4943 (4)	0.0260 (4)
H7	0.4543	0.2170	0.5397	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0202 (8)	0.0223 (7)	0.0297 (13)	0.0005 (6)	-0.0001 (7)	0.0027 (7)
C4	0.0233 (9)	0.0369 (9)	0.0323 (13)	0.0006 (7)	0.0030 (8)	0.0051 (8)
C3	0.0172 (8)	0.0356 (10)	0.0380 (12)	0.0008 (7)	0.0036 (8)	0.0068 (8)
N3	0.0293 (7)	0.0286 (6)	0.0242 (9)	-0.0071 (5)	-0.0034 (8)	0.0010 (6)
N2	0.0173 (6)	0.0196 (6)	0.0262 (8)	-0.0004 (5)	0.0005 (6)	-0.0007 (6)
N1	0.0247 (7)	0.0232 (6)	0.0274 (8)	-0.0002 (5)	-0.0003 (6)	0.0013 (6)
O1	0.0286 (7)	0.0373 (6)	0.0311 (9)	-0.0060 (5)	0.0047 (6)	0.0014 (6)
O2	0.0347 (7)	0.0438 (8)	0.0432 (10)	-0.0032 (6)	-0.0100 (6)	0.0205 (7)
Cl1	0.01823 (18)	0.02836 (18)	0.0328 (2)	-0.00189 (13)	-0.00026 (19)	0.0061 (2)
C8	0.0231 (8)	0.0202 (7)	0.0219 (9)	-0.0046 (6)	-0.0016 (7)	0.0000 (6)
C9	0.0231 (8)	0.0295 (9)	0.0382 (12)	0.0013 (7)	-0.0040 (8)	0.0089 (8)
C10	0.0161 (7)	0.0326 (8)	0.0415 (12)	0.0018 (6)	-0.0002 (8)	0.0085 (9)
C5	0.0210 (8)	0.0190 (6)	0.0214 (8)	-0.0021 (6)	-0.0001 (6)	-0.0009 (6)
C6	0.0202 (7)	0.0256 (7)	0.0333 (12)	0.0044 (6)	-0.0007 (8)	0.0034 (7)
C7	0.0196 (8)	0.0278 (8)	0.0307 (10)	0.0016 (6)	0.0022 (7)	-0.0005 (7)

Geometric parameters (\AA , $^\circ$)

C2—N1	1.316 (2)	N1—H1	0.92 (2)
C2—N2	1.343 (2)	C8—C7	1.381 (2)
C2—H2	0.9300	C8—C9	1.381 (2)
C4—C3	1.343 (3)	C9—C10	1.384 (3)
C4—N1	1.382 (2)	C9—H9	0.9300
C4—H4	0.9300	C10—C5	1.388 (2)
C3—N2	1.393 (2)	C10—H10	0.9300
C3—H3	0.9300	C5—C6	1.396 (2)
N3—O1	1.220 (2)	C6—C7	1.382 (3)
N3—O2	1.232 (2)	C6—H6	0.9300
N3—C8	1.474 (2)	C7—H7	0.9300
N2—C5	1.425 (2)		
N1—C2—N2	108.78 (15)	C7—C8—C9	122.31 (17)
N1—C2—H2	125.6	C7—C8—N3	119.25 (15)
N2—C2—H2	125.6	C9—C8—N3	118.43 (16)
C3—C4—N1	107.45 (16)	C8—C9—C10	118.58 (16)
C3—C4—H4	126.3	C8—C9—H9	120.7
N1—C4—H4	126.3	C10—C9—H9	120.7
C4—C3—N2	106.90 (16)	C9—C10—C5	120.04 (15)
C4—C3—H3	126.5	C9—C10—H10	120.0

N2—C3—H3	126.5	C5—C10—H10	120.0
O1—N3—O2	124.04 (17)	C10—C5—C6	120.53 (17)
O1—N3—C8	118.59 (14)	C10—C5—N2	119.73 (15)
O2—N3—C8	117.37 (15)	C6—C5—N2	119.73 (15)
C2—N2—C3	107.90 (15)	C7—C6—C5	119.50 (15)
C2—N2—C5	126.14 (14)	C7—C6—H6	120.2
C3—N2—C5	125.95 (15)	C5—C6—H6	120.2
C2—N1—C4	108.96 (16)	C8—C7—C6	119.02 (16)
C2—N1—H1	127.3 (13)	C8—C7—H7	120.5
C4—N1—H1	123.7 (13)	C6—C7—H7	120.5
N1—C4—C3—N2	0.1 (2)	C8—C9—C10—C5	0.7 (3)
N1—C2—N2—C3	0.8 (2)	C9—C10—C5—C6	0.4 (3)
N1—C2—N2—C5	179.69 (15)	C9—C10—C5—N2	179.43 (17)
C4—C3—N2—C2	-0.6 (2)	C2—N2—C5—C10	176.61 (17)
C4—C3—N2—C5	-179.45 (15)	C3—N2—C5—C10	-4.7 (3)
N2—C2—N1—C4	-0.7 (2)	C2—N2—C5—C6	-4.4 (3)
C3—C4—N1—C2	0.4 (2)	C3—N2—C5—C6	174.27 (17)
O1—N3—C8—C7	-7.6 (2)	C10—C5—C6—C7	-0.8 (3)
O2—N3—C8—C7	171.90 (17)	N2—C5—C6—C7	-179.81 (15)
O1—N3—C8—C9	171.10 (16)	C9—C8—C7—C6	1.1 (3)
O2—N3—C8—C9	-9.4 (2)	N3—C8—C7—C6	179.81 (16)
C7—C8—C9—C10	-1.5 (3)	C5—C6—C7—C8	0.0 (3)
N3—C8—C9—C10	179.81 (16)		

Hydrogen-bond geometry (Å, °)

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
N1—H1···C11 ⁱ	0.92 (2)	2.08 (2)	2.9976 (17)	178 (2)
C9—H9···C11	0.93	2.80	3.5898 (19)	144
C2—H2···C11 ⁱⁱ	0.93	2.52	3.4286 (17)	166
C4—H4···O2 ⁱ	0.93	2.29	3.181 (2)	161

Symmetry codes: (i) $-x+3/2, y+1/2, z-3/2$; (ii) $x-1/2, -y+1/2, z-1$.

6.4 Acknowledgement

We wish to thank the University KwaZulu-Natal and the NRF for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NR2034).

6.5 References

- Bruker (2008). APEX2, SAINT-Plus, XPREP and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Coberan, R. & Peris, E. (2008). *Organometallics*, 27, 1954–1958.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* 45, 849–854.
- Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.

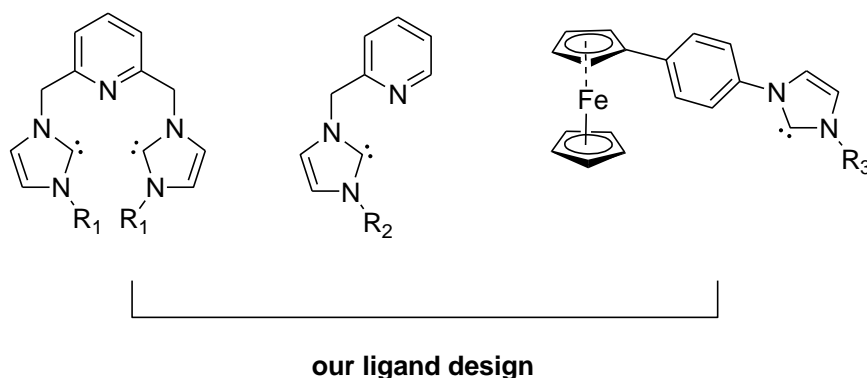
- Gayathri, P., Thiruvalluvar, A., Srinivasan, N., Jayabharathi, J. & Butcher, R. J. (2010). *Acta Cryst.* E66, o2519.
- Gnanamgari, D., Sauer, E. L. O., Schley, N. D., Butler, C., Incarvito, C. D. & Crabtree, R. H. (2009). *Organometallics*, 28, 321–325.
- Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2010). *J. Appl. Cryst.* 43, 665–668.
- Ibrahim, H., Bala, M. D. & Omondi, B. (2012). *Acta Cryst.* E68, o2305.
- Ishihara, M., Tonogaki, M., Ohba, S., Saito, Y., Okazaki, M., Katoh, T. & Kamiyama, K. (1992). *Acta Cryst.* C48, 184–188.
- Scheele, U. J., Meyer, F. & Dechert, S. (2007). *Tetrahedron Lett.* 48, 8366–8370.
- Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
- Singh, A. K., Kumar, P., Yadav, M. & Pandey, D. S. (2010). *J. Organomet.Chem.* 695, 567–573.
- Singh, A. K., Kumar, P., Yadav, M. & Pandey, D. S. (2011). *Bull. Chem. Soc. Jpn*, 84, 205–210.
- Spek, A. L. (2009). *Acta Cryst.* D65, 148–155.
- Zheng, Z., Geng, W.-Q., Wu, Z.-C. & Zhou, H.-P. (2011). *Acta Cryst.* E67, o524.

Chapter seven

Summary and conclusions

7.1 Project summary

Herein is presented an overview of the project and concluding remarks on achievements of the overall objectives of the project. The project was based on the synthesis of imidazolium salts with three different frameworks. As *N*-heterocyclic carbene ligand precursors; the design of the salts was based on achieving desirable overall properties in the transition metal-NHC complexes to be derived from them. The metals were also chosen based on their environmentally benign nature and possible catalytic potentials. The relative abundance and competitive pricing of iron, cobalt and nickel make them affordable alternatives to expensive platinum group metals which have dominated organometallic catalysis. In this thesis; all the new compounds ranging from the NHC precursors, the intermediate Ag-NHCs to the cobalt and nickel-NHC complexes were fully characterized by available and suitable analytical, spectroscopic and in some instances crystallographic tools and were confirmed to be of acceptable purity.



$R_1 = -CH_3, -C_2H_5, -CH_2(CH_2)_2CH_3, -CH_2CH(CH_3)_2, -CH_2(CH_2)_4CH_3, -CH_2C_6H_5$
 $R_2 = -C_6H_4NO_2, -C_6H_4COCH_3, -C_6H_4CN, -CH_2CHCH_2, -CH_2CH_2CHCH_2, -CH_2(CH_2)_2CHCH_2$
 $R_3 = -CH_2CHCH_2, -CH_2CH_2CHCH_2, -CH_2(CH_2)_2CHCH_2$

Figure 7.1: Summary of the three series of NHC ligands in this report.

The first series of imidazolium salts built around a pincer CNC architecture were synthesized via an improved solvent-free technique that simplified previous cumbersome methods for their synthesis and isolation. Detailed in chapter two of this thesis the results were published in the Elsevier journal *Tetrahedron Letters*.

The second series of imidazolium salts contain a picolyl moiety and were synthesized via modification of established procedures through the use of 2-bromomethylpyridine hydro bromide as the source of the pyridine based *N*-donor. The afforded functionalised imidazolium salts were obtained in excellent isolated yields.

Using standard techniques for the synthesis of ferrocenylphenyl imidazole and subsequent coupling with terminal alkenyl bromides in refluxing acetonitrile afforded good to excellent isolated yields of the corresponding ferrocenyl functionalised series of salts.

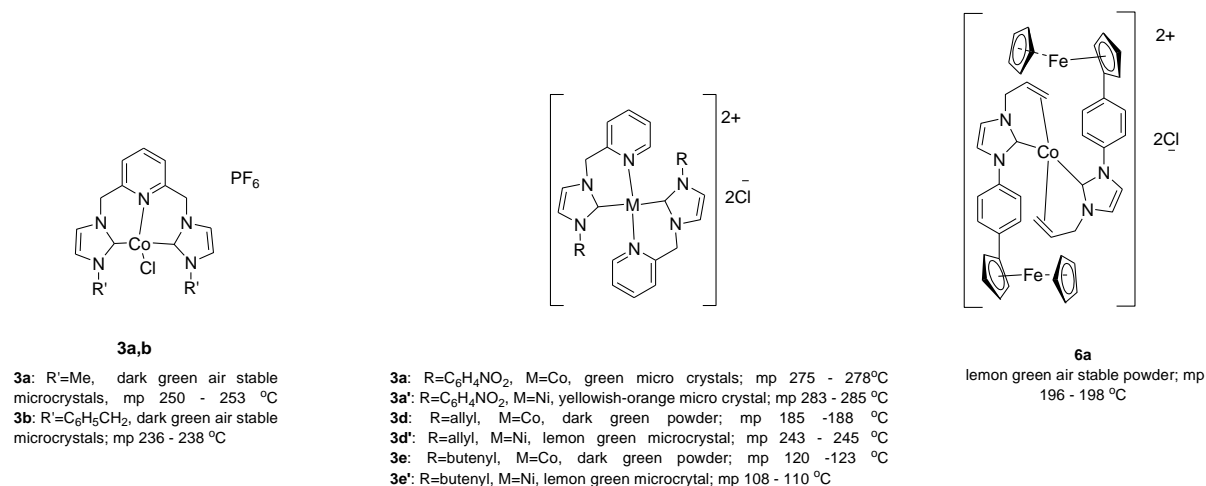


Figure 7.2: Summary of synthesized NHC-Metal complexes.

All the synthesized cobalt and nickel-NHC complexes have the metal in the +2 state of oxidation and showed appreciable activity in catalyzing the arylation of aryl amines with phenyl halides using only 1 mol% catalyst loading. Based on the results obtained, mechanistic pathways were proposed for the catalysis.

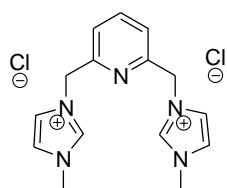
7.2 Conclusions

Several new NHC-ligand precursors were successfully synthesized and characterized. The ligand precursors yielded M-NHC complexes of Co and Ni in fair to good isolated yields via transmetalation from corresponding Ag-NHC complexes. Both the *in situ* generated and

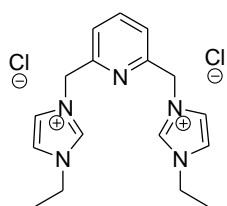
isolated M-NHC complexes have shown appreciable activities in the activation of C-N coupling of aryl bromides with aryl amines leading to good isolated yields of diarylamines comparable to those obtained with Pd-, Pt-, Ir- and Ru-NHC catalyst systems. This is an immense contribution to the field of organometallic chemistry and homogeneous catalysis of environmentally benign and readily available metals.

7.3 Summary of all the major compounds synthesised and characterised

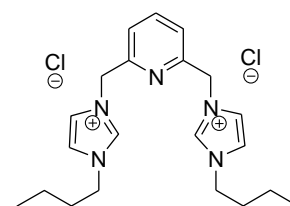
7.3.1 Salts



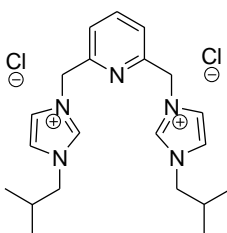
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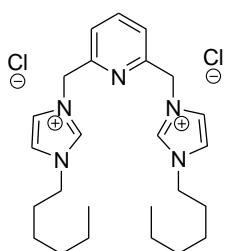
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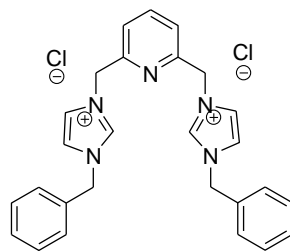
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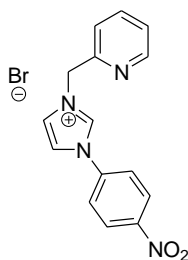
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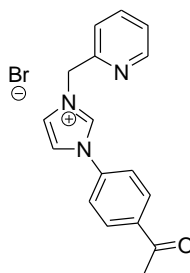
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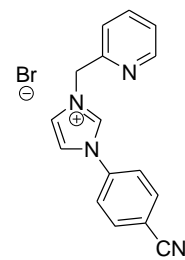
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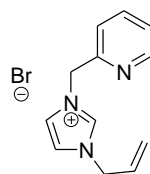
4.1a



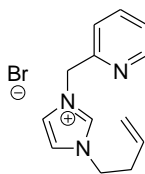
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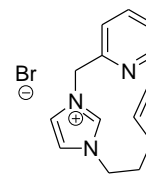
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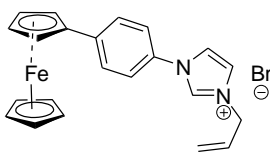
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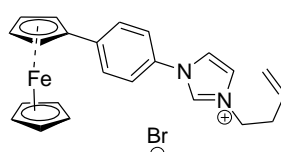
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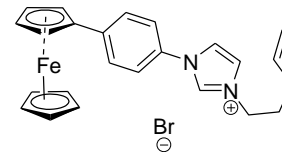
4.1f



4.4a

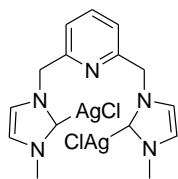


4.4b

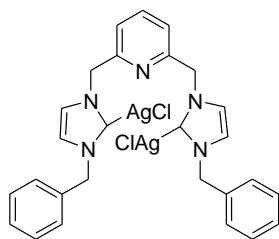


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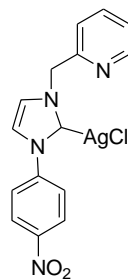
7.3.2 NHC-Ag complexes



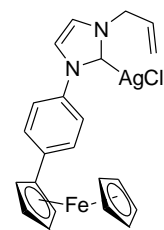
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3.2b

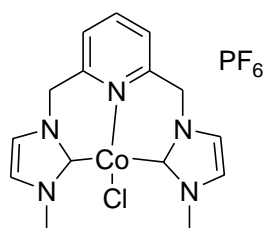


4.2a

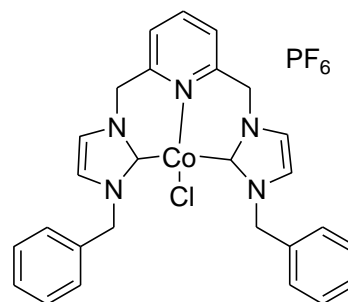


4.5a

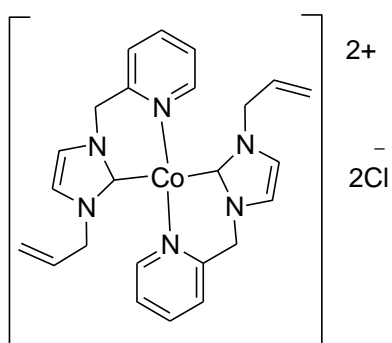
7.3.3 NHC-Co(II) complexes



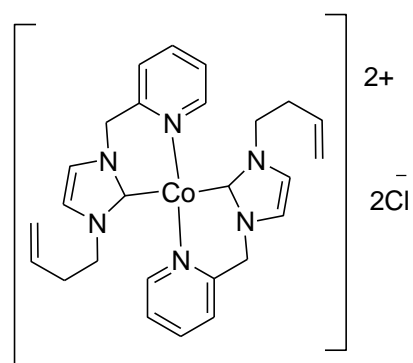
3.3a



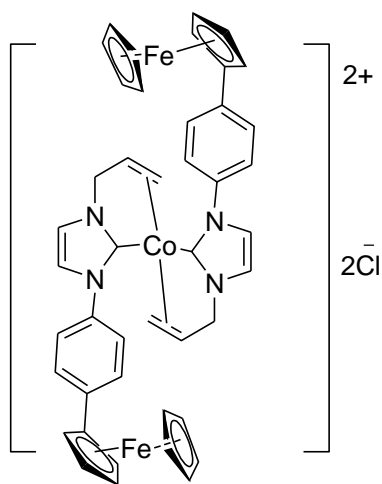
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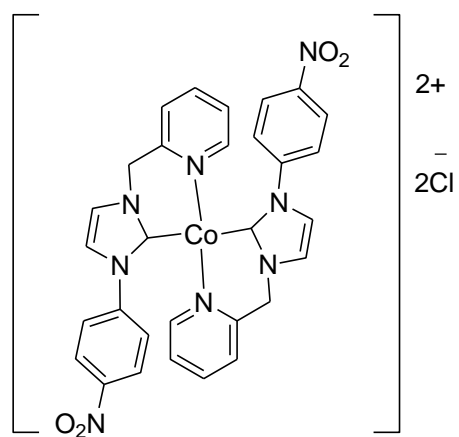
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4.3e

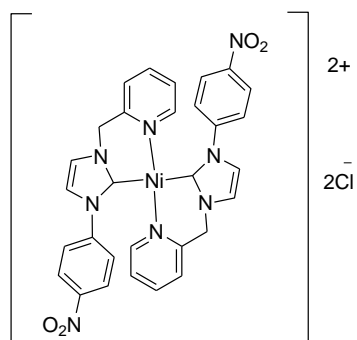


4.6a

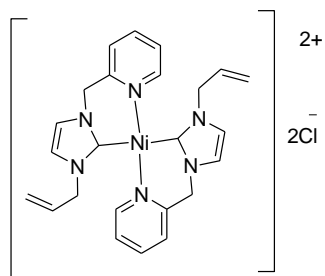


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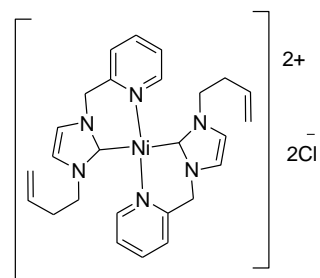
7.3.4 NHC-Ni(II) complexes



4.3a'

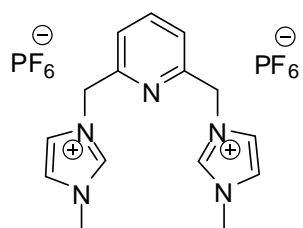


4.3d'

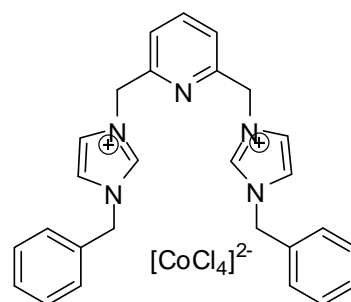


4.3e'

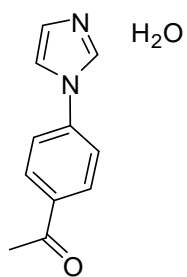
7.3.5 Others



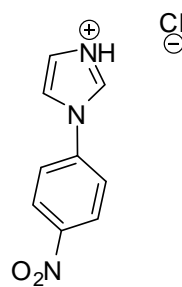
C1a



C1b



5.1



6.1