Group 8 Transition Metal Complexes Bearing Donor-Functionalised NHC Ligands

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By

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Declaration of Originality

I, Andrew Wheals, declare that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

Table of Contents

List of Abbreviations

[Ru]	Ruthenium complex
Ar	Aryl
Cat.	Catalyst
$C^{NHC}C^{NHC}$	1,1'-methylenebis(3-methylimidazol-2-ylidene) (see Appendix B)
COSY	Correlation Spectroscopy
DIPP	2,6-diisopropylphenyl
ESI-MS	Electron Spray Ionisation-Mass Spectrometry
HMBC	Heteronuclear multiple bond correlation
HOMO	Highest occupied molecular orbital
HSQC	Heteronuclear single quantum coherence
J	Scalar coupling constant (NMR)
KHMDS	Potassium hexamethyldisilazide
L	Ligand
LC	Liquid Chromatography
LUMO	Lowest unoccupied molecular orbital
m	Meta
m/z	Mass-to-charge ratio
Mesityl	1,3,5-trimethylphenyl
MPV	Meerwein-Ponndorf-Verley
MS	Mass spectrometry
NC^{NHC}	1',3-dimethyl-1,2'-dibenzo[d]imidazol-2-ylidene (See Appendix B)
NHC	*N*-heterocyclic carbene
N-het	*N*-heterocycle
NMR	Nuclear Magnetic Resonance Spectroscopy
NOESY	Nuclear Overhauser Effect Spectroscopy
o	Ortho
p	Para
PCy_3	Tricyclohexylphosphine
p-cym	*Para*-cymene (1-methyl-4-(propan-2-yl)benzene)
q_{surf}	Partial charge of the most negatively charged surface atom
RT	Room temperature
δ	Chemical shift (ppm)

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Abstract

This thesis describes the synthesis of donor-functionalised *N*-heterocyclic carbene (NHC) pre-ligands, the synthesis of group 8 metal complexes bearing donor-functionalised NHC ligands and the application of Ru(II) η^6-arene complexes containing donor-functionalised NHC ligands as catalysts for transfer hydrogenation reactions.

The first part of this thesis describes the synthesis and characterisation of three pre-ligands: two novel compounds constituted of one NHC donor and one *N*-heterocyclic *N*-donor (**2.3**, (NC^{NHC})I and **2.4**, (NC^{NHC})BPh$_4$)), one constituted of two NHC donors (**2.8**, (C^{NHC}C^{NHC})Br$_2$).

The second part of this thesis describes the synthesis and characterisation of two novel Ru(II) complexes bearing the bidentate ligand, NC^{NHC}, (**3.1**, RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$]BPh$_4$ and **3.2**, [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$) and two novel Ru(II) complexes bearing the *bis*-NHC ligand, C^{NHC}C^{NHC}, (**3.3**, [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ and **3.4**, [RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$).

The third part of this thesis describes the application of **3.3** and **3.4** as catalysts for the transfer hydrogenation reaction in 2-propanol. Both complexes were found to be active in the conversion of a range of ketones and 4-chlorobenzonitrile. Complex **3.3** was found to be more active in the conversion of all substrates, this activity has been attributed to the dissociation of the more weakly π-donating η^6-benzene ligand to form the active catalyst.

Chapter 1

Introduction:
Group 8 transition metal complexes bearing donor-functionalised NHC ligands

1.1. Organometallic complexes as catalysts

Organometallic complexes are metal complexes in which at least one metal atom is directly bonded to a carbon.[1] The organic components (ligands) of these complexes may also form coordination bonds with the metal atom *via* heteroatoms such as nitrogen, oxygen and phosphorous. Ligands may be designed to act as spectator ligands, occupy one or several coordination sites, introduce chirality to the complex, control steric properties, or alter the electronic properties of the complex. The ligands are usually anionic atoms (such as halides) or compounds (such as acetylacetonate), acting to stabilise the charge of an oxidised metal, or neutral donor compounds such as phosphines, amines or *N*-heterocycles.

Organometallic complexes have the ability to act as a catalyst, reducing the activation energy and increasing the rate of a chemical reaction. They have been widely applied in many important industrial processes. Some well-known examples include: hydroformylation to make aldehydes as feedstocks for plasticisers, detergents, fragrances and pharmaceuticals;[2] olefin metathesis to make petroleum products, propylene, pharmaceuticals, and cosmetics;[3–5] small molecule activation for the production of fertilisers from N_2 or the use of CO_2 as a chemical feedstock;[6,7] and transfer hydrogenation as an alternative to the use of hazardous H_2 in coal liquefaction and the processing of vegetable oils.[8]

This thesis focuses on organometallic complexes of group 8 transition metals with *N*-heterocyclic carbene (NHC) ligands. Specifically, multidentate donor-functionalised NHC ligands, including NHC ligands with *N*-heterocyclic secondary donors (NHC-*N*-het) and bidentate chelating NHC ligands in which the second donor is an additional NHC (*bis*-NHC) will be discussed, with a focus on the synthesis of their complexes. The application of group 8 metals bearing bidentate ligands containing NHC donors in the catalytic transfer hydrogenation of ketones and activation of CO_2 are also discussed.

1.2.   The *N*-heterocyclic carbene ligand motif

A carbene is a neutral, divalent carbon with two unshared valence electrons and an empty orbital.[9] The NHC is a heterocyclic species constituted of a carbene carbon and at least one nitrogen in the ring structure. Due to their enhanced stability, they are the largest subgroup of persistent or stable carbenes, and have been widely used as ligands in homogenous catalysis since the isolation of the first free NHC in 1991.[10] While many NHC motifs exists, derived from different azolium rings, the imidazolium derivative is by far the most well-known (Figure 1.1).[9]
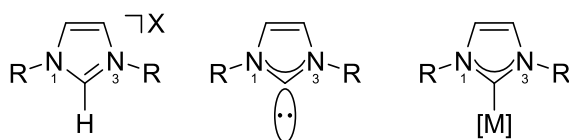
Figure 1.1. General structure of the imidazolium pre-cursor (left), the imidazole-2-ylidene free NHC (middle) and the NHC bound to a metal (right).

The electronic configuration of the imidazolium derived NHC is best described by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) being an sp^2-hybridised lone pair and an unoccupied p-orbital at the C^2 carbon, respectively.[9] The adjacent nitrogen atoms are σ-electron-withdrawing which stabilises the carbene by lowering the energy of the sp^2 hybridised orbital, and π-electron-donating, raising the energy of the empty p-orbital. Together these effects create a greater HOMO-LUMO gap, and so stabilise the carbene.

The behavior of the NHC species as a ligand is characterised by the neutral two electron σ-donor properties of the central carbene carbon, with minimal π-backbonding, allowing rotation about the C-M bond (Figure 1.1). These are similar to the characteristics of phosphine coordination, indeed NHCs were originally considered a replacement for phosphine ligands.[11,12] NHCs are typically better electron-donors than phosphines, leading to stronger ligand-metal bonds, which are reflected in greater M-C dissociation energies and shorter bond lengths.[12–14] In addition, phosphines undergo P-C bond cleavage and NHC ligands are not susceptible to this,[15] leading to complexes that are highly resistant to decomposition.[16]

NHCs are predominantly synthesised by deprotonation of their corresponding azolium salt precursor. Diverse libraries of NHC ligands have resulted from the ease with which the *N*-substituents may be altered; this allows the fine-tuning of steric and electronic properties of the resulting metal complexes.[17] (For a detailed discussion of NHC ligand synthesis see Chapter 2).

1.2.1. Donor-functionalised NHC ligands

Functionalisation of the azolium salt precursor with substituents containing donor groups (N, P, O, S or a second NHC) results in a multidentate ligand architecture, in which the NHC ligand may occupy multiple coordination sites of the metal atom.[18] This can stabilise the complex by occupying free coordination sites,[18,19] and may allow weakly donating groups capable of hemilabile binding to temporarily generate free coordination sites, which is useful for substrate binding during catalysis.[20]

The utility of donor-functionalised NHC ligands became apparent in their complexes with Pd(II) and their application as catalysts in C-C coupling reactions.[21,22] A series of Pd(II)-Me complexes bearing donor-functionalised NHC ligands have been prepared (notable examples shown in Figure 1.2). These catalysts exhibited higher stability and exceeded all existing turnover numbers (TON) for the Heck and Suzuki coupling reactions. Subsequent studies compared the activity of a Pd(II) complex containing two non-donor-functionalised NHC's (**I**) to that of a complex with a bidentate NHC ligand (**II**) in a Heck coupling reaction (Figure 1.2). At a loading of 0.001 mol%, **II** demonstrated a TON of 48 200 after 24 hours, while **I** demonstrated a TON of only 18 000 after the same amount of time in promoting the Heck coupling reaction of 4-bromoacetophenone and *n*-butyl acrylate.[21]
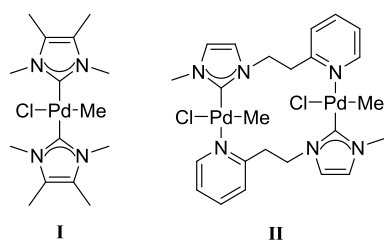
Figure 1.2. Pd(II)-Me complexes bearing monoNHC ligands (**I**) and *bis*-donor-functionalised NHC ligands (**II**) used in C-C coupling reactions. [21,22]

Recently, bidentate NHC ligands have proved fruitful substitutes for bidentate phosphines in ruthenium complexes used for direct hydrogenation reactions.[8] Previously, complexes with NHC ligands for direct hydrogenation reactions were scarce due to the high susceptibility of M-C^{NHC} towards reductive elimination.[23,24] The use of a bidentate NHC ligand was proposed as a potential strategy to help stabilise the M-C^{NHC} bond towards reductive elimination; this was achieved in 2009 with the first Ru(II)-NHC complex reported to be stable under strongly reducing conditions.[25]

1.2.2. NHC-Pincer ligands

Introduction of *N*-substituents containing donor atoms to both nitrogen atoms of an imidazolyl unit leads to a potential tridentate ligand. The NHC-pincer ligand is a specific tridentate system of the general formula DYD', where Y denotes the central atom and D/D' the sidearm donor atoms (Figure 1.3). Pincer ligands bound to a metal atom adopt a planar geometry, resulting in a meridional configuration in which three adjacent coordination sites within the same plane are occupied. This constrained configuration confers high thermal stability to the resulting transition metal complexes by inhibiting decomposition pathways.
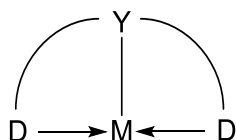
Figure 1.3. General structure of a pincer ligand, Y = central donor (e.g. phenyl, pyridyl, NHC); D = sidearm donor (N, P, O, S or NHC) and M = metal center.

The use of central units with strong σ-electron bonding character along with strongly coordinating side arms confers high thermal stability, for example Shaw *et al*. reported a Ni(II) complex containing a PCP ligand remained stable up to 240 °C.[26] Conversely, the use of weakly coordinating sidearms can lead to monodentate (κ^1), bidentate (κ^2) and tridentate (κ^3) coordination modes, as is demonstrated in dissociative equilibrium of the Pd(II) complex containing an SNS pincer ligand with hemilabile thioether sidearms (Figure 1.4).[27]
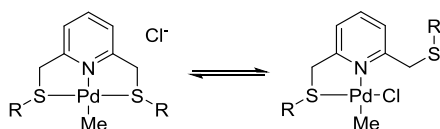
Figure 1.4. Equilibrium between κ^3 and κ^2 coordination modes.

Pincer ligands containing a single NHC moiety as the central donor and hemilabile pendant donor groups are of interest due to their ability to form organometallic complexes that bind with a variety of different coordination modes and enhanced catalytic activity over analogues in which the pendant arms are strongly binding.[28–31]

1.3. Group 8 metal complexes containing multidentate NHC ligands

The replacement of phosphine ligands in well-known complexes with NHC ligands became a popular trend due to the advantages detailed above.[11,32] The improved group 8 metal complexes with NHC ligands that result from these studies were particularly well demonstrated by the development of second generation Grubbs' catalysts (Figure 1.5).
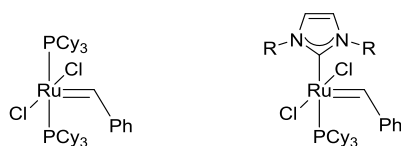
Figure 1.5. Grubbs' catalysts, first (left) and second (right) generation.

The replacement of one tricyclohexylphosphine (PCy₃) in the first generation Grubbs' catalyst with an NHC introduced air and moisture stability to the Ru(II) complexes, making the catalysts easier to handle and greatly enhancing their activity and thermal stability.[4] This was due to the stronger σ-donating character of the NHC, giving the complex a 10^4-fold greater affinity for the π-acidic olefinic substrate.[9,33] Since this revelation, group 8 organometallic complexes have found a great diversity of important applications in metathesis, reduction, polymerisation and C-X bond forming reactions.[5,10–15]

1.3.1. Ruthenium complexes bearing donor-functionalised NHC ligands

Donor-functionalised NHC ligands were first introduced as ligands for group 8 transition metals with the synthesis of the Ru(II) *bis*-NHC pincer ligand **III** (Figure 1.6).[41,42] Complex **III** was found to be a highly efficient catalyst for the transfer hydrogenation of ketones to alcohols, reaching TON's of up to 126 000; the oxidative cleavage of olefins with NaIO₄ and **III** was also shown to be successful with yields ranging from 23-99% depending on substrate used.

III
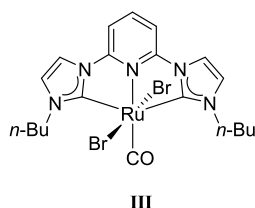
Figure 1.6. The first Ru complex bearing donor-
functionalised NHC ligand **III** [41,42]

Following the report of complex **III**, several Ru complexes with donor-functionalised NHC ligands have shown excellent activity for other catalytic reactions. Notable examples include chiral aryloxide-NHC complexes for asymmetric ring-opening/cross metathesis reactions,[43] anionic phenyl-NHC complexes for dye-sensitised solar cells[44] and hydrogen borrowing transformations,[45,46] and tethered NHC-η^6-arene ruthenium complexes for biphasic hydrogenation of styrene and CO_2.[47]

1.3.2.   NHC Ru(II) arene complexes as catalysts for the transfer hydrogenation of ketones

Hydrogenation is a fundamental chemical transformation and finds uses in a wide range of industrial applications, from the processing of food to the petrochemical industry and in the production of pharmaceuticals.[48] Direct hydrogenation, the addition of H_2 across a double bond, requires the substrate, a metal catalyst and pressurised H_2 gas. While this is a powerful reaction, spanning from the reduction of unfunctionalised alkenes to the enantioselective reduction of imines and ketones, it requires the use of hazardous pressurised H_2 gas.[49]

An attractive alternative to direct hydrogenation is transfer hydrogenation, which adds hydrogen to an unsaturated molecule from a non-H_2 source. This eliminates the hazards of handling pressurised H_2 cylinders by utilizing inexpensive and readily available alternatives such as 2-propanol; the major side product from the oxidation of 2-propanol (acetone) may also be easily recycled.[8]

Pioneering work by Hans Meerwein in the 1920's demonstrated the transfer hydrogenation of ketones in the presence of a secondary alcohol over aluminium *iso*-propoxide as the catalyst (MVP reaction).[50] Mechanistic studies have shown a cyclic transition state in the MPV reduction, in which the oxygen of both the carbonyl substrate and the secondary alcohol donor bind to the metal to facilitate the hydrogen transfer (Figure 1.7).[51]
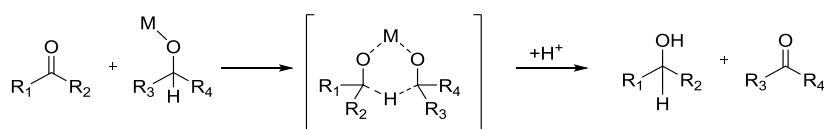
Figure 1.7 Transfer hydrogenation of ketones *via* the cyclic transition state in the MPV reduction.

It was not until the 1970's that group 8 transition metal homogenous complexes were introduced to the field of transfer hydrogenation. The tris-phosphine complex, [RuCl2(PPh3)3] was found to be active in the transfer hydrogenation of acetophenone with 2-propanol at elevated temperatures.[52–54] Twenty years later the influence of the base emerged, with a 10^3-10^4 fold increase in activity seen in the [RuCl2(PPh3)3] promoted transfer hydrogenation upon the addition of a catalytic amount of NaOH.[55] Indeed, the previously inactive RuH4(PPh3) was able to catalyse the reduction of

cyclohexanone at similar rates as [RuCl$_2$(PPh$_3$)$_3$] upon addition of NaOH. The presence of the base facilitates the formation of an *iso*-propoxide complex, which may then undergo *β*-hydride elimination to form the mono-hydride intermediate, and release acetone.[55]

Recently, Ru(II) complexes with both η^6-arene and bidentate NHC ligands have become a popular focus as catalysts for transfer hydrogenation reactions.[35] The first such example (**IV**, Figure 1.8) contained an oxazolidinone substituent binding to the metal through the nitrogen atom, and was found to be active as a catalyst for the transfer hydrogenation of ketones.[56] However, its use was limited to less sterically demanding substrates and required the addition of AgPF$_6$ to activate the precatalyst by abstracting the chloride ligand; the reaction reached only 10% yield after 24 hours the absence of AgPF$_6$. Two years later, a Ru(II) complex bearing a 5-membered chelating *bis*-NHC ligand (**V**, Figure 1.8)[57] was shown to be an active catalyst for transfer hydrogenation reactions using 2-propanol, including the reduction of CO$_2$ to formate.[38]

Since then, investigations into the effect of the pendant arm of the donor-functionalised NHC ligands and the influence of the η^6-arene ring on the efficiency of Ru complexes with both η^6-arene and donor-functionalised NHC ligands has become a focus, with promising results[56,58–60] (for more a more detailed discussion see Chapter 4).
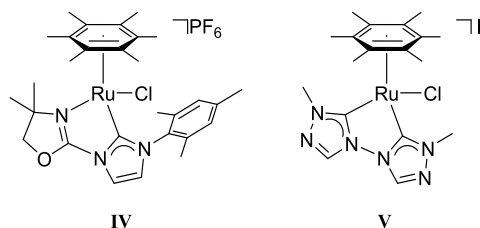
Figure 1.8 The first donor-functionalised NHC Ru(II) η^6-arene complex (**IV**) and the 5-membered chelating *bis*-NHC (**V**).[57]

1.3.3. Iron complexes bearing NHC-pincer ligands for catalysis

Iron is the most abundant transition metal on the planet, thus it is relatively cheap and is also environmentally benign. It has been shown to be a viable alternative to expensive precious metals such as Ru, Rh and Pd in many catalytic transformations.[34] In spite of these benefits, investigations into the chemistry of iron complexes bearing donor-functionalised NHC ligands only began to surface in 2004.[61] While donor-functionalised NHC complexes of iron in a variety of oxidation states are known,[34] we focus herein on Fe(II) complexes of NHC-pincer ligands, as these are scarce.

The first Fe(II) complex bearing a pincer ligand with NHC donor groups was introduced by Danopoulos in 2004 (**VIa**, Figure 1.9).[62] The ligand consisted of two imidazol-2-yl NHC moieties

linked by a 2,6-substituted central pyridyl *N*-donor (C^{NHC}NC^{NHC}). Several Fe(II) complexes coordinated by this ligand were synthesised, the structures of which varied according to the synthetic route and Fe(II) precursor used. The C^{NHC}NC^{NHC} complex **VIa** was later used as a catalyst for the cross-coupling of aryl Grignard reagents with bromoalkanes, successfully promoting the coupling of bromocyclohexane and *p*-tolylmagnesium bromide in 94% yield after 30 minutes.[63] The low valent Fe(0) dinitrogen complex **VIb** (Figure 1.9) was also employed as a pre-catalyst for the hydroboration of 4-methyl-1-pentene leading to an 81% yield; however this complex was outperformed by the analogous bis(imino)pyridine (NNN donor) complex and further investigations were not undertaken.[64] A coordinatively saturated Fe(II) complex, in which the imidazol-2-ylidene NHC moieties were instead replaced with 1,2,3-triazol-5-ylidene moieties, was also recently reported (**VIIa,b,** Figure 1.9).[65]

VIa X = Br	**VIIa** Ar = DIPP	**VIII**
VIb X = N$_2$	**VIIb** Ar = Mesityl	
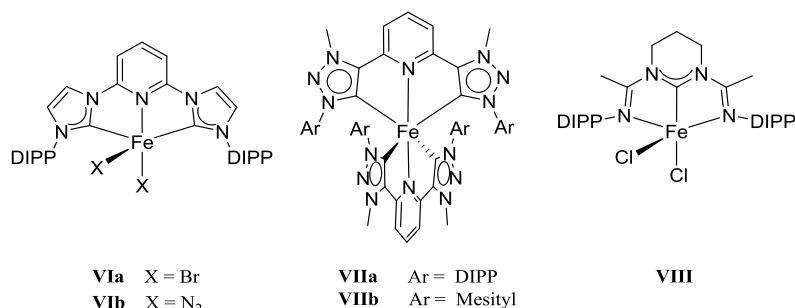
Figure 1.9. Fe(II) complexes bearing pincer ligands with NHC donors from Danopoulos (**VIa**),[62] Chirik (**VIb**),[64] Koga (**VIIa,b**)[65] and Byers (**VIII**).[66]

Complexes containing pincer ligands with a single NHC moiety as the central donor and hemilabile pendant donor groups are relatively rare. Such a complex was reported in 2012 by Byers *et al.,*[66] the central NHC donor is a 4,5,6-trihydropyrimidylidene with bis(imino) pendant *N*-donors (**VIII**, Figure 1.9). To date, this remains the only Fe(II) complex bearing an NHC-pincer ligand in which the NHC is the central donor; it is thus of interest to develop an Fe(II) catalyst bearing an NHC-pincer ligand with hemilabile side arms based on ligand architectures other than the reported bis(imino)-NHC (**VIII**, Figure 1.9).

1.4. Carbon dioxide as a chemical feedstock

Utilisation of carbon dioxide as a chemical feedstock has gained much attention over the past decade.[6] Approximately 220 megatonnes of CO_2 are currently utilised annually, with 70% of this covered by its conversion to other chemicals.[67] The majority of these conversions lie within a few

chemical production processes: the Bosch-Meiser process for urea production using CO_2 and ammonia; and the Kolbe Schmitt synthesis of salicylic acid _via_ nucleophilic addition of sodium phenoxide to CO_2. using phenol which uses organometallic complexes as catalysts for insertion into or polymerisation of epoxide[68]

Recently, carboxylation of C-B, C-X and C-H bonds with CO_2 has become an attractive approach for the incorporation of CO_2 into chemical feedstocks.[6] Ru(II) complexes have shown promise in several such CO_2 transformation reactions, such as hydroformylation,[69,70] alkoxycarbonylation,[71] hydrogenation[38,72] and reductive deoxygenation in the methylation of amines.[67] A reaction that has shown promise for late transition metal complexes with NHC ligands is the carboxylation of phenylacetylene by insertion of CO_2 into the terminal C-H bond.[73–76] However, there has yet to be an example of this reaction catalyzecatalysed by a Ru(II) complex.

1.5.   Goals of this work

Transfer hydrogenation and CO_2 utilisation are important chemical transformations: the former achieves a challenging reduction with high activation energy under mild conditions, and the latter reuses and adds value to an environmental pollutant and industrial waste product. Ru(II) complexes bearing chelating _bis_-NHC or bidentate NHC-_N_-het ligands have shown promise as catalysts for transfer hydrogenation reactions and CO_2 activation.[8,38,56,58–60] In addition, an Fe(II) complex bearing a donor-functionalised NHC ligand has yet to be applied as a catalyst for the activation of CO_2, where Ru(II) complexes have shown catalytic activation reactivity.[6]

The first aim of this work is to improve the synthesis of NHC pre-ligands containing a secondary donor, either an _N_-heteroaromatic _N_-donor or an additional NHC donor. A bidentate NHC-_N_-het ligand that forms a 5-membered chelate ring upon complexation to Ru(II) or Fe(II) is desirable to mimic the structure formed by NHC-imino ligands (such as **VIII**, Figure 1.9).

Secondly, we aim to use these bidentate NHC pre-ligands to make a series of Ru(II) complexes with η^6-arene co-ligands. In addition the synthesis of Fe(II) complexes bearing an NHC-pincer ligand previously reported by our group[28,29] will be investigated.

Finally, the group 8 complexes produced will be tested as catalysts for two reactions: (1) the insertion of CO_2 into the terminal C-H bond of phenylacetylene, and (2) the transfer hydrogenation of ketones using 2-propanol. A comparison will be made between the catalytic activity of complexes bearing either η^6-benzene or η^6-_p_-cymene for the transfer hydrogenation of acetophenone using 2-propanol, to test the proposed hypothesis that the rate limiting step is the dissociation of the η^6-arene ligand.

Chapter 2

Improved routes to imidazolium salts as donor-functionalised NHC precursors

2.1. Introduction

Since the isolation of the first free *N*-heterocyclic carbene (NHC) in 1991[10] and subsequent catalytic studies,[77] NHC's have become an attractive class of ligand due to their strong σ-donating character and ease of tune-ability.[18] Conventional synthetic routes to the azolium salt precursors allow the substituents on the nitrogen atoms to be easily modified to introduce bulky groups or groups capable of binding to a metal atom.

2.1.1. Synthesis of bidentate NHC-*N*-donor ligands

Donor-functionalised ligands bearing both an NHC group and a second *N*-heteroaromatic (*N*-het) *N*-donor are a commonly found combination;[19,78,79] the strongly σ-donating carbene forms a strong bond to the metal, while the *N*-het introduces hemilability at a neighbouring coordinating site. *N*-hets are also tolerant of strongly basic conditions, making them ideal to withstand the strongly basic reaction conditions used to generate carbenes.[18]

The azolium salt pre-ligands are typically synthesised *via* one of three approaches: (a) substitution of an alkyl halide containing the secondary donor moiety with an *N*-substituted imidazole,[21,78] (b) Cu(I) catalysed *N*-arylation with *N*-heteroaromatic halides,[80–83] or (c)-(e) cyclisation of the imidazole ring (Scheme 2.1).[84–86] Approach (a) generates a pre-ligand in which the NHC is joined to the *N*-het by a linker group (e.g. an alkyl chain) while approaches (b) through to (e) generate an NHC directly bound to the *N*-het by an N-C^{Ar} bond.

The first approach is usually performed in acetone and a slight excess of NaI. This facilitates a Finkelstein reaction, increasing the reactivity of the alkyl halide and generating the imidazolium iodide salt.[21,78]
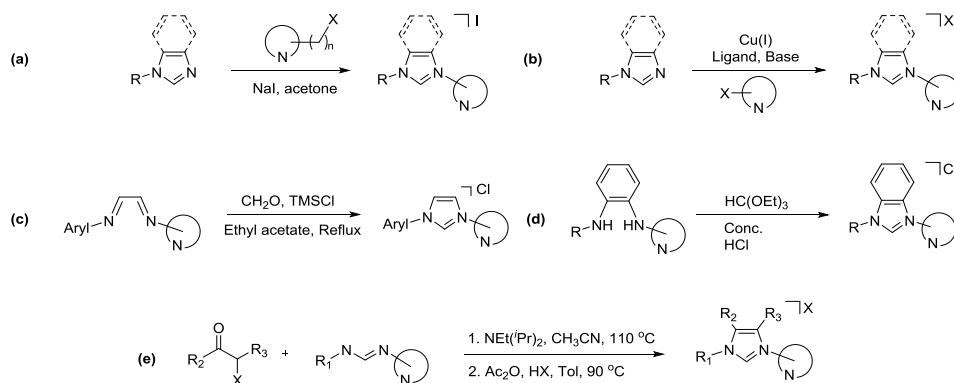
Scheme 2.1. Synthetic approaches to NHC-*N*-het azolium salt precursors (a) S_N2 halide substitution,[21,78] (b) Cu(I) catalysed *N*-arylation, [80–83] and (c)-(e) imidazole cyclisation.[84–86]

The Cu(I) catalysed *N*-arylation reaction is a popular method to functionalise imidazoles with *N*-heteroaromatic substituents by the formation of the N-C^{Ar} bond (Scheme 2.1 b).[8–17] Cu(I) is used as a catalyst to promote this reaction and the use of simple ligands such as diamines,[80,87,88] 1,10-phenanthrolines[89,90] and 1,2,3-benzotriazole,[91] has been particularly successful, as these catalytic conditions have been shown to tolerate a wide range of *N*-het substrates. However, these reactions require a stringent workup step to remove the Cu(I) which can lead to low yields. An alternative, metal-free nucleophilic aromatic substitution is also available,[92] and provides a cleaner approach, however this is limited to pyrimidines or *N*-hets bearing electron withdrawing substituents.

Cyclisation of appropriate substrates to form the azolium ring is an attractive route for the synthesis of NHCs bearing bulky, poorly nucleophilic substituents. For the synthesis of imidazolium salts, a diimine may be cyclised with paraformaldehyde in ethyl acetate (Scheme 2.1 c);[84] however, this reaction has so far been limited to *N*-aryl glyoxal diimines. Electron rich *N*-substituents on the diimine lead to C2 alkylated imidazolium salts *via* self-condensation[93] and less sterically hindered glyoxal diimines are prone to hydrolysis, leading to additional side products.

Benzimidazolium salts may be synthesised by cyclisation of an *N,N'*- disubstituted *o*-phenylenediamine with triethyl orthoformate (HC(OEt)$_3$) and conc. HCl (Scheme 2.1 d).[94] Although preparation of the diamine precursor involves metal catalysed reactions, access to non-symmetrical benzimidazolium salts is made possible by sequential palladium catalysed amination of *o*-aryl dihalides.[79]

A cyclisation shown in Scheme 2.1 e, allows access to a range of highly substituted and non-symmetrical imidazolium salts.[86] This two-step reaction generates the imidazolium salt in high yields, however, it requires the synthesis of specific formamidine and α-halo ketone substrates.

Recently, a metal free and facile alternative to the synthesis of *N*-het functionalised azole compounds, that uses simple commercially available reagents and is mediated by inexpensive $POCl_3$, has been developed (Scheme 2.3).[95] This reaction replaces the current low yielding methods which use harsh reaction conditions,[96,97] or expensive phosphonium reagents,[98–100] for the synthesis of 2-aminosubstituted heterocyclic templates for biologically active compounds. This direct amination has been used to couple a wide scope of amide and urea derived substrates to NHC pre-cursors, including imidazole and benzimidazole, resulting in the desired *N*-donor-NHC scaffold. A one-pot method is also available, in which the urea derivative is made *in situ* with *o*-phenylenediamine and triphosgene.[95]

2.1.2. Synthesis of chelating *bis*-NHC Ligands
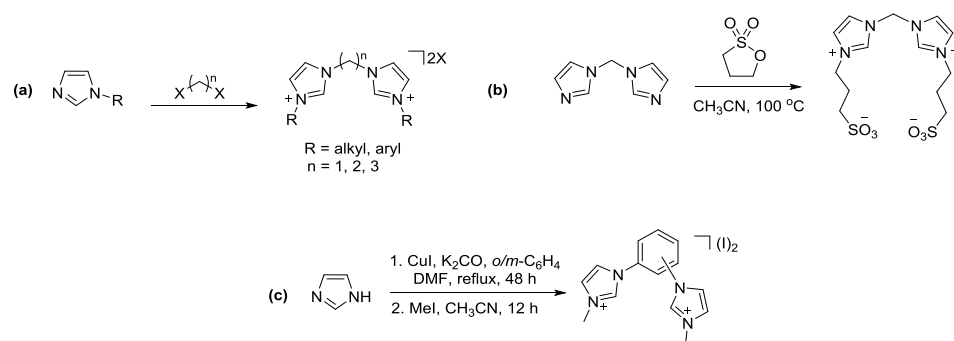
Scheme 2.2 Synthetic approaches to *bis*-NHC imidazolium salt precursors, (a) alkyl halide bridge *N*-substitution, (b) terminal *N*-substitution, (c) *o/m*-phenyl bridge.

Bidentate ligands bearing two strongly σ-donating NHC groups increase the stability of complexes in comparison to complexes bearing two monodentate-NHC ligands through the chelate effect.[19,101] Symmetrical, bidentate *bis*-NHC ligands are readily accessible from the substitution of alkyl dihalides with *N*-substituted imidazoles in non-polar solvents (Scheme 2.2a).[102,103] This has produced a wide scope of *N*-substituted bis-imidazolium halide salts with both alkyl[104,105] and aryl substituents.[106] When the imidazoles are tethered prior to functionalisation, this can lead to the introduction of interesting functionalities such as water soluble anionic groups (Scheme 2.2b).[107,108]

Bridging groups based on rigid aromatic linkers between the two NHC rings can also be introduced.[39,109] These are synthesised by first attaching imidazole rings to an aromatic di-halide ring using an Ulmmann reaction,[110] and subsequently methylating with iodomethane to produce the imidazolium salts (Scheme 2.2c).[109]

2.2. Scope of this chapter

This chapter describes the synthesis of a new NHC-*N*-heteroaromatic (NC^{NHC}) salt *via* an improved one-pot method that has not previously been employed, and a known *bis*-NHC (C^{NHC}C^{NHC}) salt. These compounds are pre-ligands for use in the following chapter.

The synthetic routes for 1'*H*-1,2'-dibenzo[d]imidazole (**2.1**), 1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**), the pre-ligand 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium ((NC^{NHC})I, **2.3**) and the novel pre-ligand 1',3-dimethyl-1,2'-dibenzo[d]imidazol-3-ium tetraphenylborate ((NC^{NHC})BPh$_4$, **2.4**) are presented in Scheme 2.3.

2.2.1. Improved, one-pot synthesis of 1'*H*-1,2'-dibenzo[d]imidazole (2.1)
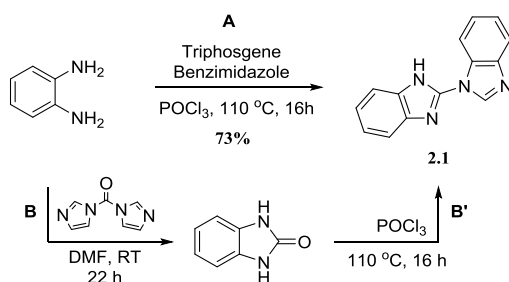
Scheme 2.3: Synthetic route for 1'*H*-1,2'-dibenzo[d]imidazole (**2.1**) *via* one-pot method (**A**) or isolated intermediate (**B**).

The one-pot, multi-component synthesis of 2-(pyrazol-1'-yl)-1*H*-benzo[d]imidazole developed by Deng *et al.*,[95] was adapted here to make 1'*H*-1,2'-dibenzo[d]imidazole (**2.1**, Route A, Scheme 2.3). The urea derivative, 1,3-dihydrobenzimidazol-2-one, was formed *in situ* by treating *o*-phenylenediamine with triphosgene, followed by POCl$_3$ mediated direct amination with benzimidazole. This method demonstrated the successful synthesis of **2.1** by this one-pot reaction, however, incomplete conversion of *o*-phenylenediamine and triphosgene to 1,3-dihydrobenzimidazol-2-one resulted in the recovery of benzimidazole as well as the desired product, and the final isolated yield of **2.1** from this one-pot process was 73%.

1'*H*-1,2'-dibenzo[d]imidazole (**2.1**) has previously been made as a by-product during the synthesis of trisbenzimidazoles in 16% yield,[111] a by-product of the synthesis of *N*-heterocyclic compounds for organic electronic devices in 25% yield,[112] and in 82% yield from 1,3-dihydrobenzimidazole-2-one (Route B', Scheme 2.3).[95] A similar yield to this literature value was found in our lab for the reaction of 1,3-dihydrobenzimidazol-2-one and benzimidazole. However, the

overall yield of **2.1** from *o*-phenylenediamine was 36%, therefore the one-pot method used herein offers a significant improvement over the previous literature preparation.

2.2.2. Syntheses of 1'-methyl-1,2'-dibenzo[d]imidazole (2.2) and 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium iodide (NC^{NHC})I (2.3)

Deprotonation of 1'*H*-1,2'-dibenzo[d]imidazole (**2.1**) with NaH and subsequent methylation with one equivalent of iodomethane resulted in the isolation of known compound 1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**) in 60% yield (Route C, Scheme 2.4).
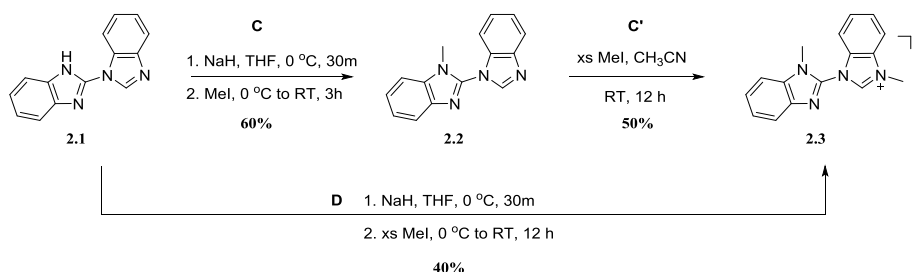
Scheme 2.4: Synthetic route for 1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**) and 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium iodide (NC^{NHC})I (**2.3**).

Following isolation of **2.2**, a second methylation with excess iodomethane in acetonitrile resulted in the precipitation of a white solid, which was collected by vacuum filtration, to give (NC^{NHC})I (**2.3**) in an overall yield of 30% (relative to 1'*H*-1,2'-dibenzo[d]imidazole, Route C', Scheme 2.4). An improved route to **2.3** directly from **2.1** was achieved in a single step: a fourfold excess of iodomethane was added to the sodium salt of **2.1**, generated *in situ* by deprotonation with NaH in THF (Route D, Scheme 2.4).

The monomethylated **2.2** has previously been prepared by heating molten benzimidazole and 1-methyl-2-chlorobenzimidazole at 125 °C in 48% yield,[113] while the iodide salt **2.3** had been obtained by anion exchange with the chloride salt,[113] which was prepared by a similar molten reaction in 82% yield. The new solution-phase methylation routes described here demonstrate an alternative but lower yielding route to **2.3**.[113]

2.2.3. Synthesis and characterisation of 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium tetraphenylborate (NC^{NHC})BPh$_4$ (2.4)

The previously isolated iodide salt (2.3) is the only form by which this cation is known. An approach to the synthesis of the novel tetraphenylborate salt of the ~~dibenzimidazole~~ cation was sought ~~because~~as it was expected this salt would be more readily isolated than the iodide salts. The BPh$_4^-$ salt was also expected to be a convenient precursor to BPh$_4^-$ salts of metal complexes to be used as catalysts. The tetraphenylborate anion is very weakly coordinating, hence tetraphenylborate salts of organometallic complexes generally have more accessible coordination sites available to bind substrates. Evaporation of acetonitrile from 2.3, and subsequent addition of NaBPh$_4$ to a methanol solution of the crude produced a precipitate which was collected by vacuum filtration and washed with methanol to give the novel pre-ligand (NC^{NHC})BPh$_4$ (2.4) in 50% yield.

Formation of the pre-ligand 2.4 was initially confirmed using ^{1}H NMR spectroscopy, with the appearance of the imidazolium proton resonance (H^{10}, Figure 2.1) at δ 10.01 ppm, and the appearance of two resonances at approximately δ 4 ppm attributed to the protons of the methyl groups of 2.4. Two NOESY correlations between the resonance due to H^{10} and the two resonances attributed to methyl groups H^1 & H^9 indicated the conformation depicted in Figure 2.1. A COSY and NOESY correlation from H^9 to C^{10} allowed assignment of each methyl resonances to their respective benzo[d]imidazole rings, and quaternary carbon resonances were assigned by HMBC correlations to methyl protons H^1 and H^9. All other resonances were assigned by HSQC and HMBC correlations and confirmed by COSY and NOESY correlations between aromatic protons (See Appendix A for full ^{1}H and ^{13}C NMR).
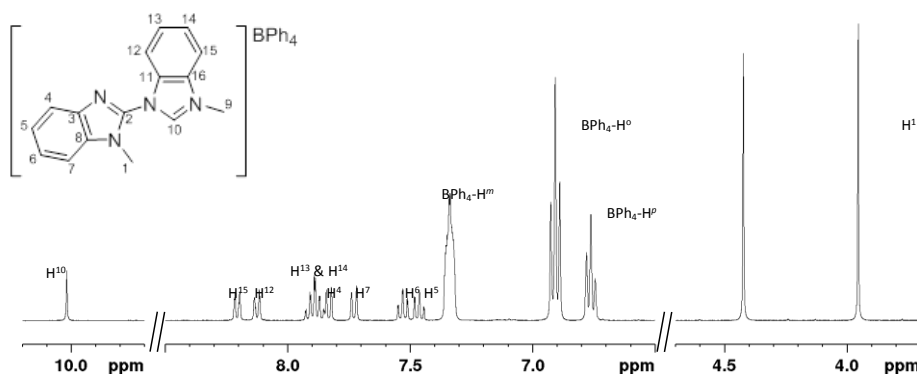

Figure 2.1. ^{1}H NMR (400 MHz, acetone-d_6, 298 K) of (NC^{NHC})BPh$_4$ pre-ligand (2.4).

The composition of (NC^{NHC})BPh$_4$ (**2.4**) was confirmed by ESI-MS with the ~~I~~identification of the cationic parent ion ([M$^+$] = 263.1) and a single anion from BPh$_4$$^-$ ([M$^-$] = 319.2).~~by ESI-MS confirmed the composition of (NC^{NHC})BPh$_4$ pre-ligand (**2.4**) suggested by the NMR data. The mass spectrum also displayed the presence of an anion as a single parent peak ([M$^-$] = 319.2) confirming the presence of the BPh$_4$$^-$ anion.~~

2.2.4.   Synthesis of 1,1'-methylenebis(3-methylimidazol-3-ium) dibromide (2.8)
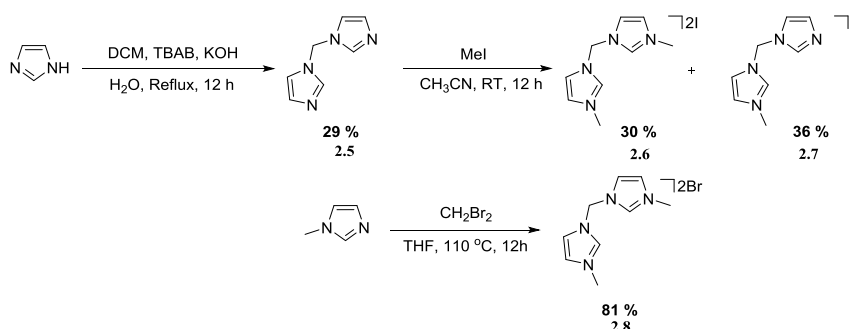
Scheme 2.5: Synthetic route for (C^{NHC}C^{NHC})I$_2$ (**2.6**), (C^{NHC}C^{NHC})I (**2.7**), and (C^{NHC}C^{NHC})Br$_2$ (**2.8**).

Initially, the pre-ligand 1,1'methylenebis(3-methylimidazol-3-ium) diiodide (**2.6**) was synthesised from the known compound bis(imidazol-1-yl)methane (**2.5**).[114] Methylation of **2.5** with excess iodomethane produced both 1-((imidazol-1-yl)methane)-3-methylimidazol-3-ium iodide (**2.7**) as a white precipitate and the doubly methylated 1,1'-methylenebis(3-methylimidazol-3-ium) diiodide (**2.6**), which remained in solution, in similar yields.

A more efficient procedure was subsequently sought, and the pre-ligand cation as 1,1'-methylenebis(3-methylimidazol-3-ium) dibromide (**2.8**) was obtained in a single step from commercially available reagents following a literature procedure.[115] Dibromomethane and 1-methylimidazole were stirred with a small volume of THF in a pressure tube in the absence of light for 12 hours. Recrystallisation from boiling methanol gave pre-ligand (**2.8**) as white needle-like crystals in 81% yield.

2.3.   Summary and conclusions

Four imidazolium salts were prepared as follows, with the aim to use these as precursors to donor-functionalised NHC ligands in subsequent work:

i. A new one-pot method, developed from a literature procedure, was used to synthesise 1'H-1,2'-dibenzo[d]imidazole (**2.1**) from o-phenylenediamine.[95] This method was more efficient and atom economical, and higher yielding previously employed synthetic routes.

ii. The iodide salt 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium iodide (NC^{NHC})I, (**2.3**) was obtained *via* a new solution phase synthesis as an alternative to the literature preparation which uses molten reactants. This new route may prove useful in the future for synthesis of thermally unstable benzimidazole derivatives as it does not rely on the extreme temperatures of molten conditions.

iii. The novel pre-ligand 1',3-dimethyl-1,2'-dibenzo[d]imidazole-3-ium tetraphenylborate ((NC^{NHC})BPh$_4$, **2.4**) was synthesised by anion exchange from the iodide salt. This compound was fully characterised by 2D NMR and MS.

Chapter 3

# Synthesis of novel Ru(II) complexes bearing bidentate NHC ligand's

3.1. Introduction

N-heterocyclic carbenes (NHC's) are encountered as versatile ligands in a large variety of organometallic and coordination complexes pertaining to almost all members of the platinum group metals.[3,4,35,116,117] Of these, many containing ruthenium and palladium are endowed with excellent catalytic properties, and have the added advantage of high levels of stability to air and moisture. In particular, group 8 metal complexes have shown promise in a diverse array of catalytic applications, including metathesis, reduction, polymerisation and C-X bond forming reactions.[5,10–15]

3.1.1. Synthesis of group 8 complexes bearing NHC ligands

The growing interest in NHC-bearing complexes over the past two decades has brought with it the need for accessible synthetic methodologies.[118] While early synthetic routes involved the isolation and handling of free carbenes,[16] requiring stringent glovebox techniques, modern routes target *in situ* formation of the carbene from the imidazolium salt precursor. For the synthesis of group 8 metal complexes bearing NHC ligands, three key routes are dominant: (a) *in situ* formation of the carbene by deprotonation in the presence of the metal precursor, (b) transmetalation from the Ag(I) intermediate, and (c) deprotonation by a metal precursor bearing an internal base (Scheme 3.1).

The first synthetic approach circumvents the isolation and handling of the free carbene simply by producing it *in situ* with a base. The high pK_a of azolium salts (ca. 16-26 in water or DMSO)[119,120] encourages the use of very strong bases such as potassium *tert*-butoxide (KO*t*Bu) or potassium hexamethyldisilazide (KHMDS). However, the sensitivity of some of these bases requires them to be handled in a glovebox or under an inert gas in a Schlenk flask, and for solvents and reagents to be stringently dried, often resulting in the use of such reagents becoming tedious. In addition, many ligands degrade under the harsh conditions of this route. Nonetheless this approach has become the most favourable for iron complexes[34] since its initial discovery in 1996 in the synthesis of an Fe(II) hexacarbene complex.[121]
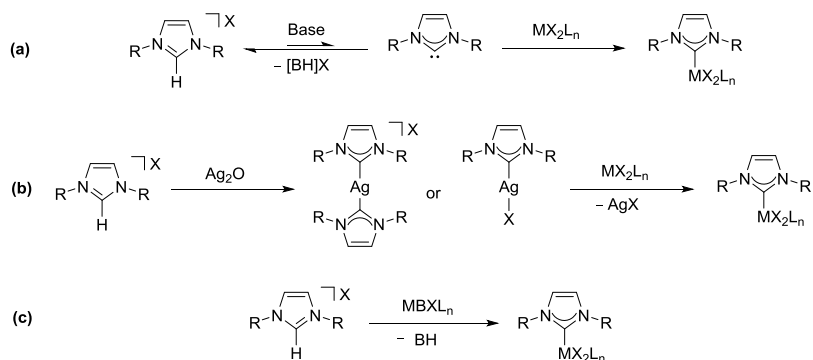
Scheme 3.1. Synthetic routes to metal complexes bearing NHC ligands (a) *in situ* carbene formation, (b) silver transmetalation, and (c) metal precursor bearing an internal base.

Silver transmetalation reactions are a popular alternative to direct metalation; silver(I) oxide (Ag$_2$O) is inexpensive, conditions may be aerobic and hydrated, and yields tend to be high with little by-product formation.[122] Silver transmetalation was first used to make group 8 metal complexes with NHC ligands in 2004, producing a simple Ru(II) arene NHC;[123] it was not until 2011 that the first Fe(II) complex bearing a donor-functionalised NHC ligand containing a secondary *N*-donor was synthesised by this method.[124] Silver carbenes are typically formed in DCM at room temperature using Ag$_2$O, although solvents such as toluene, THF, CH$_3$CN and MeOH are also common.[122]

In 2004, the Fe(II) precursor, [Fe(N(SiMe$_3$)$_2$)], bearing two equivalents of a strong internal base was used to synthesise the first Fe(II) complex bearing an NHC pincer ligand.[62] While the preparation and handling of [Fe(N(SiMe$_3$)$_2$)$_2$] is made challenging due to its moisture sensitivity, the reaction proceeds with high yields and the amine may be removed *in vacuo*.

3.1.2. Scope of this chapter

This chapter presents the synthesis of several novel Ru(II) complexes bearing donor-functionalised NHC ligands containing at least one NHC donor, the formation of a novel bimetallic Ru(II) bidentate *bis*-NHC complex, and the attempted synthesis of an Fe(II) complex bearing a pincer ligand with an NHC central donor and two *N*-donor side arms.

3.2. Synthesis of Ru(II) complexes bearing donor-functionalised NHC ligands

3.2.1. Synthesis and characterisation of RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (3.1)

While the chloride and iodide salts of the organic dibenzimidazoliums **2.3** & **2.4** are known compounds, the NC^{NHC} carbene derived from these has not previously been used as a ligand in metal complexes.
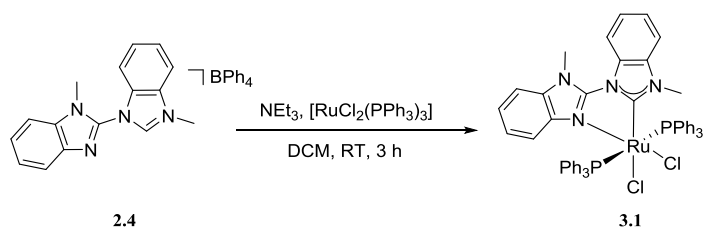

Scheme 3.2. Synthesis of novel Ru(II) complex bearing the NC^{NHC} ligand, RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (**3.1**).

Complexation of **2.4** with Ru(II) (Scheme 3.2) was achieved through *in situ* formation of the carbene from the novel NC^{NHC} tetraphenylborate salt **2.4**. [RuCl$_2$(PPh$_3$)$_3$] was chosen as the metal precursor due to the relative lability of the phosphine ligands and its precedence as a precursor to Ru(II) complexes bearing NHC ligands.[3] The carbene of (NC^{NHC})BPh$_4$ (**2.4**) was formed *in situ* using the weak base triethylamine (NEt$_3$) which is volatile, allowing easy removal, and addition of [RuCl$_2$(PPh$_3$)$_3$] leads to the complexation of Ru(II) with the bidentate ligand and loss of one phosphine ligand within 1 hour. Addition of pentane to the golden-brown solution led to the precipitation of both (HNEt$_3$)BPh$_4$ and a brown impurity that is unobservable by ^{1}H NMR spectroscopy. Filtration and subsequent addition of pentane to the golden yellow filtrate led to the precipitation of RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (**3.1**) as a pale orange powder in 24% yield. This simple approach demonstrated the successful synthesis of **3.1**.

Formation of the complex **3.1** was confirmed by ^{1}H NMR spectroscopy, with a significant shift of the methyl ^{1}H resonances (Figure 3.1) compared to the resonances of the methyl groups of the un-coordinated ligand. Integration of the large peaks in the aromatic region of the ^{1}H NMR spectrum, corresponding to the coordinated triphenylphosphine (PPh$_3$) protons, led to the conclusion that two PPh$_3$ remained bound to the Ru(II) centre. The *trans*-geometry of the coordinating phosphines was confirmed by ^{31}P NMR spectroscopy, which displayed a single ^{31}P resonance at δ 26.67 ppm (relative to free PPh$_3$, δ -6.0 ppm, Figure 3.1). Resonances were assigned using 2D NMR spectroscopy (HSQC, HMBC, COSY and NOESY), and the composition of the molecular unit of **3.1** was confirmed by

ESI-MS with identification of the cationic parent ion at 958.2 *m/z* (See Appendix A for full ^{1}H and ^{13}C NMR).
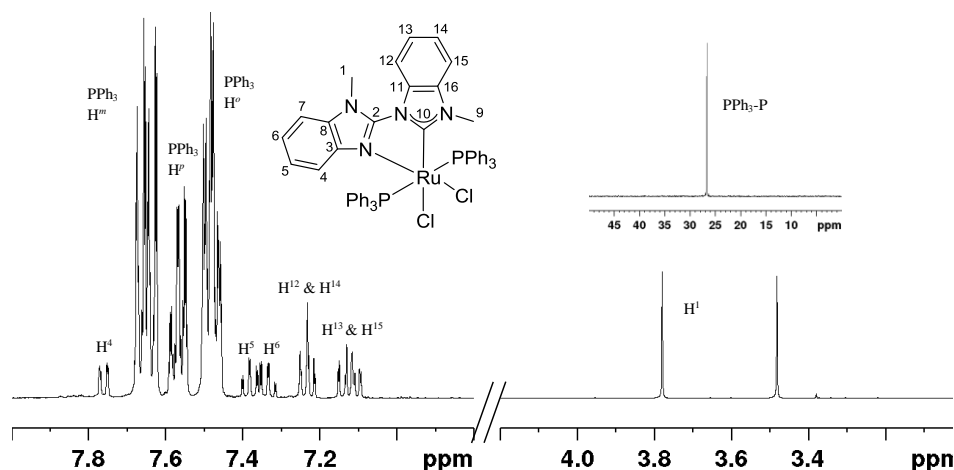
Figure 3.1. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) and inset ^{31}P NMR (160 MHz, CD$_2$Cl$_2$, 298 K) of [RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$] (**3.1**). Resonance of H^7 overlaps PPh$_3$-H^o multiplet.

3.2.2. Synthesis and partial characterisation of [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$ (3.2)

Ruthenium complexes bearing donor-functionalised NHC ligands in addition to η^6-arene co-ligands are effective catalysts for a number of organic transformations reactions.[37–40] Due to the simplicity of the reaction and use of inexpensive reagents, silver transmetalation (Scheme 3.1, Route b) is the most popular approach for the synthesis of such complexes.[47,125] Recent success in our lab using Ag(I) transmetalation to synthesise Ru(II) arene complexes bearing NHC ligands[29] indicated this would be a suitable approach for the synthesis of the remaining Ru(II) arene complexes in this chapter.
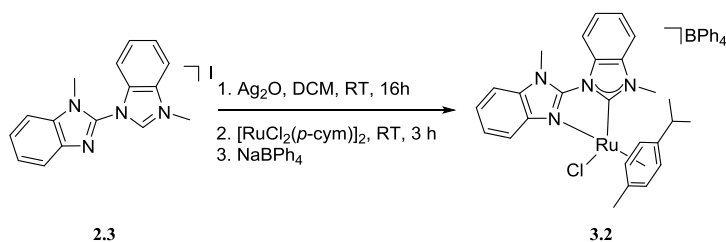
Scheme 3.3. Synthesis of novel Ru(II) arene complex bearing the NC^{NHC} ligand, RuCl$_2$(NC^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.2**).

Initial attempts to isolate [RuCl(NC^{NHC})(η^6-p-cym)]BPh$_4$ using (NC^{NHC})BPh$_4$ (**2.4**) by silver transmetalation were unsuccessful. However, formation of the mono-NC^{NHC} Ag(I) intermediate *in situ* from the iodide salt **2.3** and Ag$_2$O, followed by transmetalation with [RuCl$_2$(η^6-p-cym)]$_2$ and anion exchange with NaBPh$_4$, led to the formation of [RuCl(NC^{NHC})(η^6-p-cym)]BPh$_4$ (**3.2**, Scheme 3.3). which was detected *in situ* by ^{1}H NMR spectroscopy. Re-crystallisation from DCM and pentane gave the product as an intractable mixture with unidentified organics. Attempts to separate these by column chromatography were unsuccessful. The parent cation of **3.2** was identified by MS, and the ^{1}H NMR spectrum was partially assigned (Figure 3.2).
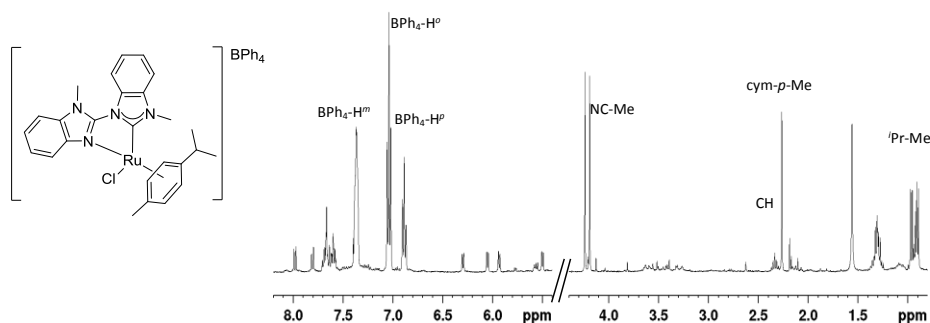
Figure 3.2. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) of [RuCl(NC^{NHC})(η^6-p-cym)]BPh$_4$ (**3.2**), unknown organic impurities are unlabelled.

3.2.3. Synthesis and characterisation of [Ag(C^{NHC}C^{NHC})]$_2$(BPh$_4$)$_2$ (3.5), [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$, (3.3) & [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]BPh$_4$, (3.4)

The Ru(II) arene complexes bearing the chelating *bis*-NHC ligand, 1,1'-methylenebis(3-methylimidazol-3-ylidene) (C^{NHC}C^{NHC}), derived from 1,1'-methylenebis(3-methylimidazol-3-ium) dibromide (**2.8**, Scheme 3.4) were sought. Several Ru(II) arene complexes bearing chelating *bis*-NHC ligands structurally similar to C^{NHC}C^{NHC} are known.[38,58,126–128] However, none contain the weakly-coordinating anion BPh$_4^-$. While PF$_6^-$ is more resistant to oxidation and reduction than BPh$_4^-$, it has a far greater surface charge (q$_{surf}$ = -0.44 vs. -0.05 for BPh$_4^-$, where q$_{surf}$ is the partial charge of the most negatively charged surface atom)[129], making BPh$_4^-$ a less coordinating anion in comparison due to its steric bulk. This means BPh$_4^-$ less likely to temporarily deactivate the catalyst by competing with a substrate for a coordination site, making BPh$_4^-$ a more desirable counterion for catalysis.
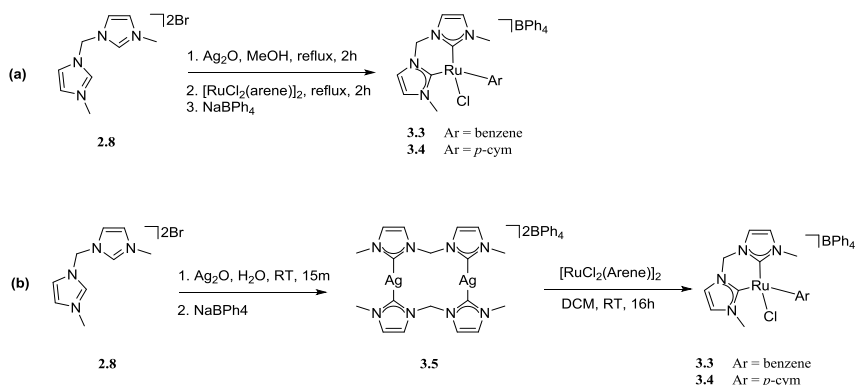
Scheme 3.4. Synthesis of Ru(II) complexes **3.3** & **3.4** bearing the $C^{NHC}C^{NHC}$ ligand by: (a) *in situ* silver transmetalation of $C^{NHC}C^{NHC}$, and (b) transmetalation from $[Ag(C^{NHC}C^{NHC})]_2(BPh_4)_2$ (**3.5**).

Approaches to the synthesis of novel Ru(II) complexes bearing the $C^{NHC}C^{NHC}$ ligand (**3.3**, **3.4** and **3.5**) are outlined in Scheme 3.4. The first attempt here (Scheme 3.4 a) followed a literature procedure for making a structurally similar complex.[38] The halide salt of the Ag(I) NHC intermediate is formed *in situ* from $(C^{NHC}C^{NHC})Br_2$ (**2.8**), and the Ru(II) arene precursor is subsequently added at reflux.[38] The appearance of a beige suspension in refluxing MeOH indicates formation of the Ag(I) NHC intermediate, along with a Ag(0) mirror on the flask. Addition of brown $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ to the suspension and stirring at reflux for 2 hours resulted in a green solution, which was dried to leave behind a green residue. The residue was redissolved in acetone and $NaBPh_4$ was added, then purification was performed by column chromatography using acetone as eluent. This yielded only a small quantity of a dark yellow powder, contaminated with unknown organic impurities.

To synthesise and isolate **3.3** and **3.4** in high purity and in greater yield, isolation of the bimetallic $[Ag(C^{NHC}C^{NHC})]_2(BPh_4)_2$ (**3.5**) was attempted *via* Route b (Scheme 3.1). The Ag(I) complex was isolated using a modified literature procedure making the analogous PF_6^- salt.[130] An aqueous solution of **2.8** and Ag_2O is stirred for a short amount of time with precipitation of **3.5** occurring after the addition of $NaBPh_4$, resulting in the isolation of **3.5** by vacuum filtration in 81% yield. which is collected in 81 % yield. The formation of the novel bimetallic complex $[Ag(C^{NHC}C^{NHC})]_2(BPh_4)_2$ (**3.5**) was confirmed using ^1H NMR spectroscopy and MS ($[M^+]$ = 284.0 *m/z*), and resonances were assigned using 2D NMR spectroscopy (Figure 3.3, See Appendix A for full ^1H and ^{13}C NMR). The relative intensities of the ligand and BPh_4^- resonances indicate there is a 1:2 ratio of cation and anion. In the PF_6^- analogue, the resonance due to H^5 is reported as a broad singlet. A very broad singlet between δ 7.0 – 6.2 ppm is observable for the BPh_4^- salt here (See Appendix A for full ^1H and ^{13}C NMR).[130]
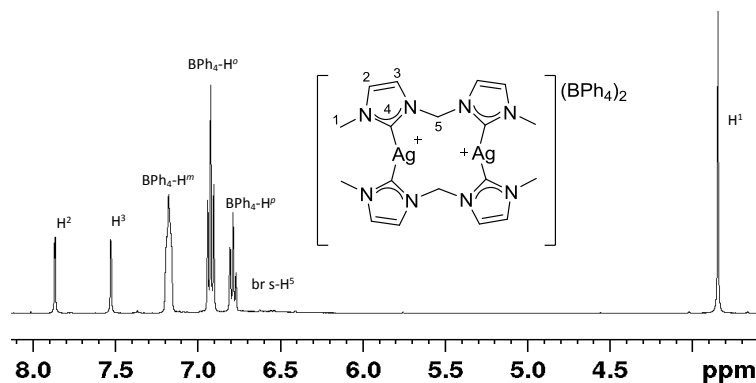
Figure 3.3. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) of [Ag(C^{NHC}C^{NHC})]$_2$(BPh$_4$)$_2$ (**3.5**).

The addition of [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$ or [RuCl$_2$(η^6-p-cym)]$_2$ to a solution of **3.5** in DCM, and subsequent purification by column chromatography on alumina with acetone:DCM (1:5) led to the recovery of [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**) and [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]BPh$_4$ (**3.4**) in 19% and 94% yield respectively. The low yield of the desired benzene analogue was accompanied by formation of a brown-black solid that separated from the product during filtration, in addition to an intractable red-brown residue that remained on the column during purification. This is due to the side-product forming (discussed in section **3.2.4** below). A similar bimetallic Ag(I) complex has been described bearing two *bis*-NHC derived from 1,1'-methylenebis(3-isopropylimidazol-3-ium) diiodide and two PF$_6^-$ anions, which was soluble in DCM and gave a 72% yield of [RuCl(*bis*-NHC)(η^6-C$_6$H$_6$)]PF$_6$ following a similar procedure.[25]

The formation of [RuCl(C^{NHC}C^{NHC}) (η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**) was confirmed by the appearance of a pair of doublets in the ^{1}H NMR spectrum with a coupling constant of J = 13.0 Hz, corresponding to the diastereotopic pair of protons H^5 & H$^{5'}$ (Figure 3.4). These protons become diastereotopic upon coordination of the ligand to the Ru(II) ion, forming a locked 6-membered chelate ring. A single resonance due to the protons of the coordinating benzene at 298 K demonstrated the free rotation of the aromatic ring faster than the NMR time scale. A NOESY correlation between the resonances due to H$^{5'}$ and H^a allowed the assignment of the methylene proton resonances; no correlation was observed between H^5 and H^a. The composition of [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**) was confirmed by ESI-MS with identification of the cationic parent ion ([M$^+$] = 390.1 m/z) and a single peak from BPh$_4^-$ ([M$^-$] = 319.2 m/z)(See Appendix A for full ^{1}H and ^{13}C NMR).
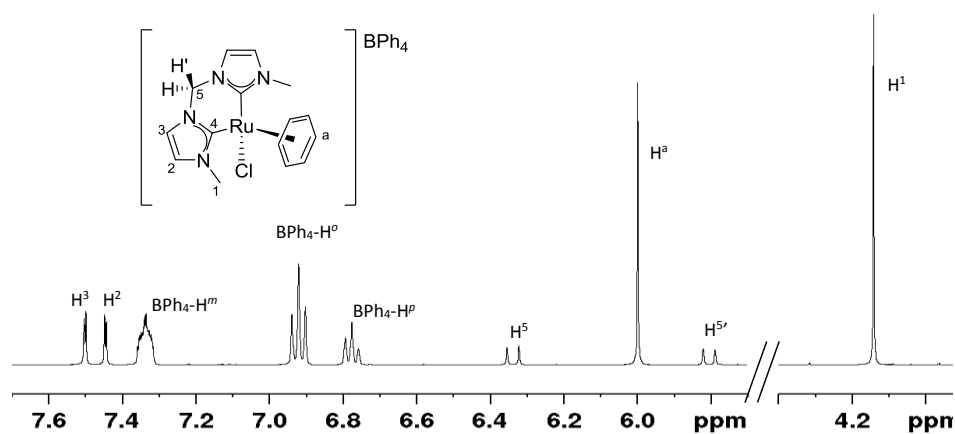
Figure 3.4. ^{1}H NMR (400 MHz, acetone-d_6, 298 K) of [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**).
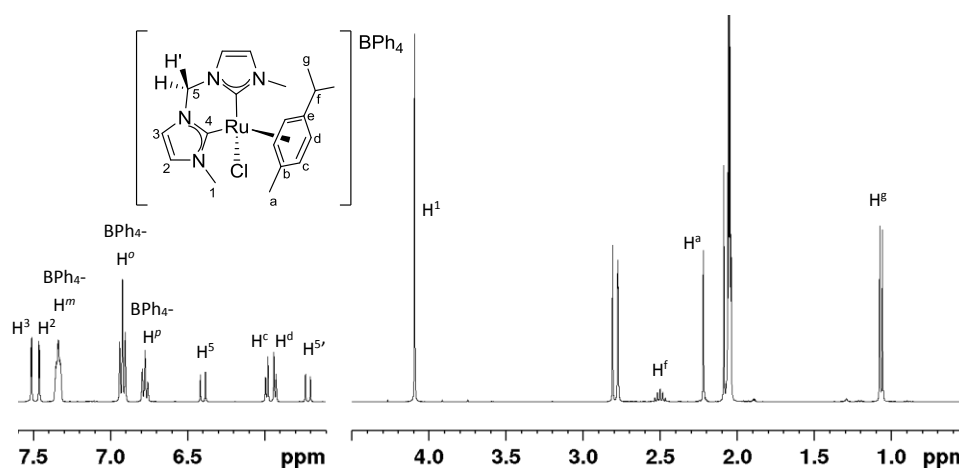
Figure 3.5. ^{1}H NMR (400 MHz, acetone-d_6, 298 K) of [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]BPh$_4$ (**3.4**).

The formation of [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]BPh$_4$ (**3.4**) was similarly confirmed by the appearance of a pair of doublets at δ 6.40 and 5.71 ppm in the ^{1}H NMR spectrum, with a coupling constant of J = 13.0 Hz (Figure 3.4). Resonances were assigned by 2D NMR (HSQC, HMBC, COSY and NOESY). A NOESY correlation between the resonances due to H$^{5'}$ and H^f allowed the assignment of the diastereotopic protons; no correlation was seen between the resonances due to H^5 and H^f. NOESY correlations between the resonances due to H$^{5'}$ and both H^a and H^g indicated free rotation of the p-cym ligand in solution faster than the NMR time scale. The composition of

[RuCl($C^{NHC}C^{NHC}$)(η^6-p-cym)]BPh$_4$ (**3.4**) was confirmed by ESI-MS with identification of the cationic parent ion ([M$^+$] = 447.1) . A single peak confirmed BPh$_4$$^-$ as the counter ion ([M$^-$] = 319.2) (See Appendix A for full ^{1}H and ^{13}C NMR).

An NMR sample of [RuCl($C^{NHC}C^{NHC}$)(η^6-p-cym)]BPh$_4$ (**3.4**) in acetone-d_6 was layered with diethyl ether, producing yellow single yellow crystals suitable for X-ray diffraction. Similarly, orange single crystals of [RuCl($C^{NHC}C^{NHC}$)(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**) were grown from an acetonitrile/diethyl ether mixture by slow evaporation.

The crystal structures of both arene complexes (**3.3** and **3.4**) reveal the expected three-legged piano-stool structural motif (Figure 3.6). The $C^{NHC}C^{NHC}$ ligand forms a 6-membered chelate with the Ru(II) centre in a boat conformation in both structures, with similar C^{NHC}-Ru-C^{NHC} bite angles of approximately 83° (Table 3.1). The solid-state structure of [RuCl($C^{NHC}C^{NHC}$)(η^6-p-cym)]BPh$_4$ (**3.4**) shows the ^{i}Pr group oriented closer to the methylene bridge of the ligand than the p-Me group; this differs to the previously reported crystal structure of this cation with the PF$_6$$^-$ anion, in which the p-Me group overlays the methylene bridge.[127] A similar crystal structure in which the chelating *bis*-NHC has ethyl *N*-substituents show similar orientation of the coordinated p-cymene in the solid state to **3.4**.[58]

Bond lengths and angles do not differ significantly between the two solid state structures of **3.3** and **3.4**, or to previously reported structures of the I$^-$ or PF$_6$$^-$ analogues of **3.4** (Table 3.1);[38,126,127] the only significant difference lies in the dihedral angles of the backbone in the $C^{NHC}C^{NHC}$ chelating ring (C1-Ns/C9-N3 and C2-N3/C9-N2). In **3.4** these angles are approximately equal whilst in **3.3** they differ by 6.5°. This pattern is also seen in the dihedral angles between the *N*-Me bonds and the carbene-Ru bond, and suggests an increased flexibility of the carbene ligand in **3.3** due to less steric bulk of the coordinated arene.
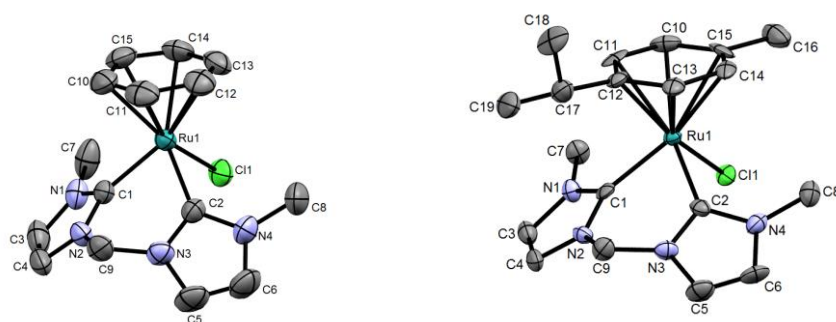

Figure 3.6. X-ray crystal structures of **3.3** (left) and **3.4** (right). (50% probability ellipsoids, hydrogen atoms and non-coordinating anions are omitted for clarity)

Table 3.1. Selected bond lengths (Å) and angles (deg) for complexes **3.3** & **3.4**.

	[RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**)	[RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.4**)
Ru1-C1	2.038(3)	2.026(8)
Ru1-C2	2.053(3)	2.009(8)
Ru1-C$_{arene}$ (Centroid)	1.745	1.728
Ru1-Cl1	2.438(1)	2.416(2)
C1-Ru1-C2	83.0(1)	83.6(3)
C1-Ru1-Cl1	87.14(9)	87.9(2)
C1-Ru1-C$_{arene}$ (Centroid)	129.00	128.87
Cl1-Ru1-C$_{arene}$ (Centroid)	126.63	126.94
N2-C9-N3	108.6(3)	110.4(7)
C1-N2-C9-N3	-49.6(4)	-45(1)
C2-N3-C9-N2	56.1(4)	46(1)
C7-N1-C1-Ru1	3.0(5)	4(1)
C8-N4-C2-Ru1	12.2(6)	-3(1)

3.2.4.   Observation of a novel homobimetallic Ru(II) complex

Albrecht *et al.*,[131] previously reported a bimetallic complex, Ru$_2$Cl$_4$(C'C')(η^6-*p*-cym)$_2$ (where C'C' = 1,1'-methylenebis(3-butylimidazol-2-ylidene), analogous to the monometallic complex [RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.4**) reported here, and in which the single C'C' unit acts as a bridging ligand between two metal centres (Figure 3.7). Similar complexes with the bidentate C^{NHC}C^{NHC} ligand seen in this chapter have been observed forming in low amounts during the silver transmetalation of bidentate *bis*-NHC ligands with [RuCl$_2$(η^6-*p*-cym)]$_2$.[127]

IX
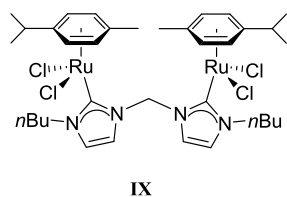
Figure 3.7. Diruthenium complex reported by Albrecht *et al.*,[131] containing a *bis*-NHC as a bridging ligand.

During the course of the transmetalation reaction of $[Ag(C^{NHC}C^{NHC})]_2(BPh_4)_2$ (**3.5**) with one equivalent of $[RuCl_2(\eta^6\text{-}p\text{-cym})]_2$ in DCM at room temperature, an aliquot was taken after 5 hours and the ^{1}H NMR spectrum revealed a mixture of two species: $[RuCl(C^{NHC}C^{NHC})(\eta^6\text{-}p\text{-cym})]BPh_4$ (**3.4**) and what was assumed to be the previously reported bimetallic complex.[131] However, upon closer inspection of the ^{1}H NMR spectrum, a pair of doublets was observed at 6.20 and 7.20 ppm, each with coupling constants of approximately $^2J_{HH}$ = 13 Hz, indicating both species contained a diastereotopic methylene bridge (Figure 3.8). This differs from the reported bimetallic complex (Figure 3.7), where the bridging structure allows free rotation about the N-C bonds of the bridging methylene carbon, resulting in the methylene protons being observed as a sharp singlet in the ^{1}H NMR spectrum. In addition, the aromatic imidazole-2-ylidene protons of the previously reported di-ruthenium complex were reported as two doublets, whereas in the ^{1}H NMR of the aliquot prepared here, four analogous doublets were seen (between 7.90 and 7.55 ppm), indicating four magnetically distinct imidazole-2-ylidene environments. Two chemically inequivalent N-CH$_3$ resonances (δ 4.20, 4.02 ppm) were also observed in the spectrum of the aliquot prepared here. Four p-cymene protons were observed as doublets between 5.42 and 5.87 ppm. Crucially, these p-cymene resonances each integrate in a 1:1 ratio with each imidazole-2-ylidene doublet. This confirms that the compound observed here is not of the type reported by Albrecht *et al.*[131] and is indeed a novel cation containing p-cymene and $C^{NHC}C^{NHC}$ ligands in equal number.

To complete the assignment, ^{1}H NMR signals correspond to isopropyl CH$_3$ groups appear as two overlapping doublets at δ 1.41 and 1.39 ppm, with coupling constants of 6.9 Hz. Mass spectrometry performed on the aliquot revealed a peak at m/z = 449.1, in addition to the peak corresponding to the cation of **3.4** ([M$^+$] = 447.1 m/z). The negative ion channel revealed only BPh$_4^-$ ([M$^-$] = 319.2 m/z). Several attempts to separate the mono and bimetallic complexes by column chromatography on both silica and alumina using a gradient elution (DCM/acetone) are yet to prove fruitful.

From the ^{1}H NMR evidence discussed and MS of the mixture, a structure corresponding to $[RuCl(C^{NHC}C^{NHC})(\eta^6\text{-}p\text{-cym})]_2(BPh_4)_2$ (**3.6**) is proposed (Figure 3.8).

The complex reported by Albrecht *et al.*,[131] requires the complexation of only 1 equivalent of the ligand to two Ru(II) centres. The addition of a second bridging ligand locks the rotational freedom about the methylene bridge with respect to the two Ru(II) centers, as evident by the diastereotopic coupling of the methylene protons. This is expected to lead to a constrained geometry in which the distance between the two Ru(II) centres is fixed.

The use of bimetallic complexes for enhancing catalytic activity has been a focus of our group, and such complexes have shown to produce enhanced catalytic efficiency over their monometallic counterparts.[132–136] This can be explained by the cooperativity between the two metal centers, which is closely related to the intermetallic distance, and rigidity of the ligand scaffold.[133,135] As such, the isolation of the putative bimetallic **3.6** became of interest in order to compare its catalytic efficiency to that of the monometallic **3.4**.

-Albrecht *et al.*,[131] reported that chelation of the C'C' ligand to form the monometallic complex could be prevented by gradually warming a frozen suspension of the Ag(I) iodide intermediate in DCM prior to adding [RuCl$_2$(η^6-*p*-cym)]$_2$. This procedure was reproduced using the isolated Ag(I) intermediate **3.5** with moderately successful results: formation of the monometallic **3.**4 was not prevented, and both the monometallic (**3.4**) and bimetallic (**3.6**) complexes formed, in a 3:2 ratio. This may be because the halide salt made *in situ* by Albrecht *et al.*,[131] has two Ag(I) ions bridged by a single 1,1'-methylenebis(3-butylimidazol-2-ylidene) with relatively strong coordinating iodide anions; this may allow the favourable formation of the bimetallic **IX** over the monometallic analogue from the frozen suspension.
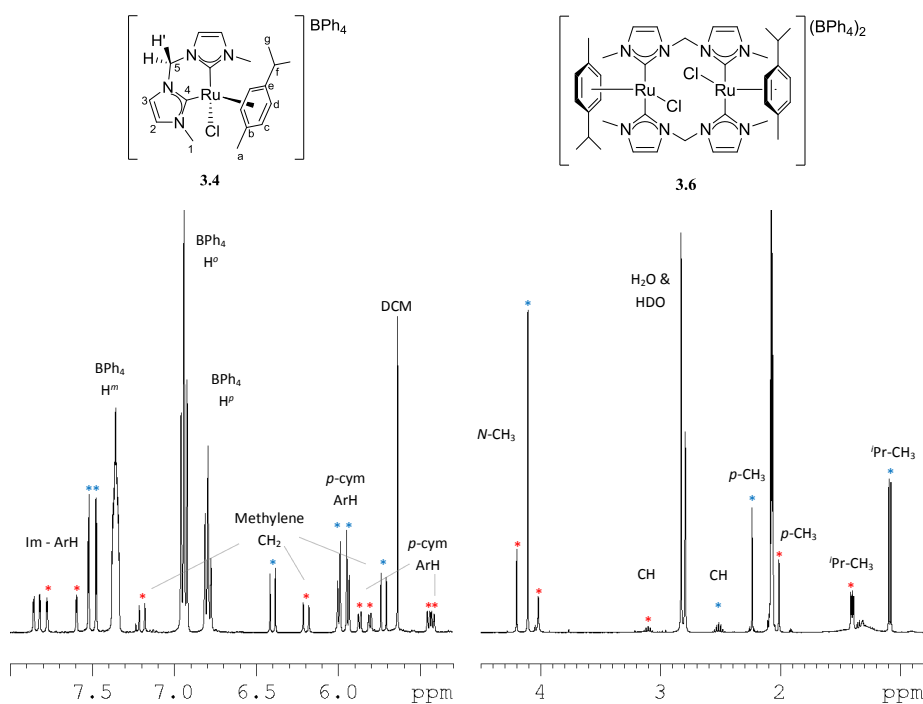
Figure 3.8. ^{1}H NMR (400 MHz, acetone-d_6, 298 K) of a mixture of [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]BPh$_4$ (**3.3**, blue, top left) and [RuCl(C^{NHC}C^{NHC})(η^6-p-cym)]$_2$(BPh$_4$)$_2$ (**3.6**, red, top right). See Figure 3.4 for resonance assignments of **3.4**.

3.3. Fe(II) complexes bearing an NHC pincer ligand

Our interest in developing group 8 complexes with ligands containing an NHC donor and hemilabile *N*-heterocyclic donor substituent (Section 3.1) led us to investigate a pincer ligand previously developed in the Messerle group. The pincer pre-ligand, 1,3-bis(pyrazol-1-yl)-imidazolium tetraphenylborate (NC^{NHC}N)BPh$_4$ (**3.7**, Figure 3.9)[28] has previously been used to make Ru(II) complexes to catalyse the transfer hydrogenation of ketones.[29] The Ru(II) complexes bearing both the hemilabile NC^{NHC}N ligand and a coordinated arene were the most successful in the transfer hydrogenation of acetophenone using 2-propanol and KOH (Scheme 3.4).
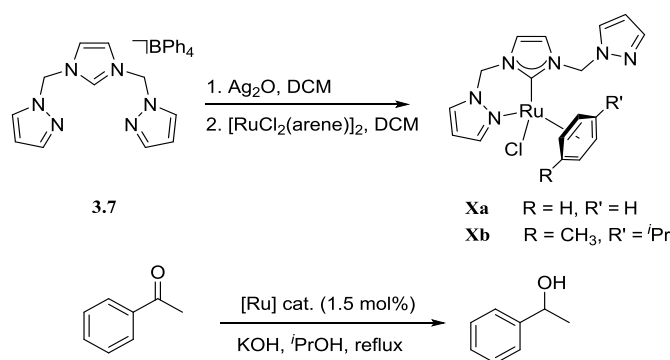
Scheme 3.4. NCN pre-ligand **3.7**, Ru(II) NHC arene complexes **Xa,b** were used as catalysts for the transfer hydrogenation of acetophenone.[29]

3.3.1. Attempted synthesis of Fe(II) complexes bearing an N^{Pz}C^{NHC}N^{Pz} pincer ligand

Recent success in our lab with the synthesis of Ir(I), Rh(I)[28] and Ru(II)[29] complexes using the NC^{NHC}N pre-ligand **3.7**,[28] (Scheme 3.5) spurred the interest in producing the first Fe(II) complex bearing an NHC ligand with *N*-hets as the pendant donors. Two synthetic routes were attempted for the synthesis of Fe(II) complexes bearing the NCN ligand, and are summarised in Scheme 3.5.

Previous reports on the synthesis of Fe(II) complexes bearing NHC ligands *via* silver transmetalation have used simple Fe(II) halide precursors such as FeX$_2$(THF)$_2$[137] or FeI$_2$,[138] and the synthesis of the Ag(I) intermediate (**3.8**, Route a, Scheme 3.5) has previously been reported from our lab group.[29] A transmetalation was therefore attempted from **3.8** to simple Fe(II) halide salts FeCl$_2$ and FeBr$_2$ in THF, DCM and acetonitrile (Route a, Scheme 3.5). However, ^{1}H NMR spectroscopy of

the crude reaction mixtures revealed only the silver intermediate **3.8** to be present. Literature transmetalations are typically performed *in situ* with a coordinating anion that may act to stabilise the transition states,[122] therefore the use of the BPh_4^- salt **3.8** may hinder the formation of the desired Fe(II) complex.

The second synthetic route attempted was developed from a literature procedure involving the *in situ* formation of $FeX[N(SiMe_3)_2]$ (X = Cl, Br) by the reaction of $KN(SiMe_3)_2$ with the corresponding Fe(II) halide.[139] A suspension of $KN(SiMe_3)_2$ in THF at -37 °C was transferred via cannula to a solution of FeX_2 in THF at -37 °C, forming a green suspension which slowly lost its colour over 3 hours. The formation of the green colour indicates the coordination of the $N(SiMe_3)_2^-$ anion to Fe(II).[140] The loss of this colour may indicate hydrolysis of the *in situ* formed $FeX[N(SiMe_3)_2]$, and may explain the recovery of **3.7** after several attempts all resulting in this observation.
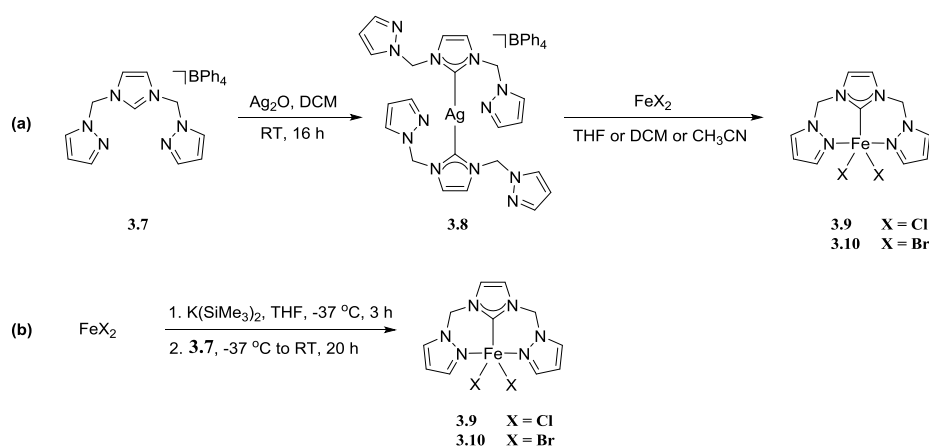
Scheme 3.5. Synthetic routes to the expected Fe(II) complexes bearing the NCN pincer ligand.

3.4. Summary

Four novel monometallic Ru(II) complexes, a novel Ag(I) complex, and a bimetallic Ru(II) complex were synthesised as follows:

i. Two Ru(II) complexes are the first examples of organometallics bearing the novel NC^NHC ligand derived from **2.3** and **2.4**. [RuCl₂(NC^NHC)(PPh₃)₂] (**3.1**) was fully characterised by 2D NMR and MS, [RuCl(NC^NHC)(η⁶-*p*-cym)]BPh₄ (**3.2**) was partially characterised by ¹H NMR and MS in a mixture containing unidentified organic impurities.

ii. The novel silver complex **3.5**, bearing the C^NHC^C^NHC ligand derived from **2.8** was prepared to be used in the synthesis of the novel Ru(II) arene complexes [RuCl(C^NHC^C^NHC)(η⁶-C₆H₆)]BPh₄

(**3.3**) & [RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.4**) by silver transmetalation. Both complexes were fully characterised by 2D NMR, MS and X-Ray crystallography.

iii. The novel homo-bimetallic Ru(II) complex (**3.6**) was observed during the synthesis of **3.4**. This complex was partially characterised by 1H NMR and MS in a mixture containing **3.4**.

iv. The attempted synthesis of an Fe(II) complex bearing the previously reported NCN pincer ligand derived from **3.7** is also described.

Chapter 4

Donor-functionalised-NHC Ru(II) Arene Complexes for Transfer Hydrogenation and CO$_2$ Activation

4.1. **Donor-functionalised-NHC Ru(II) arene complexes for the transfer hydrogenation of ketones**

In 2011, Albrecht *et al.*,[128] studied the catalytic activity of a series of Ru(II) η^6-arene complexes bearing donor-functionalised NHC ligands (Figure 4.1) for the transfer hydrogenation of ketones using 2-propanol. The series consisted of Ru(II) complexes bearing NHC ligands with hemilabile donor groups (**XIa-c**), a chelating *bis*-NHC ligand (**XIIa,b**) and a mono-NHC ligand (**XIII**). All complexes showed good to moderate activity, achieving 98% conversion to the product after 24 hours, with complex **XIIa** demonstrating the highest activity (90% conversion after 5 hours). The mono-NHC complex **XIII** by comparison reached only 63% conversion after 30 minutes; this increased to 79% upon addition of AgPF$_6$.

XIa **XIb** **XIc** **XIIa** R = R' = H **XIII**
                                  XIIb R = Me, R' = *i*Pr
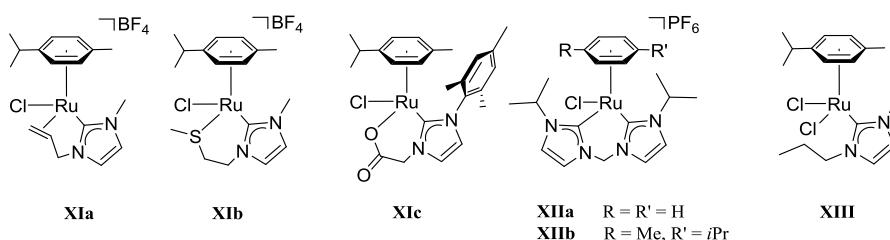
Figure 4.1. Ru(II) arene complexes bearing donor-functionalised NHC ligands.[25]

As a result of this success with chelating *bis*-NHC ligands, several reports of Ru(II) transfer hydrogenation catalysts appeared in the literature, with donor-functionalised NHC ligands consisting of primary amine,[141] *N*-heterocyclic[142] and chiral carboxyl[143] donors. In particular, pendant methoxy functionalities showed promise due to their ability to facilitate the β-hydride elimination of 2-propanol through hydrogen bonding interactions, rather than coordinating to the metal.[144] Indeed,

several Ru NHC complexes incorporating pendant methoxy groups have been successful in the hydrogenation of alkenes and metathesis.[145,146]

In order to understand the role of each feature of donor-functionalised NHC Ru(II) arene complexes has on the transfer hydrogenation of ketones, Papish *et al.*[58] investigated a series of complexes altering the arene (**XIVa-c**, Figure 4.2), and changing the type of pendant moiety from alkoxy (**XIVb**) to alkyl (**XV**) to a chelating *bis*-NHC (**XVI**) for complexes bearing the η^6-*p*-cym ligand.

Complex **XIVa** was shown to be the most active in the transfer hydrogenation of acetophenone using 2-propanol with 94% yield after 3 hours. The most striking result of this study was the comparison of activity within the first hour for complex **XIVa** versus **XIVb,c**: the complexes with more strongly π-donating arene ligands, *p*-cymene and hexamethylbenzene, resulted in yield of only 47 and 42% after 1 hour, respectively.

XIVa	arene = C_6H_6
XIVb	arene = *p*-cym
XIVc	arene = C_6Me_6
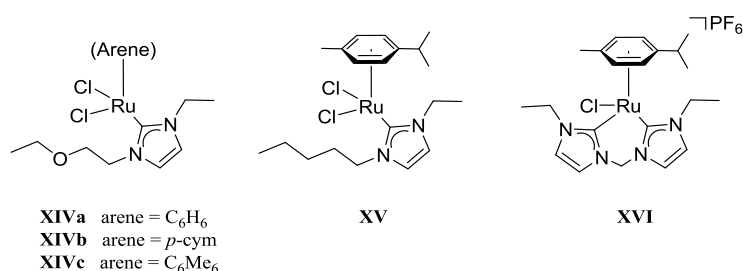
Figure 4.2. Ru(II) donor-functionalised NHC complexes for the transfer hydrogenation of ketones.

To investigate the source of the arene influence in complexes **XIVa-c**, variable-temperature NMR was performed on the pre-catalysts. This demonstrated that arene loss or ring slip is likely the step that forms the active catalyst; as expected the weakest π-donor, C_6H_6, was observed to be completely uncoordinated at 80 °C, whereas *p*-cym and C_6Me_6 remained partially coordinated at 80 °C. This trend corresponds to the activity of the complexes towards transfer hydrogenation, and the rate limiting step of the catalytic cycle was therefore hypothesised to be the total or partial loss of the coordinated arene (Figure 4.3 a).
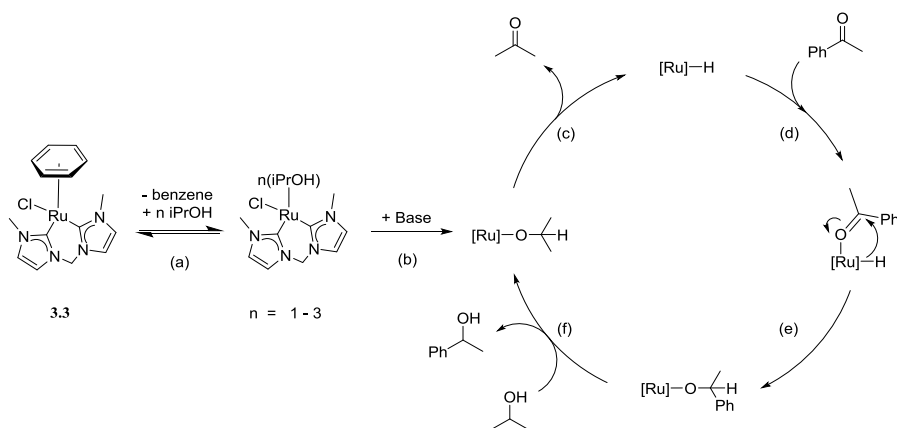
Figure 4.3. Mechanism proposed by Papish *et al.*[58] for the transfer hydrogenation of acetophenone in 2-propanol by donor-functionalised NHC Ru(II) arene complexes.

The *bis*-NHC complex **XVI** bearing *p*-cymene outperformed its ether-functionalised mono-NHC counterpart **XVb** in the first hour. It is possible that a chelating *bis*-NHC may better facilitate the dissociation of the arene ligand, leading to a highly active and stable catalyst for the transfer hydrogenation of ketones.

4.2. Ru(II) arene donor-functionalised NHC complexes for the carboxylation of phenylacetylene with CO_2

The utilisation of CO_2 as a chemical feedstock is an important reaction.[6] The incorporation of CO_2 into phenylacetylene has been a model reaction for the carboxylation of terminal alkynes, and several transition metals bearing NHC ligands have proved to be successful catalysts for this reaction.[73–76] While the overall reaction is atom neutral, current methodologies rely on the use of stoichiometric amounts of base. Ruthenium complexes can undergo insertion into C-H bonds,[35] and have shown promise in CO_2 reductioon,[38,67,69–72] but have not yet been applied to this reaction.
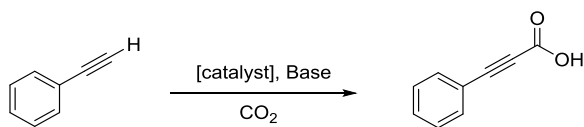
Scheme 4.1. Insertion of CO_2 into the terminal C-H bond of phenylacetylene.

4.2.1. Scope of this chapter

This chapter discusses the application of the Ru(II) arene complexes **3.3** and **3.4**, bearing the chelating $C^{NHC}C^{NHC}$ ligand, as catalysts for the transfer hydrogenation reaction of a range of ketones and nitriles, as well as the application of complex **3.4** as a catalyst for the carboxylation of phenylacetylene.

4.3. Transfer hydrogenation reactions ~~catalyze~~catalysed by complexes 3.3 and 3.4

The catalytic activity of **3.3** and **3.4** in the transfer hydrogenation with 2-propanol was tested on a range of substrates, including acetophenone, 4-methylacetophenone, 4-nitroacetophenone, 2-hexanone and 4-chlorobenzonitrile. Results can be seen in Table 4.1.
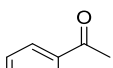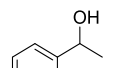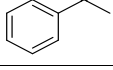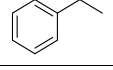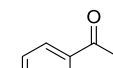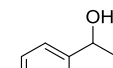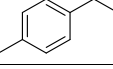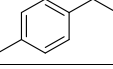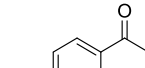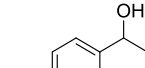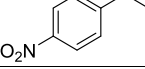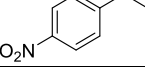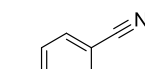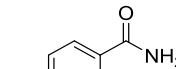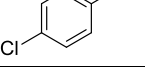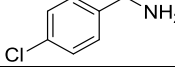
Catalyst **3.3** was found to be an effective catalyst for the conversion of acetophenone to 1-phenylethanol and showed a higher activity than **3.4** with a turnover frequency (TOF) of 81 at 1 hour, and reaching 88% conversion after 2 hours (Table 4.1, entry 2). Catalyst **3.4** did not promote comparable levels of conversion after 4 hours, and only demonstrated a TOF of 41 at 1 hour (Table 4.1, entry 2).

The effects of varying the electronic properties of the substrate were investigated using *para*-substituted acetophenones with electron-donating (Me) or -withdrawing (NO$_2$) groups (Table 4.1, entries 3-6) The moderately electron rich substrate 4'-methylacetophenone (Table 4.1, entries 3 and 4) resulted in a decrease in efficiency of conversion by both catalysts **3.3** and **3.4**, reaching only 65 and 37% conversion to product after 1 hour respectively. This is likely due to the decreased electrophilicity of the carbonyl group of the substrate, slowing down the transfer of the Ru hydride to the substrate (Figure 4.3, e). It was expected that the strongly electron-withdrawing NO$_2$ group would significantly increase the electrophilicity of the carbonyl group and hence result in high activity, however, no conversion was observed after 4 hours (Table 4.3, entry 6). This is likely due to the substrate being in-compatible with the base, corresponding to the observation of a deep red precipitate forming upon addition of KOH to this reaction mixture; the conversion of 4'-nitroacetophenone has been reported in base-free conditions.[58,128]

Reduction of 4-chlorobenzonitrile did not occur, instead the hydrolysis product 4-chlorobenzamide was produced very slowly with both complexes, reaching 36 and 14% conversion for catalysts **3.3** and **3.4** respectively (Table 4.1, entry 7 and 8). This likely occurs *via* addition of the hydroxide anion to the activated substrate, with low conversion rates reflecting the catalytic quantity of the base, and minimal water content of the solvent. Given excess water, this hydrolysis is expected to occur at a much higher rate.

The only difference between catalysts **3.3** and **3.4** is the arene ligand (η^6-benzene vs. η^6-*p*-cym, respectively). According to the mechanism for Ru(II) arene complexes bearing donor-functionalised NHC ligands proposed by Papish *et al.*[58] the dissociation of the ligand is the rate limiting step (Figure 4.4 a). As expected, complex **3.3** bearing the less π-donating η^6-benzene outperformed complex **3.4**.

Table 4.1. Catalytic transfer hydrogenation of ketones and 4-chlorobenzonitrile in 2-propanol.[a]

Entry	Substrate	Product	Catalyst	Conversion, %[c]				TOF (h^{-1}) at 1h
				0.5 h	1 h	2 h	4 h	
1			**3.3**	74	81	88	89	81
2			**3.4**	27	41	59	67	41
3			**3.3**	35	49	64	65	49
4[b]			**3.4**	15	25	37	37	25
5[d]			**3.3**	-	-	-	-	-
6[b]			**3.4**	0	0	0	0	0
7			**3.3**	8	11	23	36	11
8[b]			**3.4**	6	7	10	14	7

[a]All reactions were performed under an inert atmosphere in anhydrous 2-propanol (5 mL), aliquots were processed according to section 5.5 unless otherwise stated. [b]Aliquots for ^{1}H NMR were prepared according to the literature procedure.[128] [c]Conversions were determined by ^{1}H NMR spectroscopy by the relative integrals of substrate to product. [d]Catalyst was not tested with 4-nitroacetophenone.

4.3.1. Comparison to catalysts in the literature

The catalytic activity of catalysts **3.3** and **3.4** towards transfer hydrogenation can be compared to similar Ru(II) arene complexes previously discussed. The *bis*-NHC Ru(II) η^6-benzene complex (**XIIa**, Figure 4.1) was able to convert benzophenone in 63 % yield after 5 hours. Both complexes **3.3** and **3.4** achieved greater yields after only 4 hours, with complex **3.3** outcompeting **XIIa** in the first 30 minutes (Table 4.1, entry 1).[128] However authors note that a dramatic increase in activity was seen when the reaction was performed under N$_2$ in a sealed Schlenk tube with degassed solvent, reaching 96 % in just 30 minutes using complex **XIa**. Activity of **XIIa** under optimal conditions was not reported. It should be noted that catalytic studies with Ru(II) arene complexes with donor-functionalised NHCs have shown little steric effect on the reaction when comparing conversions of acetophenone to benzophenone, and the two substrates are comparable.[8]

The *bis*-NHC Ru(II) η^6-*p*-cym catalyst **XVI** (Figure 4.3) achieved 60 % conversion after 1 hour in identical conditions to those reported in this thesis.[58] This Ru(II) η^6-*p*-cym containing complex was outperformed by the similar η^6-benzene containing complex **3.3** reported here, reaching 81% conversion after 1 hour. This may also be compared to the complex bearing the η^6-*p*-cym ligand **3.4**, which achieved only 41 % after 1 hour. During the transfer hydrogenation reactions, it was noted that the complex forms a precipitate in 2-propanol, hence this difference may be due to the solubility of the weakly-coordinating counter ions, where **XVI** bearing PF_6^- could be more soluble than **3.4** bearing BPh_4^-, resulting in a higher concentration of the active catalyst and hence a higher catalytic activity.

4.4.   Phenylacetylene carboxylation by C-H insertion of CO_2

The catalytic activity of **3.4** in the carboxylation of terminal alkynes (Scheme 4.1) was tested on phenylacetylene. In the presence of a slight excess of Cs_2CO_3 in DMF and at 1 atm of CO_2, complex **3.4** was found to produce phenylpropiolic acid in less than 5% conversion at room temperature. Higher temperatures may be required for this reaction using Ru(II) arene complexes. As this reaction has been demonstrated at relatively low temperatures with other transition metals,[73,74,76] no further investigations with this complex were performed.

4.5.   Summary

The catalytic activity of novel Ru(II) arene complexes bearing chelating *bis*-NHC ligands was tested in the transfer hydrogenation of acetophenone in 2-propanol with the following results:

i.   Complex **3.3** was more active than **3.4** in the transfer hydrogenation of selected ketones and 4-chlorobenzonitrile, with **3.3** and **3.4** converting acetophenone to 1-phenylethanol in 81 and 41 % yield within the first hour, respectively.

ii. The activity of complexes **3.3** and **3.4** were found to be reduced with substrates containing electron donating substituents on the aromatic ring. The conversion of 4'-nitroacetophenone was found to be non-compatible with the catalytic conditions used here.

iii. The difference in activity is attributed to the relative π-donating strength of the arene ligands; the less donating η^6-benzene leads to higher activity, particularly within the first hour. This is explained by the mechanism outlined by Papish *et al.*[58] in which the rate limiting step is the dissociation of the arene ligand to form the active catalyst.

Chapter 5

Conclusions and Future Work

5.1.   Conclusions

This thesis describes the improved syntheses of bidentate donor-functionalised *N*-heterocyclic carbene pre-ligands and the synthesis and characterisation of several Ru(II) complexes bearing these ligands. The catalytic activity of two of the produced Ru(II) complexes were tested for the transfer hydrogenation of carbonyl compounds, and in the carboxylation of phenylacetylene.

Chapter 2 describes a new one-pot method developed from a literature procedure for the synthesis of 1'*H*-1,2'-dibenzo[d]imidazole (**2.1**). The 73% yield of **2.1** from *o*-phenylenediamine is a significant improvement over existing literature syntheses of this compound. Compound **2.1** was used as a precursor to the novel bidentate donor-functionalised pre-ligand (NC^{NHC})BPh$_4$ (**2.4**), which was fully characterised by 2D NMR spectroscopy and MS.

Chapter 3 describes the synthesis and characterisation of a series of Ru(II) complexes. Two novel complexes, RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (**3.1**) and [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.2**), were synthesised using the pre-ligand **2.4** and partially characterised using 2D NMR and MS. The novel complexes, [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ (**3.3**) and [RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.4**), synthesised using the known pre-ligand (C^{NHC}C^{NHC})Br$_2$ (**2.8**) and fully characterised using 2D NMR, MS and X-ray crystallography.

Chapter 4 describes the application of **3.3** and **3.4** as a catalyst for the transfer hydrogenation of a range of ketones and also 4-chlorobenzonitrile. Complex **3.3** was found to be an efficient catalyst for the transfer hydrogenation of acetophenone in 2-propanol in the presence of KOH, reaching 81 % conversion within the first hour. Complex **3.4** was found to be a far less efficient catalyst for the same transformation. This is explained by a previously proposed mechanism in which the dissociation of the arene ligand is the rate limiting step, and it is clear that the η^6-benzene ligand of **3.3** dissociates more readily than the η^6-*p*-cym ligand of **3.4** to produce the active catalyst.[58]

5.2.   Future work

The enhanced activity of **3.3** over **3.4** as catalysts for the transfer hydrogenation of acetophenone using 2-propanol (Table 4.1, entries 1 & 2) is explained by the mechanism proposed by Papish *et al.*,[58] in which the rate limiting step is the dissociation of the arene ligand (Figure 4.3 a). It has been noted that incorporation of a non-coordinating ether functionality into an NHC ligand leads to complexes with enhanced catalytic activity for this reaction.[144] This is a result of the O of the non-coordinating ether facilitating the β-hydride elimination of 2-propanoate to form the metal hydride intermediate. However, complex **XIVb** bearing an NHC with a pendant methoxy group gave similar conversions to its alkyl counterpart, **XV** (Figure 4.2).[58] This is likely because dissociation of η^6-*p*-cym is the rate limiting step, as opposed to formation of the ruthenium hydride intermediate (Figure 4.3). Upon replacement of η^6-*p*-cym with a weaker π-donating arene such as η^6-benzene, it is possible that the β-hydride elimination of 2-propanol becomes the rate limiting step.

The activity of a Ru(II) complex bearing an ether functionalised NHC ligand and the η^6-benzene co-ligand in the transfer hydrogenation of ketones has yet to be investigated. If the rate of β-hydride elimination is slower than η^6-benzene dissociation, it is expected that a complex bearing an ether functionalised NHC ligand would outperform a non-functionalised derivative. To investigate this, a series of complexes with a range of ether functionalised NHC ligands will be produced.

Figure 5.1 contains a series of proposed complexes to be used as catalysts in the transfer hydrogenation of ketones to determine the effect of: (1) pendant functionalised NHC ligands vs. non-pendant ether functionalised NHC ligands (**XVIIa** and **XVIIIa** *vs.* **XVIIb** and **XVIIIb**), and (2) monoNHC *vs.* chelating *bis*-NHC ligands with the η^6-benzene co-ligand (**XVIIa,b** *vs.* **XVIIIa,b**). If β-hydride elimination is slower than dissociation of η^6-benzene, then **XVIIb** and **XVIIIb** are expected to outcompete their non-ether-functionalised counterparts.

XVIIa	X = CH$_2$	**XVIIIa**	X = CH$_2$
XVIIb	X = O	**XVIIIb**	X = O
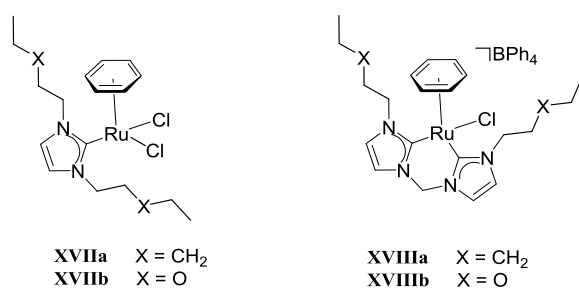
Figure 5.1 Proposed Ru(II) η^6-benzene complexes with pendant ethoxy functional groups (**XVIIb** & **XVIIIb**) and without (**XVIIa** & **XVIIIa**).

Chapter 6

Experimental

6.1. General procedures

Ruthenium(III) Cchloride Hhydrate was purchased from Precious Metals Online P/L and used without further purification. All other chemicals were purchased from Sigma Aldrich Company Inc. or Alfa Aesar Inc. and used as received. $RuCl_2(PPh_3)_3$,[147] $[RuCl_2(\eta^6-C_6H_6)]_2$,[37] $[RuCl_2(\eta^6-p-cym)]_2$,[37] bis(imidazol-1-yl)methane (**2.5**),[114] 1,1'-methylenebis(3-methylimidazol-3-ium) diiodide (**2.6**),[115] 1-((imidazol-1-yl)methane)-3-methylimidazol-3-ium iodide (**2.7**),[115] 1,1'-methylenebis(3-methylimidazol-3-ium) dibromide (**2.8**),[115] 1,3-dihydrobenzo[d]imidazole-2-one,[148] 1,3-bis(pyrazol-1-yl)-methylimidazolium tetraphenylborate (**3.7**)[28] and $[Ag(NC^{NHC}N)_2]BPh_4$[29] were prepared according to literature procedures.

For the manipulation of air sensitive materials and preparation of metal complexes, solvents were either dispensed from an LC Technology Solutions Inc. solvent purification system or dried and distilled according to literature procedures[149] and stored under nitrogen or argon in glass ampoules fitted with Youngs© Teflon valves. Compressed gas cylinders of argon (>99.5 %) and carbon dioxide (>99.5 %) were obtained from British Oxygen Company (BOC Gases). Air sensitive samples were prepared in an argon filled glovebox in an NMR tube fitted with a Youngs© Teflon valve. All Deuterated solvents were purchased from Cambridge Isotopes and used as received. All deuterated solvents for possible air sensitive samples were opened and stored in an argon filled glovebox over activated 3 Å molecular sieves.

6.1.1. Characterisation Techniques

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AvanceIII Nanobay orand DPX400 spectrometer both operating at 400 MHz (^1H) orand 100 MHz (^{13}C). All spectra were collected by the author at 298 K and chemical shifts (δ) are quoted in ppm. Coupling constants (J) are quoted in Hz and carry uncertainties of ±0.05 Hz for ^1H and ^{13}C. ^1H and ^{13}C NMR chemical shifts were internally referenced to residual solvent resonances.[150] Multiplicity of NMR resonances are reported using the following abbreviations: s, singlet; d; doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sept, septet; br, broad.

Proton and carbon resonances for new compounds were assigned using COSY (Correlation Spectroscopy), NOESY (Nuclear Overhauser Effect Spectroscopy), HMBC (^{1}H- ^{13}C) (Heteronuclear Multiple Bond Coherence), HSQC (^{1}H- ^{13}C) (Heteronuclear Single Quantum Coherence) experiments. All NMR data were acquired and processed using TopSpin^{TM} version 3.5 from Bruker NMR software.

Single crystal X-ray analyses were carried out at the Mark Wainwright Analytical Centre, University of New South Wales, Sydney by Dr. Samantha Binding and Mathew Peterson. X-ray diffraction measurements were carried out on a Bruker Kappa APEXII CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). All structures were solved by direct methods or Superflip and the full-matrix least-square refinements were carried out using OLEX2 running SHELXL or CRYSTALS program suite.

Mass spectra were acquired at the Biomolecular Frontiers Research Centre at Macquarie University using a 6300 Series Ion Trap Liquid Chromatography Mass Spectrometer (ESI-LC/MS). The ionised compound of interest or cationic fragment of the organometallic complex is defined as M$^+$.
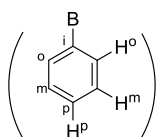
Note on BPh$_4$ counter anion: ^{1}H and ^{13}C NMR resonances for the tetraphenyl borate anion, BPh$_4^-$, have been assigned according to the labels shown to the left.

~~**Note on BPh$_4$ counter anion:** ^{1}H and ^{13}C NMR resonances for the tetraphenyl borate anion, BPh$_4^-$, have been assigned according to the labels shown to the left.~~

~~X-Ray crystallography~~

~~Mass spectra were acquired at the Biomolecular Frontiers Research Centre at Macquarie University using a 6300 Series Ion Trap Liquid Chromatography Mass Spectrometer (ESI-LC/MS). The ionised compound of interest or cationic fragment of the organometallic complex is defined as M$^+$.~~

6.2. Synthesis of Ligands

1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**) and 1',3-dimethyl-1,2'-dibenzo[d]imidazol-3-ium iodide (**2.3**) have previously been prepared,[113] but literature containing this molten-imidazole procedure was not accessible, and solution phase syntheses were thus developed.
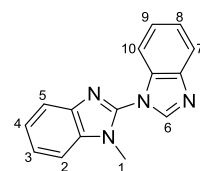
6.2.1. 1'*H*-1,2'-bibenzo[d]imidazole, (2.1)
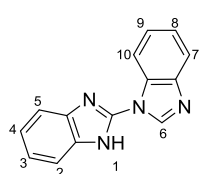
1'*H*-1,2'-bibenzo[d]imidazole was synthesised following a modification of the literature procedure.[95] Triphosgene (1.39 g, 4.68 mmol) was slowly added to a stirring suspension of *o*-phenylenediamine (1.52 g, 14.0 mmol) in POCl$_3$ (13 mL, 140 mmol). The suspension was allowed to stir at room temperature for 30 min and benzimidazole (1.66 g, 14.0 mmol) was added, before heating to reflux and stirring for 16 h. The resulting suspension was poured into an ice-water bath, the pH was adjusted to 10 by the addition of conc. NaOH and the suspension stirred at room temperature for 2 h. The off white precipitate was collected by vacuum filtration, re-dissolved in acetone and filtered, then dried *in vacuo* to yield 1'*H*-1,2'-bibenzo[d]imidazole (**2.1**) as a beige solid.

Yield: 2.04 g, 10.3 mmol, 73.3%.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.79 (s, 1H, **H^6**), 8.51 (d, *J* = 8.1 Hz, Ar**H**), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, Ar**H**), 7.64 (m, 2H, Ar**H**), 7.48 (m, 1H, Ar**H**), 7.41 (m, 1H, Ar**H**), 7.28 (m, 2H, Ar**H**) ppm.

6.2.2. 1'-methyl-1,2'-dibenzo[d]imidazole, (2.2)

A 60% dispersion of NaH in mineral oil (0.17 g, 4.23 mmol) was slowly added to a stirring solution of 1'*H*-1,2'-bibenzo[d]imidazole (**2.1**), (0.99 g, 4.23 mmol) in THF (20 mL) at 0 °C, and allowed to warm to room temperature over 30 min. The reaction mixture was cooled to 0 °C and iodomethane (0.32 mL, 5.14 mmol) was added dropwise, before warming to room temperature and stirring for 3h. The solvent was evaporated *in vacuo* then the residue re-dissolved in DCM (20 mL). The DCM solution was washed with water (3 x 20mL) and brine (20 mL), then dried over MgSO$_4$, filtered, and evaporated to dryness to yield a brown oil. The product was purified by column chromatography (Silica, ethyl acetate) to yield 1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**), as a beige solid.

Yield: 0.75g, 2.54 mmol, 60.0%.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.23 (s, 1H, **H^1**), 7.92 (m, 1H, Ar**H**), 7.84 (m, 1H, Ar**H**), 7.59 (m, 1H, Ar**H**), 7.54 (m, 1H Ar**H**), 7.50 – 7.39 (m, 4H, Ar**H**) ppm.

6.2.3. 1',3-dimethyl-1,2'-dibenzo[d]imidazol-3-ium iodide, ((NC^{NHC})I, 2.3)
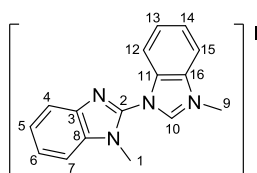
1'-methyl-1,2'-bibenzo[d]imidazole (**2.2**), (0.26 g, 1.05 mmol) was dissolved in the minimum amount of acetonitrile in a 15 mL pressure tube, to which excess iodomethane (0.26 mL, 4.19 mmol) was added. The solution was stirred in the absence of light at room temperature for 12h, during which 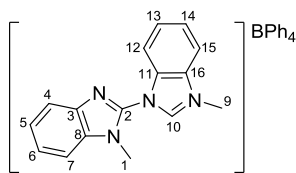time a white precipitate formed. The white precipitate was collected by vacuum filtration to yield 1',3-dimethyl-1,2'-dibenzo[d]imidazol-3-ium iodide (**2.3**) as a white solid, which was partially characterised.

Yield: 0.156 g, 0.34 mmol, 38 %.

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.38 (s, 1H, **H^{10}**), 8.23 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, Ar**H**), 8.08 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, Ar**H**) 7.89-7.77 (m, 4H, Ar**H**), 7.52 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 3.44 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 4.26 (s, 3H), 3.90 (s, 3H) ppm.

ESI-MS (CH3CN): *m/z:* 263.1 (100 %, [M$^+$])

6.2.4. 1',3-dimethyl-1,2'-dibenzo[d]imidazol-3-ium tetraphenylborate ((NC^{NHC})BPh$_4$, 2.4)

The tetraphenylborate salt (**2.4**), was synthesised using a similar procedure to that above. 1'-methyl-1,2'-dibenzo[d]imidazole (**2.2**) (0.857 g, 3.45 mmol) was dissolved in the minimum amount of acetonitrile in a 15 mL pressure tube, to which excess iodomethane (0.86 mL, 13.8 mmol) was added. The solution was stirred in the absence of light at room temperature for 12h, during which time a white precipitate formed. The acetonitrile was evaporated *in vacuo* and the residue re-dissolved in the minimum amount of methanol, to which NaBPh$_4$ (1.19 g, 10.1 mmol) was added and stirred for 15 mins, the precipitate was collected by vacuum filtration to yield 1',3-dimethyl-1,2'-bibenzo[d]imidazol-3-ium tetraphenylborate (**2.4**), as a light tan powder.

Yield: 1.01 g, 1.73 mmol, 50.1%.

^{1}H NMR (400 MHz, Acetone-d_6): δ 10.02 (s, 1H, **H^{10}**), 8.21 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, **H^{15}**), 8.12 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, **H^{12}**), 7.91 (m, 1H, **H^{14}**), 7.87 (m, 1H, **H^{13}**), 7.83 (d, $^{3}J_{HH}$ = 8.0, 1H, **H^{4}**), 7.73 (d, $^{3}J_{HH}$ = 8.1 Hz, **H^{7}**), 7.53 (d, $^{3}J_{HH}$ = 8.1, 1H, **H^{6}**), 7.46 (d, $^{3}J_{HH}$ = 8.0, 1H, **H^{5}**), 7.34 (m, 8H, BPh$_4$-**H^{m}**), 6.91 (m, 8H, BPh$_4$-**H^{o}**), 6.76 (m, 4H, BPh$_4$-**H^{p}**), 4.42 (s, 3H, **H^{9}**), 3.95 (s, 3H, **H^{1}**) ppm.

^{13}C {^{1}H}NMR (100 MHz, Acetone-d_6): δ 164.95 (q, $^{1}J_{BC}$ = 49.4 Hz, BPh$_4$-**C^{q}**), 144.02 (**C^{10}**), 141.64 (**C^{3}**), 139.90 (**C^{2}**), 137.03 (BPh$_4$-**C^{m}**), 136.60 (**C^{8}**), 133.03 (**C^{16}**), 132.57 (**C^{11}**), 129.58 (**C^{13}**), 129.00 (**C^{14}**), 126.02 (BPh$_4$-**C^{o}**), 125.60 (**C^{6}**), 124.52 (**C^{5}**), 122.25 (BPh$_4$-**C^{p}**), 121.16 (**C^{4}**), 115.49 (**C^{15}**),

114.96 (C^{12}), 112.09 (C^7), 35.00 (C^9), 31.40 (C^1) ppm.

ESI-MS (CH$_3$CN): *m/z* : 263.1 (100 %, [M$^+$])

6.3. Synthesis of Novel Complexes

6.3.1. [RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$], (3.1)
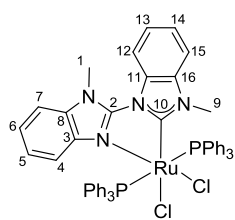
To a Schlenk flask under N$_2$ containing a stirring solution of (NC^{NHC})BPh$_4$, (**2.4**), (0.100 g, 0.171 mmol) and trimethylamine (0.12 mL, 0.855 mmol) in dry DCM (20 mL) was added RuCl$_2$(PPh$_3$)$_3$ (0.164 g, 0.171 mmol). The deep red solution was stirred at room temperature for 3 h, at which point a golden brown solution remained. The solvent was reduced *in vacuo* and pentane added, causing the precipitation of a green residue. The suspension was filtered through glass fiber and diethyl ether was added to the yellow filtrate causing the precipitation of RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (**3.1**) as an orange powder.

Yield: 38.5 mg, 0.040 mmol, 23.5 %.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.76 (m, 1H, **H^4**), 7.70-7.60 (m, 16H, PPh$_3$-**H^m**), 7.60-7.52 (m, 8H, PPh$_3$-**H^p**), 7.52-7.43 (m, 16H, PPh$_3$-**H^o**), 7.47 (m, 1H, **H^7**), 7.38 (m, 1H, **H^5**), 7.33 (m, 1H, **H^6**), 7.24 (m, 1H, **H^{12}**) 7.23 (m, 1H, **H^{14}**), 7.13 (m, 1H, **H^{13}**), 7.11 (m, 1H, **H^{15}**), 3.78 (s, 3H, **H^1**), 3.48 (s, 3H, **H^9**) ppm.

^{31}P NMR (160 MHz, CD$_2$Cl$_2$): δ 26.67 (s) ppm.

^{13}C {^{1}H}NMR (100 MHz, DMSO-*d$_6$*): δ 153.06 (**C^{10}**), 142.68 (**C^2**), 141.67 (**C^3**), 135.64 (**C^8**), 133.35 (d, $^1J_{PC}$ = 103.5 Hz, PPh$_3$-**C^{ipso}**), 132.32 (d, $^3J_{PC}$ = 9.8 Hz, PPh$_3$-**C^m**), 132.24 (d, $^4J_{PC}$ = 2.7 Hz, PPh$_3$-**C^p**), 131.23 (**C^{16}**) 128.88 (d, $^2J_{PC}$ = 12.0 Hz, PPh$_3$-**C^o**), 129.09 (**C^{11}**), 123.51 (**C^5**), 123.40 (**C^{14}**), 122.87 (**C^{6PP}**), 122.35 (**C^{13}**), 120.12 (**C^4**), 110.80 (**C^{12}**), 110.30 (**C^7**), 108.36 (**C^{15}**), 31.14 (**C^1**), 27.66 (**C^9**) ppm.

ESI-MS (CH$_3$CN): *m/z*: 958.2 (100%, [M$^+$])

6.3.2. [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$, (3.2)
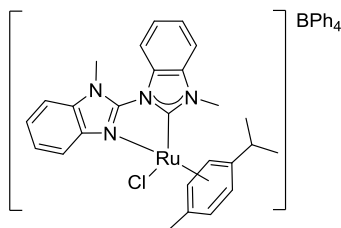
To a solution of (NC)I, (**2.3**), (37.8 mg, 0.097 mmol) in dry DCM (10 mL) was added Ag$_2$O (16.8 mg, 0.073 mmol) and the suspension was stirred at room temperature for 16 h in the absence of light. A cloudy beige suspension remained, to which [RuCl$_2$(η^6-~~C$_6$H$_6$~~*p*-cym)]$_2$ (29.7 mg, 0.048 mmol) was added and the suspension stirred at room temperature for 2h. NaBPh$_4$

(33.2 mg, 0.097 mmol) was added and the suspension was stirred for 15 min. The suspension was filtered through celite in air and the solvent removed *in vacuo* to yield [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.2**), as a crude red oil contaminated with unknown organics. Purification was attempted by column chromatography (silica, acetone:DCM 1:1) and recrystallisation from acetonitrile and diethyl ether. [RuCl(NC^{NHC})(η^6-*p*-cym)]BPh$_4$ (**3.2**), was partially characterised by ^{1}H NMR and mass spectrometry as below:

<u>^{1}H NMR (400 MHz, CD$_2$Cl$_2$):</u> δ 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.69-7.52 (m, 6H), 7.35 (m, 8H, BPh$_4$-**H^m**), 7.02 (t, $^3J_{HH}$ = 7.4 Hz, 8H, BPh$_4$-**H^o**), 6.86 (t, $^3J_{HH}$ = 7.1 Hz, 4H, BPh$_4$-**H^p**), 6.26 (d, $^3J_{HH}$ = 6.1 Hz, 1H, cym-Ar**H**), 6.01 (d, $^3J_{HH}$ = 5.9 Hz, 1H, cym-Ar**H**), 5.90 (d, $^3J_{HH}$ = 6.0, 1H, cym-Ar**H**), 5.46 (d, $^3J_{HH}$ = 5.9, 1H, cym-Ar**H**), 4.19 (s, 3H), 4.12 (s, 3H), 2.31 (sept, *J* = 6.9, 1H, cym-C**H**), 2.23 (s, 3H, cym-*p*-C**H$_3$**), 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 3H, cym-^{i}Pr-C**H$_3$**), 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 3H, cym-^{i}Pr-C**H$_3$**) ppm.

<u>ESI-MS (CH$_3$CN): *m/z:*</u> 533.1 (100 %, [M]$^+$)

6.3.3. [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$, (3.3)
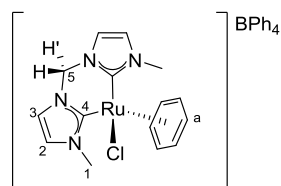
To a stirring suspension of [Ag(C^{NHC}C^{NHC})]$_2$(BPh$_4$)$_2$ (**3.5**), (0.13 g, 0.107 mmol) in dry DCM (10 mL) was added [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$ (0.054 g, 0.107 mmol) and the suspension was stirred at room temperature for 16h. The suspension was filtered through celite and the solvent evaporated *in vacuo* to leave behind an orange oil. The product was purified by column chromatography (Al$_2$O$_3$, acetone:DCM 1:5) and the solvent was evaporated to yield [RuCl(C^{NHC}C^{NHC})(η^6-C$_6$H$_6$)]BPh$_4$ as an crystalline orange powder.[29]

<u>Yield:</u> 27.0 mg, 0.038 mol, 19%.

<u>^{1}H NMR (400 MHz, Acetone-*d$_6$*):</u> δ 7.49 (d, $^3J_{HH}$ = 2.0 Hz, 2H, **H^3**), 7.45 (d, $^3J_{HH}$ = 2.0 Hz, 2H, **H^2**), 7.34 (m, 8H, BPh$_4$-**H^m**), 6.92 (t, $^3J_{HH}$ = 7.4 Hz, 8H, BPh$_4$-**H^o**), 6.78 (t, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$-**H^p**), 6.29 (d, $^3J_{HH}$ = 12.9 Hz, 1H, **H^5**), 5.98 (s, 6H, **H^a**), 5.76 (d, $^3J_{HH}$ = 12.9 Hz, 1H, **H$^{5'}$**), 4.13 (s, 6H, **H^1**) ppm.

<u>^{13}C {^{1}H}NMR (100 MHz, Acetone-*d$_6$*):</u> δ 175.26 (**C^4**), 164.97 (q, $^1J_{BC}$ = 49.4 Hz, BPh$_4$-**C^{ipso}**), 137.06 (BPh$_4$-**C^m**), 126.00 (BPh$_4$-**C^o**), 124.74 (**C^2**), 122.25 (BPh$_4$-**C^p**), 90.96 (**C^a**), 62.70 (**C^5**), 38.47 (**C^1**) ppm.

<u>ESI-MS (CH$_3$CN): *m/z:*</u> 391.0 (100 %, [M]$^+$)

6.3.4. [RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh$_4$, (3.4)
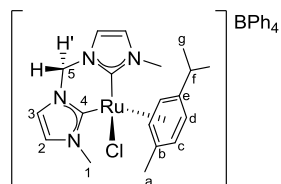
To a stirring suspension of [Ag($C^{NHC}C^{NHC}$)]$_2$(BPh$_4$)$_2$ (**3.5**) (0.12 g, 0.098 mmol) in DCM (10 mL) was added [RuCl$_2$(η^6-p-cym)]$_2$ (0.06 g, 0.098 mmol) and the suspension was stirred at room temperature for 16 h. The suspension was filtered through celite and the solvent evaporated *in vacuo* leaving behind a red oil. The product was purified by column chromatography (Al$_2$O$_3$, acetone:DCM 1:5) and recrystallised from DCM/Et$_2$O to yield [RuCl($C^{NHC}C^{NHC}$)(η^6-p-cym)]BPh$_4$ **3.4** a bright yellow powder.

<u>Yield:</u> 0.14 g, 0.18 mmol, 93.6 %.

<u>^{1}H NMR (400 MHz, Acetone-d_6):</u> δ 7.51 (d, $^3J_{HH}$ = 2.0 Hz, 2H, **H^3**), 7.46 (d, $^3J_{HH}$ = 2.0 Hz, 2H, **H^2**), 7.34 (m, 8H, BPh$_4$-**H^m**), 6.92 (t, $^3J_{HH}$ = 7.4 Hz, 8H, BPh$_4$-**H^o**), 6.77 (t, $^3J_{HH}$ = 7.2 Hz, BPh$_4$-**H^p**), 6.40 (d, $^3J_{HH}$ = 13.0 Hz, 1H, **H^5**), 5.98 (d, $^3J_{HH}$ = 6.3 Hz, 2H, **H^c**), 5.93 (d, $^3J_{HH}$ = 6.3 Hz, 2H, **H^d**), 5.71 (d, $^3J_{HH}$ = 13.0 Hz, 1H, **H$^{5'}$**), 4.09 (s, 6H, **H^1**), 2.50 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, **H^f**), 2.22 (s, 3H, **H^a**), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 6H, **H^g**) ppm.

<u>^{13}C {^{1}H}NMR (100 MHz, Acetone-d_6):</u> δ 176.22 (**C^4**), 164.07 (q, $^1J_{CB}$ = BPh$_4$-**C^{ipso}**) 137.06 (BPh$_4$-**C^m**), 126.00 (BPh$_4$-**C^o**), 124.78 (**C^2**), 122.23 (**C^3**), 121.28 (BPh$_4$-**C^p**) 107.92 (**C^e**), 105.49 (**C^b**), 93.23 (**C^c**), 87.45 (**C^d**), 62.60 (**C^5**), 38.48 (**C^1**), 32.79 (**C^f**), 22.97 (**C^g**), 18.60 (**C^a**) ppm.

<u>ESI-MS (CH$_3$CN): *m/z*:</u> 447.1 (100 %, [M]$^+$)

6.3.5.   [Ag($C^{NHC}C^{NHC}$)]$_2$(BPh$_4$)$_2$, (3.5)
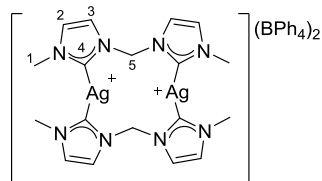
The title complex was prepared by a modified literature procedure.[130] To a stirring solution of ($C^{NHC}C^{NHC}$)Br$_2$ (**2.8~~IV~~**) (0.41 g, 1.20 mmol) in distilled water (25 mL) was added excess Ag$_2$O (0.69 g, 3.00 mmol). The solution was stirred at room temperature in the absence of light for 30 min. The suspension was filtered through celite, and NaBPh$_4$ (0.41 g, 1.20 mmol) was added to the filtrate, causing a white suspension to form. The precipitate was collected by vacuum filtration and dried *in vacuo* to give [Ag($C^{NHC}C^{NHC}$)]$_2$(BPh$_4$)$_2$ (**3.5**), as an off white powder.

<u>Yield:</u> 0.59 g, 0.49 mmol, 80.9 %.

<u>^{1}H NMR (400 MHz, DMSO-d_6):</u> δ 7.87 (d, $^1J_{HH}$ = 1.7 Hz, **H^2**), 7.53 (d, $^1J_{HH}$ = 1.7 Hz, **H^3**), 7.17 (m, 16H, BPh$_4$-**H^m**), 6.92 (t, $^1J_{HH}$ = 7.4 Hz, 16H, BPh$_4$-**H^o**), 6.78 (t, $^1J_{HH}$ = 7.4 Hz, 8H, BPh$_4$-**H^p**), 6.75 (br s, 4H, **H^5**) 3.39 (s, 12H, **H^1**) ppm.

<u>^{13}C {^{1}H}NMR (100 MHz, DMSO-d_6):</u> δ 163.34 (BPh$_4$-**C^{ipso}**) 135.52 (BPh$_4$-**C^m**), 125.29 (BPh$_4$-**C^o**), 124.32 (**C^2**), 121.68 (**C^3**), 121.51 (BPh$_4$-**C^p**), 63.05 (**C^5**), 38.51 (**C^1**) ppm.

<u>ESI-MS (CH$_3$CN): *m/z*:</u> 284.0 (100%, [M]$^+$)

6.3.6.   [RuCl(C^NHCC^NHC)(η^6-p-cym)]₂(BPh₄)₂, 3.6
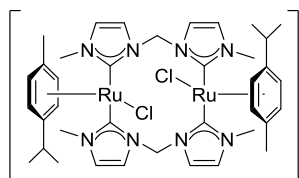
The title complex was prepared along with [RuCl(C^NHCC^NHC)(η^6-p-cym)]BPh₄ (**3.4**) in an identical procedure. As above, to a stirring suspension of [Ag(C^NHCC^NHC)]₂(BPh₄)₂ (**3.5**) (0.12 g, 0.098 mmol) in DCM (10 mL) was added [RuCl₂(η^6-p-cym)]₂ (0.06 g, 0.098 mmol) and the suspension was stirred at room temperature for 16 h. The suspension was filtered through celite and the solvent evaporated *in vacuo* leaving behind a red oil containing both **3.4** and **3.6**. Purification was attempted by column chromatography (silica, gradient elution acetone:DCM) with unsuccessful results. [RuCl(C^NHCC^NHC)(η^6-p-cym)]₂(BPh₄)₂ (**3.6**), was partially characterised by ^1H NMR and mass spectrometry as a mixture containing **3.4,** as below:

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<u>^1H NMR (400 MHz, Acetone-d_6):</u> δ 7.84, 8.60, 7.76, 7.58 (4 x d, $^3J_{HH}$ = 2.0 Hz, 8H, Im**H**), 7.18 (d, $^3J_{HH}$ = 13.7 Hz, 2H, NC**H**HN), 6.18 (d, $^3J_{HH}$ = 13.7 Hz, 2H, NCH**H**N), 5.85, 5.79, 5.42, 5.40 (4 x d, $^3J_{HH}$ = 6.0 Hz, 8H, cym-Ar**H**), 3.08 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, cym-C**H**), 1.99 (s, 6H, p-C**H₃**), 1.38 (d, $^3J_{HH}$ = 6.9, 12H, *i*Pr-C**H₃**) ppm.

<u>ESI-MS (CH₃CN):</u> *m/z:* 449.1 (100%, [M]⁺)

6.4.   General procedure for transfer hydrogenation reactions

All experiments were performed under N₂ using standard Schlenk techniques. Commercially available 2-proponol was distilled and stored over 3 Å molecular sieves. Aliquot purification was performed in open air with commercially available hexane and diethyl ether without further purification.

In a typical run, the catalyst (**3.3** or **3.4**, 0.010 mmol) was added to a two-neck round bottom flask, to which dry 2-propanol (4 mL) and the substrate (1.00 mmol) were added. The suspension was subjected to three freeze-thaw-degas cycles and then placed in an oil bath at 85 °C for 5 min. KOH (5.7 mg, 0.100 mmol) in 2-propanol (1 mL) was added to the mixture, which was stirred at 85 °C under a condenser.

At the desired sampling time, a 0.2 mL aliquot of the reaction mixture was drawn *via* a syringe and quenched with pentane (1.0 mL). The mixture was filtered through celite which was washed with DCM (3 x 1 mL) and the organic mixture washed with 1M HCl (1 mL). The organic solvent was removed under reduced pressure at room temperature. The residue was dissolved in CDCl₃ and analysed by ^1H NMR. Percent conversions were determined by comparing the integrations of aromatic peaks from the substrate and product.

6.5. General procedure for phenylacetylene CO_2 insertion

All experiments were performed under N_2 using standard Schlenk techniques. DMF was collected from an SPS and stored over 3 Å molecular sieves under N_2. Following acidification, work-up was performed in open air with commercially available reagents.

In a typical run, phenylacetylene (25 μL, 0.227 mmol) and the complex (0.014 mmol) were added to a suspension of cesium carbonate (0.089 mg, 0.273 mmol) in dry DMF (2.5 mL). The suspension was subjected to three freeze-thaw-degas cycles, the flask backfilled with CO_2 from a balloon on the final cycle. The suspension was allowed to stir at room temperature for 24 h. After 24 h, 1 M LiCl (20 mL) was added and the pH adjusted to < 1 using conc. HCl. The organics were extracted with diethyl ether (3 x 20 mL) and the combined organics dried over Mg_2SO_4, filtered and evaporated to dryness to yield the crude product.

The residue was dissolved in $CDCl_3$ and analysed by ^{1}H NMR. Percent conversions were determined by comparing the integrations of aromatic peaks from the substrate and product.

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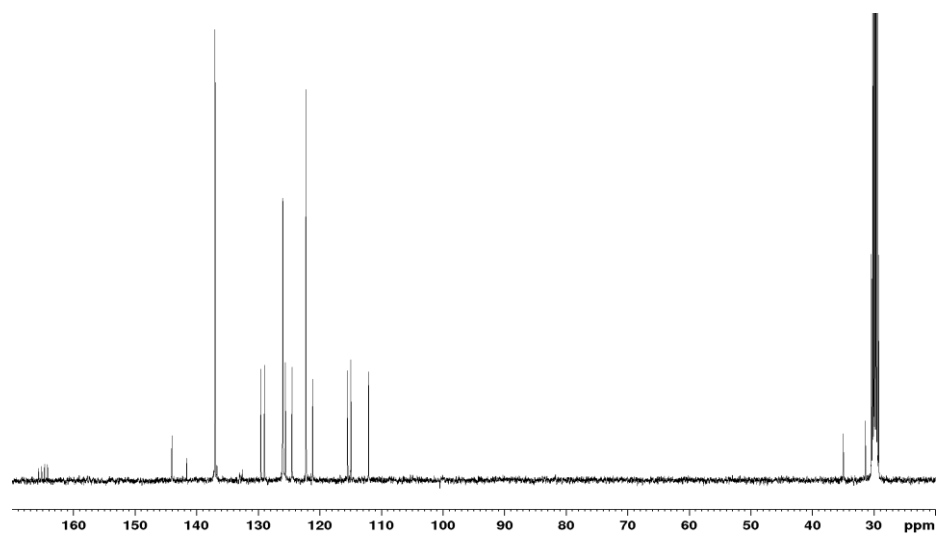
Appendix A: Spectral Data

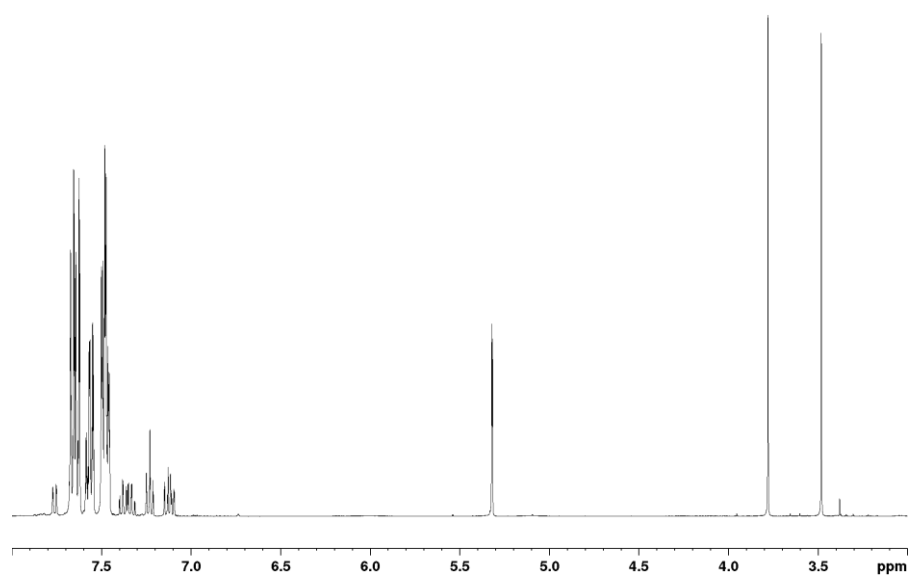**(NC$^{\text{NHC}}$)BPh$_4$ (2.4)**

^{1}H NMR (400 MHz)
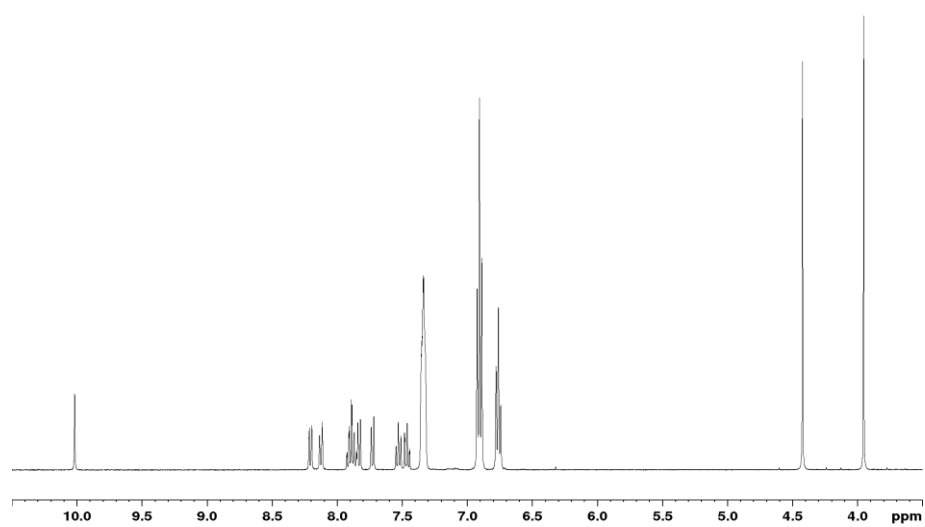
^{13}C NMR (100 MHz)

RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$ (3.1)

^{1}H NMR (400 MHz)

^{13}C NMR (100 MHz)
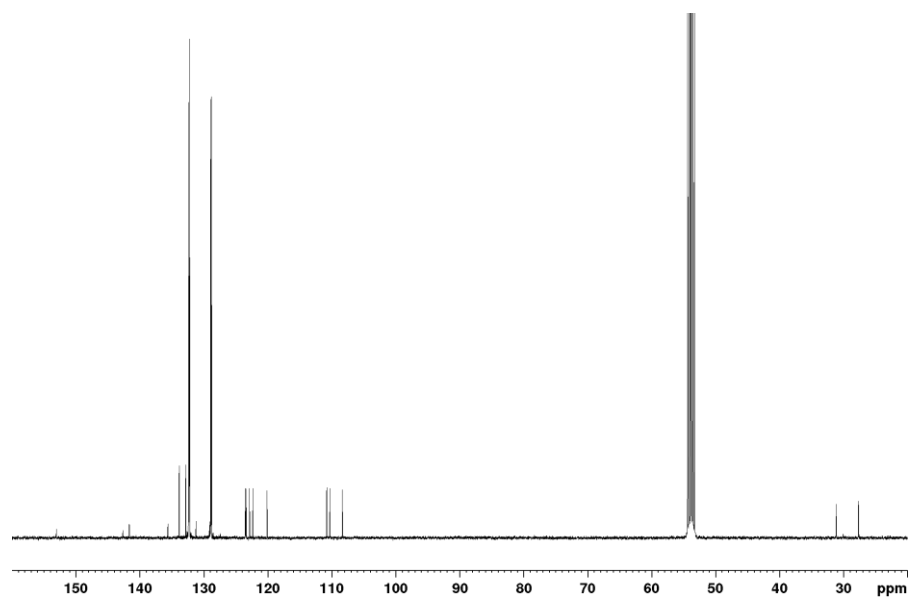
[RuCl(C^{NHC}C^{NHC})(η^6-C_6H_6)]BPh_4 (3.3)

^{1}H NMR (400 MHz)
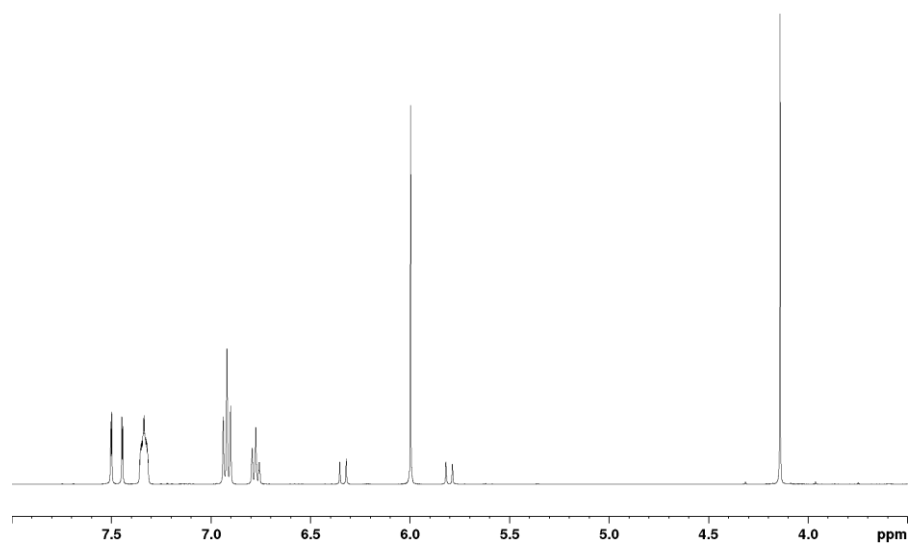
^{13}C NMR (100 MHz)
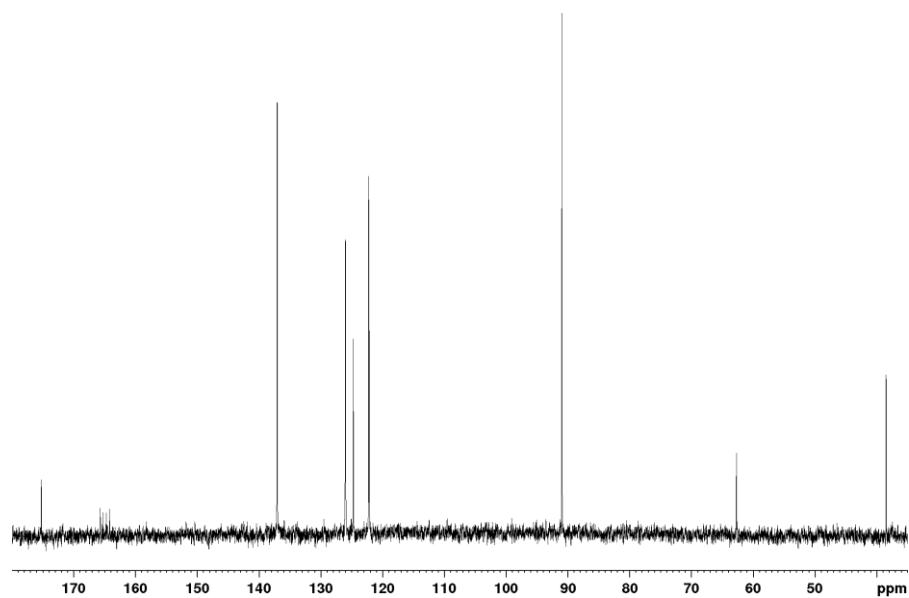
[RuCl(C^{NHC}C^{NHC})(η^6-*p*-cym)]BPh_4 (3.4)

^{1}H NMR (400 MHz)
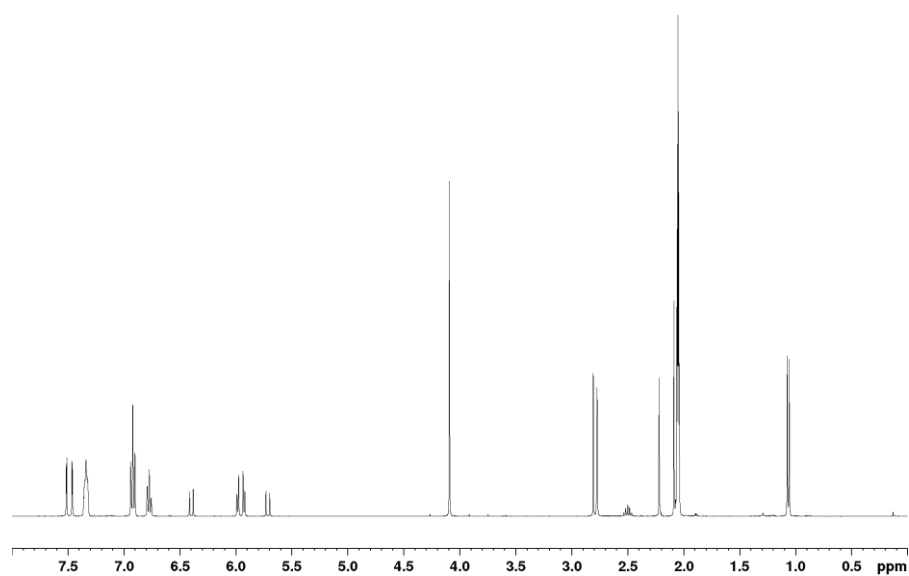
^{13}C NMR (100 MHz)
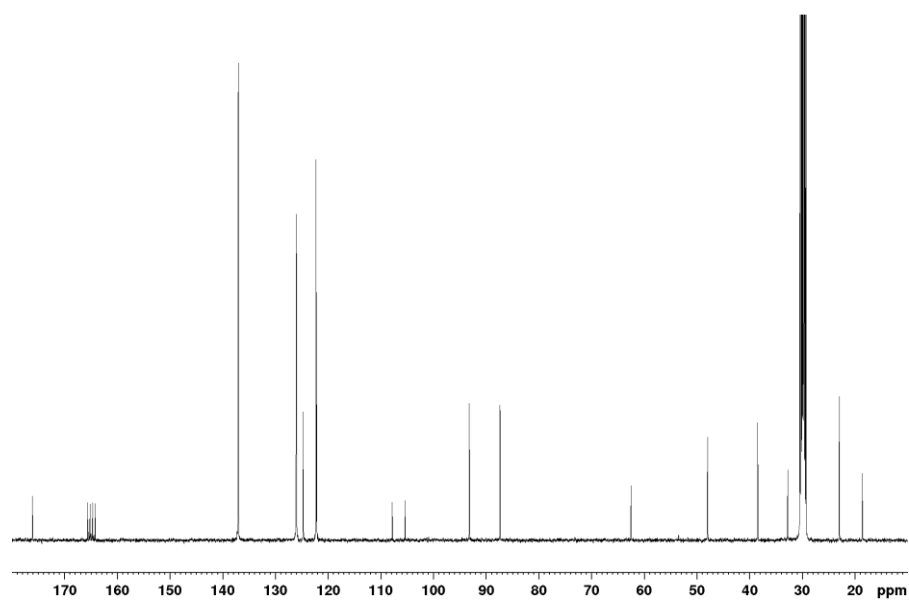
[Ag(C^{NHC}C^{NHC})]$_2$(BPh$_4$)$_2$ (3.5)

^{1}H NMR (400 MHz)
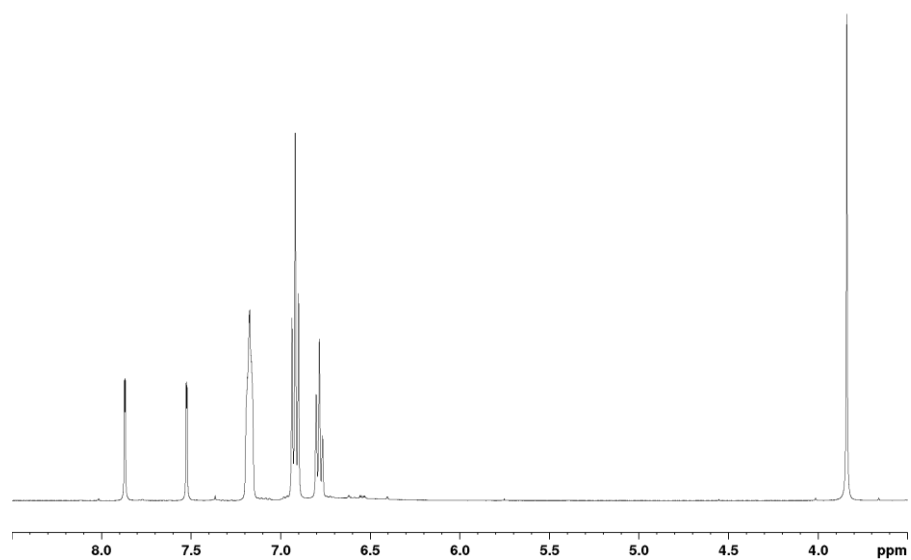
^{13}C NMR (100 MHz)
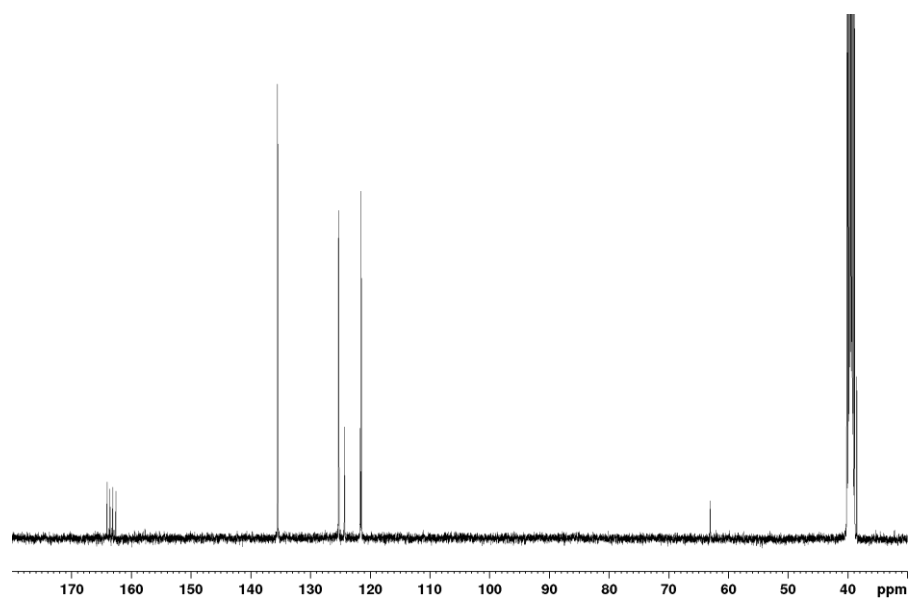
Appendix B: List of Numbered Compounds

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

VIa X = Br	
VIb X = N$_2$	

VIIa Ar = DIPP	
VIIb Ar = Mesityl	

VIII

IX

Xa R = H, R' = H	
Xb R = CH$_3$, R' = ^{i}Pr	

XIa

XIb

XIc

XIIa R = R' = H	
XIIb R = Me, R' = iPr	

XIII

XIVa arene = C$_6$H$_6$	
XIVb arene = p-cym	
XIVc arene = C$_6$Me$_6$	

XV

XVI

XVIIa X = CH$_2$	
XVIIb X = O	

XVIIIa X = CH$_2$	
XVIIIb X = O	

2.1

2.2

(NC^{NHC})I
2.3

(NC^{NHC})BPh$_4$
2.4

2.5

2.6

2.7

(C^{NHC}C^{NHC})Br$_2$
2.8

RuCl$_2$(NC^{NHC})(PPh$_3$)$_2$
3.1

[RuCl(NC^{NHC})(p-cym)]BPh$_4$
3.2

[RuCl(C^{NHC}C^{NHC})(C$_6$H$_6$)]BPh$_4$
3.3

[RuCl(C^{NHC}C^{NHC})(p-cym)]BPh$_4$
3.4

[Ag(C^{NHC}C^{NHC})]$_2$(BPh$_4$)$_2$
3.5

[RuCl(C^{NHC}C^{NHC})(p-cym)]$_2$(BPh$_4$)$_2$
3.6

(NC^{NHC}N)BPh$_4$
3.7

[Ag(NC^{NHC}N)]BPh$_4$
3.8

3.9   X = Cl
3.10   X = Br

Appendix C: X-Ray Crystallographic Data

Table AC.1. Crystallographic parameters for [RuCl($C^{NHC}C^{NHC}$)(η^6-C_6H_6)]BPh$_4$ (**3.3**).	
Formula	C$_{38}$ H$_{38}$ N$_4$ Cl B Ru
Space Group	P 2$_1$/n
Cell Lengths	**a** 10.206(3) **b** 20.456(7) **c** 16.049(5)
Cell Angles	**α** 90 **β** 90.762(13) **γ** 90
Cell Volume	3350.32
Z, Z'	**Z**: 4 **Z'**: 0
R-Factor (%)	5.05

Table AC.1. Crystallographic parameters for [RuCl($C^{NHC}C^{NHC}$)(η^6-p-cym)]BPh$_4$ (**3.4**).	
Formula	C$_{43}$ H$_{46}$ N$_4$ Cl B Ru
Space Group	P 2$_1$ 2$_1$ 2$_1$
Cell Lengths	**a** 10.0308(8) **b** 14.0422(10) **c** 26.1734(18)
Cell Angles	**α** 90 **β** 90 **γ** 90
Cell Volume	3689.64
Z, Z'	**Z**: 4 **Z'**: 0
R-Factor (%)	6.71