UNIVERSITY OF SOUTHAMPTON

FACULITY OF SCIENCE AND ENGINEERING

School of Chemistry

Studies of *N*-Heterocyclic Carbenes Functionalised with a Cyclopentadienyl Type Moiety

by

Stephen Paul Downing

Thesis for the degree of Doctor of Philosophy

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UNIVERSITY OF SOUTHAMPTON

ABSTRACT

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New NHC ligands functionalised with indenyl and fluorenyl moieties have been synthesised. A number of metal complexes containing these ligands have also been synthesised and many characterised by X-ray crystallographic techniques.

A number of imidazolium salts functionalised with a cyclopentadienyl type moiety have been synthesised including: 1-[2-(9-9H-fluorenyl)ethyl]-3-(2,6-diisopropylphenyl)-2H-imidazol-1-ium bromide; 1-[2-(2,7-di-tert-butyl-9H-fluoren-9-yl)-ethyl]-3-(2,6-diisopropyl-phenyl)-3H-imidazol-1-ium bromide; 3-(2,6-diisopropylphenyl)-1-[2-(3H-inden-1-yl)-ethyl]-2H-imidazolium bromide; 3-(2,6-Diisopropyl-phenyl)-1-[2-(3H-(4,7-dimethyl)inden-1-yl)-ethyl]-3H-imidazolium bromide.

A number of main group metal complexes with ligands derived from the imidazolium salts have been synthesised including: 1-[2-(9-Fluorenyl)ethyl]-3-(2,6 di-iso-propylphenyl)-imidazol-2-ylidene potassium; 1-[2-(inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-1-ylidene potassium; 1-[2-((3,5-dimethyl)inden-1-yl)ethyl]-3-(2,6 diisopropyl-phenyl) -imidazol-1-ylidene potassium; 1-[2-(9-[2,7-Di-tert-butylfluorenyl)ethyl]-3-(2,6-di-iso-propylphenyl)-imidazol-2-ylidene potassium; 1-[2-(9H-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3H-imidazol-1-yl silver bromide; 1-[2,5-dimethyl-2-(inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl)-3H-imidazol-1-yl silver bromide; 1-[2-(9H-fluoren-9-yl)ethyl]-3-(2,6 di-iso-propylphenyl)-2H-imidazol-1-ylidene zinc HMDS bromide; 1-[2-(9H-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-2H-imidazol-1-ylidene zinc neopentyl bromide;1-[2-(1-3H-indenyl)ethyl]-3-(2,6 di-iso-propylphenyl)-2H-imidazol-1-ylidene copper bromide.

A number of early transition metal complexes with ligands derived from the imidazolium salts have been synthesised including: 3-(2,6-Diisopropyl-phenyl)-1-[2-(fluorenyl-9-yl)-ethyl]-imidazol-2-ylidene titanium dimethylamide chloride; 3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(2,5-(dimethylindenyl)-ethyl]-imidazol-2-ylidene zirconium trichloride; 3-(2,6-Diisopropyl-phenyl)-1-[2-(1-indenyl)-ethyl]-imidazol-2-ylidene vanadium dimethylamide bromide; 3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(2,5-dimethyl)indenyl)-ethyl]-imidazol-2-ylidene vanadium dichloride; Bis[3-(2,6-Diisopropyl-phenyl)-1-[2-(9H-fluoren-9-yl)-ethylimidazol-2-ylidene] chromium dibromide.

The following late transition metal complexes with ligands derived from the imidazolium salts have been synthesised: 3-(2,6-Diisopropyl-phenyl)-1-[2-(9-9H-fluorenyl)-ethyl]-imidazol-2-ylidene –rhodium COD bromide; 3-(2,6-Diisopropyl-phenyl)-1-[2-(3-1H-indenyl)-ethyl]-imidazol-2-ylidene –rhodium COD bromide; 3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(4,7-dimethyl)-1H-indenyl)-ethyl]-imidazol-2-ylidene –rhodium COD chloride; 3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]-1H-indenyl)ethyl]-imidazol-2-ylidene rhodium carbonyl; 3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]indenyl)ethyl]-imidazol-2-ylidene –Iridium biscarbonyl; 3-(2,6-Diisopropyl-phenyl)-1-[2-(9-9H-fluorenyl)-ethyl]-imidazol-2-ylidene -nickel bromide (II); 3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]-1H-indenyl)ethyl]-imidazol-2-ylidene -nickel bromide (II).

3-(2,6-Diisopropyl-phenyl)-1-[2-(9-9H-fluorenyl)-ethyl]-imidazol-2-ylidene -nickel bromide (II) was shown to be an active catalyst for ethylene polymerisation.

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Abbreviations

DCM	dichloromethane
THF	tetrahydrofuran
THT	tetrahydrothiophene
DMSO	dimethylsulfoxide
NMR	nuclear magnetic resonance
ppm	parts per million
eV	electron Volt
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
NHC	*N*-heterocyclic carbene
HMDS	hexamethyldisilazide
LDA	lithium di-*iso*-propyl amine
COD	cyclooctadiene
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadiene
iMes	1-3-di(1,3,5-trimethylphenyl)imidazol-2-ylidene
BuLi	butyllithium
n	normal
sec	secondary
tert	tertiary
M	A metal
pK_a	acid dissociation constant
Z	Number of molecules in unit cell
V	Volume of unit cell

Chapter 1

Introduction to Carbene and Cyclopentadienyl Ligands

1 Introduction to Carbene and Cyclopentadienyl Ligands

1.1 Carbenes

Carbenes are defined as chemical entities containing two-coordinate carbon atoms with two non-bonding electrons and no formal charge on the carbon.[1] They are generally highly transient species and not isolable unless stabilised.

Skell reported the first intentional use of a carbene in organic chemistry in 1958,[2] but it was not until 1964 that the first metal complex containing a carbene was reported by Fischer,[3] introducing carbenes to the repertoire of organometallic chemistry.

1.2 Singlet and Triplet Carbenes

1.2.1 Electronic Structure of Singlet and Triplet Carbenes

The ground-state spin multiplicity, Figure 1.1, is a fundamental feature of carbenes that dictates their reactivity.[4] The carbene ground-state is related to the relative energy of the σ and p_π orbitals. The singlet ground-state is favoured by a large σ-p_π separation; Hoffmann determined that a value of at least 2 eV is necessary to impose a singlet ground state, where as, a value below 1.5 eV leads to a triplet state.[5]

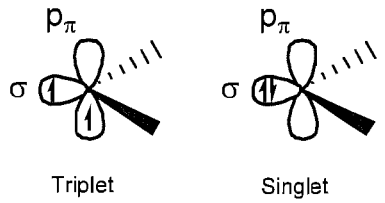


Figure 1.1 Electronic configuration of triplet and singlet carbenes.

The substituents next to the divalent carbon play an important role in the determination of the multiplicity.[6,7,8] The σ non-bonding orbital is inductively stabilised by σ-withdrawing groups, while the p_π orbital is left unchanged, this increases the σ-p_π separation which favours the singlet state. The opposite is true for σ-donating groups.

Mesomeric effects can play a more significant role than inductive effects.[9,10] Mesomeric effects are caused by the introduction of interaction between the p_π orbital of the carbene and the π-orbitals of the surrounding groups. In the case of singlet carbenes with two π-donating groups α- to the divalent carbon (OR, SR, NR_2, PR_2, etc.) the energy of the vacant p_π orbital is increased. Since the energy of the σ-orbital remains much the

same, the σ-p_π separation is increased stabilising the singlet state. Donation of lone pairs from both substitiuents, as is the case where the divalent carbon is the C-2 carbon formed from a imidazole based hetero cyclic ring, gives a three-centre four-electron system, giving the carbon -hetero atom bonds some multiple-bond character and the carbene carbon a slight negative charge, Figure 1.2.

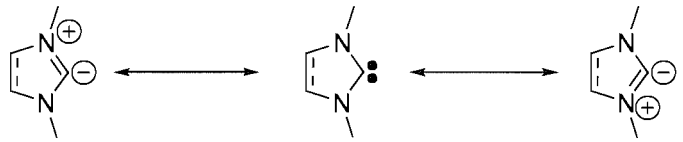
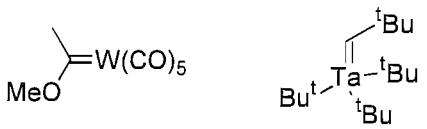


Figure 1.2 Electron delocalisation in imidazol-2-ylindenes and imidazolin-2-ylidenes.

The filled σ-orbital renders the carbene nucleophilic, and the empty p_π orbital electrophilic, therefore singlet carbenes are ambiphilic. However, they are often prevented from acting as electrophiles by electron donation into the formally empty p_π orbital by the surrounding substituents. Triplet carbene tend to react as biradicals.

1.2.2 Schrock and Fischer Carbene Complexes

When complexed to a metal, singlet carbenes of the type CR(XR'), where X = hetero atom, are called Fischer type carbene complexes and triplet carbenes are called Schrock type carbene complexes. Fischer reported the first carbene metal complex **1.1** in 1964.[3] It was not until 1974 that Schrock reported the first alkylidene complex **1.2**.[11]



1.1 **1.2**

Figure 1.3 The first Fischer and Schrock type carbene complexes.

Fischer carbene complexes have electron donating substituents located on the carbene carbon and are electrophilic in nature. The HOMO centred on the metal and the LUMO centred on the carbene carbon. Schrock carbene complexes tend to have hydrogen or alkyl substitution on the carbene carbon and act as nucleophiles and form olefinic-type bonds, Figure 1.4.[12] Also of note is that Schrock carbene complexes exhibit much more π-back-bonding therefore more M-C double bond compared to Fischer carbenes.

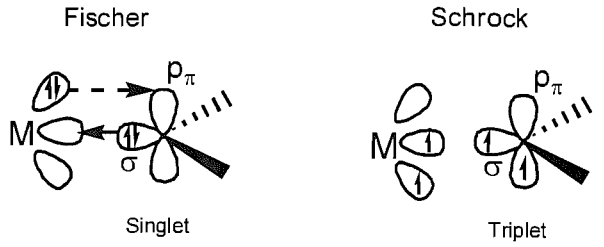
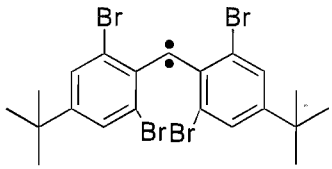


Figure 1.4 Orbital diagram of Fischer and Schrock carbenes.

1.3 Stable Carbenes

1.3.1 Stable Triplet Carbenes

Due to their highly reactive nature and affinity for electrons it is extremely difficult to produce a stable triplet carbene. One of the most stable triplet carbenes **1.3**, Figure 1.5, was reported by Tomioka *et al.* in 1996,[13] the carbene has a half life of sixteen seconds in solution and is indefinitely stable if frozen in a THF glass. To date, no triplet carbenes have been isolated in the crystalline state.



1.3

Figure 1.5 The most stable triplet carbene synthesised to date.

1.3.2 Stable Singlet Carbenes

There are many different types of stable singlet carbenes known in the literature. The vast majority of singlet carbenes are of the diamino-type, as nitrogen substitution of the carbene carbon offers the best combination of electronic and mesomeric effects to stabilise the carbene.[9,10] However, there are also examples known where one of the amino substituents is replaced by a different hetero-atom. These include the examples shown in Figure 1.6: cyclic imidazolin-2-ylidenes **1.4**,[14] tetrahydropyrimid-2-ylidenes **1.5**,[15] imidazol-2-ylidenes **1.6**,[16] 1,2,4-triazol-5-ylidenes **1.7**,[17] 1,3-thiazol-2-ylidenes **1.8**[18], and acyclic diamino-**1.9**,[19] aminooxy- **1.10**[20] and animothiocarbenes.[20] Of these, the vast majority of examples in the literature are based on imidazol-2-yilenes and imidazolin-2-ylidenes, due to the facile synthesis of these species.[21]

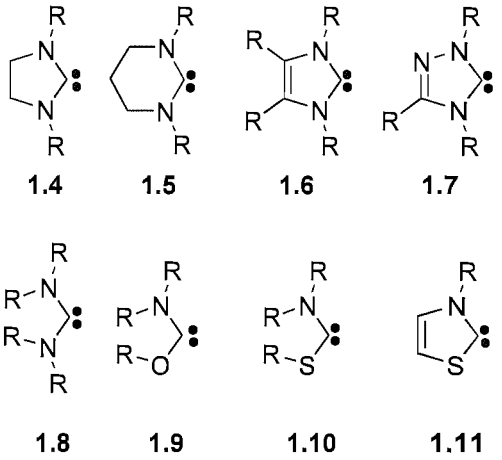
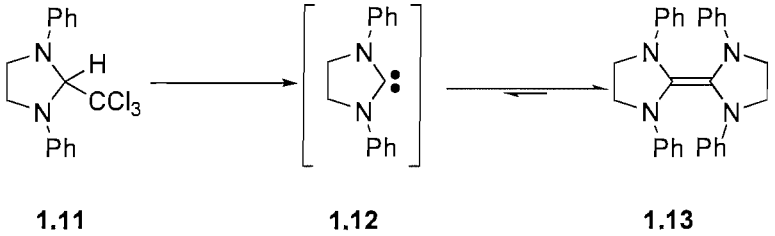


Figure 1.6 Examples of the types of amino-substituted stable singlet carbenes known in the literature.

One of the typical reactions of unstabilised singlet carbenes is to form electron-rich olefins, Scheme 1.1. This dimerisation can be prevented by adding steric bulk to the carbene to slow the kinetics of the reaction. Wanzlick made attempts to isolate a free carbene, 1,3-diphenylimidazolium-2-ylindene **1.12** by the thermal elimination of chloroform from **1.11**, but only the electron-rich olefin **1.13** was identified.[22] However, in the case of unsaturated NHCs the equilibrium is shifted to give free NHC.



Scheme 1.1 Wanzlick's attempt at synthesising a free imidazol-2-ylindene.

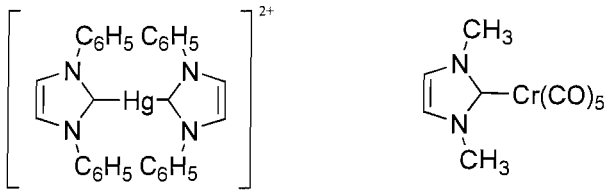
The eponymous Wanzlick equilibrium between the free carbene and the dimer has now recently been shown to exist for a limited number of systems.[23,24,25] The stability of the carbenes to withstand dimerisation was increased by the neighbouring π system (imidazol-2-ylidene and benzylimidazol-2-ylidene). With this understanding of electronic stabilisation sterically unhindered free singlet carbenes have been isolated.[1]

1.4 The Early Days of *N*-Heterocyclic Carbenes

1.4.1 The First Metal NHC Complexes

The first *N*-heterocyclic carbene complexes were reported simultaneously by Öfele **1.14**[26] and Wanzlick *et al.* **1.15**[27] in 1968, Figure 1.7. Both groups synthesised their metal

complexes by reacting the imidazolium salt with a metal compound of sufficient basicity to deprotonate the imidazolium salt and generate the free carbene *in situ* which in turn gave the metal complex.

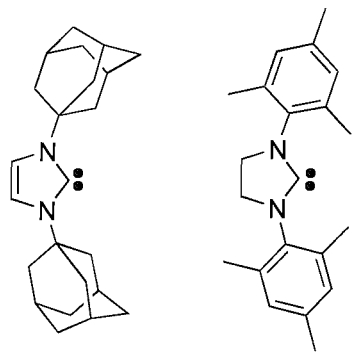


1.14 **1.15**

Figure 1.7 The first transition metal NHC complexes isolated by Öfele and Wanzlick *et al.*

1.4.2 The First Stable Crystalline Carbene

In 1991, Arduengo isolated the first crystalline carbene, 1,3-di-1-adamantylimidazol-2-ylidene **1.16**.[28] It was claimed that the ability to isolate this complex was due to its steric and electronic properties, however it was later shown that the steric factors are not so important, in the case of imidazole-type carbenes, by the isolation of less sterically encumbered imidazol-2-ylidenes.[1] Arduengo then went on to show that the saturated imidazolin-2-ylidenes **1.17** could also be isolated.[29]



1.16 **1.17**

Figure 1.8 The first stable crystalline imidazol-2-ylidene and imidazolin-2-ylidene isolated by Arduengo.

It was the isolation of what were previously thought unstable compounds that has led to the recent surge in interest in carbene compounds and their complexes over the last 15 or so years. Ever since the isolation of carbenes as bottleable compounds their inorganic and organometallic chemistry has gained enormously in versatility and depth,

such is the interest in NHC complexes that several reviews have been made in the area in recent years.[21,30,31,32,33,34,35,36]

1.5 *N*-Heterocyclic Carbene Complexes

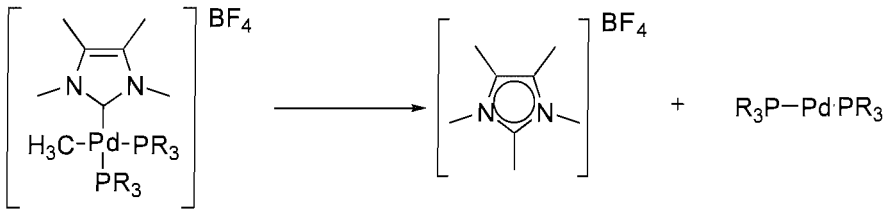
Although they are interesting species in themselves, *N*-heterocyclic carbenes are of more interest to organometallic chemist when complexed to metals. There are however, a few examples of NHCs being used as catalysts in organic transformations, Nolan reported *N*-heterocyclic carbenes as versatile nucleophilic catalysts for transesterification/acylation reactions[37]; later Nolan also reported the synthesis of phosphorus esters by transesterification mediated by N-heterocyclic carbenes.[38] In 1995, Hedrick reported the use of NHCs as catalysts for the ring opening polymerisation of lactides. Hedrick used the alcohol adducts of saturated NHCs as the catalyst precursors.[39]

1.5.1 Properties of N-Heterocyclic Carbenes as Ligands

There is a striking similarity between NHCs and trialkylphosphines, particularly the ligand properties and metal complex synthesis.[40,41] *N*-Heterocyclic ligands are two-electron σ-donors with little π-accepting ability.[42,43] The reason for this lack of π-accepting ability is that the lone pairs from the N-substituents are donating electron density into the π orbitals and raising the energy level of the orbital. They are more comparable to P-, N-, O-donating ligands rather than classical Schrock or Fischer carbenes.[32] Nolan concluded that NHCs act as better donors than the best phosphine donor ligands with the exception of the sterically demanding bis(adamantyl) carbene.[44]

N-Heterocyclic carbene have the adventitious property of forming strong bonds to metal centres, especially late transition metals, with little tendency for dissociation.[45] However the case for early metals is less clear, but in the case of groups 4 and 5 the NHC may be able to dissociate.[46] In the case of the f-block metals, current research suggests that the carbenes may be very labile.[36]

Although many consider them as completely inert, metal to *N*-heterocyclic carbene bonds can display reactivity such as metal to metal transfer,[47,48] and also alkyl-carbene elimination reactions, Scheme 1.2, and insertion to metal-carbene bonds[49] which have clear implications for complex synthesis and catalysis.[50]



Scheme 1.2 Reaction showing a carbene-alkyl elimination from a palladium complex.

1.5.2 Metals

Herrmann summed up the potential of NHCs as ligands by saying '*N-heterocyclic carbenes have become universal ligands in organometallic and inorganic chemistry. They not only bind to any transition metal, be it in a high or low oxidation state, but also to main groups elements such as beryllium, sulphur and iodine.*'[21]

The chemistry of NHC complexes with late transition metals is now well established and there are a multitude of examples in the literature. However, much less is known about the NHC complexes of early transition metals as there have only been a relatively few reports to date, especially of group 4, 5 metals with simple NHC ligands.[51,52]

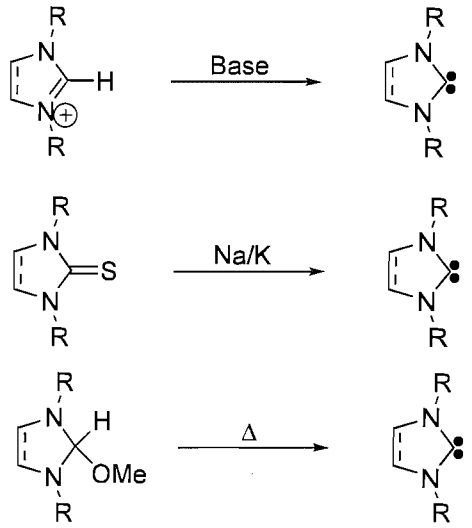
1.6 Synthetic Routes to *N*-Heterocyclic Carbene Complexes

NHC complexes to almost all of the metals in the periodic table are known. However, the preparation of these compounds is based mainly on four methods: (i) complexation of the free carbene, (ii) *in situ* deprotonation of imidazolium salts, (iii) cleavage of electron-rich olefins by low oxidation state metal complexes and (iv) NHC transfer reactions from readily available NHC complexes.

1.6.1 Complexation of Preformed NHC Ligands.

Various methods have been employed to prepare the free NHCs from suitable precursors, Scheme 1.3. The imidazolium salts can be deprotonated by NaH and KO^{t}Bu or dimsyl-anions in THF.[1,28] The use of NaH in liquid ammonia has also been reported, and is a high yielding and general method.[53,54] In some case the use of KHMDS proves to be the best method of deprotonation.[55] The use of LDA has also been reported.[56] Cyclic thioureas can be converted to the free NHC by reaction with sodium or potassium metal.[16] 1,3-Bis-*neo*-pentylbenzimidazolin-2-ylidene has been isolated using this method.[57] Elimination of small molecules such as chloroform[22] or methanol[58,59] has also been used.

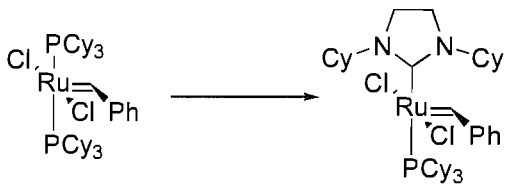
It is also possible to produce the free carbene from the imidazolium salt by direct electrochemical reduction.[60]



Scheme 1.3 General methods for the formation of a free carbenes.

The main advantage of using the preformed, free NHCs is that less consideration has to be given to the nature of the metal centre. Other methods may require the presence of basic groups or other special reactivity of the metal centre.

The preformed NHC can react with a variety of metal complexes. Examples include reaction of the free NHC with $[Cl_2M(COD)]_2$ (M = Rh, Ir) to cleave the dimer and give the monomeric complex.[61] Phosphine displacement is another common method for the production of NHC complexes, reaction of bis(tri-*ortho*-tolylphosphine)palladium (0) with free NHCs gives either the mono or bis-carbene complex dependant on the sterics of the NHC.[62] One of the best examples of phosphine exchange is shown in Scheme 1.4, the synthesis of Grubbs' second generation catalyst **1.19** from the first generation catalyst **1.18**.[63]



1.18 **1.19**

Scheme 1.4 Synthesis of Grubbs' second generation catalyst form the first generation catalyst, SIMes, - PCy_3.

Coordinated solvents such as THF can also be exchanged.[64]

1.6.2 In Situ Deprotonation of Ligand Precursors

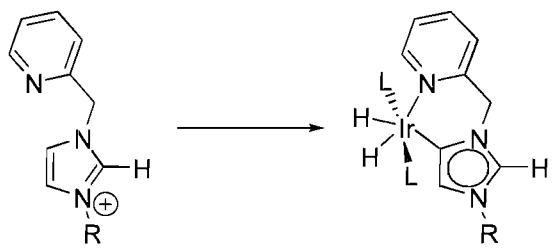
The *in situ* complexation of the ligand has the advantage of not having to prepare the free NHC. In cases where the carbene is unstable or difficult to handle, this approach may be the only means to prepare the desired complex.

Imidazolium salts can be deprotonated *in situ* by a basic metal complex: Öfele prepared some of the first *N*-heterocyclic carbene complexes with this method.[26,65] The limitation of this method is that the appropriate metal precursor needs to be readily available.

Deprotonation by basic anions is also possible. Metal alkoxides or acetate salts are frequently used; one potential problem of this method is that the counter ion from the imidazolium salt is incorporated into the new metal complex. Wanzlick synthesised one of the first reported HNC complexes from mercury acetate using this method.[22] Similarly palladium (II) and nickel (II) complexes have been prepared.[54,66,67]

The reaction of rhodium and iridium alkoxides with imidazolium salts also leads to the NHC complexes at room temperature.[54,68] Basic silver(I) oxide [69] or silver carbonate[70] are useful precursors to silver NHC complexes, which are useful as transfer reagents.

There are examples in the literature where the direct reaction of an imidazolium salt with a basic metal complex leads to an 'abnormal' binding mode, in which the carbene is formed on a carbon other than the C-2 carbon. In one example reported by Crabtree, Scheme 1.5, a pyridyl functionalised imidazolium salt **1.20** is reacted with an iridium hydride complex to give an imidazole-5-ylidene **1.21**.[71]

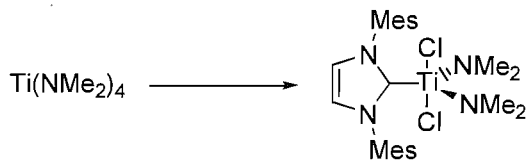


1.20 **1.21**

Scheme 1.5 Formation of a non-classically bonded *N*-heterocyclic carbene, $IrH_5(PPh_3)_2$, refluxing THF.

An example that is important in the case of early transition metals is the deprotonation of an imidazolium salt by coordinated amide ligand.[51] In the example in

Scheme 1.6 two equivalents of imidazolium salt are deprotonated, but only one is seen in the complex **1.22**; this gives some insight into the strength of the early metal carbene bond.

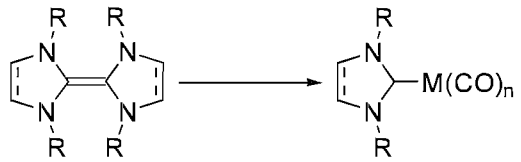


1.22

Scheme 1.6 In situ deprotonation of an imidazolium salt by an early transition metal amide, 1,3-bis(mesityl)imidazole, THF, RT, overnight.

1.6.3 Cleavage of Electron-Rich Olefins

One of the earlier methods to form NHCs was to thermally cleave electron rich enetetramines, Scheme 1.7, with a metal precursor usually a carbonyl. Heating of tetraaminoethylenes **1.23** in refluxing toluene in the presence of suitable precursors such as manganese, iron, ruthenium cobalt or nickel carbonyls gives the corresponding NHC complexes **1.24**.[72,73,74] The exchange of phosphines is also possible for example in the Wilkinson catalyst.[75]



1.23 **1.24**

Scheme 1.7 Cleavage of an electron rich olefin by a metal carbonyl, metal carbonyl, refluxing toluene.

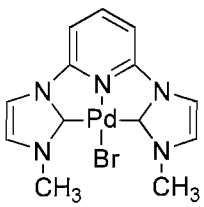
1.6.4 Ligand Transfer Reactions

Carbene transfer from NHC complexes of chromium, molybdenum, and tungsten pentacarbonyl is possible. The NHC ligands have been successfully transferred to rhodium (I), palladium (II), platinum (II), copper (I), silver (I) and gold (I).[47,48] Both silver and gold NHC complexes have received attention as NHC transfer reagents in recent years.[34]

1.7 Functionality and Design of *N*-Heterocyclic Carbene Complexes

1.7.1 Catalysis – Late Transition Metals

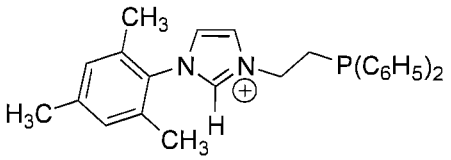
NHC complexes have proved to be extremely popular as catalysts, due to their similarity to already established phosphine ligand complexes. After initial patent reports; the first publications of the use of NHC complexes in catalysis appeared in 1995, with the description of the Heck coupling of aryl bromides and chlorides.[54] Carbene catalysts have many advantages over phosphine catalysts; they are structurally rigid, and the carbene is more tightly bound leading to less desolvation of the ligand, in turn leading to less catalyst decomposition and deactivation, they also have a long shelf life and are stable to oxidation and are easy to access compared to phosphine ligands. In addition, the steric characteristics of the NHC ligands are fundamentally different to the phosphines, the phosphines are generally considered as cones whilst the NHCs are considered as wedges. A catalyst **1.25**, Figure 1.9, that is extremely stable as a result of its 'pincer-type' tridentate C,N,C- ligand has been reported by Crabtree[76] and others. This catalyst can remain active for the coupling of aryl bromides at 184 °C in air.



1.25

Figure 1.9 A highly stable C,N,C tridentate catalyst for Heck coupling reactions.

Fürstner has demonstrated a general and user friendly approach for the Suzuki coupling of aryl chlorides, generating the catalyst in situ from palladium acetate and imidazolium salt.[77] The best results being obtained from 1,3-bis(isopropyl)imidazolium salt.[78] Highly active and very stable catalysts for Heck, Suzuki and Sonogashira couplings were found in certain palladium (II) complexes of NHCs with dangling N-substituents.[79] High efficiencies in Heck coupling of aryl bromides were reported by Nolan, who used palladium in the presence of C,P chelating NHC ligands derived from a sterically demanding imidazolium salt **1.26**.[80]

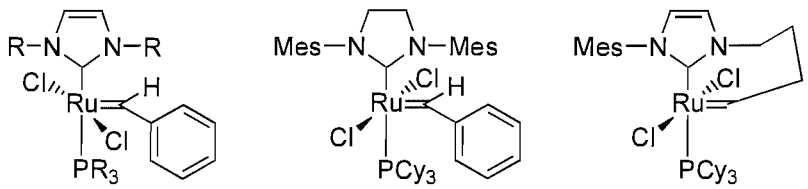


1.26

Figure 1.10 An imidazolium salt that is a precursor for a highly actively Heck catalyst.

Another important class of catalysts are olefin metathesis catalysts: overviews of this area have been given by Grubbs[81] and Fürstner.[82]

Grubbs reported the saturated NHC complex **1.29** in Figure 1.11 as an improvement on his second generation catalyst **1.28**.[83] Using a saturated NHC further stabilises the complex, due to the increased strength of the metal to carbene bond in saturated systems. Also shown in Figure 1.11 is an example of a functionalised NHC tethered with a Schrock carbene **1.30** reported by Fürstner.[84]

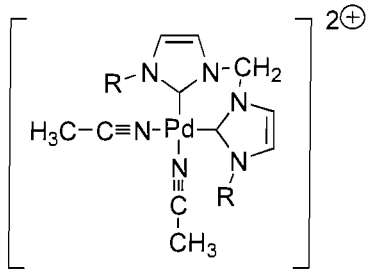


R = Aryl; R' = CH_3, Cyclohexyl

1.28 **1.29** **1.30**

Figure 1.11 A series of Grubbs type catalysts, containing *N*- heterocyclic imidazoles.

Yet another catalytic application was found in 2001: dicationic palladium (II) NHC complexes such as **1.31** in Figure 1.12 catalyse the copolymerisation of ethylene and CO under mild conditions and low pressure.[85]



R = mesityl, methyl

1.31

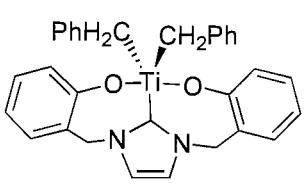
Figure 1.12 An effective ethylene-carbon monoxide co-polymerisation catalyst.

There are a few examples in the literature of asymmetric catalysis using chiral NHC complexes. For example the Burgess and Pfaltz groups have both reported chiral complexes based on NHC ligands functionalised with oxazoline units.[86,87]

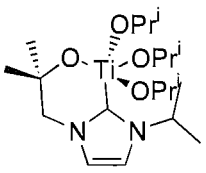
Due to the costs of the precious metals involved in catalysis, research was conducted to investigate ways to prevent catalyst leaching. One way of doing this is to anchor the catalyst to a solid support either polystyrene[88,89] or PEG.[90]

1.7.2 Catalysis – Early Metals

There are sparingly few examples in the literature of early metal NHC catalysts Figure 1.13. In one example reported by Arnold an alkoxy tethered NHC titanium complex **1.32** is able to catalyse the polymerisation of lactides.[91] Another example by Kawaguchi is a titanium bis(phenoxy)complex **1.33** capable of polymerising ethylene.[92] In another paper by McGuiness, the catalytic activity of first row early to middle transition metals with a bis(carbene)pyridine ligand **1.34** is discussed.[93] This ligand system is also discussed in a paper by Danopoulos.[94]



1.32



1.33

M = Ti, V, Cr, Mn

1.34

Figure 1.13 Examples of early transition metal catalysts.

While the catalytic activity of late transition metal complexes is well established, and comparable to the well understood phosphine systems, the early metals still need

investigation. However, this is complicated by the fact that the NHC ligand is more labile when complexed to an early transition metal[46]; it is apparent that early transition metals require extra functionality on their NHCs to improve the stability of the complexes to enable their use as catalysts.

1.8 Cyclopentadienyl Ligands

Ferrocene was first synthesised albeit serendipitously in 1948 by Miller, Tebboth and Tremain.[95] It was not until 1952 that the true structure of ferrocene was realised independently by Wilkinson[96] and Fischer.[97] Sandwich complexes are now known for a wide variety of metals in the periodic table.[95]

The indenyl analogue of ferrocene was first synthesised by Wilkinson in 1953.[98] More recently the indenyl effect has been studied; indene rings can undergo ring slippage from η^5 to η^3 hapticity, potentially increasing the reactivity of the complexes by coordinative unsaturation.[99]

1.8.1 Catalysts – Metallocene Complexes.

Marks reports catalytic hydroamination reactions of olefins with lanthanide bent metallocene complexes.[100,101] Bergman discovered that zirconocene bis(amide) could catalyse the addition of amines across alkynes and allene.[102] Such is the interest in the area that Doye published a microreview dedicated to group 4 metal complexes as hydroamination catalysts.[103]

1.8.2 Catalysts – Ansa Metallocene Complexes

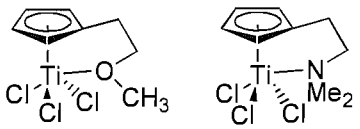
Also of great interest are *ansa*-bridged cyclopentadienyl complexes where the cyclopentadinyl rings are joined by a bridge of some description to prevent mutual rotation of the rings and control the stereochemistry of the catalytic product. The main use of these ligands is with zirconium in the polymerisation of propylene. [104,105]

The fundamental work into the use of metallocenes for polymerisation was carried out by Brintzinger[106] and Ewen[107].

Bercaw reports a series of complexes in which adding steric bulk to a cyclopentadieneyl ring changes the tacticicity of the product from syndiotactic to isotactic.[104] Undheim reported a variation on the simple *ansa* bridge by using a spirane-bridged *ansa* cyclopentadienyl-fluorenyl catalyst, the *ansa* bridge acts as the stereochemical control.[105]

1.8.3 Constrained-Geometry Cyclopentadienyl Complexes

Qichen reported the first example of a chelated cyclopentadienyl ligand on a titanium half-sandwich complex **1.35**, Figure 1.14.[108] With the discovery by Flores of the pendant aminoalkyl effect on the catalysis of olefins, effort has been focussed on the production of new more active and stable catalytic systems of this type.[109]

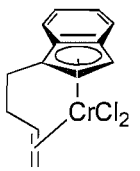


1.35 **1.36**

Figure 1.14 The first geometry-constrained cyclopentadienyl complex, reported by Qichen and the first geometry-constrained cyclopentadiene complex used in catalysis.

In 1998, Rausch investigated the effect of changing the sterics of the pendant anime group in both cyclopentadienyl and indenyl complexes of titanium and found that increasing the steric bulk decreases the catalytic activity for the polymerisation of olefins.[110] Later, chromium complexes containing geometry-constrained Cp ligands became of interest. Huang synthesised chromium complexes containing both pyridyl and aniline fictionalised Cp rings and these offered good catalytic activities.[111] Enders reports quinoline functionalised cyclopentadienyl complexes of chromium.[112]

Zagarian reported a number of nickel complexes containing indenyl ligands functionalised with pendant groups and the tuning of the pendant hemilabile moiety in order to improve catalysis, also described is how the pendant amino group helps prevent phosphine coordination improving the catalytic potential.[113] Later Zagarian reported similar complexes but with a cyclopentadiene tethered to an olefin ligand **1.37**, Figure 1.15, this ligand system was intended to help stop decomposition.[114]



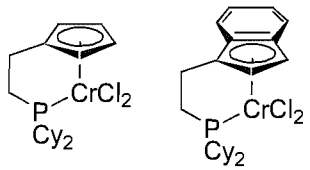
1.37

Figure 1.15 An olefin substituted indenyl complex.

In 2000, Hessen reported a geometry constrained titanium complex with an amide functionalised cyclopentadienyl moiety, which offers olefin polymerisation.[115] Hessen

also reported a vanadium complex with a geometry-constrained Cp amine ligand; unfortunately, this offers no catalytic activity.[116]

In 2006, Cole-Hamilton reported a geometry-constrained phosphine cyclopentadienyl ligand. Complexes of this ligand with cobalt, rhodium and iridium were tested for alcohol carbonylation.[117] Also reported by Jensen are constrained-geometry phosphine cyclopentadienyl **1.38** and geometry-constrained phosphine-indene **1.39** complexes of chromium and their use in olefin polymerisation.[118]



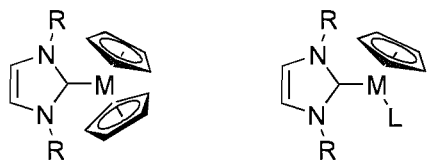
1.38 **1.39**

Figure 1.16 Geometry-constrained phosphine complexes of cyclopentadienyl and indenyl reported by Jensen.

Also discussed in the literature are constrained-geometry cyclopentadienyl ligands with anionic substituents namely amides, titanium dichloride complexes of these ligands act as a co-catalyst for the polymerisation of ethylene.[119] Such is the interest a review was recently written in this area.[120]

1.9 Complexes Containing Both Cyclopentadienyl Rings and NHC Ligands

Both NHCs and cyclopentadienyl ligands are now both ubiquitous in organometallic chemistry; however there are relatively few examples in the literature of complexes containing both these entities, and these all comprise of metallocene complexes **1.40** and half sandwich or piano stool complexes **1.41**.



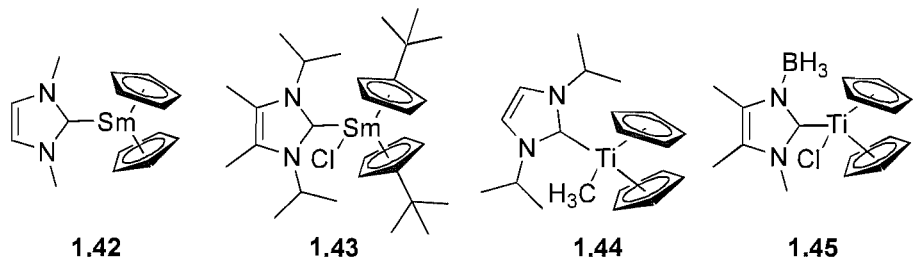
1.40 **1.41**

Figure 1.17 General form of metallocene NHC complex and a half sandwich complex containing an NHC.

1.9.1 Metallocene Complexes Containing an NHC

Metallocene complexes of samarium containing an NHC **1.42** were reported in 1994 by Arduengo *et al.*[121] The complexes consist of samarium with two pentamethyl cyclopentadienyl rings and either one or two NHC ligands. Samarium(III) analogues **1.43** were reported by Baudry-Barbier in 1998;[122] these complexes were tested for isoprene polymerisation but showed disappointing activity.

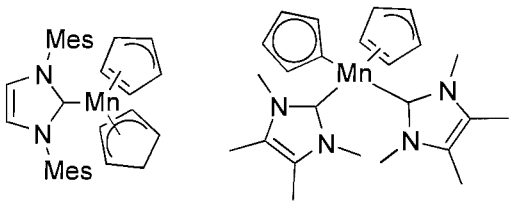
There are very few examples of early transition metal complexes containing both a cyclopentadienyl ring and an NHC; however, complexes based on titanocene **1.44** and zirconocene were published in 2002 by Erker.[123] These cationic complexes contain two cyclopentadienyl groups, an NHC and a methyl group to complete the coordination sphere. Also reported by Wacker in 2002 was a titanocene complex which contains a negatively charged borane substituted NHC **1.45**.[124]



1.42 **1.43** **1.44** **1.45**

Figure 1.18 Selected examples of metallocene NHC complexes.

Complexes containing manganese, cyclopentadienyl rings and NHCs have been reported by Cowley Figure 1.19.[125] Two of the complexes contain a bis-aryl NHC and two Cp rings **1.46** and the other contains two tetramethyl NHCs and two cyclopentadienyl rings **1.47**. However, in both cases the cyclopentadienyl rings are reported as having a less than η^5 interaction with the metal centre.



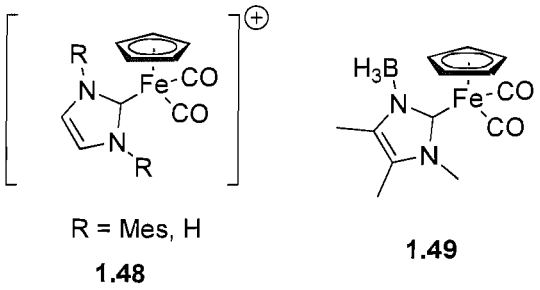
1.46 **1.47**

Figure 1.19 Manganocene NHC Complexes.

1.9.2 Half Sandwich Complexes

Half sandwich complexes are of the type $(Cp)M(NHC)(Ligand)_x$ and also sometimes referred to as piano stool complexes. These complexes are of interest due to their potential catalytic properties.

As early as 1979, Angelici reported the synthesis of iron half sandwich carbonyl complexes by the reaction of diamines with dithiocarbene complexes of iron.[126] Later in 1995, Fehlhammer reported the reaction of an iron cyano complex with a diamine to form an iron half sandwich complex **1.48**.[127] Half sandwich complexes of iron have been reported by Toupet [128] containing a single cyclopentadienyl ring and also a single NHC with the rest of the coordination sphere filled by ligands such as carbonyl or acetonitrile. Also reported by Wacker is an iron half sandwich complex containing a negatively charged borane substituted NHC **1.49**.[124]



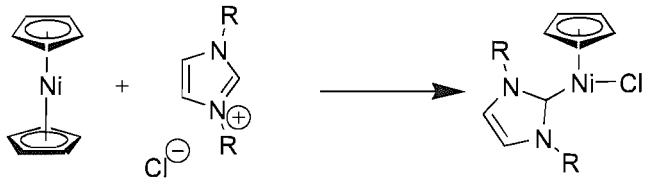
R = Mes, H

1.48

1.49

Figure 1.20 Selected iron half sandwich complexes.

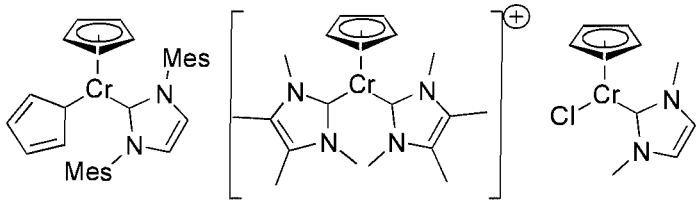
There have been several reports of half sandwich complexes containing nickel. The first reported half sandwich NHC complex of nickel was reported in 1999 by Cowley.[129] It was synthesised by reacting nickelocene with a bulky preformed carbene to give the half sandwich complex; it is interesting to note that one of the cyclopentadienyl rings becomes η^1. In 2000 the same group reported a more facile synthesis of nickel half sandwich complexes, Scheme 1.8.[130] This was achieved by taking nickelocene and reacting it directly with the IMes·HCl to give the corresponding chloride complex **1.50**. Later, in 2005, it was reported by Nolan that this route could be generalised and applied to a number of imidazolium salts.[131]



1.50

Scheme 1.8 A general facile reaction to synthesise nickel chloride half sandwich complexes.

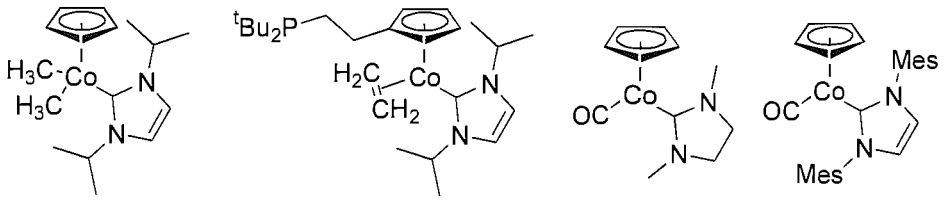
The first half sandwich NHC complex of chromium **1.51** was reported in 1999.[129] It is interesting to note that as well as being the first chromium half sandwich complex it is the first thermally stable chromium complex containing two cyclopentadienyl ligands (η^1 and η^5) and a simple two-electron donor. Previously, it was thought that linked cyclopentadienyl ligands would be required to isolate chromocene with a simple two electron donor, for example a monocarbonyl complex. In 1999, Tilset reported the reaction of chromocene and IMes.HCl to give the half sandwich chloride complex **1.53**, in an analogous reaction to nickelocene.[132] Another group of chromium complexes have been reported by Jolly[133] The reaction of $CrCl_2Cp(THF)$ with tetramethyl NHC displaces the THF and introduces the NHC ligand. This compound **1.52** was investigated for catalytic activity, however it was found to be disappointing.[134]



1.51 **1.52** **1.53**

Figure 1.21 Selected chromium half sandwich complexes.

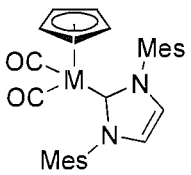
In 1991 Delgado described the mechanism of formation of a cobalt half sandwich NHC carbonyl complex. **1.54** [135] In 2001 Butenschön, reported the reaction of a phosphine functionalised Cp ethylene complex and an NHC, the NHC displaced the phosphine to give the half sandwich complex **1.55**.[136] A complex of cobalt **1.56** reported in the literature by Baird in 2002[137] was made by the NHC phosphine exchange with $CpCo(PPh_3)Me_2$ but was only synthesised in low yields. Half sandwich complexes of cobalt were reported by Tilset.[138] Reacting either Cp or Cp^* cobalt dicarbonyl or di(ethylene) with IMes gives the corresponding complex **1.57**.



1.54 **1.55** **1.56** **1.57**

Figure 1.22 Selected cobalt half sandwich complexes.

Half sandwich complexes of molybdenum and tungsten have been reported by Dioumaev in 2003, Figure 1.23.[139] These complexes consist of IMes, Cp, two carbonyls and a hydride. After hydride transfer to $Ph_3C^+B(C_6F_5)_4^-$ the cation formed is an example of a complex in which the IMes is not an innocent ligand and the crystal structure show some interaction between the phenyl ring and the metal.

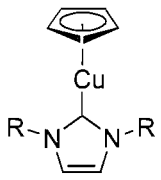


M = Mo, W

1.58

Figure 1.23 Half sandwich complexes of molybdenum and tungsten.

In 2006 Wang reported the first syntheses of copper(I) half sandwich complexes, Figure 1.24, **1.59**;[140] the paper describes several complexes with different NHC substitution. A point of interest is that these complexes are not entirely thermally stable and decompose upon heating.



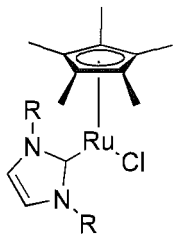
R = ^{i}Pr, ^{t}Bu, Mes, 2,6 diisopropylphenyl

1.59

Figure 1.24 Copper half sandwich complexes.

In 1999, Nolan described the synthesis of a ruthenium half sandwich complex **1.60**[44]. A number of bulky NHCs were reacted with $(Cp^*RuCl)_4$ to give the corresponding half sandwich complex. A later paper[141] compared IMesRuCp*Cl and Cy_3PRuCp*Cl as a olefin metathesis catalyst and show the carbene outperforms the phosphine complex.

Later, Nolan reported the complex synthesised with the bulky 1,3-bis(IPr)imidazol-2-ylidene.[142] Also in 2000, Baratta reported an improved synthesis of ruthenium half sandwich complexes.[143] By reacting Cp^*RuOMe with an imidazolium salt the carbene is formed *in situ*. Later in 2002 Baratta reported a number of new complexes with different functionality of the ligands.[144]

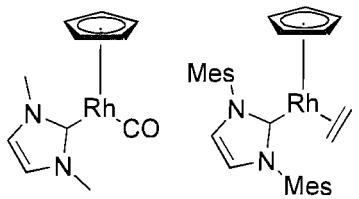


R = Mes, 2,6-diisopropyl, Tol, Cy, ^{i}Pr

1.60

Figure 1.25 Structure of half sandwich ruthenium complexes.

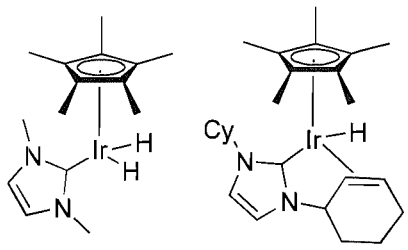
As early as 1986 Macomber and Rogers reported rhodium half sandwich complex CpRh(CO)-1,3-dimethylimidazolindin-2-ylidene **1.61**.[145] Both Rh(I) and Rh(III) half sandwich complexes were reported by Tilset in 2004.[138] The Rh(I) complex **1.62** contains ethylene whereas the Rh(III) complex contains chloride ligands to complete the coordination sphere.



1.61 **1.62**

Figure 1.26 Complexes of rhodium.

Yamaguchi has reported a series of investigations about iridium NHC half sandwich complexes and their catalytic oxidation of alcohols.[146,147,148] Also described is the facile CH activation of complexes containing ansa cyclopentadiene moieties. In 2000 Herrmann reported an iridium complex **1.64** in which a cyclohexyl substituent has become C-H activated.[149] In 2006, Peris also reports a series of iridium half sandwich complexes in which the alkyl group of the NHC has become C–H activated.[150] In 2005, Heinesky reported a half sandwich complex **1.63** containing a bis-carbene ligand as well as coordinated dihydrogen.[151] Also in 2005 Lammertsma [152] reports a NHC Cp^*iridium containing a phosphinidine ligand.



1.63 1.64

Figure 1.27 Selected examples of iridium half sandwich complexes.

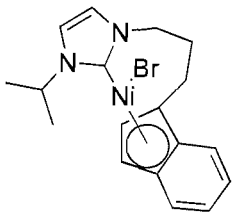
Recently Calhorda and Herrmann, describe the coordination of both cyclopentadienyl and indenyl into an iridium NHC COD complex, and performed DFT calculations associated with the system.[153]

As can be seen these complexes are rare for the early transition metals but are more common for the late transition metals. It should be noted that these NHC complexes are generally limited to Cp or Cp^* and only one mention of complexes containing indenyl ligands are mentioned. The ligands when combined with different metals offer numerous opportunities for catalysis.

1.10 Aims

As described previously sandwich complexes containing both an NHC and a cyclopentadienyl ligand are known, but until the publication of our group's communication, in early 2006, complexes in which the NHC is tethered to the cyclopentadienyl moiety were unknown.[154]

Recently in 2007, Shen reported a nickel complex containing an NHC functionalised with an indenyl group.[155] This complex has a similar architecture to the compounds described later, but differs in the fact a three carbon bridge is used to link the MHC and indenyl moieties, also the NHC is functionalised with a alkyl group not a aryl one. Shen made attempts to synthesise the aryl version but these were unsuccessful. Additionally the nickel complex was synthesised from the NHC lithium indenyl complex, which was formed *in situ*, the free NHC has not been isolated.



1.67

Figure 1.28 Shen's indenyl NHC nickel complex **1.67**.

It was hoped to be able to synthesise complexes containing a ligand in which the NHC is tethered to cyclopentadienyl type moieties, cyclopentadienyl, indenyl and fluorenyl, Figure 1.29.

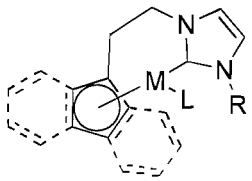


Figure 1.29 General architecture of proposed ligand system.

There are many intriguing points of tuning available on the generic architecture suggested above; firstly, an obvious point of modification would be to the R-group on the imidazole, as this would have effects on both the sterics and electronics of the carbene. Working along the ligand, there is the possibility of altering the back bone of the imidazole-2-ylidene ring either by adding electron withdrawing or donating groups or by using a saturated imidazol-2-ylidene ring. The bridge could be another site of modification, the number of atoms in the bridge could be altered leading to different chelate ring sizes, or chiral centres could be placed in or next to the bridge to enable stereochemical control of the final complexes. Finally, there is great potential for modification in the cyclopentadienyl ring system. The ring system could be changed from cyclopentadienyl to indenyl then to fluorenyl, this in itself will have effects on the electronics of the complexes. Alkyl groups could be added to the ring systems, this would have effects on the steric of the metal centre but also on the electronics of the ring.

It is hoped that the chemistry of this ligand can be established for a range of transition metals. It could be envisaged that for late transition metals the ligand will act as a rigid bidentate ligand, whilst in the case of early metals, hemilability may be possible and the carbene allowed to act as a much more labile moiety. In this respect, some catalysis of metal complexes containing this ligand system could be investigated.

In order to achieve these aims, firstly synthetic routes needed to be found to the imidazolium salt precursors. No cyclopentadienyl type imidazolium salts were previously known in the literature.

A suitable method needed to be found to generate the free ligand. In order for the ligand to coordinate to a metal in its monodentate form only the free NHC has to be formed, there are many methods known to do this as previously discussed. For the ligand to act as a bidentate donor, then the cyclopentadienyl ring also needs to be deprotonated, there are also methods known to achieve this. However, the method chosen has to be compatible with both these functional groups in the ligand and not lead to any further unexpected reactions.

Reliable ways of forming the metal complexes with the isolated free ligands would need to be investigated.

Other ways of forming the metal complexes, without the use of the free ligand, such as the use of silver carbene complexes as transfer reagents could be another avenue of research.

One intriguing avenue of research is that this ligand system could be used to synthesise hetero-bimetallic systems in which one metal centre forms an NHC complex whilst the other forms a cyclopentadienyl type complex. These systems may be of use in dual catalytic systems.

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Chapter 2

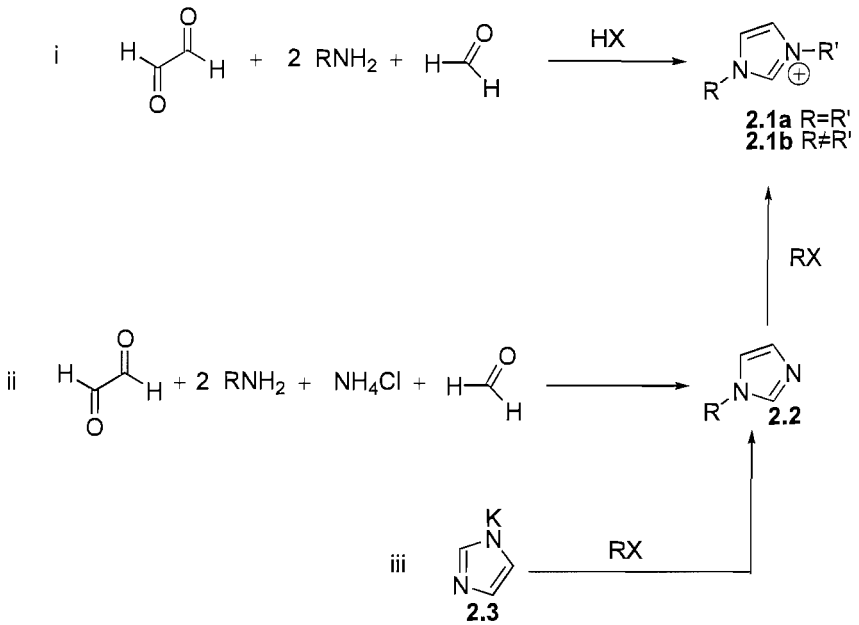
Imidazolium Salt Synthesis

2 Imidazolium Salt Synthesis

2.1 Background

2.1.1 Previous Syntheses of Imidazolium Salts

Most easily available are stable *N*-heterocyclic carbenes derived from imidazole, not least because numerous imidazolium precursors can be made by various reliable routes.[1] The carbenes and imidazolium salt precursors under investigation in this thesis are based on imidazolium salts.

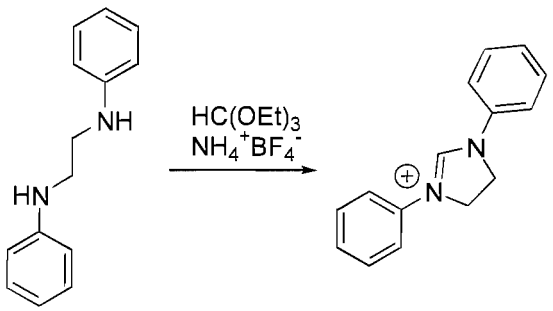


Scheme 2.1 Synthetic methods for making symmetrical and unsymmetrical imidazolium salts.

The most straightforward route to imidazolium salts **2.1** is the one-pot synthesis from glyoxal, primary amine and formaldehyde, route i, Scheme 2.1; this method gives access to symmetrically substituted imidazolium salts **2.1a**. To synthesise the more interesting unsymmetrical imidazolium salts **2.1b** a variation on this route is required, route ii. Generally, the *N*-substituted imidazole **2.2** is synthesised, either from glyoxal, amine, ammonium chloride and formaldehyde. Quaternisation with a reactive, usually primary, alkyl halide then takes place. The limitation of this method is that one of the *N*-substituents is derived from the reactive alkyl halide. An alternative route, iii, uses potassium imidazolide **2.3** as the starting material. Its use may simplify the reaction but

also is subject to limitations regarding the nature of the substituents that can introduced to the imidazole, as again only the more reactive primary alkyl halides are generally useful.

The orthoformate route, Scheme 2.2, coverts 1,2-diamines into aryl-substituted imidazolinium salts. This route can be applied to both symmetrically and unsymmetrically substituted bis(aryl) imidazolinium salts **2.5**. The are a number of useful routes to the starting 1,2-diarylamines **2.4**.[2]

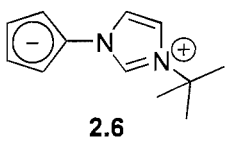


2.4 **2.5**

Scheme 2.2 Synthesis of a bis-aryl substituted imidazolium salt.

2.1.2 Imidazolium Salts Containing a Cyclopentadienyl Moiety

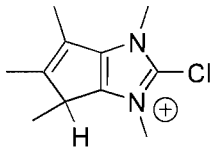
There are only a few examples in the literature to date of an imidazolium salts containing cyclopentadiene type moieties. In 2004, Coleman and Green reported a zwitterionic imidazolium compound **2.6**, Figure 2.2, in which the cyclopentadienide was linked directly to the imidazolium nitrogen.[3] There is no evidence in the literature of the carbene being formed, it may be that this salt cannot be deprotonated to form the carbene. However, the carbene derived from this compound is not expected to bind to a metal in the bidentate mode, as the strain in the chelate would be too great.



2.6

Figure 2.1 A zwitterionic salt containing a cyclopentadienide moiety.

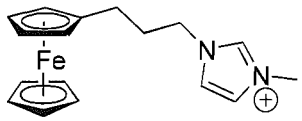
Arduengo reported an imidazolium fused cyclopentadienyl system **2.7**, Figure 2.2.[4] The carbene is formed by the unusual oxidative addition of a metal into the carbon chlorine bond. This ligands forms metallocene type complexes with fused *N*-heterocyclic carbene type ligands. This system will offer the wrong binding motif for the system we wish to investigate as this ligand gives bimetallic complexes, whereas we wish to investigate bidentate systems.



2.7

Figure 2.2 A fused cyclopentadienyl imidazolium salt.

A series of ferrocene linked imidazolium salts **2.8** have been reported by Murray, Figure 2.3.[5] The ferrocene units in these linked imidazolium salts are too stable to be converted to the cyclopentadienyl imidazolium salt, by removal of the iron.



2.8

Figure 2.3 Ferrocene linked imidazolium salt.

2.2 Aims

It was hoped to be able to synthesise novel imidazolium salts functionalised with cyclopentadienyl type moieties (cyclopentadienyl, indenyl and fluorenyl) and that different substitution patterns could be included within the ligand system, both on the cyclopentadienyl type moiety and on the imidazolium ring. If possible, it was hoped to be able to find a general method that can be applied to the different ring systems with various substitution patterns. These salts will be used as proligands, to synthesise the free anionic carbene compounds, metal complexes and other ligand transfer reagents, including silver carbene complexes.

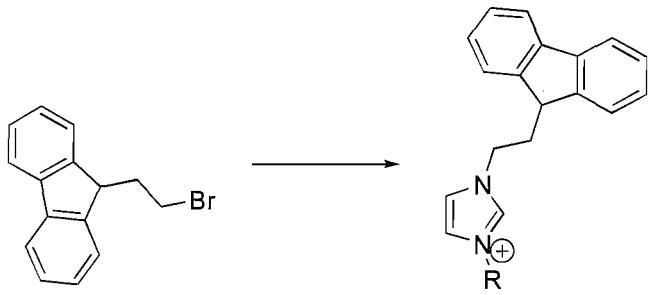
The target that was initially investigated was the cyclopentadienyl functionalised imidazolium salts, because of the generality of cyclopentadienyl compared to fluorenyl and indenyl ligands. After initial difficulties in synthesising the cyclopentadienyl salts, attention moved to the fluorenyl and indenyl imidazolium salts that were then envisaged to be more facile to synthesise.

2.3 Fluorene Functionalised Imidazolium Salt Synthesis

2.3.1 Unsubstituted-Fluorenyl Imidazolium Salt Synthesis

Bromoethylfluorene was synthesised according to literature methods.[6] As expected, when the bromoethylfluorene **2.9** was reacted with 2,6-diisopropylphenyl- and

mesityl- imidazoles by heating in refluxing dioxane for one week, the desired imidazolium salts **2.10a** and **2.10b** respectively were obtained in good yields, Scheme 2.3. The reaction could be scaled up to provide *ca.* 50 g quantities of imidazolium salts without any loss in yield. The products were purified by precipitation from DCM and ether to remove the unreacted starting materials. The imidazolium salts formed very hydroscopic powders that quickly became waxy and then sticky on exposure to air. After drying azeotropically with toluene, analytically pure materials were obtained.



2.9

2.10a R = 2,6-di-*iso*-propylphenyl
2.10b R = mesityl

Scheme 2.3 Synthesis of fluorenyl imidazolium salts. Reaction conditions: substituted imidazole, dioxane, 100 °C, 1 week.

The identities of the desired products were confirmed by analytical and spectroscopic methods. The imidazolium salts can be clearly identified by positive ion electrospray mass spectrometry, as the peak from the cation gives an unambiguous signal. Additionally in the ^{1}H-NMR spectra, a peak at around 10 ppm is distinctive for the imidazolium proton in these systems. Attempts to produce X-ray quality crystals of the unsubstituted-fluorenyl functionalised imidazolium salts were unsuccessful.

2.3.2 Substituted-Fluorenyl Imidazolium Salts

It was envisaged that adding substitution to the fluorenyl ring could improve the properties of the ligand in metal complexes. As problems were being encountered in the isolation of metal complexes with the unsubstituted-fluorene system, it was decided to investigate if adding simple alkyl groups to the ring system would enable crystallisation by changing the solubility characteristics of the complexes. It could also be envisaged that the addition of alkyl groups could affect the chemistry of the fluorenyl ring although the effects would be predicted to be subtle and a lengthy investigation would be required to fully explore these effects.

There are a number of possibilities for substitution of the fluorenyl ring system. The fluorenyl ring can be substituted symmetrically with alkyl **2.12**[7], **2.13**[8] or aryl **2.14**[9] groups or asymmetrically **2.11**[10]. Asymmetric substitution is of interest because it may enable chiral metal complexes to be formed, which in turn could be applied to asymmetric catalysis.

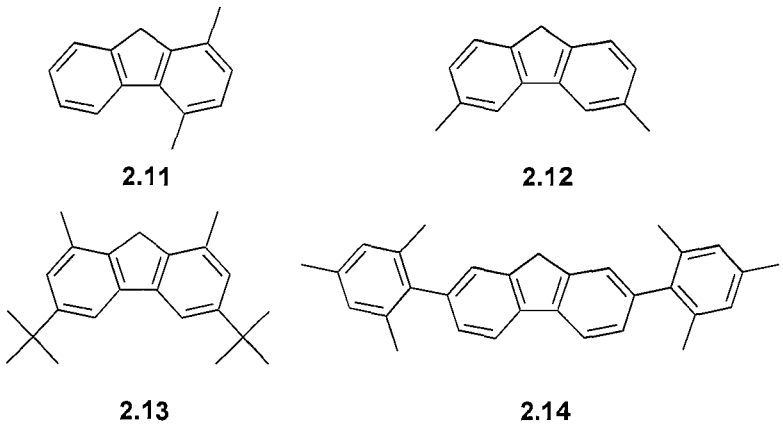
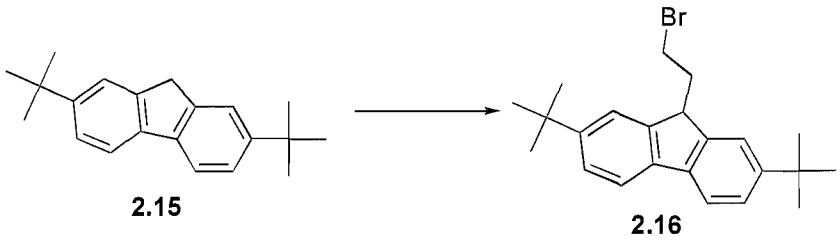


Figure 2.4 Selected examples of different alkyl and aryl substitution patterns known for fluorene.

2,7-Di-*tert*-butylfluorene **2.15** was synthesised according to literature methods.[11] 2,7-Di-*tert*-butylfluorene was chosen in the first instance for its facile synthesis as compared to other substitutions on fluorene. The synthesis involved the transfer of *tert*-butyl groups from 2,6-di-*tert*-butylcresol to the fluorene in nitromethane using aluminium chloride as a catalyst. Other substitution patterns on fluorene often require the synthesis of a biphenyl system which is then ring closed to form the fluorene ring system. In future, it may be possible to fully investigate the effects of changing the substitution patterns in the fluorenyl ring system.

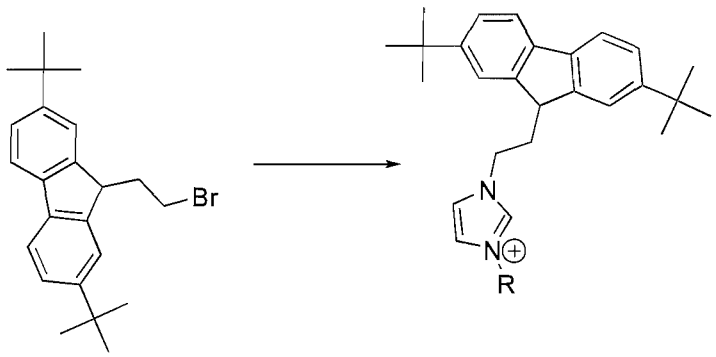
Using the analogous method for the synthesis of bromoethylfluorene,[6] the novel 9-(2-bromoethyl)-(2,7-di-*tert*-butyl)fluorene **2.16** was synthesised, Scheme 2.4. 2,7-Di-*tert*-butyl-fluorene was deprotonated with BuLi in ether at – 78 °C and then 3 eq. of dibromoethane added. After stirring overnight, the addition of water, and the removal of the volatiles the crude product was obtained. The product was crystallised by cooling a hot saturated petrol solution to -30 °C. The product was obtained as colourless crystals.



2.15 **2.16**

Scheme 2.4 Synthesis of the novel 2,7-(2-bromoethyl)di-tert-butylfluorene. Reaction conditions: BuLi, ether, -78 °C – RT, 4 eq. dibromoethane, , -78 °C – RT.

Reaction of **2.16** with *N*-substituted imidazoles gave the desired imidazolium salts. Both the 2,6-diisopropylphenyl- **2.17a** and mesityl- **2.17b** imidazolium salts have been synthesised, Scheme 2.5. **2.11** and the *N*-substituted imidazole were heated to 100 °C in dioxane for one week. After removal of the volatiles, the salt was precipitated from DCM and ether. Again as in the unsubstituted case, these salts were highly hydroscopic but after being dried azeotropically analytically pure imidazolium salts were obtained.



2.16

2.17a R = 2,6-di-*iso*-propylphenyl
2.17b R = mesityl

Scheme 2.5 Synthesis of a substituted-fluorenyl imidazolium salt. Reaction conditions: substituted imidazole, dioxane, 100 °C, 1 week.

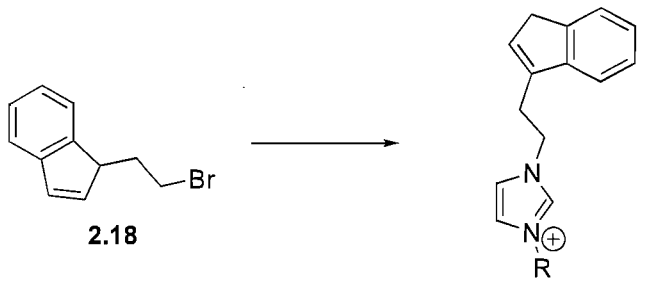
2.3.3 Summary

It has been shown that a range of fluorenyl functionalised imidazolium salts can be synthesised, with various substitution patterns on both the imidazole and the fluorenyl portions. It would be expected that these methods could be further extended to other substitution patterns.

2.4 Indenyl Imidazolium Salt Synthesis

2.4.1 Unsubstituted-Indene Imidazolium salt synthesis

Reacting the known 2-bromoethylindene **2.18** [12] with substituted imidazoles resulted in the synthesis of the desired imidazolium salts **2.19a-e**, Scheme 2.6. Bromoethylindene and the appropriate imidazole were reacted in refluxing dioxane for up to one week, alkyl imidazoles reacting more expeditiously than aryl ones. After precipitation from DCM and ether, the desired imidazolium salts were obtained. This reaction was shown to be general to a number of differently substituted imidazoles, alkyl and aryl including 2,6-diisopropylphenyl-, phenyl-, *ortho*-tolyl-, mesityl-, tertbutyl- and methyl- imidazole. The indene imidazolium salts were extremely hydroscopic, but after drying azeotropically analytically pure imidazolium salts were obtained.



2.18

2.19a R = *tert*-butyl
2.19b R = phenyl
2.19c R = *ortho*-tolyl
2.19d R = mesityl
2.19e R = 2,6-di-*iso*-propylphenyl

Scheme 2.6 Synthesis of indenylethyl substituted imidazolium salt. Reaction conditions: 1 eq. substituted imidazole, dioxane, 100 °C, 1 week, 50-80%.

The formation of the imidazolium salt is clearly identified by the appearance of a new peak in the ^{1}H-NMR spectra around 10 ppm, distinctive for the imidazolium proton, and further confirmed by electrospray mass spectrometry and elemental analysis.

During these reactions, it appears that the geometry of the double bond in the five-membered ring of the indene shifts from 1,2 to 2,3, Scheme 2.6. It could be conceived that the imidazole is acting as a base, causing deprotonation and catalysing the rearrangement of the indene ring to the more thermodynamically stable isomer. The new double bond position was assigned from the NMR spectra, the previously diastereotopic protons, now appear as one signal in the imidazolium salt.

Attempts were made to grow X-ray quality crystals of all the indenyl imidazolium salts synthesised:

3-(Phenyl)-1-[2-(3*H*-inden-1-yl)-ethyl]-2*H*-imidazolium bromide **2.19b** was crystallised, by cooling from the hot reaction mixture in dioxane, in the triclinic space group P-1 with a= 8.2154(8) Å, b = 8.7904(8) Å, c = 15.2315(15) Å, α = 75.607(4)°, β = 79.709(3)°, γ = 85.148(4)° V = 1047.37(17) Å^3 and D_{calcd} = 1.444 Mg M^{-3} for Z = 2. Data were collected at 120(2)K on a Bruker-Nonious KappaCCD diffractometer. Least squares refinement of the model based on 4820 unique reflections (R_{int} = 8.63%) converged to a final R_1 = 5.18% ($I > 2(I)$) and R_w^2 = 8.47%. See Table 2.1 for full details. Two molecules of dioxane are also present in the unit cell and were modelled successfully without any splitting.

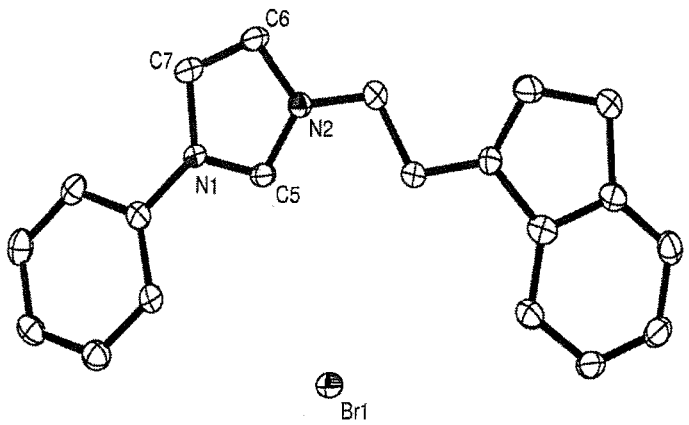


Figure 2.5 ORTEP representation of 3-(Phenyl)-1-[2-(3H-inden-1-yl)-ethyl]-2H-imidazolium bromide **2.19b** showing 50% probability ellipsoids. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: N(1)-C(5) 1.338(4); N(1)-C(7) 1.383(4); N(1)-C(19) 1.448(4); N(2)-C(5) 1.327(4); N(2)-C(6) 1.384(4); N(2)-C(8) 1.467(4); C(6)-C(7) 1.342(5); N(2)-C(5)-N(1) 108.7(3).

The X-ray crystal structure confirms the NMR assignment of the location of the double bond in the indene ring system as seen by the flat geometry at the bridge head atom. The bond lengths and angles found in this imidazolium salt lie in the range previously reported.[13] In the crystal structure, the molecules form a layered structure with dioxane present in the voids. There is one molecule of dioxane present in the asymmetric unit, the dioxane was modelled in the usual manner and was modelled as existing in one orientation,

although no interaction appears to exist with the imidazolium salt molecules.

Unfortunately, despite efforts, no other unsubstituted-indenyl imidazolium salts could be crystallised.

2.4.2 Substituted-Indene Imidazolium Salts

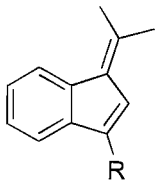
Like the fluorenyl case, problems were encountered trying to isolate the metal complexes of the unsubstituted-indenyl functionalised carbenes, so it was decided to investigate the possibility of adding alkyl groups to substitute the indenyl ring system. It was hoped that adding alkyl groups to the indenyl ring may improve the properties of the ligand and its complexes.

It was envisaged that adding alkyl groups may alter the solubility characteristics to enable the complexes to be crystallised. As in the fluorenyl case, it could be predicted that the alkyl groups will have subtle effects on the chemistry of the ligand.

There are two general options for substituting an indenyl ring, either on the five membered ring, or the 6 membered ring, it would be expected that alterations to the five membered ring would have more effect on the sterics at the metal centre whilst altering the six membered ring would have less. It is also conceivable that the indene could be substituted in both rings. One difficultly is that like substituted cyclopentadiene rings indene rings have a tendency to add new groups in a geminal fashion to the 5 membered ring,[14,15] which is unsuitable for use as a bidentate ligand as this would prevent deprotonation of the five membered ring to form an aromatic system.

There are a few examples of indene ring systems where there is substitution on the 2-postion, in order to achieve this Grignard reagents are used.[16] This requires starting from the 2-indenone. Consequently, there are only a few examples of 1,2 or 2,3 substituted indenes and these tend to be limited to simple alkyl groups such as methyl and ethyl.[17,18] This may be a path of research for future work, but has not yet been explored.

1,3 disubstituted indenes are known in the literature but these are generally synthesised via the benzofulvene, followed by a reduction step or contain silyl groups to prevent geminal substitution.[19]



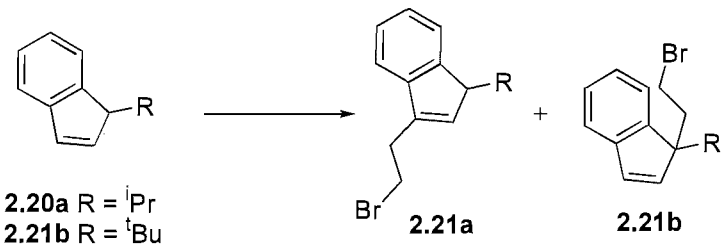
R = alkyl

2.20

Figure 2.6 An example of a benzofulvene used to synthesise 1,3-substituted fulvenes.

Attempts were made to synthesise indene systems that were substituted in the 1,3-positions however attempts to achieve this failed as the second substitution also partially occurred at the 3-position giving a product that could not be used as a bidentate ligand. Initially 1-isopropylindene **2.20a** was reacted with nBuLi followed by dibromoethane, unfortunately this lead to a mixture of the desired product **2.21a** and the geminal substituted product **2.21b**, Scheme 2.7. The same was then tried with 1-*tert*-butylindene **2.20b** in the hope that the increased steric bulk would prevent geminal substitution, however this was not the case and again the geminal isomer contaminated the final product.

Attempts were made to isolate the desired 1,3 disubstituted compounds from the mixture, unfortunately these mixtures resisted separation.



2.20a R = ^{i}Pr
2.21b R = ^{t}Bu

2.21a **2.21b**

Scheme 2.7 Attempted synthesis of a 3-substituted bromoethyl fluorene leading to a mixture of 1-,3- and 3,-3, substituted indenes.

Due to the difficultly in isolating, a 3-substituted-1-(2-bromoethyl)indene attention turned to substituting the phenyl ring of the indene. It was discovered in the literature that 4,7-dimethylindene **2.23** could be synthesised in a facile manner from the reaction of 2,5-hexandione with cyclopentadiene in sodium ethoxide solution.[20] There are also other substituted indenes known in the literature, **2.22**[21], **2.24**, **2.25**[22] are selected examples, but **2.22** was chosen initially because of the ease of synthesis compared to other substituted indenes.

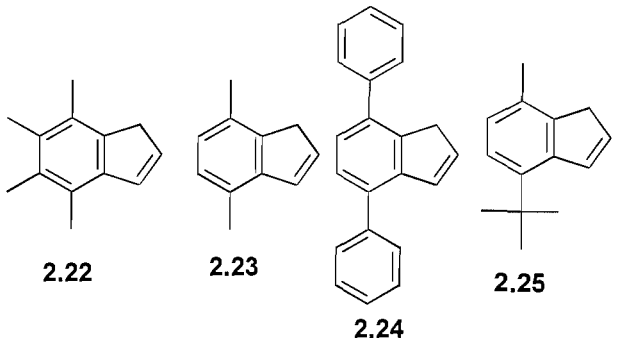
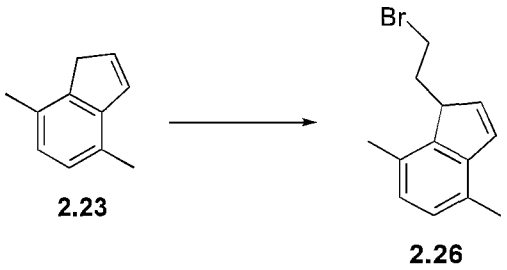


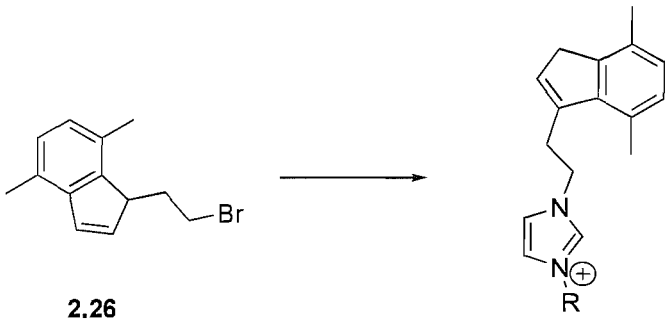
Figure 2.7 Differently substituted alkyl and aryl indenes.

It was envisaged that 4,7-dimethylindene **2.23** should react in a similar way to indene so an analogous route to the method for indene was used to synthesise the bromoethyl compound. On treatment with n-BuLi in ether followed by subsequent addition of 3 eq. of dibromoethane the desired 1-(2-bromoethyl)-(4,7-dimethylindene) was synthesised in good yields. It was hoped that clean material could be obtained by distillation in a similar manner to bromoethyl indene, indeed distillation of the crude product gave the clean 1-(2-bromoethyl)-4,7-dimethylindene **2.26**.



Scheme 2.8 Synthesis of 1-(2-bromoethyl)-4,7-dimethylindene **2.26**. Reaction conditions: nBuLi, ether, -78 °C – RT, 4 eq. dibromoethane, , -78 °C – RT.

Subsequent reaction of the isolated indene with 2,6-diisopropyl imidazole gave the desired imidazolium salt in high yields. This salt was extremely hydroscopic and the purification had to be carried out expeditiously to prevent an oil being formed, leading to loss of product during handling. Azeotropically drying followed by prolonged exposure to vacuum was required to obtain the salt as a powder, rather than a sticky oil.



2.26

2.27 R = 2,6-diisopropylphenyl

Scheme 2.9 Synthesis of the imidazolium salt. Reaction conditions: 1 eq. substituted imidazole, dioxane, 100 °C, 1 week, 50-80%.

Again, the same shift of the double bond from 2,3 to 1,2 is observed in the substituted indenyl system.

Only the imidazolium salt synthesised from 2,6-diisopropylphenyl imidazole was synthesised. Although it would be expected that this method could be generalised to any imidazole.

3-(2,6-Diisopropyl-phenyl)-1-[2-(3H-(4,7-dimethyl)inden-1-yl)-ethyl]-3H-imidazolium bromide **2.27** was crystallised, from a saturated DCM solution layered with ether, in the monoclinic space group $C_{2/c}$ with a= 28.8436(13) Å, b = 9.2261(4) Å, c = 25.4781 Å, $\alpha = 90°$, $\beta = 123.067(2)°$, $\gamma = 90°$ $V = 5681.9(4)$ Å^3 and $D_{calcd} = 1.320$ Mg M^{-3} for Z = 8. Data were collected at 120(2)K on a Bruker-Nonious KappaCCD diffractometer. Least squares refinement of the model based on 6548 unique reflections ($R_{int} = 7.85\%$) converged to a final $R_1 = 5.49\%$ ($I > 2(I)$) and $R_w^2 = 12.95\%$. See Table 2.1 for full details. One molecule of DCM is also present in the unit cell and was modelled successfully, when split equally into two orientations, with restrains placed on the central carbon atom.

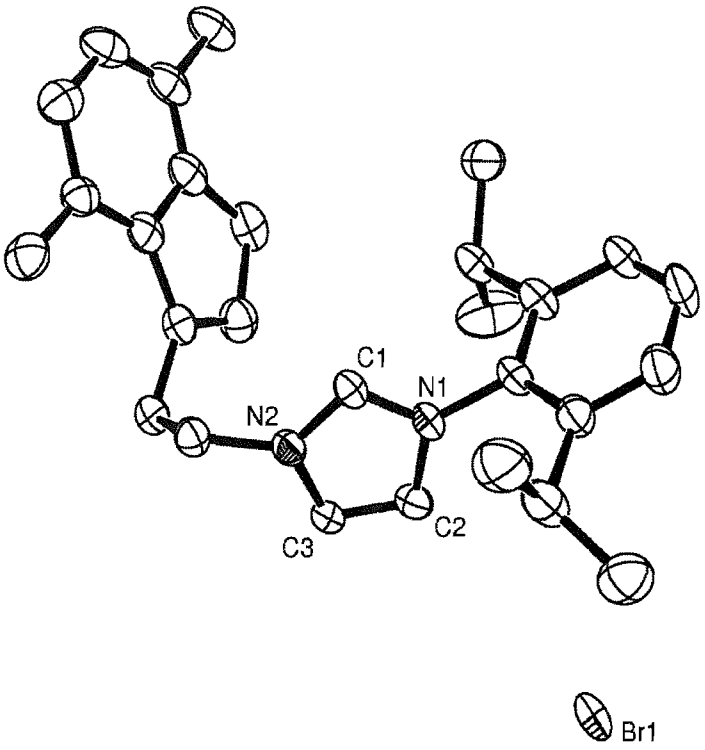


Figure 2.8 ORTEP representation of 3-(2,6-Diisopropyl-phenyl)-1-[2-(3H-(4,7-dimethyl)inden-1-yl)-ethyl]-3H-imidazolium bromide **2.27** showing 50% probability ellipsoids. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard N(1)-C(1) 1.342(4); N(1)-C(2) 1.379(4); C(1)-N(2) 1.317(4); N(2)-C(3) 1.370(4); C(3)-C(2) 1.356(5); C(1)-N(1)-C(2) 108.3(3); C(1)-N(1)-C(17) 125.8(3); C(2)-N(1)-C(17) 125.8(3); N(2)-C(1)-N(1) 108.8(3); C(1)-N(2)-C(3) 108.8(3); C(2)-C(3)-N(2) 107.7(3)

The bond lengths and angles found lie within the previously reported values.[13] The molecule of DCM that was present in the asymmetric unit, had to be modelled as split in two orientations, the central carbon was restrained to keep the same position and thermal parameters in both molecules. When compared to the previous imidazolium salt this one takes a more contorted orientation, this may simply be due to the *iso*-propyl groups preventing the molecule from lying in a plane in the crystal.

2.4.3 Summary

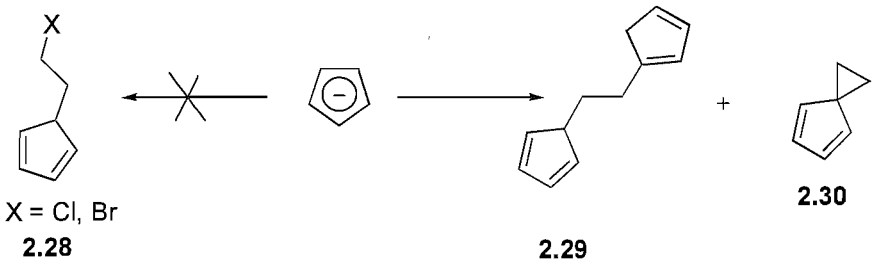
A number of indenyl functionalised imidazolium salts have been synthesised, and it had been shown that the quaternisation method can be applied to both unsubstituted- and substituted- indenes. One substituted-indene functionalised imidazolium salt has been

synthesised, although it would be expected this method could be applied to a number of other imidazoles as well as 2,6-diisopropylphenyl imidazole. A further path of research could be to investigate the effects of changing the substitution on indene more fully.

2.5 Towards the Synthesis of a Cyclopentadienyl Imidazolium Salt

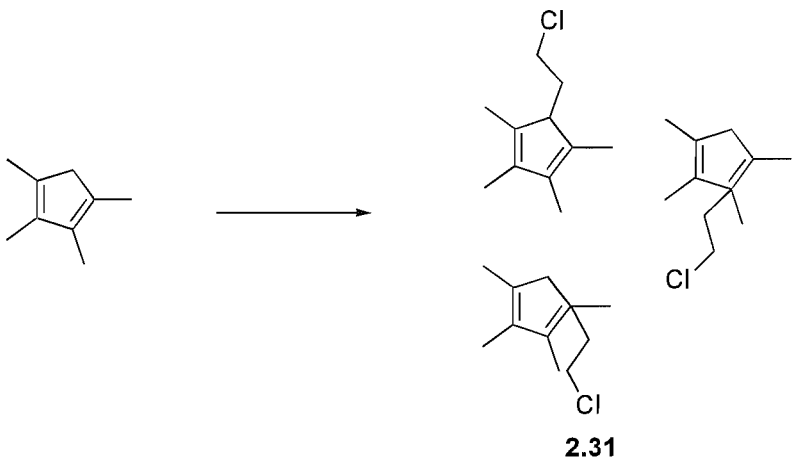
2.5.1 Analogous Methods

Methods to make bromo- or chloro- ethylcyclopentadiene **2.28** or pure 1-(haloethyl)-2,3,4,5-(tetramethylcyclopentadiene) are not known in the literature, also methods for other leaving groups are not known. Reaction of lithium or sodium cyclopentadienide with dibromoethane leads to the spiro-heptadiene product **2.30** or the *ansa*-bis-Cp **2.29**, Scheme 2.10.



Scheme 2.10 The reaction of cyclopentadienide with dibromoethane.

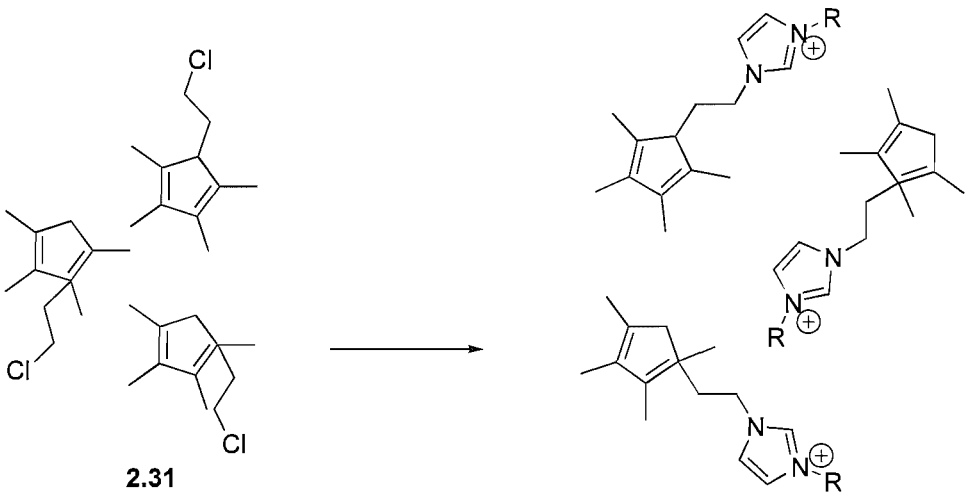
In the reaction of tetramethylcyclopentadiene with a di-substituted ethylene, an amount of geminal substitution takes place leading to unwanted geminal isomers **2.31**, Scheme 2.11.



Scheme 2.11 Synthesis of a mixture of tetramethylcyclopentadienylethylchlorides. Reaction conditions: nBuLi, ether, room temperature followed by dichloroethane, 1 week, room temperature.

This lack of routes to pure bromo- or chloro- ethylcyclopentadienes **2.28** or bromo- or chloro- ethyl(tetramethyl)cyclopentadienes **2.31** hampered efforts to make the cyclopentadienyl functionalised imidazolium salts by analogous methods to the indenyl and fluorenyl analogues. It was hoped that by using the impure mixtures available from known syntheses[23] to synthesise a mixture of imidazolium salts that it may be possible to isolate the pure imidazolium salt we desired.

A mixture of chloroethylcyclopentadienes **2.31** was reacted with 2,6-diisopropylphenylimidazole to give a mixture of imidazolium salts. The ^{1}H-NMR spectrum of the resulting mixture was extremely complicated but it was clear there were a number of compounds present in the mixture. Attempts to isolate the desired isomer proved unsuccessful, and unfortunately, by NMR the majority of the product appeared to be geminally substituted product. This was later confirmed by X-ray structure analysis, the geminal coupling to the cyclopentadiene ring is clearly seen. The ring itself appears to be highly disordered, with different isomers occupying the same space, and cannot be modelled in a satisfactory manner. The resulting products were isolated and later subject to further reactions.



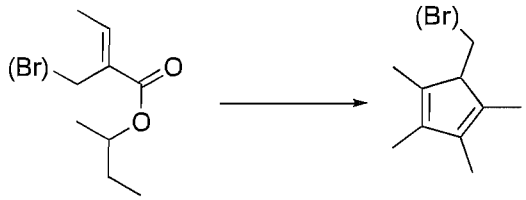
2.31

2.32 R = 2,6-di-*iso*-propylphenyl

Scheme 2.12 Synthesis of a mixture of imidazolium salts, from a mixture of tetramethylcyclopentadienylethyl chlorides. Reaction conditions: 2,6-diisopropylphenylimidazole, dioxane, 100°C, 1 week.

2.5.2 Attempts to Synthesis a Bromomethylcyclopentadiene

It was hoped that a way of synthesising a bromo- or chloro- methylcyclopentadiene **2.34** could be found. A route was chosen based on the cyclisation of the 2-butyl tiglic acid ester, Scheme 2.13.[24], using a starting material modified with a bromide. It was hoped that by adding a bromine to one of the methyl groups, that on cyclisation, the bromomethyl(tetramethyl)cyclopentadiene would form. Unfortunately, **2.23** did not cyclise on reaction with toluene sulphonic acid.



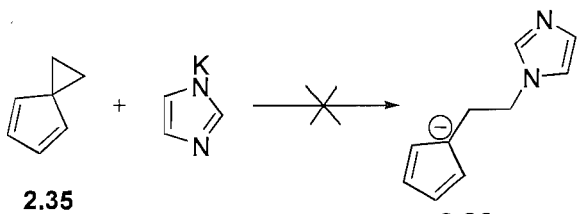
2.33 **2.34**

Scheme 2.13 Cyclisation of tiglic acid.

This lack of a suitable synthesis for a haloethylcyclopentadiene hampered efforts to synthesis the cyclopentadienyl analogue. A search of the literature also revealed that other leaving groups are also unknown. As an analogous route to the successful synthesises for indenyl and fluorenyl could not be followed attempts were made to synthesise the cyclopentadienyl imidazolium salt by other methods.

2.5.3 Spiro-substituted Cyclopentadiene

It was thought that a spiropropane substituted cyclopentadiene may act as a suitable analogue for a haloethylcyclopentadiene. The reaction between spiro-heptadiene **2.35** and a dialkyl potassium phosphide is known[25] and it was hoped this could be applied to potassium imidazolide, in a reaction where imidazolide acts as a neucleophile and attacks the spiro-carbon, which ring opens. The cyclopentadienyl imidazole **2.36** synthesised which could then be converted to the imidazolium salt by reaction with an alkyl halide, however even after prolonged periods of heating no reaction was observed.

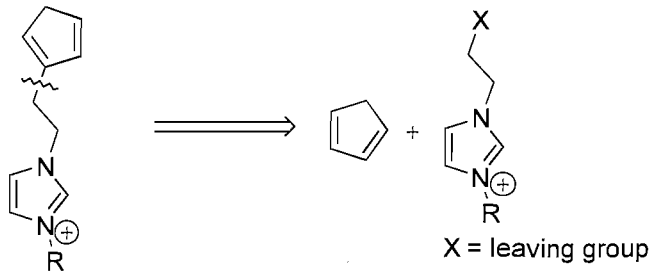


2.35 **2.36**

Scheme 2.14 Attempted synthesis of a cyclopentadienylethyl imidazole.

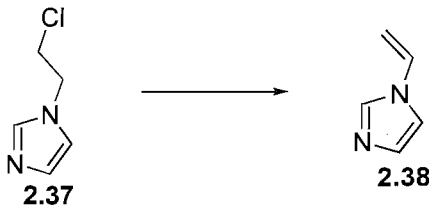
2.5.4 A Different Disconnection Method

Instead of trying to form the cyclopentadienyl-substituted imidazolium salt from an 'alkyl-cyclopentadiene' and an imidazole, an alternative disconnection route was attempted in which the substituted imidazolium salt would be synthesised from an 'alkyl-imidazole' and cyclopentadiene.



Scheme 2.15 A different disconnection approach.

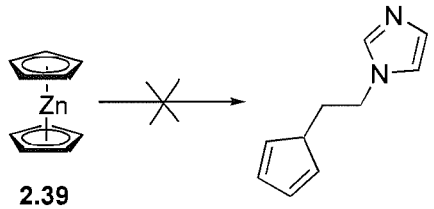
Sodium or lithium cyclopentadiene were reacted with chloroethylimidazole **2.37**, unfortunately the only identifiable compound that could be isolated from the reaction mixture was the elimination product, vinylimidazole **2.38**. A black intractable solid was also produced, possibly the product from the polymerisation of chloroethyl imidazole. Bromoethylimidazole was not tried, as it was believed to be unstable and likely to spontaneously polymerise.



Scheme 2.16 The unwanted synthesis of vinylimidazole.

It is well known that cyclopentadienide sometimes acts as a very poor neucleophile.[26] It was hoped that if a less basic and more nucleophilic cyclopentadienyl compound could be found then the elimination may be prevented and substitution increased. Attempts were made to use the readily available and more nucleophilic dicyclopentadienyl zinc **2.39**,[27] however, at room temperature no reaction appeared to take place and increasing the temperature lead to polymerisation of the chloroethylimidazole. It was shown in a another paper that adding a phosphine to the reaction would increase the reactivity of the dicyclopentadienyl zinc by changing the coordination to η^1.[28] Triphenyl

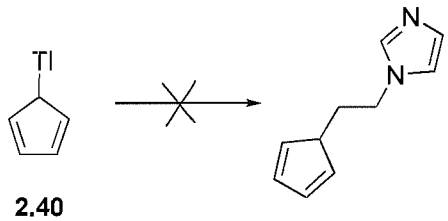
phosphine was added, unfortunately, this had no effect and the reaction still did not proceed.



2.39

Scheme 2.17 Attempted synthesis of cyclopentadienylethylimidaole.

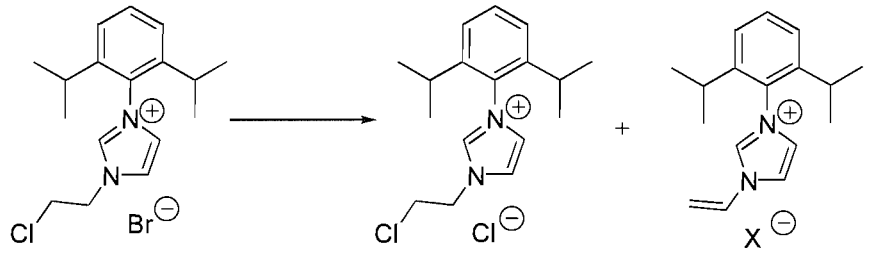
Thallium cyclopentadienide **2.40**[29] is a cyclopentadienyl neucleophile that is also considered less basic than sodium or potassium cyclopentadienide, evidence of this is the fact that it is synthesised using aqueous methods. Thallium cyclopentadiene and chloroethyl imidazole were combined in ether, unfortunately, none of the desired product was observed and only the starting materials were seen.



2.40

Scheme 2.18 Attempted synthesis of cyclopentadienylethylimidaole

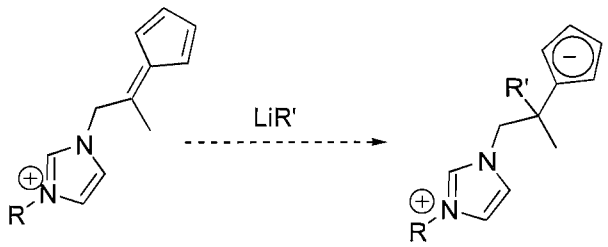
It was thought that by using the chloroethyl imidazolium salt **2.41** it may be possible to access the cyclopentadienyl imidazolium salt directly, and may be also benefit from increased reactivity from the charged imidazolium ring. Indeed the reactivity of the compound was increased but the desired product was not seen, several products were observed; the elimination product **2.43**, the chlorine-bromine exchanged product **2.42** and the tentatively assigned thallium bromide carbene of the imidazolium salt.



2.41 2.42 2.43

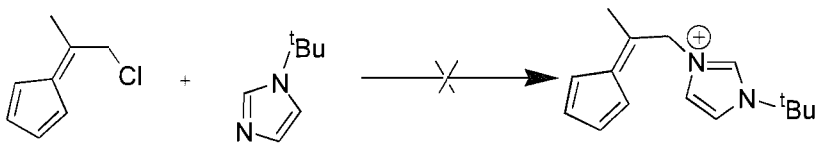
2.5.5 Fulvenes

It was envisaged that a fulvene may be a suitable precursor from which to synthesise the desired imidazolium salts. It was hoped that if a fulvene imidazolium salt could be synthesised, then it could be converted to the cyclopentadienide moiety by the addition of an alkyl lithium or similar reagent



Scheme 2.19 Proposed synthesis of a cyclopentadienide ligand from a fulvene intermediate.

An attempt was made to react 6-chloromethyl-6-methylfulvene **2.44**,[30] prepared by the literature method, with *tert*-butyl-imidazole to form the imidazolium salt. The reaction proved unsuccessful, this may have been due to thermal lability of the chloromethyl fulvene leading to decomposion before the reaction could take place.

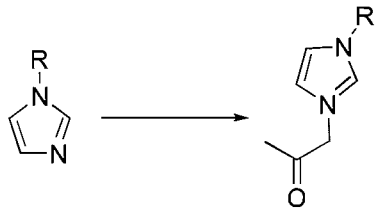


2.44 2.45

Scheme 2.20 Attempted preparation of fulvene imidazolium salt.

It was envisaged that iodomethylmethylfulvene might react more quickly and quaternise before the decomposition took place. The synthesis of iodomethylmethylfulvene was attempted using the analogous method to the chloro-derivative using iodoacetone, but the product could not be isolated.

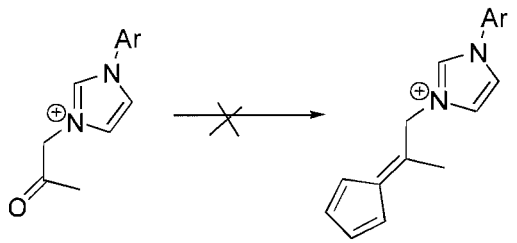
It was hoped to be able to form a fulvene substituted imidazolium salt from a ketone substituted imidazolium salt such as **2.46**. Firstly, a method had to be found to synthesise the ketone imidazolium salt. This was achieved by the reaction of chloroacetone with an imidazole in dioxane. In the case of the more reactive alkyl imidazoles, as the chloroacetone was added to the stirred mixture of imidazole in dioxane an exotherm was noticed. The reason for this vigorous reaction may be due to the carbonyl group activating the chloride.



2.46

Scheme 2.21 Synthesis of a carbonyl functionalised imidazolium salt. Reagents and conditions: chloroacetone, dioxane, up to 100 °C overnight.

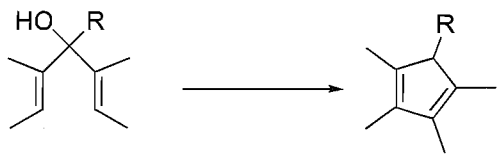
The reaction of the ketone substituted imidazolium salt with cyclopentadiene to form the fulvene was attempted using the method of Little.[31] Unfortunately, the desired product could not be identified; it is feasible that the acidic imidazolium proton interferes with this reaction.



Scheme 2.22: Attempted formation of fulvene-carbene. Reaction conditions: Cyclopentadiene, MeOH, Pyrrollidine.

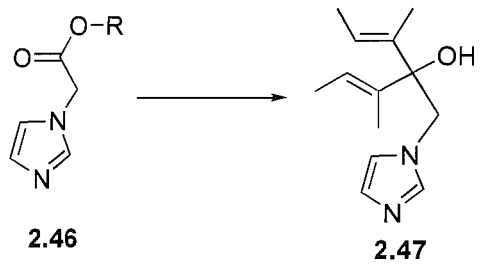
2.5.6 Imidazole Ester

A synthetic route that involved the cyclisation of an acyclic-diene was envisaged.



Scheme 2.23 Intended Cyclisation

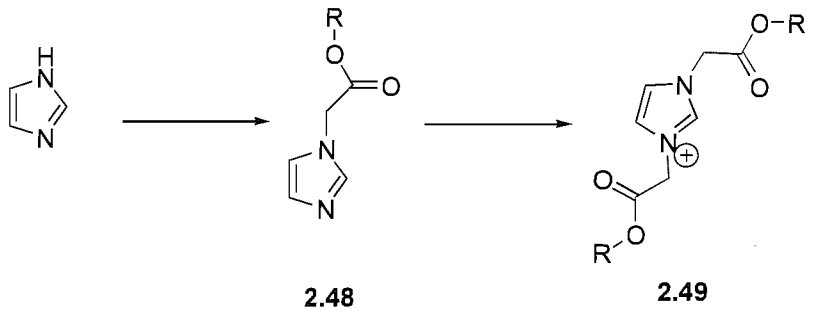
It was hoped that the R-group could be an imidazole, so attempts were made to synthesise the diene substituted imidazole. It was hoped that the addition of 2 equivalents of butenyl lithium to an imidazole ester would yield the desired product. This required the synthesis of the imidazole ester, which has not been reported.



2.46 **2.47**

Scheme 2.24 Intended formation of diene-ol

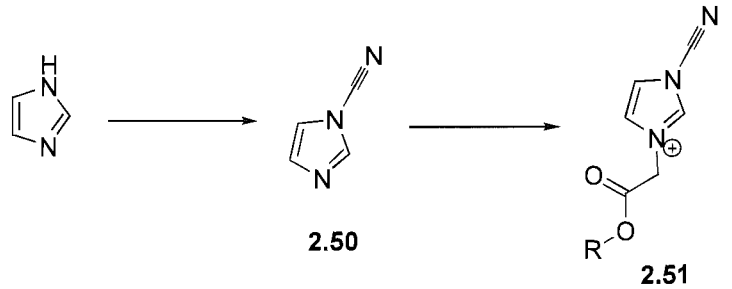
This required the formation of the compound **2.46**. This however proved to be harder than first envisaged. First, it was hoped that treating imidazole and the bromoester with base would form the desired product **2.48** however; a large amount of quaternised product **2.49** was detected. This quaternisation also happened with the chloro analogue. This undesired quaternisation took place because the desired product is more reactive towards quaternisation than the imidazole towards substitution.



2.48 **2.49**

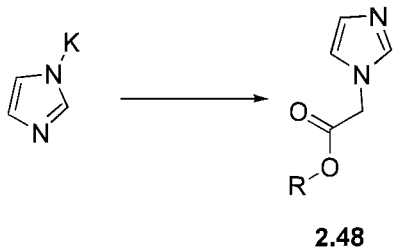
Scheme 2.25 Attempted preparation of **2.48** leading to an imidazolium salt.

Protection of the imidazole with a nitrile group followed by quaternisation with the bromo ester worked in good yields but unfortunately, the deprotection step to remove the nitrile failed.



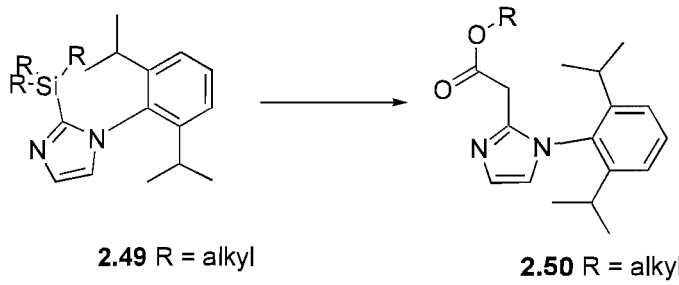
Scheme 2.26 Formation of **2.51**.

Finally reacting potassium imidazolide with the chloroester at low temperatures gave the desired product **2.48** in reasonable yield.



Scheme 2.27 Synthesis of **2.48**

Unfortunately, reaction of the imidazolium ester with butenyl lithium or Grignard failed to give the desired product; it was thought the acidic protons of the imidazole might interfere with the reaction so attempts were made to protect the imidazole at the C-2 position with a silyl protecting group. Attempts to protect the imidazole ester with a silyl protecting group failed, presumably, because the ester interfered with the deprotonation step. However, protecting an aryl imidazole succeeded. On quaternisation, the ester attacked the C-2 'protected' position rather than the N-3 position as desired. Different silyl protecting groups were tried including triisopropylsilyl in the hope the added bulk may prevent C-2 substitution, but the same substitution still took place.



Scheme 2.28 Formation of the undesired product **2.50**

2.5.7 Summary

A number of methods using different disconnection approaches have been attempted in order to synthesise the cyclopentadienyl imidazolium salt, but still none have yet proven fruitful.

The biggest difficultly proved to be the lack of a synthesis to give a halo-alkyl substituted cyclopentadiene, which would have been envisaged to give a facile synthesis of the imidazolium salt, analogous to the indene and fluorene cases. Routes involving the spirocyclopentadiene also proved fruitless.

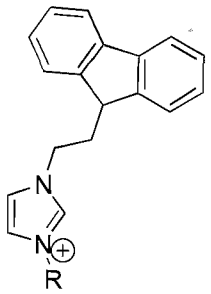
Using cyclopentadienyl nucleophiles failed as these caused elimination rather than the desired substitution.

A useful method has been found to synthesise ketone substituted imidazolium salts. Attempts to form the fulvenes from these failed.

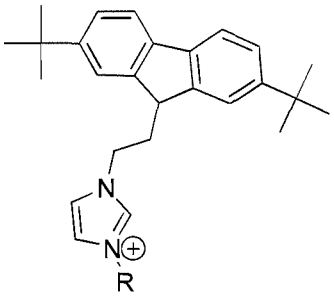
Attempts to build a cyclopentadienyl ring on the imidazole and imidazolium salts failed, due to the acidic nature of the C-2 proton. Attempts to protect this proton resulted in unexpected substitution reactions on quaternisation.

2.6 Conclusions

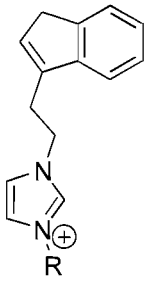
A number of imidazolium salts have been synthesised, **Figure 2.9**.



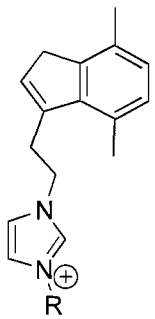
2.10a R = 2,6-di-*iso*-propylphenyl
2.10b R = mesityl



2.17a R = 2,6-di-*iso*-propylphenyl
2.17b R = mesityl



2.19a R = *tert*-butyl
2.19b R = phenyl
2.19c R = *ortho*-tolyl
2.19d R = mesityl
2.19e R = 2,6-di-*iso*-propylphenyl



2.27 R = 2,6-diisopropylphenyl

Figure 2.9 Functionalised imidazolium salts synthesised.

Indenyl and fluorenyl imidazolium salts have been synthesised in a facile manner. It has been shown that the reaction should be expected to work for a variety of substitution patterns on the indenyl or fluorenyl rings.

A facile route to a carbonyl substituted imidazolium salt has been found.

Despite attempting numerous approaches, a synthetic method for the production of a cyclopentadienyl imidazolium salt has yet to be found.

2.7 General Experimental

2.7.1 Instrumentation

Proton NMR spectra were recorded on a Bruker Avance DPX300, at 300 MHz or a Bruker Advance DPX400 spectrometer at 400 MHz. ^{13}C and $^{13}C\{^{1}H\}$ NMR spectra were recorded on the same spectrometers at 75 MHz and 100 MHz, respectively. The NMR spectra were referenced to the residual solvent signals.

Low resolution mass spectra were collected on a Micromass Platform II spectrometer. High resolution mass spectra were collected on a Bruker Apex III spectrometer.

Elemental analyses were carried out by the microanalytical laboratory at the Department of Health and Human Sciences, London Metropolitan University. All analyses were carried out in duplicate with both results agreeing closely. Air-sensitive samples were supplied in glass tubes sealed under vacuum.

2.7.2 Solvents

Solvents were purchased from Fisher Chemicals. All solvents for moisture sensitive reactions were dried and distilled before use. Petroleum ether 40/60 was dried over sodium benzophenone ketyl and is referred to as petrol in this section, diglyme (approx 1 ml/L) was added to increase the solubility. Diethyl ether was dried over sodium benzophenone ketyl and is referred to as ether in this section. Toluene was dried over molten sodium. THF was dried over sodium benzophenone ketyl. DCM was dried over powdered calcium hydride. Benzene was dried over sodium benzophenone ketyl and stored in an ampoule over 4 Å molecular sieves under N_2.

$CDCl_3$ was dried over 4 Å molecular sieves and stored over fresh sieves. CD_2Cl_2 was dried over calcium hydride and stored over 4 Å molecular sieves. d_8-THF was dried over NaK alloy and stored over 4 Å molecular sieves.

2.7.3 Compounds

Indene; fluorene; 1,2-dibromoethane; 2,5-hexanedione; BuLi (2.5 M in hexanes) and dicyclopentadiene were all purchased from Aldrich Chemicals.

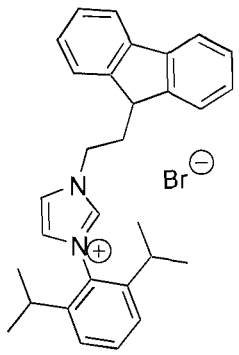
The following compounds were prepared according to literature methods: bromoethylfluorene;[32] di-*tert*-butylfluorene;[11] *tert*-butylimidazole; phenylimidazole; tolylimidazole; mesitylimidazole[33] and 2,6-diisopropylphenylimidazole.[34]

2.7.4 General

Air-sensitive reactions were carried out using standard Schlenk techniques or in a catalytically dried and deoxygenated M. Braun glovebox (<2 ppm O_2). All air-sensitive solids were stored in the glovebox. Imidazolium salts were also stored in the glovebox due to their hydroscopic nature.

2.8 Experimental

1-[2-(9-9*H*-Fluorenyl)ethyl]-3-(2,6-diisopropylphenyl)-2*H*-imidazol-1-ium bromide 2.10a



A glass ampoule fitted with a PTFE stopcock containing 9-(2-bromoethyl)-9H-fluorene (18 mmol, 5.0g); 2,6-diisopropylphenylimidazole (18 mmol, 4.2g) and dioxane (100 ml) was heated to 100 °C for 5 days. After removal of the volatiles, the residue was dissolved in the minimum amount of DCM (*ca.* 5 ml). This solution was then added slowly to ether (100 ml). The resulting solid was filtered, washed with diethyl ether (100 ml); and dried under vacuum. The solid was dried azeotropically with toluene. The product was isolated as above giving an off-white solid. (4.6g, 50%.)

^{1}H ($CDCl_3$, 300 MHz): 10.45 (1H, s, imidazolium-H); 7.75 (2H, d, J = 7.5 Hz, ArH) 7.63 (2H, d, J = 8.0 Hz, ArH); 7.46 (1H, t, J = 8.5 Hz, ArH); 7.37 (2H, t, J = 7.5 Hz, ArH); 7.29 (2H, d, J = 7.5 Hz, ArH); 7.23 (2H, d, J = 8.0 Hz, ArH); 7.16 (1H, s, NCH); 6.90 (1H, s, NCH); 4.46 (2H, m, CH2); 4.19 (1H, t, J = 5.0 Hz, Fluorenyl-H); 2.9 (2H, m, CH2); 2.15 (2H, sept, J = 6.5 Hz, $CH(CH_3)_2$); 1.19 (6H, d, J = 6.5 Hz, $CH(CH_3)_2$); 1.19 (6H, d, J = 6.5 Hz, CH(CH3)2).

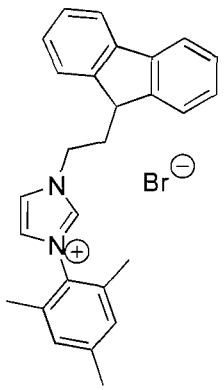
$^{13}C\{^1H\}$ ($CDCl_3$, 300 MHz): 145.2 (Ar); 145.1 (Ar); 141.0 (Ar); 138.1 (imidazolium -CH); 131.8 (NCH); 130.1 (Ar); 127.7 (NCH); 127.5 (Ar); 124.8 (ArH); 124.5 (ArH); 123.6 (ArH); 123.2 (ArH); 120.1 (ArH); 47.6 (CH2); 44.9 (Fluorenyl-CH); 33.9 (CH_2); 24.4 ($CH(CH_3)_2$); 24.2 ($CH(CH_3)_2$).;15.2 ($CH(CH_3)_2$).

Calculated (%) C, 71.85, H, 6.63, N, 5.59; Found C, 71.92, H, 6.57, N, 5.60.

MS ES+: 421 (M-Br-)+

M.P.: 155 °C (ether).

1-[2-(9*H*-Fluoren-9-yl)-ethyl]-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium bromide 2.10b



An ampoule containing 9-(2-bromoethyl)-9*H*-fluorene (18 mmol, 15 g); mesitylimidazole (18 mmol, 3.4 g) and dioxane (100 ml) was heated to 100 °C for 5 days. The volatiles were removed and the residues were dissolved in the minimum amount of DCM (5 ml). The solution was then added slowly to ether (100 ml). The resulting solid was filtered and washed with diethyl ether (100 ml); and dried under reduced pressure. The solid was dried azeotropically with toluene. The product was isolated as a white solid (6.6g , 79%). The product was stored in a glovebox due to its hydroscopic nature, when left in air the product would rapidly form an oil.

^1H ($CDCl_3$, 300 MHz): 10.36 (1H, m, imidazolium-H); 7.70 (2H, m, Ar); 7.55 (2H, m, Ar); 7.38 (2H, m, Ar); 7.30 (2H, m, Ar); 6.94 (2H, s, Ar); 6.77 (1H, m, imid-H); 6.73 (1H, m, imid-H); 4.35 (2H, t, J = 7.0 Hz, NCH_2); 4.24 (1H, t, J = 5.0 Hz, fluorenyl-H); 3.01 (2H, td, J = 7.0, 5.0 Hz, CH_2); 2.92 (3H, s, mesityl-CH_3); 1.99 (6H, s, mesityl-CH_3)

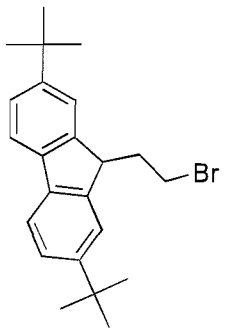
$^{13}C\{^1H\}$ (CDCl3, 75 MHz): 145.1 (Ar); 141.7 (Ar); 141.3 (Ar); 138.2 (Ar); 134.1 (Ar); 130.6 (ArH); 129.8 (CH, NCH); 127.8 (CH, NCH); 127.7 (ArH); 124.8 (ArH); 122.7

(ArH); 122.0 (ArH); 120.1 (ArH); 47.5 (NCH_2); 45.0 (Fluorenyl *C*H); 33.5 (CH_2-fluorenyl); 21.0 (CH_3); 17.8 (CH_3)

MS (ES+): 379.3 (M^+)

MP: 155 °C (DCM/ether)

2-(2,7-Di-*tert*-butyl-9H-fluoren-9-yl)-ethyl-1-bromide 2.16

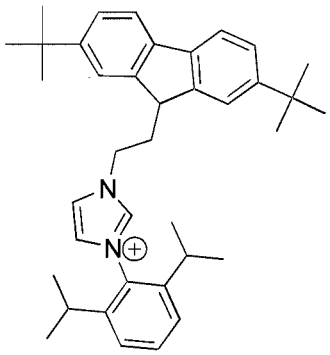


Di-*tert*-butylfluorene (36 mmol, 10g) was dissolved in ether (150 ml). The solution was cooled to –78 °C, BuLi (2.5 M in hexanes, 36 mmol, 15 ml) was added and the solution allowed to warm to room temperature and left to stir for 2 hours. The solution was recooled to –78 °C and 1,2-dibromoethane (100 mmol, 18.5g)was added. The reaction was allowed to stir overnight, the volatiles were removed under reduced pressure and the product recrystalised from petrol to give the product as a colourless crystalline material (8.1 g, 82%).

^1H ($CDCl_3$, 300 Hz): 7.68 (2H, d, J = 8 Hz, Ar); 7.59 (2H, m, Ar); 7.45 (2H, dd, J = 7,2 Hz); 4.16 (1H, t, J = 6 Hz, fluorene-H); 3.43 (2H, t, J = 8 Hz, CH2); 2.55 (2H, q, J = 8 Hz, CH_2); 1.45 (18H, s, ^{t}Bu).

$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 150.0 (Ar); 138.5 (Ar); 124.5 (Ar); 120.7 (Ar); 119.3 (ArH); 46.5 (CH, fluorenyl H); 37.0 ($BrCH_2$) 34.9(*C*, ^{t}Bu); 31.7 (*C*H, ^{t}Bu); 30.9 (CH_2).

1-[2-(2,7-Di-tert-butyl-9H-fluoren-9-yl)-ethyl]-3-(2,6-diisopropyl-phenyl)-3H-imidazol-1-ium bromide 2.17a

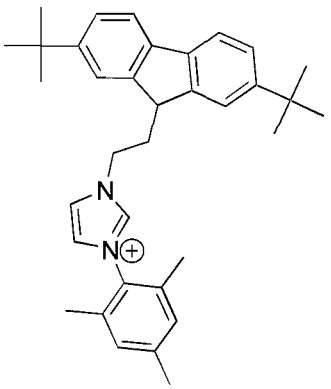


Di-*tert*-butylbromoethylfluorene (21 mmol, 8.0 g); 2,6 diisopropylimidazole (21 mmol, 4.8 g) and dioxane (100 ml) were heated at 100 °C under reduced pressure for 3 days. The reaction mixture was dried and the residues stirred with ether/petrol (50/50, 25 ml), the residues were filtered and dried. The resulting solid was dried azeotropically with toluene, the toluene was removed under reduced pressure, to give the desired product (11.3 g, 88%).

^{1}H ($CDCl_3$, 300 Hz): 10.39 (1H, s, imidazolium-H); 7.62 (1H, m, Ar); 7.59 (2H, m, Ar); 7.39 (3H, m, Ar); 1.17 (2H, d, J = 8Hz); 7.10 (2H, d, J = 7Hz, Ar); 7.03 (1H, m, Ar); 4.47 (2H, t, J = 5 Hz, NCH_2); 4.15 (1H, t, J = 5 Hz, fluorenyl-H); 2.80 (2H, q, J = 7 Hz, CH2); 2.11 (2H, quin, J = 6 Hz, iPrH); 1.33 (18H, s, ^{t}Bu); 1.14 (6H, d, J = 6 Hz, ^{i}PrMe); 1.04 (6H, d, J = 6 Hz, iPrMe).

^{13}C{^{1}H} ($CDCl_3$, 75 MHz): 149.5 (Ar); 145.4 (Ar); 144.8 Ar); 137.5 (Ar); 130.8 (ArH); 128.0 (ArH); 125.3 (ArH) 124.9 (ArH); 124.1 (ArH) 123.8 (ArH) 21.6 (ArH); 119.4 (ArH); 47.8 (CH_2N); 46.4 (fluorenyl-H) 34.5 (CH_2); 31.7 (^{t}BuMe); 28.5 (H, ^{i}Pr); 27.5 (C, ^{t}Bu); 24.4 (Me, ^{i}Pr); 24.2 (Me, ^{i}Pr).

1-[2-(9*H*-Fluoren-9-yl)-ethyl]-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium bromide 2.17b



An ampoule containing 9-(2-bromoethyl)-9*H*-fluorene (5.0 g, 18 mmol), mesitylimidazole (3.4 g, 18 mmol) and dioxane (100 ml) was heated to 100 °C for 5 days. The volatiles were removed and the residues were dissolved in the minimum amount of DCM (5 ml). The solution was then added slowly to ether (100 ml). The resulting solid was filtered and washed with diethyl ether (100 ml), and dried under reduced pressure. The solid was dried azeotropically with toluene. The product was isolated as a white solid (6.6g , 79%)

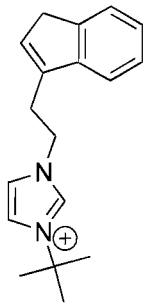
^{1}H ($CDCl_3$, 300 Hz): 10.36 (1H, m, imidazolium-H), 7.70 (2H, m, Ar), 7.55 (2H, m, Ar), 7.38 (2H, m, Ar), 7.30 (2H, m, Ar), 6.94 (2H, s, Ar), 6.77 (1H, m, imid-H), 6.73 (1H, m, imid-H), 4.35 (2H, t, J = 7.0 Hz, NCH_2), 4.24 (1H, t, J = 5.0 Hz, fluorenyl-H), 3.01 (2H, td, J = 7.0, 5.0 Hz, CH_2), 2.92 (3H, s, mesityl-CH_3), 1.99 (6H, s, mesityl-CH_3)

^{13}C{^{1}H} ($CDCl_3$, 75 MHz): 145.1 (Ar), 141.7 (Ar), 141.3 (Ar), 138.2 (CH, imid), 134.1 (Ar), 130.6 (ArH), 129.8 (CH, imid), 127.8 (CH, imid), 127.7 (ArH), 124.8 (ArH), 122.7 (ArH), 122.0 (ArH), 120.1 (ArH), 47.5 (NCH_2), 45.0 (Fluorenyl *C*H), 33.5 (*C*H_2-fluorenyl), 21.0 (*C*H_3), 17.8 (*C*H_3)

MS (ES+): 379.3 (M^+)

MP: 155 °C (DCM/ether)

3-(*tert*-Butyl)-1-[2-(3*H*-inden-1-yl)-ethyl]-2*H*-imidazolium bromide 2.19a



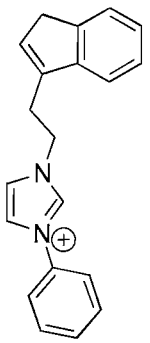
1-(2-Bromoethyl)-1H-indene (2.0 mmol, 4.4 g) and *tert*-butylimidazole (2.0 mmol, 2.5 g) were dissolved in dioxane (50 ml) and heated to 110 °C for 1 week. The dioxane was removed under reduced pressure and the resulting viscous residue was dissolved in DCM and precipitated with ether. The resulting viscous product was dried azeotropically with toluene. After removal of the toluene under reduced pressure the residue was washed with ether and dried under vacuum to give an off white powder (6.0 g, 86%)

^{1}H ($CDCl_3$, 300 MHz): 10.23 (1H, s, imidazolium-H); 7.64 (1H, t, J =2 Hz, *H*C=CH); 7.39 (1H, t, J =2 Hz, *H*C=CH); 7.31-7.28 (1H, m, Ar); 7.23-7.21 (1H, m, Ar); 7.12-7.03 (2H, m, Ar); 6.34 (1H, s, indene-CH); 4.66 (2H, t, J = 7 Hz, CH_2); 3.19 (2H, s, indene-CH_2); 3.13 (2H, t, J =7Hz, CH_2); 1.49 (9H, s, ^{t}Bu)

^{13}C{^{1}H} ($CDCl_3$, 75 MHz): 143.8 (Ar); 138.6 (ArH); 135.3 (Ar); 131.2 (ArH); 127.8 (Ar); 125.9 (ArH); 124.7 (ArH); 123.6 (ArH); 122.5 (ArH) 119.1 (ArH) 118.3 (ArH); 59.9 (Me_3C); 48.6 (CH_2); 37.7 (CH_2); 29.8 (CH_3); 28.42 (CH_2)

Mass Spec (ES+) 267.1 M^+

3-Phenyl-1-[2-(3H-inden-1-yl)-ethyl]-2H-imidazolium bromide 2.19b



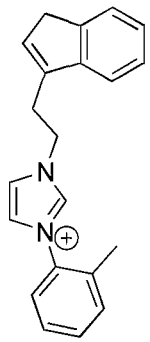
1-(2-Bromoethyl)-1H-indene (1.0 mmol, 2.2 g) and phenylimidazole (1.0 mmol, 1.4 g) were dissolved in dioxane (50 ml) and heated to 110 °C for 1 week. X-ray quality

crystals were obtained when the reaction mixture was cooled as colourless needles. The crystals were washed with ether and dried under reduced pressure. The product was dried azeotropically with toluene, removal of the toluene gave the product as a colourless crystalline material. Yield (3.1 g, 86%)

^{1}H ($CDCl_3$, 300 MHz): 10.84 (1H, s, imidazolium-H); 7.71 (2H, dt, J = 14, 2 Hz, Ar); 7.66-7.63 (2H, m, Ar); 7.45-7.34 (5H, m, Ar); 7.18-7.02 (2H, m, Ar); 6.41 (1H, s, indene-CH); 4.84 (2H, t, J = 7 Hz, CH_2); 3.27 (2H, s, indene-CH_2); 3.23(2H, t, J =7Hz, CH_2)

^{13}C{^{1}H} ($CDCl_3$, 300 Hz): 143.8 (Ar); 138.6 (Ar) 135.3 (ArH); 134.2 (Ar); 131.4 (ArH); 130.3 (ArH); 129.9 (ArH); 126.1 (ArH); 125.0 (ArH); 123.8 (ArH); 123.6 (ArH); 121.6 (ArH); 120.3 (ArH); 118.6 (ArH); 48.9 (CH_2); 37.9 (CH_2); 28.5 (CH_2)

3-(2-methylphenyl)-1-[2-(1-3H-indenyl)-ethyl]-2H-imidazolium bromide 2.19c



1-(2-Bromoethyl)-1H-indene (1.0 mmol, 2.2 g) and *tert*-butylimidazole (1.0 mmol, 1.6 g)) were dissolved in dioxane (50 ml) and heated to 110 °C for 1 week. After removal of the volatiles under reduced pressure, the resulting solid was dissolved in DCM and precipitated with ether. The solid was filtered and dried azeotropically. Removal of the toluene gave the product as a colourless powder. Yield (3.0 g, 79%).

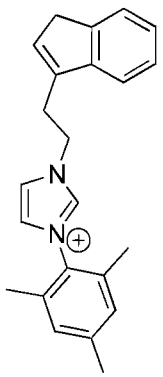
^{1}H ($CDCl_3$, 300 Hz): 10.27 (1H, t, J = 1 Hz, imidazolium-H); 7.80 (1H, t, J = 1 Hz, CH=C*H*); 7.42-7.35 (3H, m, Ar); 7.31-7.17 (6H, m, Ar); 6.50 (1H, s, indene-CH); 5.00 (2H, t, J = 7 Hz, CH_2); 3.30 (4H, m, CH_2 and indene CH_2); 2.12 (3H, s, Me)

^{13}C{^{1}H} ($CDCl_3$, 75 Hz): 144.1 (Ar); 144.1 (Ar) 138.8 (Ar) 137.4 (ArH); 133.67 (Ar); 133.18(ArH); 132.0 (ArH) 131.0 (ArH); 127.7 (ArH); 126.4 (ArH); 126.1 (ArH);

125.2 (ArH); 124.0 (ArH); 123.3 (ArH); 122.7 (ArH); 118.7 (ArH); 49.3 (CH_2); 38.1 (CH_2); 28.6 (CH_2); 17.6 (CH_3)

MS (ES^+) 301.0 (M^+)

3-(2,3,5-trimethylphenyl)-1-[2-(3H-inden-1-yl)-ethyl]-3H-imidazolium bromide 2.19d



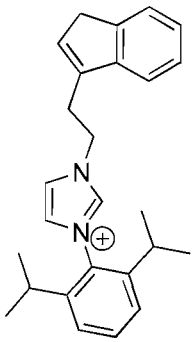
1-(2-Bromoethyl)-1H-indene (1.0 mmol, 2.2g) and mesitylimidazole (1.0 mmol, 1.9 g) were dissolved in dioxane (50 ml) and heated to 110 °C for 1 week. After removal of the volatiles under reduced pressure, the resulting solid was dissolved in DCM and precipitated with ether. The solid was filtered and dried azeotropically. Removal of the toluene gave the product as a colourless powder. Yield 2.8 g, 68%

^1H ($CDCl_3$, 300 Hz): 9.97 (1H, t, *J* =1 Hz, imidazolium-H); 7.95 (1H, t, *J* = 1Hz, CH=C*H*); 7.37 (2H, t, *J* =8 Hz, Ar) 7.22-7.10 (2H, m, Ar); 7.02 (1H, t, *J* = 1 Hz, CH=C*H*); 6.86 (2H, s, Ar); 6.44 (1H, s, indene-CH); 3.28 (4H, m CH_2); 3.23 (2H, s, indene CH_2); 2.32 (3H, s, Me); 1.83 (6H, s, Me)

$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 143.9 (Ar); 143.8 (Ar); 138.6 (ArH); 133.9 (Ar); 131.7 (ArH); 130.4 (ArH); 128.0 (ArH); 126.2 (ArH); 125.0 (ArH); 123.8 (ArH); 123.6 (ArH); 122.7 (ArH); 118.8 (ArH); 49.0 (CH_2); 37.9 (CH_2); 28.3 (CH_2); 20.8 (CH_3); 17.2 (CH_3)

MS (ES^+) 329.1 M^+

3-(2,6-Diisopropylphenyl)-1-[2-(3H-inden-1-yl)-ethyl]-2H-imidazolium bromide 2.19e



1-(2-Bromoethyl)-1H-indene (90mmol, 20g) and 2,6-diisopropylphenylimidazole (90 mmol, 21g) were dissolved in dioxane (100 ml) and heated to 110 °C for 1 week. The dioxane was removed under reduced pressure and the resulting viscous residue was dissolved in DCM and precipitated with ether. The resulting viscous product was dried azeotropically with toluene. After removal of the toluene under reduced pressure the residue was washed with ether and dried under vacuum to give an off white powder (25 g, 61%.)

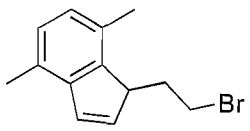
^{1}H ($CDCl_3$, 400 MHz): 10.13 (1H, s, imidazolium-H); 8.01 (1H, s, Ar); 7.43-7.36 (3H, m, Ar); 7.23-7.11 (5H, m, Ar); 6.99 (1H, s, NCH); 6.48 (1H, s, NCH);5.10 (2H, t, J = 6.5 Hz, CH_2); 3.30 (2H, t, J = 6.5Hz, CH_2); 3.21 (2H, s, indenyl-CH2); 2.02 (2H, sept, J = 7Hz, ipr-CH) 1.06 (6H, d, J = 7 Hz, iPr-CH_3); 0.97 (6H, d, J = 7 Hz, ipr-CH_3).

$^{13}C\{^{1}H\}$ (CDCl3, 100 MHz): 144.3 (Ar); 143.1 (Ar); 137.8 (ArH); 137.1 (Ar); 130.8 (ArH); 127.2 (Ar); 125.4 (ArH); 124.3 (ArH) 124.2 (ArH); 123.6 (ArH); 123.0 (ArH); 122.8 (ArH); 118.0 (ArH); 48.1 (CH_2); 37.1 (CH_2); 27.6 (CH) 27.6(CH_3); 23.2 (CH_3).

MS, ES+ 371 (M+, 100%).

Calculated (%) C, 68.44, H, 6.13 N, 5.32, found C, 68.45, H, 6.20 N, 5.23.

1-(2-Bromoethyl)-4,7-dimethyl-1H-indene 2.26



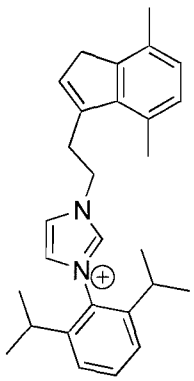
(125 mmol, 18 g) 4,7-dimethylindene was treated with 1eq. of BuLi (2.5 M in hexanes, 125 mmol, 50 ml) in ether (500 ml) at -78°C. After warming to room temperature for 2h; the solution was again cooled to -78°C and 3 eq. of dibromoethane (375 mmol, 69 g) was added. The solution was allowed to stir overnight. Water 200 ml was added, after separation, the organics were dried ($MgSO_4$). The solvent was evaporated under vacuum to leave a dark oil. The resulting oil was distilled (100 °C, 1 Torr); to give a light yellow to orange oil (22.9 g, 75%). The resulting product was kept under nitrogen in the freezer.

^1H ($CDCl_3$, 400 MHz): 7.20 (1H, d, J = 7.5 Hz, ArH); 7.14-7.10 (3H, m, 1-H); 6.90 (1H, dd, J = 5, 3 Hz, 2-H); 3.94-3.92 (1H, m, 3-H); 3.50-3.45 (2H, m, BrCH2); 2.93-2.84 (1H, m, BrCH2CH2); 2.61 (6H, s, 2 x CH3); 2.28-2.20 (1H, m, BrCH2CH2).

$^{13}C\{^1H\}$ ($CDCl_3$, 100 MHz): 142.2; 141.3; 134.9 128.7; 128.7; 126.7; 126.4; 125.6; 47.6; 31.3; 29.5; 17.2; 16.6.

EI MS: 250, 252 (M+.)

3-(2,6-Diisopropyl-phenyl)-1-[2-(3H-(4,7-dimethyl)inden-1-yl)-ethyl]-3H-imidazolium bromide 2.27



1-(2-Bromo-ethyl)-4,7-dimethyl-1H-indene (22.6 g, 90.0 mmol) and 2,6-diisopropylphenylimidazole (21.0 g, 90.0 mmol) were dissolved in dioxane (100 ml) and heated to 110 °C for 1 week. The dioxane was removed under vacuum and the resulting solid was dissolved in DCM and precipitated with ether. The resulting solid was dried

azeotropically with toluene. After removal of the toluene under reduced pressure the residue was washed with petrol and dried under vacuum to give an off white powder (26 g, 61%.)

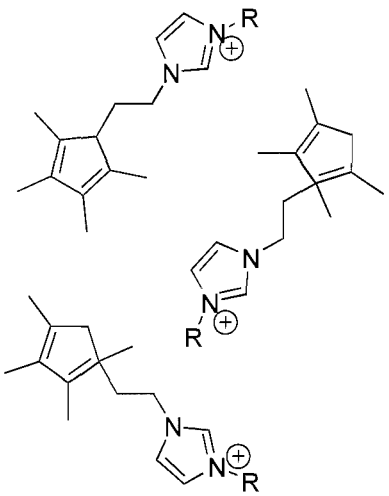
^{1}H (CDCl3, 300 MHz): 10.34 (1H, s, imidazolium H); 7.68 (1H, s, ArH); 7.48-7.42 (1H, t, J = 6Hz, ArH); 7.23-7.20 (3H, m, ArH); 7.00 (1H, s,) 6.88 (2H, q, J = 8 Hz, ArH); 6.30 (1H, s, 2-H); 5.11 (2H, t, J = 6 Hz, CH_2); 3.47 (2H, bs, CH_2); 3.06 (2H, s, 3-H); 2.53 (3H, s, CH3); 2.18 (3H,s , CH3); 2.16 (2H, sept, J = 7Hz, CH(CH3)2); 1.15 ((6H, d, J = 7Hz, CH(CH3)2); 1.04 ((6H, d, J = 7Hz, CH(CH3)2).

^{13}C{^{1}H} ($CDCl_3$, 75 MHz): 145.3; 143.8; 140.9; 140.6; 138.5; 131.9; 131.8; 131.0; 130.8; 130.1; 129.8; 126.5; 124.7; 123.6; 123.2; 49.8; 36.6; 31.5; 28.7; 24.3; 24.2; 20.2; 18.2.

Calculated (%) C, 70.14, H, 7.36, N, 5.84. found C, 69.90, H, 7.37, N, 5.77

MS ES+: 400 M+

3-(2,6-Diisopropyl-phenyl)-1-[tetramethylcyclopentadienyl]-imidazolium chlorides 2.32



R = 2,6diisopropylphenyl

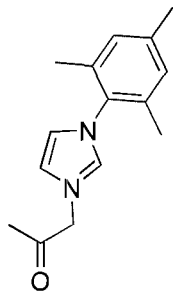
Chloroethyl-2,3,4,5-tetramethylcyclopentadienes (20 mmol, 3.7 g) and 2,6-diisopropylphenylimidazole (20 mmol, 4.6 g) were heated under partial vacuum at 140°C for 4 days in a thick wall glass ampoule equipped with a Youngs' valve. After cooling the resulting solid is dissolved in the minimum of THF and precipitated by addition of ether. This was repeated until the impurities were removed (by ^{1}H NMR spectroscopy). The product is a pale brown powder (*ca* 50% yield).

MS ES^+:321 $(M\text{-}Cl^-)^+$.

^1H NMR ($CDCl_3$): 10.85 (0.8H, bs) and 10.96 (0.2H, bs) imidazolium proton; 7.49 (1H, t, J = 8 Hz, ArH); 7.47 (1H, s, backbone-CH); 7.26 (2H, d, J = 8 Hz, ArH); 7.10 (1H, s, backbone-CH); 5.88 (0.8H, bs) and 5.75 (0.2H, bs) CpH; 4.73 (0.2H, m CpH); 4.03 (1.6H, two multiplets) and [5.01 (0.2H, bs), 4.30 (0.1H, bs)] bridge. 2.23 (4H, m, bridge and CH isopropyl); 1.86-1.75 (6H, m, cp-Me); 1.23-0.98 (18H, m, cp-Me and isopropyl Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.0 (C, Ar); 145.3 (C, Ar); 139.5 (C, Cp); 134.4 (CH, Ar); 131.7 (CH, Cp); 130.3 (CH, Ar); 124.53 (CH, Ar); 123.5 (CH, Ar); 123.2 (CH, Ar); 47.5 (CH_2, Bridge); 36.6 (CH_2, Bridge); 28.7 (CH, isopropyl), 24.2 (CH_3, isopropyl); 21.7 (CH_3, CpMe); 12.6 (CH_3, CpMe).

Calculated (%) C, 75.61, H, 9.03, N, 6.78 Found: C, 75.52, H, 8.96, N, 6.82

1-(2-Oxopropyl)-3-(2,4,6-trimethylphenyl)-3H-imidazol-1-ium bromide 2.46



An ampoule containing mesitylimidazole (40 mmol, 7.4 g), chloroacetone (40 mmol, 3.6 ml) and dioxane (100 ml) were heated to 100 °C overnight under partial vacuum. The volatiles were removed under reduced pressure and the residues dissolved in the minimum of DCM (5 ml) and then poured into ether (250 ml). The product was then isolated by filtration and dried under vacuum. The product was isolated as a white powder (9.6 g, 87%).

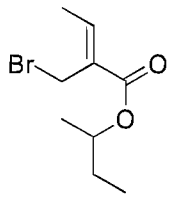
NMR (^1H, $CDCl_3$): 9.90 (1H, m, imid-H), 8.07 (1H, m, NC*H*), 7.10 (1H, m, NC*H*), 9.95 (2H, s, Ar), 6.06 (2H, s, NCH_2CO), 2.34 (3H, s, Ar*Me*), 2.30 (3H, s, $COCH_3$), 2.03 (6H, s, Ar*Me*).

NMR ($^{13}C\{^1H\}$, $CDCl_3$): 199.2, (*C*O), 141.2, (Ar), 138.9 (Imid-H), 134.3, (Ar), 130.7 (Ar), 129.8 (*C*H), 125.0 (*C*H), 122.1 (ArH), 58.6 (CH_2), 27.4, (NCH_2CO), 21.0 (CH_3), 17.4 (CH_3)

MS (ES^+): 243 M^+

MP 201 °C (dec.)

(Z)-2-Bromomethyl-but-2-enoic acid *sec*-butyl ester 2.33



Method as Helvetica Chimica Acta, **1984**, 414 substituting 3-hydroxy-2-methylene-butyric acid *sec*-butyl ester for 3-hydroxy-2-methylene-butyric acid *tert*-butyl ester.

^1H NMR (300 MHz, $CDCl_3$) 6.98 (1H, q, J = 7Hz, CH); 4.90 (1H sextet, J = 6Hz, CH); 4.18 (2H, s, CH_2Br); 1.85 (3H, d, J -= 7Hz, CH_3) 1.63-1.51; (2H, m, CH_2); 1.20 (3H, d, J = 6Hz, CH_3); 0.87 (3H, t, J = 8Hz, CH_3)

^{13}C NMR (75 MHz, $CDCl_3$) 177.4 (C=O); 142.7 (CO_2CH); 130.8 (C); 73.3 (CH); 28.8 (CH_2); 24.1 (CH_2); 19.4 (CH_3) 15.9 (CH_3); 9.6 CH_3)

MS CI 235, 237 ($M+H^+$, 100%)

Table 2.1 Crystallographic parameters for compounds from this chapter

Identification code	**2.19b**	**2.27**
Empirical formula	$C_{24}H_{27}BrN_2O_2$	$C_{29}H_{37}BrCl_2N_2$
Formula weight	455.39	564.42
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	$C_{2/c}$
Unit cell dimensions	a = 8.2154(8) Å	a = 28.8436(13) Å
	α= 75.607(4)°.	α= 90°.
	b = 8.7904(8) Å	b = 9.2261(4) Å
	β= 79.709(3)°.	β= 123.067(2)°.
	c = 15.2315(15) Å	c = 25.4781(12) Å
	γ = 85.148(4)°.	γ = 90°.
Volume	1047.37(17) $Å^3$	5681.9(4) $Å^3$
Z	2	8
Density (calculated)	1.444 Mg/m^3	1.320 Mg/m^3
Absorption coefficient	1.985 mm^{-1}	1.655 mm^{-1}
F(000)	472	2352
Crystal size	0.80 x 0.08 x 0.04 mm3	0.30 x 0.20 x 0.10 mm3
Theta range for data collection	3.05 to 27.89°.	3.11 to 27.79°.
Index ranges	-10<=h<=10	-37<=h<=37
	-11<=k<=11	-11<=k<=11
	-19<=l<=19	-33<=l<=33
Reflections collected	17769	58044
Independent reflections	4820 [R(int) = 0.0863]	6548 [R(int) = 0.0785]
Completeness to theta = 27.89°	96.2 %	99.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9248 and 0.2996	0.8520 and 0.6366
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4820 / 0 / 263	6548 / 0 / 332
Goodness-of-fit on F2	1.040	1.040
Final R indices [I>2sigma(I)]	R_1 = 0.0518, wR^2 = 0.0847	R_1 = 0.0549, wR^2 = 0.1295
R indices (all data)	R_1 = 0.0925, wR^2 = 0.0964	R_1 = 0.0938, wR^2 = 0.1484
Largest diff. peak and hole	0.486 and -0.461 $e.Å^{-3}$	1.272 and -0.442 $e.Å^{-3}$

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Chapter 3

Synthesis of Main Group Carbene Complexes

3 Main Group Chemistry

3.1 Aims

Attempts to prepare main group, namely groups 1, 2, 11, 12, 13 and 14, complexes of the NHCs derived from the imidazolium salts described in the previous chapter are described in this chapter. It was hoped that the monodentate NHC complexes could be synthesised, as well as the bidentate indenyl-, fluorenyl- NHC complexes. The existence of two C-H acidic sites of different pK_a (i.e. at the C2 of the imidazolium salt and the cyclopentadiene ring) raises the question of selective mono- or di-deprotonation which may lead to different binding modes of the deprotonated entity to a transition metal (monodentate, chelate bidentate or bridging.)

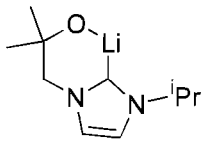
As well of being of interest in their own right, these complexes could also be used as ligand transfer reagents to synthesise transition metal complexes. The s-block, especially lithium, sodium and potassium, and silver complexes were of special interest as ligand transfer reagents. Attempts to isolate and fully characterise by a variety of methods including X-ray structure analysis where possible are described below.

3.2 Group 1 Complexes

3.2.1 Previous Examples

Isolated Group 1 NHC salts are still rare, but Arnold has shown these to be effective transmetalation regents.[1]

There are a limited number of examples of lithium carbene complexes; the first crystallographicaly characterised example was reported by Arduengo in 1999.[2] In 2004, Arnold reported the lithium imidazole-2-ylidene complex **3.1**, Figure 3.1, containing a tethered alkoxide group.[3] The only other reported example of lithium NHCs is of a borane substituted NHC.[4]

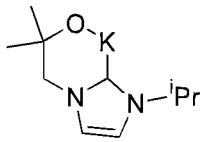


3.1

Figure 3.1 A lithium imidazole-2-ylidene.

Arnold also reported the first potassium imidazol-2-ylidene **3.2**, Figure 3.2, the example contains the same ligand system as in the lithium example above.[1]

To date, the only other example is from the communication resulting from this work.[5]



3.2

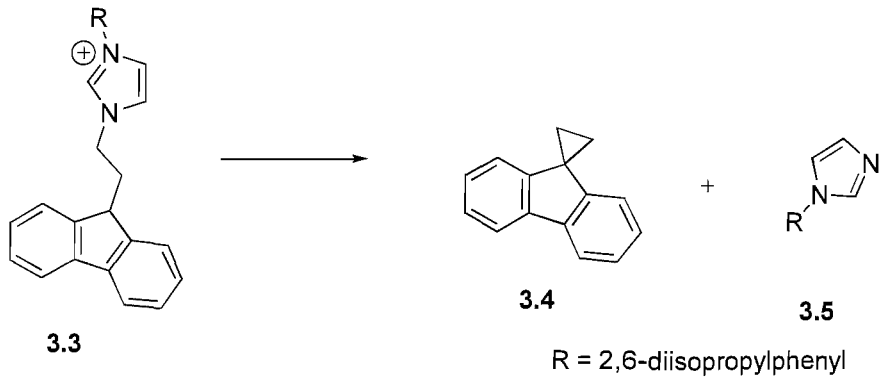
Figure 3.2 The first reported potassium imidazole-2-ylidene.

No sodium or caesium NHC complexes have yet been reported.

Our aim was to synthesise a compound containing a lithium or potassium cyclopentadienyl moiety and a free carbene in order to use it as ligand transfer reagent for the synthesis of transition metal complexes. It may be envisaged that this NHC functionality of this compound may interact with the coordination sphere of the Group 1 metal.

3.2.2 Attempted Synthesis of Lithium Complexes

Attempts were made to synthesise the lithium fluorenyl carbene from the imidazolium salt **3.3** and two equivalents of ^{n}BuLi. Attempts to crystallise the lithium fluorenyl functionalised NHC led to crystalline materials that were characterised by X-ray crystallographic analysis as 2,6-diisopropylphenylimidazole **3.5** and the spiro cyclopropyl-fluorene **3.4**, Scheme 3.1. It is unclear how these by-products were formed, but it could be envisaged that the fluorenyl is deprotonated first to form the zwitter ionic imidazolium salt, and that the bridge head carbon attacks the bridge and the substituted-imidazole is lost as a leaving group. Deprotonation was also attempted with LiHMDS but this lead to the same decomposition as with ^{n}BuLi, the mechanism for this decomposition is unclear.



Scheme 3.1 Decomposition of imidazolium salt during attempted deprotonation.

3.2.3 Sodium Compounds

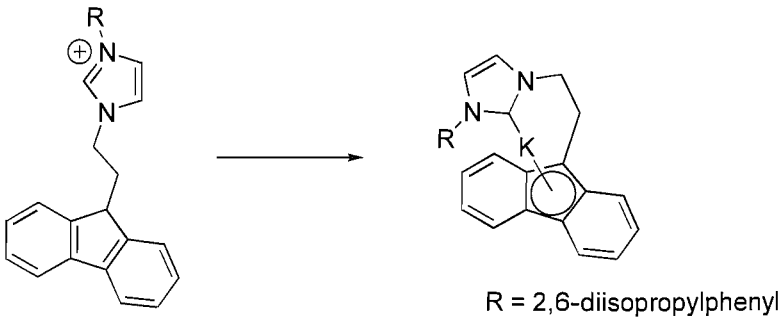
Attempts were made to use NaHMDS to deprotonate the fluorenyl imidazolium salt, but unfortunately, the desired product could not be identified, again the 2,6-diisopropylimidazole **3.5** and spirofluorene **3.4** compounds were identified by NMR spectroscopy.

3.2.4 Potassium Compounds

Attempts were made to deprotonate the fluorenyl imidazolium salt with KHMDS or KH in various solvents. In this case the formation of the desired potassium fluorenyl carbene **3.6** was identified, by NMR spectroscopy, but the desired product could not be isolated from the reaction mixture, which contained 2,6-diisopropylphenylimidazole **3.5** and the spiro cyclopropane fluorenyl compound **3.4**. Washing with petrol removed the spiro cyclopropane fluorenyl compound, but did not remove the 2,6-diisopropylphenylimidazole. Attempts to dissolve the 2,6-diisopropylphenylimidazole in ether also resulted in the potassium fluorenyl carbene being dissolved and also was accompanied by some decomposition, an explanation for this could be the ether displaces the NHC.

A synthetic method for producing pure potassium fluorenyl NHC **3.6** was discovered serendipitously when an NMR experiment was carried out to investigate the reaction of KHMDS with the fluorenyl imidazolium salt in d_6-benzene. The NMR spectra appeared to show that none of the expected product was present and that complete decomposition had taken place. On closer examination, the NMR tube was seen to contain X-ray quality, extremely small, bright orange crystals. The X-ray structure of these crystals was determined and indeed showed that the crystals were the desired material and

were only sparingly soluble in benzene, which accounts for the low quality of the ^{1}H-NMR spectrum of the deprotonation mixture.



3.3 **3.6**

Scheme 3.2 Direct synthesis of fluorenyl potassium NHC. Reagents and conditions: 2 eq. KHMDS, benzene

The fluorenyl potassium NHC **3.6** crystallised, from the reaction of **3.3** and KHMDS in benzene, in the monoclinic space group $P2_1/n$ with a = 20.531(7) Å, b = 13.027(4) Å c = 23.378(8) Å, α = 92.220(5)°. V = 6248(4) Å^3 and D_{calcd} = 1.141 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6715 unique reflections (R_{int} = 11.36%) converged to a final R_1 = 6.62% ($I > 2(I)$) and Rw^2 = 15.2%. The asymmetric unit cell contained three molecules of benzene that are not shown in the ORTEP diagrams. Two of the molecules of benzene were modelled normally, the third was highly disordered and could not be adequately modelled, so was accounted for by removing the electron density form the density map using PLATON-squeeze.[6]

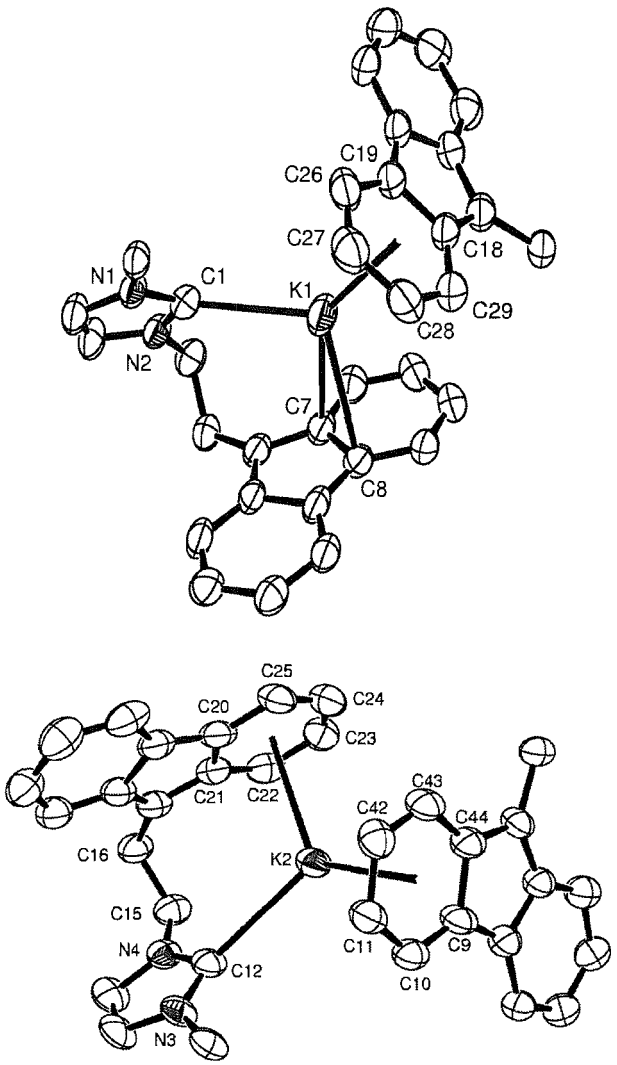


Figure 3.3 ORTEP representation of the coordination sphere of K in the two repeat units of the chain structure of **3.6** with 50% probability ellipsoids. H atoms, the phenyl rings and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-K(1) 2.896(5); C(7)-K(1) 2.941(5); C(8)-K(1) 3.014(5); C(48)-K(1) 3.244(5); C(12)-K(2) 2.911(5); C(20)-K(2) 3.177(5); C(21)-K(2) 3.018(5); C(22)-K(2) 3.029(5); C(23)-K(2) 3.142(5); C(24)-K(2) 3.252(5); C(25)-K(2) 3.287(5); N(2)- C(1)-K(1) 127.7(3); N(1)-C(1)-K(1) 125.1(3); N(2)-C(1)-N(1) 102.6(4); N(4)-C(12)-K(2) 123.7(3); N(3)-C(12)-K(2) 130.5(3).

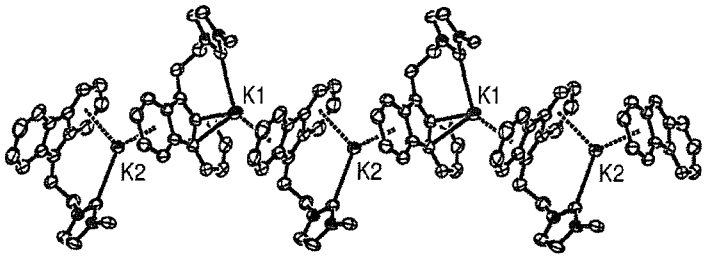


Figure 3.4 ORTEP representation of the chain structure of **3.6** with 50% probability ellipsoids. H atoms, the phenyl rings and solvent molecules are omitted for clarity.

The structure comprises polymeric 'zigzag' chains with potassium and bridging fluorenyl units, Figure 3.4. Two types of alternating repeat units featuring potassium atoms with different coordination spheres are observed.

Assuming that the longest potassium-fluorene interaction can be estimated by the sum of the ionic radius of potassium and the van der Waals radius of the carbon neighbour, the coordination sphere of K(1) comprises of one η^4 ring and one η^2 ring sandwiching the metal, whilst in K(2) there are two η^4 rings. The tethered NHC group completes the coordination sphere of both the potassium atoms. The K-$C_{carbene}$ distances (2.896 – 2.911 Å) are much shorter than those observed previously (3.048 Å)[1], possibly due to the geometry of the system. The crystallographic C(12) carbon deviates slightly from planarity (angle sum (355 – 356°), while the angle between the plane of the imidazole-2-ylidene ring and the K – C vector is in the range 22 -24°. There are three molecules of benzene in the asymmetric unit, although only two of these could be modelled in a satisfactory manner. The third had to be accounted for in the density map using Squeeze.[6] It was believed that these molecules of benzene were important for the formation of the crystals.

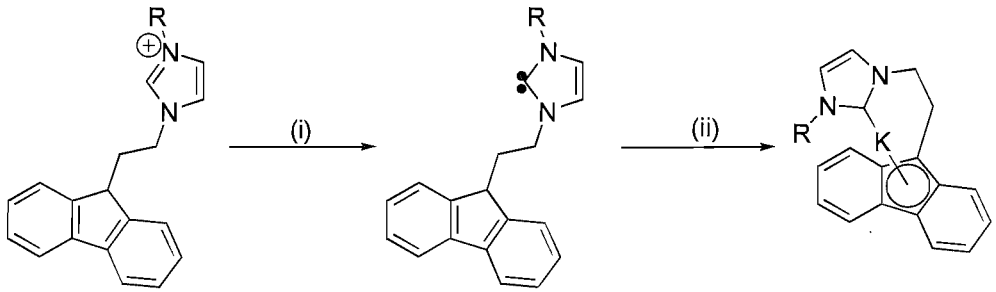
An NMR spectrum of the crystalline material was collected in d_8-THF. The $^{13}C\{^1H\}$ NMR spectrum shows a high-frequency $C_{carbene}$ chemical shift (at 206.9 ppm), this is in agreement with the only other reported potassium NHC complex(208.4 ppm). The appearance of a symmetric NMR spectrum suggests that unlike the crystal structure there is no chirality in the complex; this may indicate that the complex is fluxional or the NHC is dissociating from the K in solution to form an uncoordinated NHC. Unfortunately the NMR spectrum could not be obtained in a non-coordinating solvent due to the poor solubility of the fluorenyl potassium complex.

The formation of potassium bromide as by product from these reactions meant that a purification method needed to be refined in order to prevent the presence of KBr in the

final product. This would occur in a simple scaled up version of the NMR experiment, it would be expected that it would be difficult to separate the KBr and fluorenyl potassium NHC. It was envisaged that a two step preparative sequence could be used: In the first step reaction of the imidazolium salt with KHMDS formed the hydrocarbon soluble NHC and insoluble potassium bromide, which was easily separated by filtration. In the second step deprotonation of the fluorene functionality with KHMDS gave the potassium fluorenyl product.

Indeed when the imidazolium salt was reacted with the first equivalent of KHMDS in benzene, giving rise to the desired NHC **3.7** partially contaminated with 2,6-diisopropylphenylimidazole, the spiro-fluorene compound and other unidentified organic compounds. Several attempts were made to purify the crude free NHC but unfortunately, none of these were successful.

The benzene solution of the crude NHC **3.7** was filtered through Celite onto a second equivalent of KHMDS and overnight a bright orange microcrystalline material formed, which was identified as the desired product **3.6**. This material was filtered then washed with petrol; after prolonged drying under vacuum the desired material with no residual benzene was obtained. The material was obtained in a yield of 60%. The material was pure by NMR spectroscopy and elemental analysis with no further purification.



3.3 **3.7** **3.6**

R = 2,6-diisopropylphenyl

Scheme 3.3 Synthesis of potassium fluorenyl NHC. Reaction conditions: (i) KHMDS, benzene, RT, 3h. (ii) KHMDS, benzene, RT, overnight.

Due to the environmental and possible health implications of using benzene routinely as a solvent, the reaction was tried in other solvents including toluene and ether; unfortunately, these reactions did not work. It is believed that the benzene may play an

important role in the crystallisation of the product, which is supported by the presence of benzene in the crystal structure.

This method described above was also shown to be applicable to the 2,7-ditertbutylfluorenyl imidazolium salt **3.8**, the yield was lower 40%. This may be attributable to the alkyl groups increasing the solubility of the product **3.10**. The material produced from this reaction was unsuitable for X-ray analysis, but again clean by elemental analysis and NMR spectroscopy.

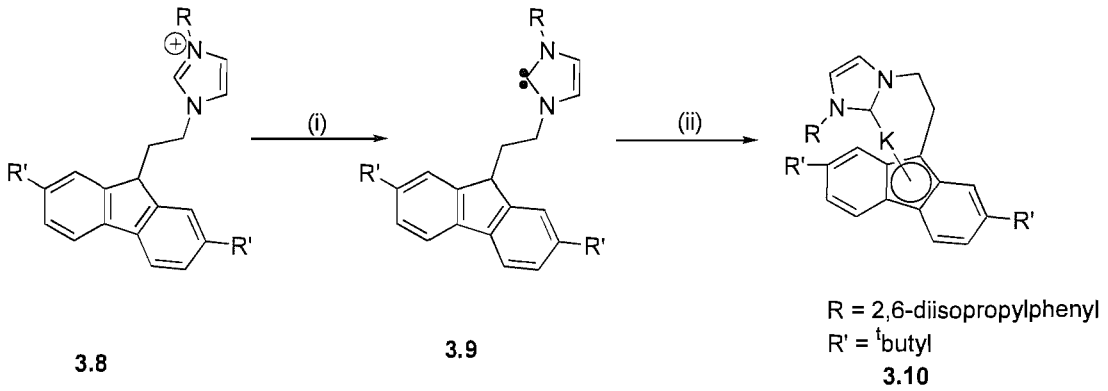
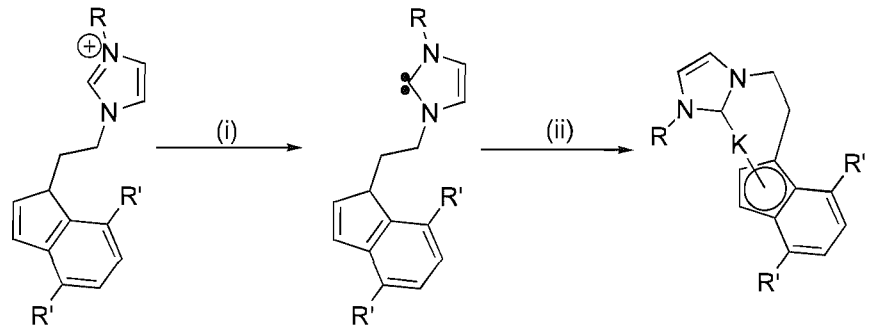


Figure 3.5 Synthesis of potassium fluorenyl NHC. Reaction conditions: (i) KHMDS, benzene, RT, 3h. (ii) KHMDS, benzene, RT, overnight

After the success of the two-step deprotonation method for the fluorenyl imidazolium salts **3.3** and **3.8**, the procedure was applied to the indene imidazolium salts. Both the unsubstituted **3.11a** and the dimethyl substituted-indene **3.11b** gave the desired products **3.13a** and **3.13b** respectively. The dimethyl substituted product **3.11b** formed more slowly compared to all the other imidazolium salts. Even though this behaviour is unclear it could be envisaged to be due to the electronic effects of the methyl groups.



R = 2,6-di-*iso*-propylphenyl
3.11a R' = H
3.11b R' = Methyl

3.12a R' = H
3.12b R' = Methyl

3.13a R' = H
3.13b R' = Methyl

Scheme 3.4 Synthesis of potassium indenyl NHC. Reaction conditions: (i) KHMDS, benzene, RT, 3h. (ii) KHMDS, benzene, RT, overnight.

The dimethyl-substituted indenyl NHC complex **3.13b** was crystallised, from a saturated solution of the compound in THF layered with petrol, in the monoclinic space group P_21/b with a = 10.4695(9) Å, b =16.6995(15) Å, c = 14.3103(12) Å, β = 92.220(5)°. V = 2462.5(4) Å^3 and D_{calcd} = 1.178 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 10116 unique reflections (Rint = 8.27%) converged to a final R_1 = 15.83% ($I > 2(I)$) and Rw^2 = 38.73%. Although the R-values are very high, the data can be used to show the overall connectivity of the system, the errors in the bond lengths are large so direct comparisons to other systems should be used with caution.

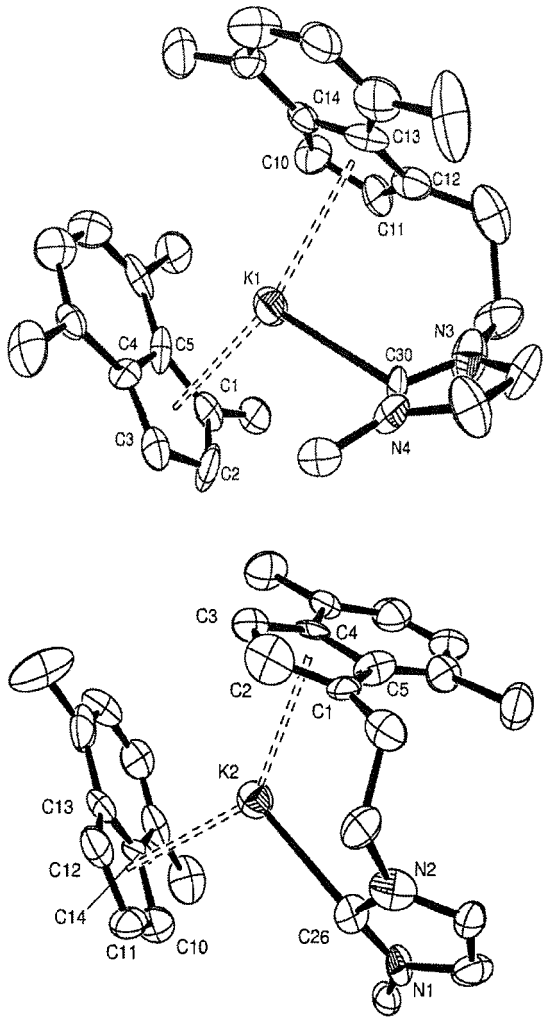


Figure 3.6 ORTEP representation of the coordination sphere of K in the two repeat units of the chain structure of **3.13b** with 50% probability ellipsoids. H atoms and the 2,6-disopropylphenyl rings expect the ipso carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: K(1)-C(1) 3.071(10); K(1)-C(2) 3.058(15);K(1)-C(3) 3.056(11); K(1)-C(4) 2.988(11); K(1)-C(5) 2.994(11); K(1)-C(10) 2.952(13); K(1)-C(11) 3.080(13); K(1)-C(12) 3.235(12); K(1)-C(13) 3.158(11); K(1)-C(14) 2.994(11); K(1)-C(30) 2.893(12); N(3)-C(30) 1.308(15); N(4)-C(30) 1.343(16); K(2)-C(1) 3.105(11); K(2)-C(2) 3.014(13); K(2)-C(3) 2.948(10); K(2)-C(4) 2.990(9); K(2)-C(5) 3.133(13); K(2)-C(10) 2.978(13); K(2)-C(11) 3.073(12); K(2)-C(12) 3.016(12); K(2)-C(13) 2.962(12); K(2)-C(14) 2.933(11); K(2)-C(26) 2.880(11); N(1)-C(26) 1.376(14); N(2)-C(26) 1.342(14); N(3)-C(30)-K(1) 125.2(9); N(4)-C(30)-K(1) 117.3(7); N(3)-C(30)-N(4) 105.2(10); N(1)-C(26)-K(2) 125.6(7); N(2)-C(26)-K(2) 119.1(7); N(2)-C(26)-N(1) 103.6(9).

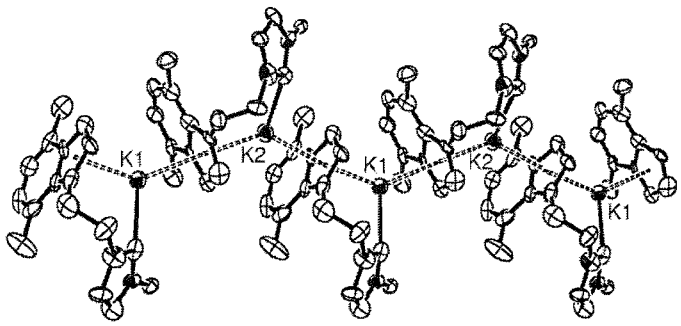


Figure 3.7 ORTEP representation of the of the chain structure of **3.13b** with 50% probability ellipsoids. H atoms and the phenyl rings of the imidazolium rings are omitted for clarity.

The structure comprises polymeric 'zigzag' chains with potassium and bridging indenyl units, in an analogous fashion to the fluorenyl potassium NHC structure. Two types of alternating repeat units featuring potassium atoms with broadly similar coordination spheres are observed.

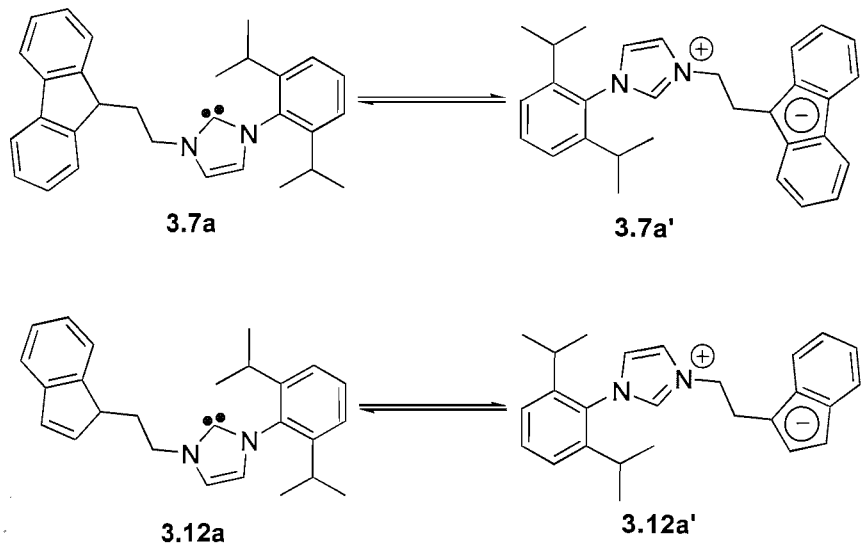
Both potassium environments consist of two η^5 indenyl rings and a coordinated NHC. The K – $C_{carbene}$ bonds lengths (2.880 - 2.893 Å) are similar to the lengths observed for the fluorenyl complex, which are shorter than previously seen. The angle between the CNC plane and the K1 – C vector is in the range 31 – 33°, whilst the angle between the CNC plane and the K2 – C vector is in the range 39 – 40°. These values are much larger than the fluorenyl case, and may indicate that the ligand is more strained, as the coordination is now to the five membered ring rather than adjoined six membered ring.

It is interesting to note that both of these potassium carbene complexes form broadly similar structures in the solid state. Both complexes have formed infinite chains where the potassium is coordinated to two cyclopentadienyl moieties and also had one coordinated NHC.

The observed order of deprotonation of the C-H acidic groups in these imidazolium salts is the opposite of that expected based on the acidity of NHCs, indenyl and fluorenyl anions in DMSO.[7,8,9] This discrepancy may be related to the kinetic nature of the products isolated and solvent effects. The loss of KBr as a precipitate from benzene may force any equilibrium established towards the free carbene in the first deprotonation.

Heating solutions of crude indene carbene **3.12a** or fluorene carbene **3.7** in d_8-THF resulted in the formation of equilibrium mixtures of the corresponding tautomers, indenyl

imidazolium salt **3.12a'** and fluorenyl imidazolium salt **3.7'**, as observed by NMR spectroscopy. The fluorene carbene produced a 1:1 mixture whereas the indene carbene gave a 3:1 mixture. The formation of these equilibrium mixtures suggests that the acidity of the NHCs compared to the indene or fluorenyl groups in these compounds are somewhat comparable.



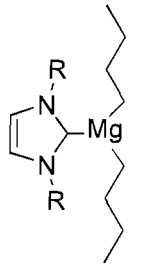
Scheme 3.5 Tautomeristion of carbene compounds.

3.2.5 Summary of Group 1 Complexes

A method has been found to prepare potassium complexes in reasonable yields. The complexes are among the few potassium carbenes that have been structurally characterised. The angles between the CNC plane and the K vectors are large indicating a weak interaction between the carbene and potassium. Methods have yet to found to synthesise sodium or lithium carbene complexes.

3.3 Group 2 Complexes

There is only one report of magnesium carbene complexes, in 1993, Arduengo reported the mesityl and adamantyl imidazol-2-ylidene adducts of dibutyl magnesium **3.16**.[10] There are no other reported group 2 complexes of carbenes.



R = mesityl, adamantyl

3.16

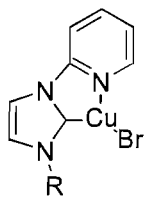
Figure 3.8 Magnesium NHC complexes.

3.3.1 Attempted Synthesis of Magnesium Complexes

Attempts were made to synthesise magnesium complexes however, the lack of reported complexes meant there are no established methods to synthesise them. Arduengo's method of adding dibutyl magnesium to the free NHC was unsuitable because the free NHC could not be isolated in our case. The imidazolium salts were added to both one and two equivalents of dibutyl magnesium. NMR spectroscopy of the products revealed that deprotonation of the imidazolium salt had taken place indicated by the disappearance of signal at around 10 ppm, however, the product could not be identified any further or isolated. It appeared even with the addition of a second equivalent of dibutyl magnesium that the second deprotonation did not take place.

3.4 Group 11 Complexes

In 1993, Arduengo reported the first copper NHC complexes. [11] In 2001, Danopoulos reported a series of pyridine-*N*-functionalised NHC carbene complexes, Figure 3.9 shows one example **3.17**.[12] In 2005, Petersen reported a series of copper alkyl carbene complexes.[13]

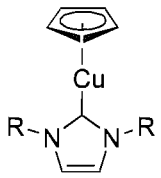


R = 2,6-diisopropylphenyl

3.17

Figure 3.9 A pyridyl-functionalised NHC complex of copper.

In 2006 Wang reported the first syntheses of copper(I) half sandwich complexes, **3.18**;[14] this paper described several complexes with different NHC substitution. These were related to our target compounds even though they do not feature tethers between the NHC and cyclopentadienyl moieties. A point of interest is that these reported complexes are not entirely thermally stable and decompose upon heating.



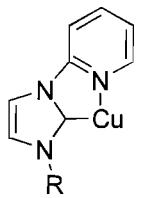
R = ^{i}Pr, ^{t}Bu, Mes, 2,6 diisopropylphenyl

3.18

Figure 3.10 Copper half-sandwich complex.

Silver complexes have been used as carbene transfer reagents. They are of interest as precursors to the ligands as they may allow transfer to late transition metals.

The first silver complexes were reported by Arduengo as early as 1993.[11] In 1998, Lin reported the facile synthesis of silver carbenes using Ag_2O acting simultaneously as silver source and base.[15] The first silver complexes containing mixed donors were reported by Danopoulos in 2000.[16] These complexes contained pyridine ligands as an extra donor.

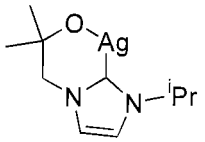


R = 2,6-diisopropylphenyl

3.19

Figure 3.11 A pyridyl-functionalised NHC complex of silver.

There are only limited examples of silver carbenes with an anionic donor described in the literature. In 2001, Arnold reports a bis-carbene alkoxide complex of silver.[17] Later in 2005, Arnold reports a mono carbene alkoxide complex.[18] These complexes were investigated as potential ligand transfer reagents for anionic carbene complexes.



3.20

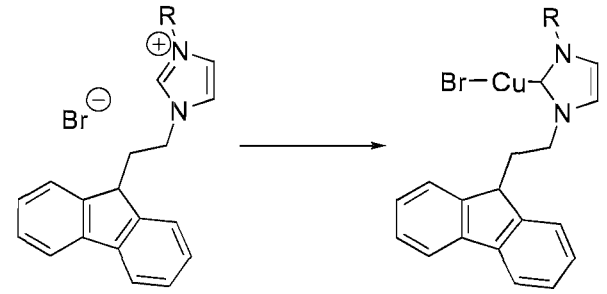
Figure 3.12 A silver NHC complex with anionic ligand.

Gold NHC complexes have remained relatively unexplored,[19] but form similar structures to silver carbenes.

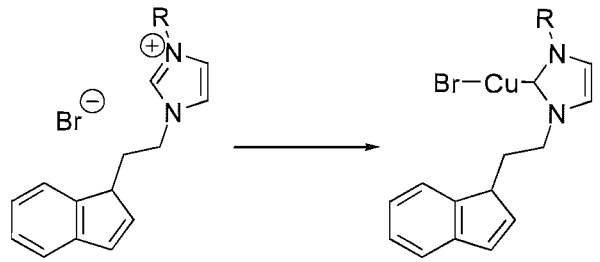
3.4.1 Synthesis of Copper Complexes

Attempts were made to react the pre-formed indenyl and fluorenyl potassium NHCs with copper (I) halides, however these reactions were unsuccessful.

The copper carbene complexes were synthesised from basic $(CuHMDS)_4$ and the imidazolium salt in toluene in an aminolysis reaction. The $(CuHMDS)_4$ acted as an in situ base to give the desired mono dentate carbene copper complexes cleanly. After washing with petrol, analytically pure product was obtained. The reaction was shown to be general for both the fluorenyl and indenyl imidazolium salts.



3.21



3.22

R = 2,6-diisopropylphenyl

Scheme 3.6 Synthesis of copper carbene complexes form the imidazolium salts. Reaction conditions: $(CuHMDS)_4$, toluene, -78 °C – RT, overnight.

Attempts were made to crystallise all the copper carbene complexes synthesised.

3.21 was crystallised, from a saturated solution of the compound in DCM layered with ether, in the orthorhombic space group P_{bca} with a = 9.5934(7) Å, b = 16.173(2) Å, c = 35.316(4) Å. V = 5479.4(10) Å^3 and D_{calcd} = 1.367 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 4942 unique reflections (R_{int} = 15.61%) converged to a final R_1 = 9.93% ($I > 2(I)$) and Rw^2 = 18.35%.

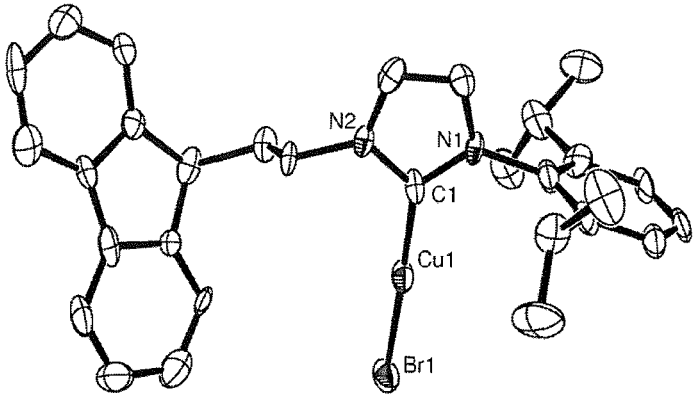


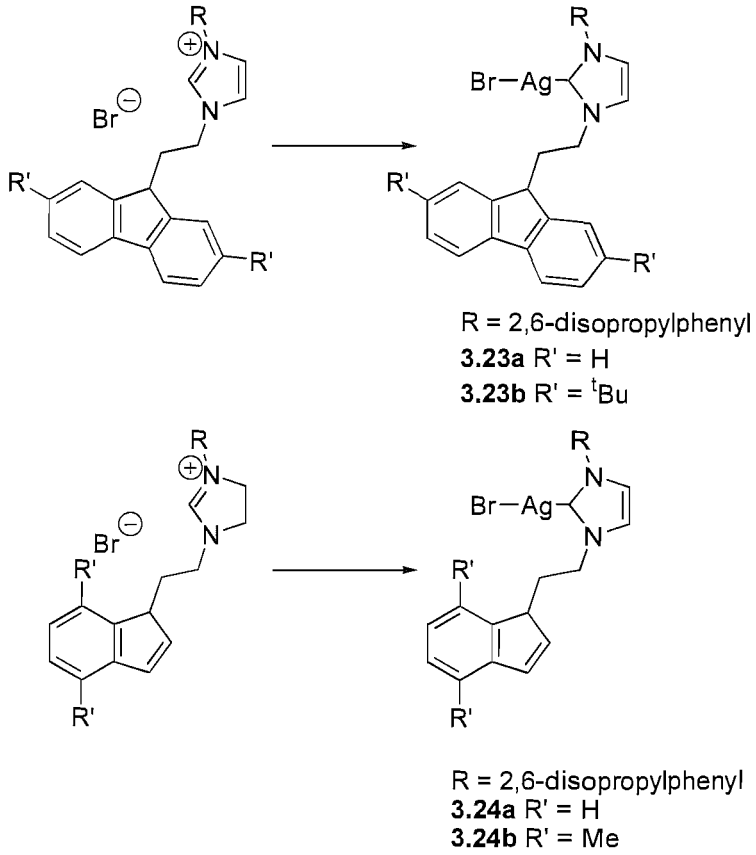
Figure 3.13 ORTEP representation of **3.21** with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Cu(1)-C(1) 1.882 (10); Cu(1)-Br(1) 2.2341 (17); C(1)-Cu(1)-Br(1) 177.2 (3).

The copper centre adopted the expected almost linear coordination sphere geometry expected for this type of complex. With an angle of 177.2° only deviating slightly form the perfect 180°. The bond lengths are in the range reported in the literature.[12]

Attempts were made to synthesise the bidentate copper complexes by treatment with an extra equivalent of KHMDS but this appeared to lead to decomposition and the desired product could not be isolated, earlier Wang reported that unlinked NHC cyclopentadienyl complexes of copper were not entirely stabile, it may be that forcing the angle way from 180° further destabilizes these complexes making them unisolable.

3.4.2 Silver Complexes

The monodentate silver complexes were synthesised in an analogous method to that reported in the literature[16] by reaction of the imidazolium salt with basic silver oxide in DCM in the presence of 4 Å molecular sieves. After being heated to reflux overnight, the solution was filtered and the volatiles removed under reduced pressure giving analytically pure product in near quantitative yields. The products were air-stable solids but decomposed slowly if exposed to light.



Scheme 3.7 Synthesis of silver carbene complexes. Reaction conditions: Ag2O, DCM, 4 Å molecular sieves, reflux, overnight.

3.24a was crystallised, from a saturated solution of the compound in DCM layered with ether, in the orthorhombic space group P_{na21} with a = 22.287(4) Å, b = 8.0426(16) Å, c = 13.609(3) Å. V = 2439.4(8) Å^3 and D_{calcd} = 1.520 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5747 unique reflections (R_{int} = 10.76%) converged to a final R_1 = 8.16% ($I > 2(I)$) and Rw^2 = 12.47%

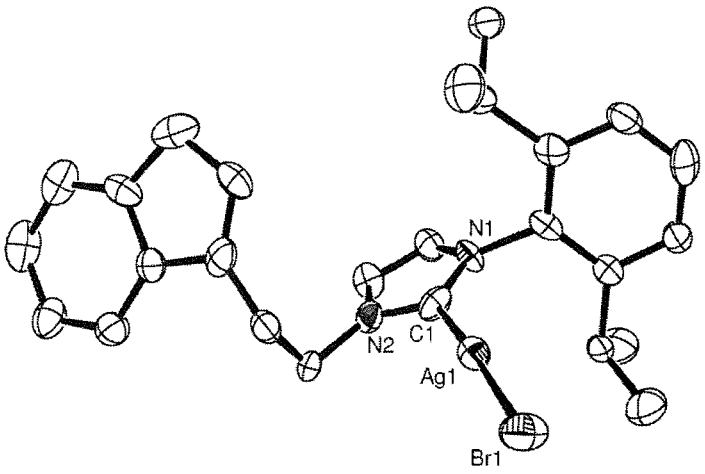
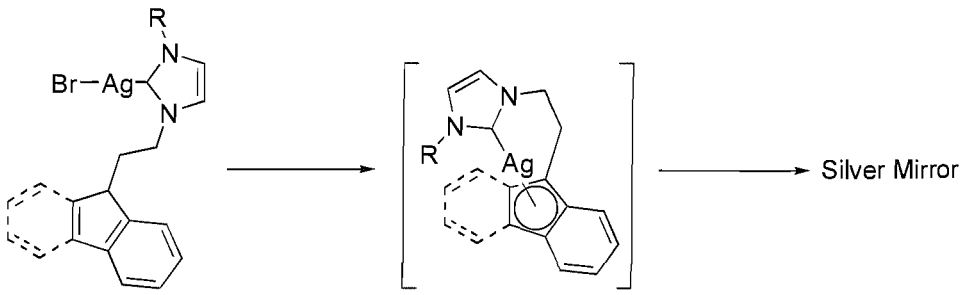


Figure 3.14 ORTEP representation of **3.24a** with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-Ag(1) 2.086(9); Ag(1)-Br(1) 2.42874(14); C(1)-Ag(1)-Br(1) 173.7(3).

The silver carbene has adopted a single carbene single bromide monomeric structure with linear geometry around the silver.

The carbene and bromine to silver bond lengths are typical of this type of silver carbene.[16] The $C_{carbene}$-Ag-Br angle is 173.7(3) close to the perfect 180° as would be expected in this type of complex. The indenyl ring shows no interaction with the metal centre.

It was hoped that the bidentate silver complexes could be synthesised as transfer reagents for the bidentate ligands, rather than just the monodentate carbenes. Attempts were made to synthesis the bidentate silver complexes by reacting the monodentate complexes with KHMDS in order to eliminate potassium bromide and leave the product. On addition of the KHMDS at -78 °C a bright orange to red colour formed, suggesting the deprotonation of the indenyl or fluorenyl ring took place. Unfortunately, on warming to room temperature a silver mirror rapidly formed in the reaction vessel, preventing any analysis of the products formed. It could be envisaged that some kind of reductive elimination is taking place although no evidence to support this has been found.



Scheme 3.8 Attempted synthesis of bidentate silver complex leading to decomposition and a silver mirror.

The imidazolium salt functionalised with a mixture of tetramethyl cyclopentadienes was also reacted with Ag_2O to give the corresponding mixture of silver carbenes. The crystal structure is shown in Figure 3.15 on page 113.

3.4.3 Summary of group 11 complexes

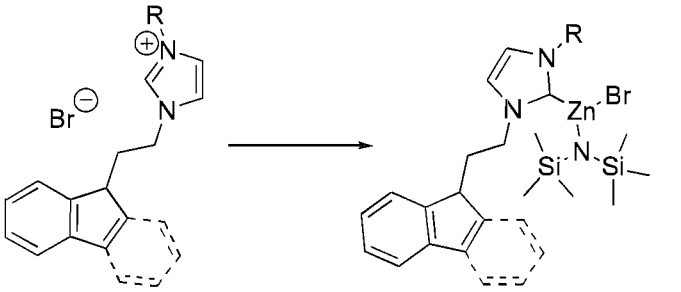
Methods have been found to synthesise monodentate NHC complexes of copper and silver, but attempts to synthesise the bidentate complexes ended in decomposition.

3.5 Group 12 Complexes

Group 12 complexes of NHCs are well known. The first zinc NHC complexes were reported by Arduengo.[10] In 2004 Buchmeiser reported a series of zinc complexes containing the IMes ligand.[20] Zinc NHC complexes have also be used to catalyse the polymerisation of D,L-lactide.[21]

3.5.1 Zinc Complexes

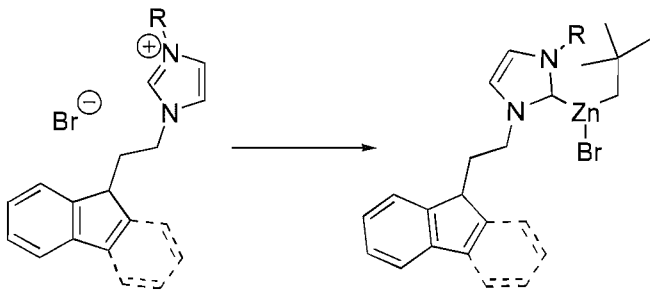
Zinc bis(HMDS) and the fluorenyl imidazolium salt were reacted with the intention of synthesising the bidentate zinc complex, NMR spectroscopy showed that only the first deprotonation had taken place to form the zinc carbene complex with a neutral fluorenyl tail **3.26**. Attempts were made to heat the reaction to drive the second deprotonation; unfortunately, no further reaction took place. The same reaction was tried with the indenyl imidazolium salt and gave the same results as the fluorenyl analogue.



R = 2,6-diisopropylphenyl
3.25 Indenyl
3.26 Fluorenyl

Scheme 3.9 Synthesis of a zinc carbene complex. Reaction conditions $Zn(HMDS)_2$, toluene, -78 °C – RT, over night.

It was hoped that by using a di-alkyl zinc reagent the reactivity would be increased allowing the second deprotonation to take place. Dineopentyl zinc was reacted with the fluorenyl imidazolium salt, only the first deprotonation took place and further heating, did not make the reaction proceed. It is believed that this is due to the second alkyl being less basic in character than the first. An equivalent of KHMDS was added to the monodentate complex it appeared by NMR that the desired reaction had taken place but the product could not be isolated.



R = 2,6-diisopropylphenyl
3.27 Indenyl
3.28 Fluorenyl

Scheme 3.10 Synthesis of a zinc carbene complex. Reaction conditions $Zn(CH_2C(CH_3)_3)_2$, toluene, -78 °C – RT, over night.

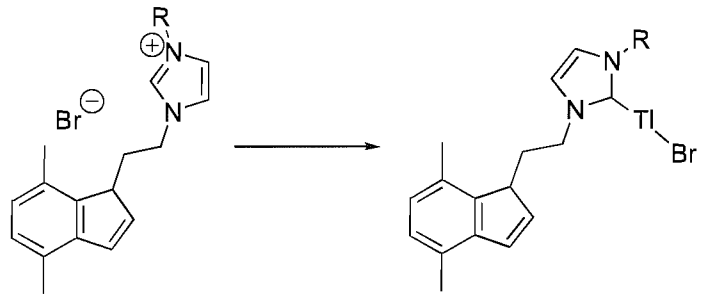
3.6 Group 13 Complexes

In 2001 Jones reported the first thallium carbene complexes, $TlCl_3$ was reacted with one and two equivalents of IMes to give the thallium complexes.[22] In 2002, Jones describes the complexes of a bis-carbene with group 13 metals.[23] In 2004, Arnold reports

the use of a thallium carbene complex as an effective carbene-transfer reagent to form rhodium complexes.[24]

3.6.1 Attempted Synthesis of Thallium Complex

Attempts were made to react TlHMDS[25] with the 2,7-dimethylindene functionalised imidazolium salt. The NMR spectrum of the crude product showed the disappearance of the signal at 10 ppm, characteristic of the imidazolium proton, unfortunately the product could not be isolated as even when exposure from light was prevented a grey metallic substance quickly formed in the material. The rapid decomposition and toxicity of the material prevented other analysis of the products.



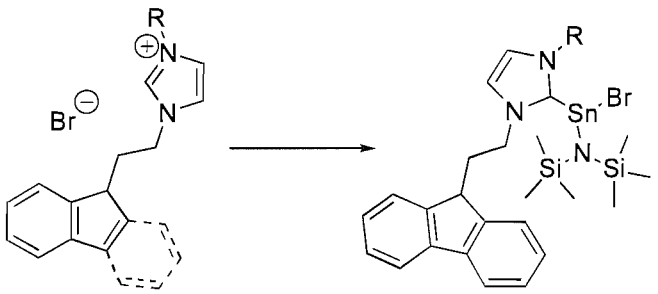
3.29

Scheme 3.11 Attempted synthesis of a thallium carbene complex. Reagents and conditions: TlHMDS, toluene, - 78 °C – RT.

3.7 Group 14 Complexes

There are limited examples of group 14 complexes in the literature. There are no imidazol-2-ylidene complexes of tin known and only one example of a saturated imidazolyl-2-ylidene complex.[26]

3.7.1 Attempted Synthesis of Tin Complexes



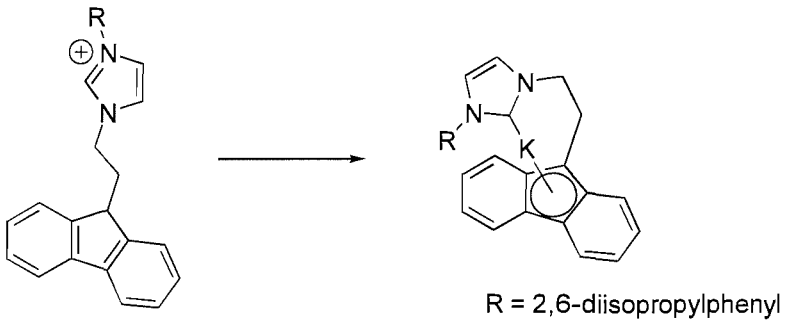
R = 2,6-diisopropylphenyl
3.30

Scheme 3.12 Synthesis of a monodentate tin NHC complex. Reagents and conditions: $Sn(HMDS)_2$, THF, -78 °C – RT, overnight.

$Sn(HMDS)_2$ was reacted with the fluorenyl imidazolium salt to give the monodentate tin carbene complex **3.30** in a crude form. The tin compounds were highly soluble in petrol and resisted attempts at crystallisation. It was hoped that by heating the crude monodentate product that the second equivalent of HMDS would react with the ligand to give the bidentate product unfortunately the reaction did not proceed any further.

3.8 Conclusions

A method has been found to isolate pure indenyl and fluorenyl potassium NHC complexes; it has been shown that the method can be applied to substituted and unsubstituted indenyl and fluorenyl systems.

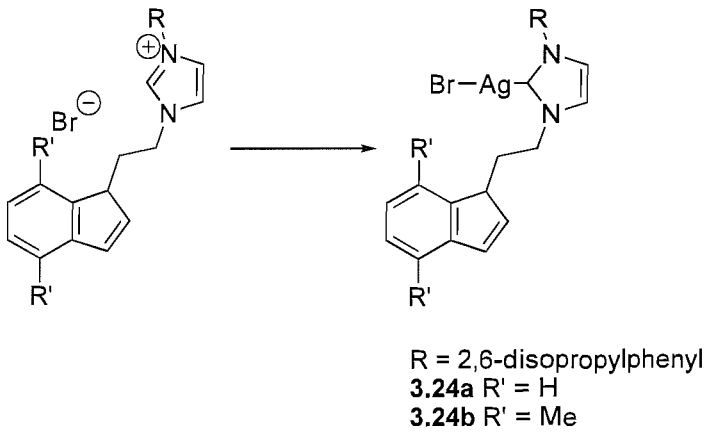


3.3 **3.6**

Scheme 3.13 Example of the formation of a potassium fluorenyl NHC complex.

The order of deprotonation in the salts is opposite to what would be expected from the pKa of the groups in DMSO.

The silver NHC and copper NHC monodentate complexes can be made in a facile manner but attempts to produce the bidentate complex resulted in decomposition. It appears that the metal is being reduced to elemental copper or silver and that the ligand is decomposing by an unknown route.



Scheme 3.14 Example synthesis of an silver carbene.

The monodentate zinc HMDS NHC and zinc neopentyl NHC complexes can be synthesised in a facile manner. Evidence was observed by NMR spectroscopy of the formation of the bidentate complexes but these could not be isolated.

Attempts were made to synthesise novel tin NHC complexes, but due to their extremely non-polar nature could not be isolated, attempts to synthesise the bidentate tin complexes were unsuccessful.

3.9 General Experimental

3.9.1 Instrumentation

Proton NMR spectra were recorded on a Bruker Avance DPX300, at 300 MHz or a Bruker Advance DPX400 spectrometer at 400 MHz. ^{13}C and $^{13}C\{^1H\}$ NMR spectra were recorded on the same spectrometers at 75 MHz and 100 MHz, respectively.

NMR spectra of the metal complexes were collected. In most cases the carbene carbon was not observed in the ^{13}C $\{^1H\}$ spectrum, this is due to the slow relaxation of the nuclei. Attempts were made to observe the expected signals from the carbene carbon by increasing the pulse delay on the spectrometer, despite extended delay and extended scans the signals could not be observed.

Low resolution mass spectra were collected on a Micromass Platform II spectrometer. High resolution mass spectra were collected on a Bruker Apex III spectrometer.

Elemental analyses were carried out by the microanalytical laboratory at the Department of Health and Human Sciences, London Metropolitan University. All analyses were carried out in duplicate with both results agreeing closely. Air-sensitive samples were supplied in glass tubes sealed under vacuum.

3.9.2 Solvents

Solvents were purchased from Fisher Chemicals. All solvents for moisture sensitive reactions were dried and distilled before use. Petroleum ether 40/60 was dried over sodium benzophenone ketyl and is referred to as petrol in this section, diglyme (approx 1 ml/L) was added to increase the solubility. Diethyl ether was dried over sodium benzophenone ketyl and is referred to as ether in this section. Toluene was dried over molten sodium. THF was dried over sodium benzophenone ketyl. DCM was dried over powdered calcium hydride. Benzene was dried over sodium benzophenone ketyl and stored in an ampoule over 4 Å molecular sieves under N_2.

$CDCl_3$ was dried over 4 Å molecular sieves and stored over fresh sieves. CD_2Cl_2 was dried over calcium hydride and stored over 4 Å molecular sieves. d_8-THF was dried over NaK alloy and stored over 4 Å molecular sieves.

3.9.3 Compounds

ZnHMDS[27], bis(*neo*-pentyl) zinc[28], CuHMDS[29] were prepared according to literature methods. Imidazolium salts were synthesised using the methods described in the previous chapter. Silver oxide was purchased from Aldrich.

3.9.4 General

Air-sensitive reactions were carried out using standard Schlenk techniques or in a catalytically dried and deoxygenated M. Braun glovebox (<2 ppm O_2). All air-sensitive solids were stored in the glovebox. Imidazolium salts were also stored in the glovebox due to their hydroscopic nature.

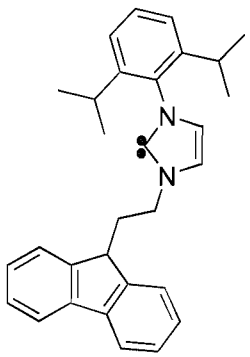
3.10 Experimental

General method for the first deprotonation of the imidazolium salts

1 eq. KHMDS (3 mmol, 600 mg) was dissolved in benzene (20 ml) and the resulting solution was added at room temperature to the imidazolium salt (3 mmol) to give a suspension. The mixture was stirred overnight. The precipitated potassium halide was removed by filtration through Celite giving rise to a solution of the crude neutral functionalised NHC. The crude products have been isolated as air sensitive powders. However, this is not necessary for routine work and the solutions of the NHCs were used for the second deprotonation as described below.

1H- data for the crude neutral species are given below.

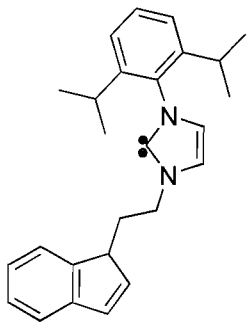
1-[2-(9H-Fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-2-ylidene 3.14



^{1}H (C_6D_6, 300 MHz): 7.71 (2H, d, J = 7 Hz, Ar); 7.64 (2H, d, J = 7 Hz, Ar) ; 7.35-7.21 (7 H, m, Ar); 6.66 and 6.53(1H each, s, imidazolium backbone); 4.11 (2H, t, J = 7 Hz,

CH_2); 4.05 (1H, t, J = 6 Hz, fluorenyl-H); 2.45 (2H, quin, J = 7Hz, 2x $CH(CH_3)_2$); 2.36 (2H, m, backbone); 1.16 (6H, d, J = 7 Hz, $CH(CH_3)_2$); 1.07 (6H, d , J = 7 Hz, $CH(CH_3)_2$).

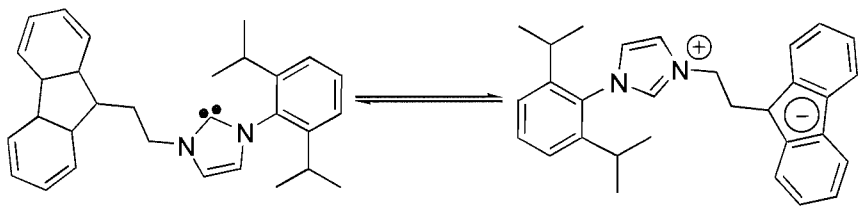
1-[2-(1H-inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-2-ylidene 3.15



The 1H-NMR (C_6D_6) spectrum of the crude product at room temperature shows broad peaks assignable to indenyl and 2,6-diisopropylphenyl aromatic protons (6.8 – 7.7 ppm); CH_2CH_2, indene and $CH(CH_3)_2$ protons (2.2 – 4.0 ppm) and $CH(CH_3)_2$ (0.8 – 1.2ppm).

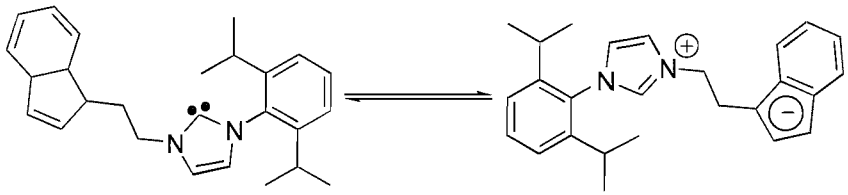
Even though the integration agrees with the proposed structure, the broadness of the spectrum inhibits further assignment.

Tautomerisation of 1-[2-(9H-Fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-1-ylidene



A solution of **3.14a** obtained as described above dissolved in THF-d_8 was placed in an NMR tube equipped with Young's valve and heated to 60 °C. The ^{1}H NMR spectrum was recorded periodically. After 8 h an equilibrium mixture was obtained comprising **3.7a** and **3.7a'** (ca 1:1). The latter was identified by the appearance of a characteristic broad peak at 11.2 ppm which was assigned to the imidazolium proton. Simultaneously, the intensity of the fluorenyl proton at 2.6 ppm decreased to one half of its original intensity. All other signals due to the aromatic, backbone and CH_2CH_2 protons broadened.

Tautomerisation of 1-[2-(3H-inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl) - imidazol-1-ylidene

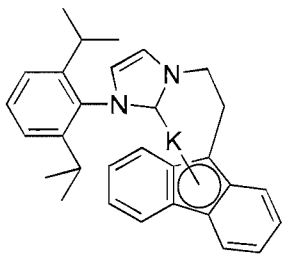


A similar behavior was observed with **3.15a** where the corresponding signals are at 11.21 ppm (imidazolium appearing) and 2.2 ppm indenyl proton decreasing in intensity. The final mixture contains *ca.* 25% **3.12a** and 75% **3.12a'**.

General Procedure for the Deprotonation of the crude carbene compounds.

The filtrate of the crude NHC obtained as described above was added to 1 eq. KHMDS and the resulting solution allowed to stir overnight. The precipitated product is then isolated by filtration, washed with benzene (2 ml); then petrol (10 ml) and dried under vacuum to afford the product (50 - 80% yield).

1-[2-(9-Fluorenyl)ethyl]-3-(2,6 di-*iso*-propylphenyl)-imidazol-2-ylidene potassium 3.6



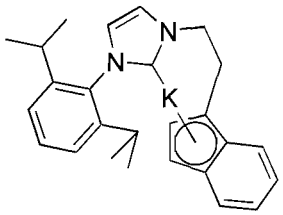
A solution of KHMDS (80 mg, 0.4 mmol) in benzene 10 ml was added to a suspension of the imidazolium salt (200 mg, 0.4 mmol) in benzene to form an orange solution. This solution became green by stirring overnight. It was filtered through Celite giving rise to the crude **3.14a** as shown by 1H-NMR spectroscopy (see above). A solution of KHMDS (80 mg, 0.4 mmol) in benzene was added to the solution of **3.14a** to give a red reaction mixture which on stirring formed slowly a red precipitate. Stirring continued overnight, the precipitate was collected by filtration and washed with benzene to give the product (90mg, 50% yield).

^{1}H (d_8-THF, 300 MHz): 8.02 (2H, d, J = 8 Hz, Ar); 7.51 (1H, s,NC*H*); 7.26 (3H, m, overlapping NC*H* and Ar); 7.12 (2 H, d, J = 7 Hz, Ar); 6.97 (3H, m, Ar); 6.58 (2H, m, Ar); 4.52 (2H, m, CH_2); 3.67 (2H, m,CH_2); 2.33 (2H, sept, J = 7 Hz, C*H*(CH_3)$_2$); 1.10 [6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$]; 0.81 [6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$];

^{13}C{^{1}H} (d_8-THF, 75 MHz): 206.9 (carbene C); 144.3 (Ar); 136.2 (Ar); 132.5 (Ar); 126.2 (Ar); 121.0 (Ar); 120.5 (Ar); 118.2 (Ar); 117.5 (Ar); 117.5 (Ar); 116.7 (Ar); 111.7 (Ar); 106.5 (Ar); 88.4 (fluorenyl C); 51.3 (*C*H_2); 26.7 (*C*H_2); 25.6 (*C*H(CH_3)$_2$); 22.0 (CH(*C*H_3)$_2$); 21.10 (CH(*C*H_3)$_2$).

Calculated(%): C, 78.56, H, 6.81, N, 6.11. Found: C, 78.41, H, 6.69, N, 5.97.

1-[2-(inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-1-ylidene potassium 3.13a



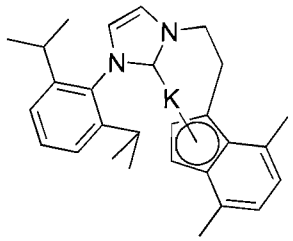
This was prepared similarly from the solution of the crude **3.15a** and KHMDS. Yield: ca 50% of red-purple air sensitive powder.

^{1}H (d^5-pyridene, 300 MHz): 7.82(1H, d, J = 8 Hz, indenyl); 7.72 (1H, d, J = 8 Hz, indenyl); 7.46-7.43 (1H, m, indenyl);7.32-7.20 (4H, m, overlapping 2,6-diisopropylphenyl aromatic and 1H indenyl aromatic); 6.98 (2H, m, indenyl); 6.75 (1H, s, carbene backbone); 6.48 (1H, s, carbene backbone); 4.45 (2H, m, NCH_2CH_2-ind); 3.59 (2H, m, NCH_2CH_2-ind); 2.93 (2H, sept, J = 7 Hz, CH(CH_3)$_2$); 1.19 (6H, d, J = 7 Hz, CH(CH_3)$_2$); 1.14 (6H, d, J = 7 Hz, CH(CH_3)$_2$).

^{13}C{^{1}H} (d^5-pyridene, 75 MHz): 211.0 (C, carbene); 147.5 (Ar); 130.2 (Ar); 129.9 (ArH); 129.5 (Ar); 128.3 (Ar); 126.6 (Ar); 125.0 (Ar); 120.8 (ArH); 120.6 (ArH); 120.1 (ArH); 117.3 (ArH); 113.9 (ArH); 104.9 (Indenyl carbon); 93.4 (Bridge CH2); 55.6 (Bridge CH2); 32.6 (isopropyl CH); 29.32 (isopropyl CH3).

Calculated(%): C, 76.05, H, 7.61 N, 6.82. Found: C, 76.00, H, 7.70, N, 6.72.

1-[2-((3,5-dimethyl)inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl) -imidazol-1-ylidene potassium 3.13b

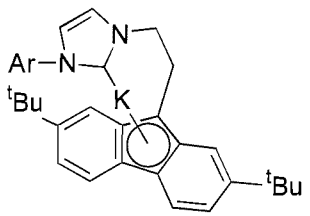


^{1}H (d_8-THF, 300 MHz): 7.22-7.09 (4H, m,); 6.98 (1H, d, J = 1 Hz, Ar*H*); 6.00 (2H, s, Ar*H*); 5.84 (1H, d, J = 4Hz, backbone); 5.58 (1H, d, J = 4Hz, backbone); 4.18-4.14 (2H, m, bridge); 3.34-3.30 (2H, m, bridge); 2.58 (2H, sept, J = 7 Hz, C*H*(CH_3)$_2$); 2.45 (3H, s, Me);2.22 (3H, s, Me); 1.05 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$); 1.00 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} (d_8-THF, 75 MHz): 209.4; 146.1; 138.3; 129.4; 128.1; 128.1; 123.9; 123.5; 123.4; 123.0; 122.2; 119.2; 119.1; 114.4; 112.1; 105.0; 90.0; 56.3; 32.8; 27.6; 23.9; 23.4; 21.6; 18.9.

Calculated (%) C, 77.01, H, 7.62, N, 6.42, Found, 76.96, H, 7.71, N, 6.34.

1-[2-(9-[2,7-Di-*tert*-butylfluorenyl)ethyl]-3-(2,6-di-*iso*-propylphenyl)-imidazol-2-ylidene potassium 3.10



Ar = 2,6-diisopropylphenyl

This was prepared similarly from the solution of the crude **3.8** and KHMDS. Yield: *ca.* 50% of deep-purple air sensitive powder.

^{1}H (THF-d_8, 300 MHz): 7.84 (2H, d, J = 8 Hz, Ar); 7.35-7.31 (2H, m, Ar); 7.29 (2H, s, Ar); 7.21-7.16 (1H, m, Ar); 7.05 (2H, d, J = 8 Hz, Ar); 6.82 (1H, d , J = 1 Hz, Ar); 6.59 (2H, dd, J = 7 ,2 Hz, Imidazole back bone); 4.48 (2H, t, J = 7 Hz, bridge); 3.63 (2H, t, J = 7 Hz, bridge); 2.24 (2H, J = 7 Hz,CHCH$_3$); 1.40 (18H, s, tBu); 0.96 (6H, d J = 7 Hz, CH_3); 0.81 (6H, d J = 7 Hz, CH_3);

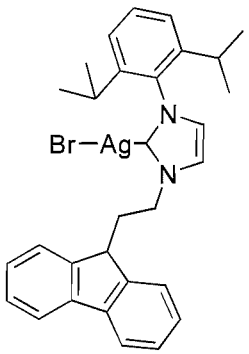
$^{13}C\{^1H\}$ (d_8-THF, 75 MHz): 209.2 (Carbene); 144.2 (Ar); 138.8 (Ar); 136.4 (Ar)132.9 (Ar); 126.2 (ArH); 126.1 (ArH); 120.9 (ArH); 119.7 (ArH);116.5 (Ar); 116.4 (ArH);106.5 (ArH); 104.7 (ArH); 88.1 (Flu); 50.1 (CH_2); 30.0 (CH_3(tBu)); 26.7 (CH_2); 25.6 (CH); 22.0 (CH_3); 21.2 (CH_3)

Calculated(%): C, 79.66, H, 8.62, N, 4.89.Found: C, 80.02, H, 8.71, N, 4.88.

General method for the synthesis of silver carbene complexes.

Imidazolium salt (1mmol); silver oxide (108 mg, 1 mmol) and 4Å molecular sieves in DCM (30 ml) were heated to reflux overnight under nitrogen in the dark. The resulting mixture was then filtered through celite and the volatiles were removed under reduced pressure to give the desired product as a solid residue which was dried under vacuum in almost quantative yield.

1-[2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl silver bromide 3.23a



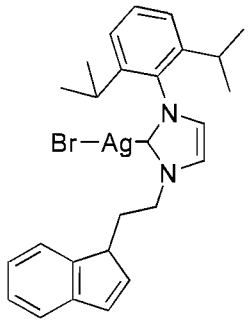
^1H ($CDCl_3$, 300 MHz): 7.80 (2H, m, Ar); 7.61 (2H, m, Ar); 7.40 (5H, m, Ar); 7.22 (2H, d, J = 8 Hz, Ar); 6.76 (1H, m, carbene backbone); 6.70 (1H, m, carbene backbone); 3.82 (2H, m, N-C*H*2CH2-Fl); 2.82 (2H, m, N-CH2C*H*2-Fl); 2.25 (2H, septet, J = 7 Hz, C*H*(CH3)2); 1.21 (6H, d, J = 7 Hz, CH(C*H*3)2); 1.08 (6H, d, J = 7 Hz, CH(C*H*3)2)).

$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 145.6 (C, Ar); 145.0 (C, Ar); 141.7 (C, Ar); 130.5 (CH, Ar) 127.8 (CH, Ar) 124.3 (CH, Ar); 124.2 (CH, Ar); 123.3 (CH, Ar) 120.9 (C, Ar); 120.2 (CH, Ar) 48.2 (Fl- CH_2CH_2N) 45.1 (*C*H, fluorene) 34.7 (Fl-*C*H_2CH_2-N); 28.2 (*C*H(CH_3)$_2$); 24.5 CH(*C*H_3)$_2$);24.34 CH(*C*H_3)$_2$).

MS ES+: 947 $[AgL_2]^+$.

Calculated for $C_{30}H_{32}N_2AgBr$ (%): C, 59.23, H,5.30, N, 4.60, Found: C, 59.36, H, 5.39, N, 4.50.

1-[2-(inden-1-yl)ethyl]-3-(2,6 di-*iso*-propylphenyl)-3*H*-imidazol-1-yl silver bromide 3.24a



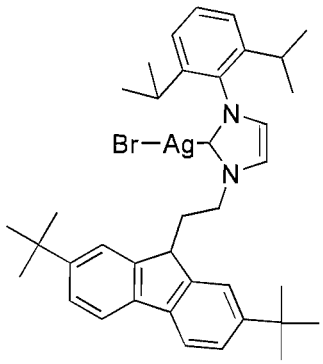
^1H ($CDCl_3$, 300 MHz): 7.42-7.13 (7H, m, aromatic); 6.95 (1H, s, carbene backbone); 6.79(1H, s, carbene backbone); 6.24 (1H, bs, indenyl H); 4.53 (2H, t, J = 7 Hz, bridge); 3.30- 8 -(2H, s, indenyl CH2); 3.13 (2H, t, J = 7 Hz, bridge); 2.15 (2H, septet, J = 7Hz, isopropyl CH); 1.95 (6H, d, J = 7 Hz, isopropyl CH3); 0.98 (6H, d, J = 7 Hz, isopropyl CH3).

$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 145.6 (C, Aromatic); 144.7 (c, aromatic); 144.2 (c, aromatic); 139.4 (c, aromatic); 131.5 (CH, aromatic); 130.5 (CH, aromatic); 126.4 (CH, aromatic); 125.2 (CH, aromatic); 124.2 (CH, aromatic); 51.1 (CH_2, bridge); 38.0 (CH_2, bridge); 29.9 (CH_2, indenyl); 28.2 (CH, isopropyl); 24.4 (CH_3, isopropyl).

MS ES+ (m/z): 847 $[AgL_2]^+$.

Calculated for $C_{26}H_{30}N_2AgBr$ (%): C, 55.43, H, 5.42 N, 5.02. Found C, 55.90, H, 5.34, N, 4.95.

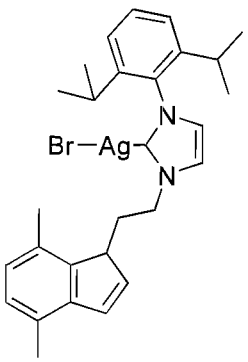
1-[5-5'-Di-tert-butyl-2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl silver bromide 3.23b



^{1}H ($CDCl_3$, 300 Mhz): 7.71 (2H, d, J = 8 Hz, Ar); 7.63 (2H, m, Ar) 7.50 – 7.43 (3H, m, Ar); 7.25 (2H, d, J = 8 Hz, Ar); 6.88 (1H, d, J = 1 Hz, NC*H*); 6.75 (1H, d, J = 1 Hz, NC*H*); 4.15 (1H, m, fluorene H); 3.95 (2H, m, NCH_2); 2.74 (2H, m, CH_2) 2.30 (2H, m, ^{i}PrH); 1.45 (18H, s, ^{t}Bu); 1.23 (6H, d, J = 7Hz); 1.08 (6H, d, J = 7Hz).

^{13}C{^{1}H} ($CDCl_3$, 75 MHz): 150.5 (C, Ar); 145.5 (C, Ar); 145.2 (C, Ar); 138.5 (C, Ar); 134.6 (C, Ar); 130.4 (H, Ar); 124.8 (C, Ar); 124.5 (H, Ar); 124.1 (s, Ar); 123.6 (s, Ar); 120.9 (s, Ar); 119.4 (s, Ar); 48.6 (CH_2N); 45.2 (Fluorene H); 43.4 (CH2); 35.2 (^{t}Bu, C); 31.6 (^{t}Bu, Me); 28.6

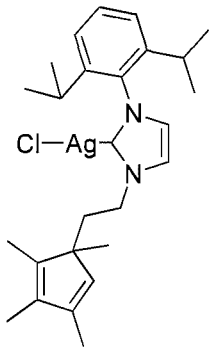
1-[2,5-dimethyl-2-(inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl silver bromide 3.24b



^{1}H ($CDCl_3$, 300 MHz): 7.47-7.40 (2H, m, Ar); 7.26 – 7.22 (3H, m, Ar); 7.06 (1H, s, Ar); 6.97 (2H, q, J = 9 Hz, Ar); 6.90 (1H d, J = 2 Hz, NC*H*); 6.24 (1H, s, indenyl-H); 4.58 (2H, t, J = 6 Hz, CH_2); 3.37 (2H, t, J = 6 Hz, CH_2); 3.19 (2H, s, indene-CH_2); 2.60 (3H, s, indene-methyl); 2.31 (3H, s, indene-methyl); 2.31 (2H, sept, J = 7 Hz, C*H*(CH_3)$_2$); 1.20 – 1.01 (12H, m, CH(C*H*$_3$)$_2$).

$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 145.6 (Ar); 143.8 (Ar); 141.2 (Ar); 134.7 (Ar); 131.6 (ArH); 130.9 (ArH); 130.5 (Ar); 129.7 (ArH); 127.7 (Ar); 126.4 (ArH); 124.2 (ArH); 123.6 (ArH); 123.6 (ArH); 120.9 (ArH); 51.7 (CH_2); 36.2 (CH_2); 32.6 (CH_2); 28.2 ($CHCH_3$); 24.5 (indene-CH_3); 24.3 (indene-CH_3); 20.1 ($CH(CH_3)_2$); 18.3 ($CH(CH_3)_2$).

1-Tetramethylcyclopentadienyl-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl silver bromide as a mixture of isomers



^1H NMR ($CDCl_3$) 7.43 (1H, m, aromatic); 7.23 (2H, aromatic); 7.09 (0.2H, m) and 7.00 (0.8 H, m, imidazole backbone due to the presence of different isomers); 6.92 (0.2H, m) and 6.88 (0.8H, m, imidazole backbone); 5.92 (0.4H, bs) and 5.76 (0.2H, bs) and 4.82-4.62 (0.4H, m, CpH); 4.15-3.90 (0.4H, m) and 4.15-3.90 (0.4H, m) and 3.80-3.60 (1.2H, m, bridge); 2.38-2.22 (2H, m, bridge); 2.18-1.98 (2H, m, isopropyl CH); 1.90-1.70 (6H, m, Cp-methyl); 1.22-0.95 (18H, m, isopropyl CH_3 and Cp methyls).

$^{13}C\{^1H$ complicated by the presence of three isomers.

MS ES^+ (m/z): 861 $[AgL_2]^+$.

Calculated for $C_{26}H_{36}N_2AgCl.2H_2O$ (%): C, 56.17, H, 7.25 N, 5.04. Found C, 56.02, H, 7.10, N, 4.55.

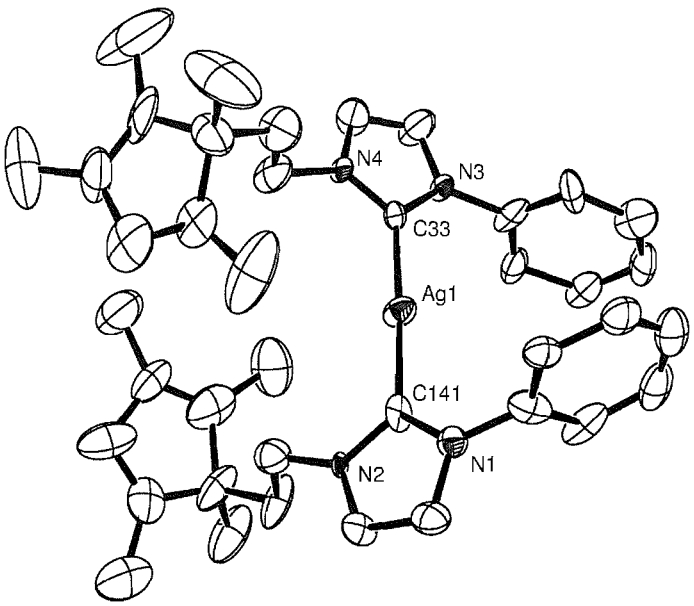
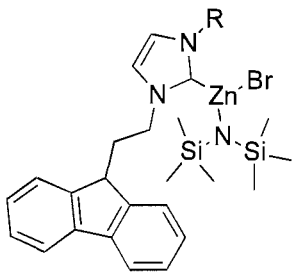


Figure 3.15 ORTEP representation of **3.21** with 50% probability ellipsoids. H atoms and isopropyl groups are omitted for clarity.

1-[2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 di-*iso*-propylphenyl)-2*H*-imidazol-1-ylidene zinc HMDS bromide 3.26



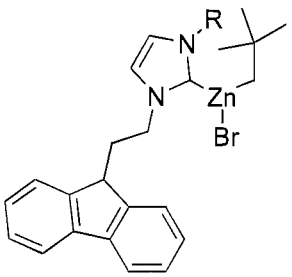
Zinc bis(HMDS) and 1-[2-(9H-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3H-imidazol-1-ium bromide were dissolved in THF and cooled to –78 °C the solutions were combined and allowed to warm to room temperature and stirred over night. The volatiles were removed and the residues were dissolved in toluene, filtration and removal ,of the volatiles gave the product as a white solid.

^{1}H (C_6D_6, 300 MHz): 7.50-7.40 (5H, m, Ar); 7.13-7.10 (4H, m, Ar); 6.91-6.84 (2H, m, Ar); 5.86 (1H, d, J = 1 Hz, NC*H*) 5.55 (1H, d, J = 1 Hz, NC*H*); 3.73-3.67 (3H, m, Fluorenyl –H and CH_2); 2.47-2.40 (2H, m, CH_2); 2.62 (2H, sept, J = 7 Hz, C*H*(CH_3)$_2$)); 1.26 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$); 0.74 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$); 0.05 (18H, s, HMDS).

$^{13}C\{^1H\}$ (C_6D_6, 75 MHz):146.2 (Ar); 145.8 (Ar); 141.0 (Ar); 134.0 (Ar); 127.9 (ArH); 125.1 (ArH); 123.9 (ArH); 120.8 (ArH); 120.3 (ArH); 47.9 (CH_2); 45.4 (Fluorenyl-*C*H); 34.1 (CH_2); 28.5 (C*H*CH_3); 25.6 (CHC*H*$_3$); 23.7 (CHC*H*$_3$); 5.46 (N[Si(*C*H_3)$_3$]$_2$).

Calculated (%) C 59.44, H 6.94, N 5.79; Found C 59.42, H, 7.01, N 5.62

1-[2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-2*H*-imidazol-1-ylidene zinc neopentyl bromide 3.28



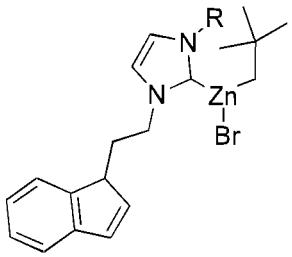
Zinc bis(neopentyl) and 1-[2-(9H-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3H-imidazol-1-ium bromide were dissolved in THF and cooled to –78 °C the solutions were combined and allowed to warm to room temperature and stirred over night. The volatiles were removed and the crude material dissolved in petrol and filtered through celite attempts to further purify the product were unsuccessful.

^1H (C_6D_6, 300 MHz): 7.51-7.48 (2H, m, Ar); 7.42-7.38 (2H,m, Ar); 7.18-7.16 (4H,m , Ar); 6.98-6.91 (2H, m, Ar); 5.91 (1H, s, NCH); 5.59 (1H, s, NCH); 3.81-3.70 (3H, m, bridge and fluorenyl-H); 2.42-2.32 (4H, m, bridge and C*H*$(CH_3)_2$); 1.21 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$); 1.20 (9H, s, neopentyl); 0.78 (6H, d, J = 7 Hz, CH(C*H*$_3$)$_2$); 0.30 (2H, s, neopentyl).

$^{13}C\{^1H\}$ (C_6D_6, 75 MHz): 146.2 (Ar); 146.0 (Ar); 141.5 (Ar); 130.8 (Ar); 129.3 (ArH); 125.1 (ArH); 124.3 (ArH); 122.8 (ArH); 120.8 (ArH); 120.2 (ArH); 47.7 (CH_2); 45.4 (Fluorenyl-CH); 35.4 (CH_2); 34.8 (neopentyl-CH_3); 33.3 (neopentyl-CH_2); 32.4 (neopentyl-C); 28.4 (C*H*$(CH_3)_2$); 25.4 (CH(C*H*$_3$)$_2$); 23.6 (CH(C*H*$_3$)$_2$).

Calculated (%) C 56.84, H 7.15, N 6.21; Found C 56.95, H, 7.06, N 6.23.

1-[2-(1-3*H*-indenyl)ethyl]-3-(2,6 di-*iso*-propylphenyl)-2*H*-imidazol-1-ylidene zinc HMDS bromide 3.27



A similar method to the above was followed.

^{1}H (C_6D_6, 300 MHz): 7.21-6.91 (6H, m, Ar); 6.96 (2H, d, J = 7 Hz, Ar); 6.07 (1H, s, indene-CH); 5.96 (1H, d, J = 1 Hz, NC*H*); 5.91 (1H, d, J = 1 Hz, NC*H*); 4.42 (2H, t, J = 7 Hz, CH_2); 2.95-2.85 (4H, m, CH_2 and indene- CH_2); 2.36 (2H, sept, J = 7 Hz, C*H*$(CH_3)_2$); 1.32 (6H, d, J = 7 Hz, CH(C*H*$_3)_2$); 0.80 (6H, d, J = 7 Hz, CH(C*H*$_3)_2$); 0.18 (18H, s, HMDS).

^{13}C{^{1}H} (C_6D_6, 300 MHz): 173.2 (carbene-C); 173.2 (Ar); 146.0 (Ar); 144.6 (Ar); 139.9 (Ar); 134.1 (Ar); 131.2 (ArH); 129.3 (Ar); 126.5 (ArH); 125.4(ArH); 124.6 (ArH); 124.3 (ArH); 123.9 (ArH); 121.4 (ArH); 119.2 (ArH); 49.5 (CH_2); 38.1 (CH_2); 29.4 (CH_2); 28.6 (CH); 25.5 (CH_3); 23.6 (CH_3); 5.5 (HMDS).

Calculated (%) C 63.88, H 5.72, N 4.97; Found C 63.61, H, 5.70, 5.05.

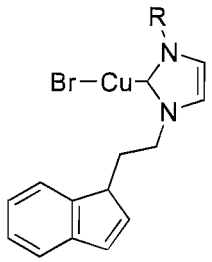
Attempted synthesis of 1-[2-(fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-2*H*-imidazol-1-ylidene zinc HMDS

1-[2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-2*H*-imidazol-1-ylidene zinc HMDS bromide and KHMDS were dissolved in THF and cooled to –78 °C the solutions were combined and allowed to warm to room temperature overnight. The volatiles were removed under vacuum and the residues dissolved in petrol and filtered through celite and the volatiles removed to give the crude product. Attempts to crystallise from petrol were unsuccessful.

^{1}H (C_6D_6, 300 MHz): 8.10 (2H, dt, J = 7, 1 Hz, Ar); 7.34 (2H, td, J = 7, 1 Hz, Ar); 7.21-6.95 (7H, m, Ar) 6.18 (1H, d, J = 1 Hz, NCH); 6.00 (1H, d, J = 1 Hz, NCH); 3.78-3.72 (2H, m, bridge); 3.52-3.47 (2H, m, bridge); 2.40 (2H, sept, J = 7 Hz, C*H*$(CH_3)_2$); 1.24 (6H, d, J = 7 Hz, CH(C*H*$_3)_2$); 0.83 (6H, d, J = 7 Hz, CH(C*H*$_3)_2$).

$^{13}C\{^1H\}$ (C_6D_6, 300 MHz): 149.7 (Ar); 144.2 (Ar); 136.5 (Ar); 133.3 (Ar); 129.3 (ArH); 127.9 (ArH); 124.2 (ArH); 123.8 (ArH); 121.6 (ArH); 120.5 (ArH); 116.3 (ArH); 59.7 (fluorenyl-C); 52.0 (CH_2); 33.2 (CH_2); 27.0 ($CH(CH_3)_2$); 24.4 $CH(CH_3)_2$); 20.0 $CH(CH_3)_2$).

1-[2-(1-3*H*-indenyl)ethyl]-3-(2,6 di-*iso*-propylphenyl)-2*H*-imidazol-1-ylidene copper bromide 3.22



Tetrakis (copper HMDS) and 1-[2-(1-3*H*-indenyl)ethyl]-3-(2,6 diisopropylphenyl)-2*H*-imidazolium bromide were dissolved in THF and cooled to –78 °C the solutions were combined and allowed to warm to room temperature and stirred over night. The volatiles were removed and the residues were dissolved in toluene, filtration and removal of the volatiles gave the product as a yellow solid. Yield

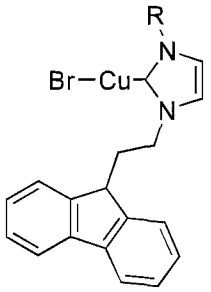
^1H (C_6D_6, 300 MHz): 7.28 (5H, m, Ar); 6.99 (2H, d, J = 7 Hz, Ar); 6.12 (1H, s, Indene-H); 6.04 (1H, d, J = 1 Hz, NCH); 6.02 (1H, d, J = 1 Hz, NCH); 4.00 (2H, t, J = 6 Hz, CH_2); 3.08 (2H, s, indene-CH_2); 2.73 (2H, t, J = 6 Hz, CH_2); 2.25 (2H, sept, J = 7 Hz, $CH(CH_3)_2$); 1.21 (6H, sept, J = 7 Hz, $CH(CH_3)_2$); 0.91 (6H, sept, J = 7 Hz, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ (C_6D_6, 75 MHz): 145.9 (Ar); 144.5 (Ar); 139.4 (Ar); 131.5 (ArH); 130.5 (ArH); 126.5 (Ar); 125.2 (ArH); 124.2 (ArH); 122.3 (ArH); 120.3 (ArH); 119.1 (ArH); 50.1 (CH_2); 38.1 (CH_2); 29.7 (CH_2); 28.5 ($CH(CH_3)_2$); 24.6 ($CH(CH_3)_2$); 24.1 ($CH(CH_3)_2$)

MS ES^+: 803 $(CuNHC_2)^+$

Calculated (%) C 60.76, H 5.88, N 5.45; Found C 60.70, H, 5.82, N 5.42.

3-(2,6-Di-*iso*-propyl-phenyl)-1-[2-(9-9*H*-fluorenyl)-ethyl]-imidazol-2-ylidene -copper bromide 3.21



^{1}H (C_6D_6, 400 MHz): 7.50 (1H, d, *J* = 8 Hz, Ar); 7.45 (1H, bs, Ar); 7.20 (2H, t, *J* = 7 Hz, Ar); 7.15 (2H, t, *J* = 7 Hz); 7.06 (1H, d, *J* = 8 Hz, Ar); 6.86 (2H, d, *J* = 8 Hz, Ar); 5.87 (1H, d, *J* = 1 Hz, NC*H*); 5.64 (1H, d, *J* = 1 Hz, NC*H*); 3.64 (1H, t, *J* = 8 Hz, CH_2); 3.32 (1H, t, *J* = 8 Hz, CH_2); 2.40-2.20 (4H, m, CH_2 and C*H*(CH_3)$_2$); 1.19 (6H, d, *J* = 7 Hz, CH(C*H*$_3$)$_2$); 0.86 (6H, d, *J* = 7 Hz, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} (C_6D_6, 100 MHz): 144.6 (Ar); 144.5 (Ar); 140.1 (Ar); 133.9 (Ar); 129.1 (ArH); 125.9 (ArH); 123.7 (ArH); 122.9 (ArH); 122.6 (ArH); 120.7 (ArH); 118.9 (ArH); 118.8 (ArH); 46.2 (CH_2); 43.8 (Fluorenyl-H); 33.7 (CH_2); 27.2 (*C*H(CH_3)$_2$); 23.3 CH(*C*H$_3$)$_2$); 22.86 CH(*C*H$_3$)$_2$)

MS ES$^+$: 903 (CuNHC$_2$)$^+$

Attempted Synthesis of 1-[2-(9*H*-fluoren-9-yl)ethyl]-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl tin HMDS bromide

Tin bis HMDS and the potassium fluorenyl NHC complex were dissolved in THF and cooled to -78°C, the mixture was allowed to return to room temperature and stirred over night. The volatiles were removed under vacuum and the crude product dissolved in petrol and filtered through celite to give the crude product. Attempts to further purify the product by crystallisation from petrol failed.

^{1}H (C_6D_6, 300 MHz): 8.35 (1H, d, *J* = 8 Hz, Ar); 7.98 (2H, f, *J* = 9 Hz, Ar) 7.60-6.71 (8H, m , Ar); 6.30 (1H, d, *J* = 1 Hz, NCH); 6.16 (1H, d, *J* = 1 Hz, NCH); 4.31-4.21 (1H, m, Fluorenyl-H); 4.19-3.92 (2H, m, bridge); 2.81-2.45 (2H, m, bridge); 2.41-2.31 (2H, m, C*H*(CH_3)$_2$); 0.92-0.79 (12H, m, CH(C*H*$_3$)$_2$); 0.06 (18H, s, HMDS).

^{13}C{^{1}H} (C_6D_6, 75 MHz): 131.2 (Ar); 129.9 (Ar); 126.6 (Ar); 125.5 (ArH); 124.7 (Ar); 124.0 (ArH); 123.6 (ArH); 123.0 (ArH); 122.3 (ArH); 121.4 (ArH); 120.2 (ArH);

51.4 (CH_2); 30.0 (CH_2); 28.8 (($CH(CH_3)_2$)); 28.5 ($CH(CH_3)_2$); 26.0 ($CH(CH_3)_2$); 25.8 ($CH(CH_3)_2$); 23.8 ($CH(CH_3)_2$); 23.4 ($CH(CH_3)_2$); 2.6 (HMDS)

Table 3.1 Crystallographic parameters for potassium carbene structures.

Identification code	**3.6**	**3.13b**
Empirical formula	$C_{72}H_{74}K_2N_4$	$C_{28}H_{33}KN_2$
Formula weight	1073.55	436.66
Temperature	120(2) K	293(2) K
Wavelength	0.6868 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/b
Unit cell dimensions	a = 20.531(7) Å	a = 10.4695(9) Å
	α = 90°.	α = 90°.
	b = 13.027(4) Å	b = 16.6995(15) Å
	β = 92.220(5)°.	β = 100.193(4)°.
	c = 23.378(8) Å	c = 14.3103(12) Å
	γ = 90°.	γ = 90°.
Volume	6248(4) $Å^3$	2462.5(4) $Å^3$
Z	4	4
Density (calculated)	1.141 Mg/m^3	1.178 Mg/m^3
Absorption coefficient	0.195 mm^{-1}	0.233 mm^{-1}
F(000)	2288	936
Crystal size	0.20 x 0.01 x 0.01 mm^3	0.08 x 0.08 x 0.08 mm^3
Theta range for data collection	1.96 to 21.19°.	2.92 to 27.58°.
Index ranges	-21<=h<=21	-13<=h<=8
	-13<=k<=13	-20<=k<=21
	-24<=l<=24	-17<=l<=18
Reflections collected	34299	19549
Independent reflections	7615 [R_{int} = 0.1136]	10116 [R_{int} = 0.0827]
Completeness to theta = 27.89°	99.8 %	95.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9980 and 0.6387	0.9876 and 0.7658
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	7615 / 0 / 700	10116 / 1 / 560
Goodness-of-fit on F2	0.922	1.282
Final R indices [I>2sigma(I)]	R_1 = 0.0663, wR^2 = 0.1520	R_1 = 0.1583, wR^2 = 0.3873
R indices (all data)	R_1 = 0.1220, wR^2 = 0.1773	R_1 = 0.2443, wR^2 = 0.4272
Largest diff. peak and hole	0.362 and -0.297 $e.Å^{-3}$	1.829 and -0.536 $e.Å^{-3}$

Table 3.2 Table of crystallographic parameters for the X-ray structures of silver and copper complexes.

Identification code	**3.24a**	**3.21**
Empirical formula	$C_{26}H_{30}AgBrN_2$	$C_{30}H_{32}BrCuN_2$
Formula weight	558.30	564.03
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	Pna21	Pbca
Unit cell dimensions	a = 22.287(4) Å	a = 9.5934(7) Å
	α = 90°.	α = 90°.
	b = 8.0426(16) Å	b = 16.173(2) Å
	β = 90°.	β = 90°.
	c = 13.609(3) Å	c = 35.316(4) Å
	γ = 90°.	γ = 90°.
Volume	2439.4(8) $Å^3$	5479.4(10) $Å^3$
Z	4	8
Density (calculated)	1.520 Mg/m^3	1.367 Mg/m^3
Absorption coefficient	2.479 mm^{-1}	2.275 mm^{-1}
F(000)	1128	2320
Crystal size	0.20 x 0.05 x 0.05 mm3	0.05 x 0.01 x 0.01 mm3
Theta range for data collection	2.94 to 32.42°.	3.01 to 27.62°.
Index ranges	-28<=h<=33	-12<=h<=11
	-10<=k<=10	-21<=k<=15
	-16<=l<=17	-46<=l<=45
Reflections collected	15263	20596
Independent reflections	5747 [R(int) = 0.1076]	4942 [R(int) = 0.1561]
Completeness to theta = 27.89°	98.5 %	77.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8861 and 0.6370	0.9776 and 0.8947
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5747 / 1 / 275	4942 / 0 / 311
Goodness-of-fit on F2	1.053	1.043
Final R indices [I>2sigma(I)]	R_1 = 0.0816, wR^2 = 0.1247	R_1 = 0.0993, wR^2 = 0.1835
R indices (all data)	R_1 = 0.1554, wR^2 = 0.1466	R_1 = 0.2033, wR^2 = 0.2337
Largest diff. peak and hole	1.226 and -0.758 $e.Å^{-3}$	1.120 and -0.665 $e.Å^{-3}$

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Chapter 4

Early Transition Metal Complexes with *N*-Heterocyclic Carbene Ligands Functionalised with Cyclopentadienyl Type Donors

4 Early Transition Metal Complexes with NHC ligands

4.1 Aims

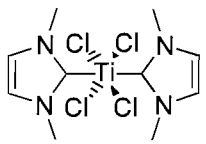
Attempts to prepare early transition metal, namely groups 4, 5 and 6, complexes containing the NHC ligands derived from the imidazolium salts discussed previously, in Chapter 1, are described in this chapter. The initial aim was to synthesise complexes with the ligand coordinating in a bidentate mode, η^5-, η^3-, η^1- fluorenyl- or indenyl- NHC complexes, although monodentate NHC complexes with dangling fluorene or indene groups may be versatile precursors for example in the rational synthesis of homo- and hetero-bimetallic complexes etc.

The synthetic methods studied include salt metathesis with the potassium indenyl- or fluorenyl- NHC complexes or more direct methods such as aminolysis reactions.

4.2 Group 4 Complexes

4.2.1 Titanium Complexes

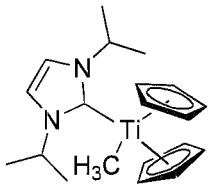
The first titanium NHC complex **4.1**, Figure 4.1, was briefly described in 1994 by Hermann. It was synthesised by reacting two equivalents of free NHC with $TiCl_4.THF_2$ and characterised by spectroscopic and analytical methods.[1]



4.1

Figure 4.1 The first NHC titanium complex reported by Hermann.

In 2002, Erker reported a titanocene methyl complex containing an NHC ligand 4.2, Figure 4.2.2 This complex contained a Cp rings and a monodentate NHC. In this example, the NHC and Cp ring are unlinked; our aim was to synthesise complexes where these two moieties are linked in a fashion analogous to the well established heteroatom functionalised ansa cyclopentadienyl complexes reported by Jutzi and others and the constrained geometry systems of Bercaw and others.

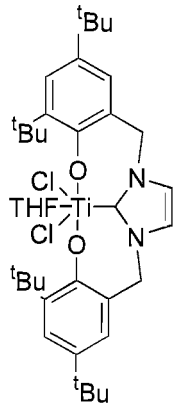


4.2

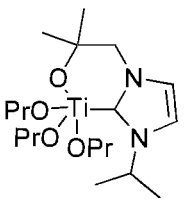
Figure 4.2 A titanocene NHC complex reported by Erker.

In 2004, Cowley reported a titanium NHC complex obtained by an aminolysis reaction, interestingly two equivalents of imidazolium salt precursor were deprotonated to give NHC ligands but only one coordinated to the metal and the other remained uncoordinated.[3] This was taken as evidence that NHCs only form weak bonds to early transition metals.

There are additional examples in the literature in which titanium complexes contain an NHC functionalised with an anionic pendant group. This is the target of our research. In 2003, Kawaguchi reported a titanium complex containing a bis-phenoxide functionalised NHC **4.3**, Figure 4.3.[4] In 2006, Arnold reported an alkoxide functionalised NHC complex of titanium **4.4**, Figure 4.3.[5] Other than the titanium complex described in this thesis these are the only published examples of titanium complexes containing an NHC functionalised with an anionic group.



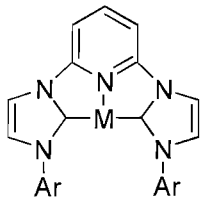
4.3



4.4

Figure 4.3 Examples of titanium complexes containing NHC ligands functionalised with anionic groups

In 2006, Danopoulos reported a bis-NHC pyridyl pincer complex of titanium **4.5**, Figure 4.4, this ligand also binds to many other early transition metals as described below.[6]



Ar = 2,6-diisopropylphenyl

4.5

Figure 4.4 Bis-NHC functionalised pyridyl ligand reported by Danopoulos.

4.2.2 Synthesis of Titanium Complexes

Attempts to synthesise bidentate Ti (IV) complexes by reacting the pre-formed potassium fluorenyl complex with $TiCl_4THF_2$ were attempted. Unfortunately, the reaction led to an insoluble yellow material that could not be characterised. Attempts were also made to react $Ti(NMe_2)_4$ with the functionalised imidazolium salts hoping that aminolysis taking place to form the desired complexes with bidentate ligand would occur after generation of the NHC by aminolysis *in-situ*. Unfortunately, the products of this reaction although soluble in organic solvents gave broad unassginable NMR spectra. The broadness of the spectrum may be due to paramagnetic impurities that could be formed by these reactions.

Partial substitution of the chloride ligands for dialkylamides would be expected to increase the solubility of the products and facilitated their characterisation by NMR. An NMR scale reaction of $Ti(NMe_2)Cl_2$ and the potassium fluorenyl NHC complex was carried out. The two reactants were dissolved in d_6-benzene and the suspension filtered through glass wool in the glove box after 2 minutes in order to remove the KCl formed. The ^{1}H-NMR spectrum of the solution consisted of a number of broad signals and could not be assigned unambiguously.

X-ray diffraction quality crystals had grown in the NMR tube after standing overnight. Under a microscope, it was seen that two types of crystals were present: dark brown-yellow crystals and colourless crystals. Both of these types of crystals were subject to X-ray analysis.

The X-ray structure of the yellow crystals was collected:

The titanium complex **4.7** was crystallised, from the reaction of $Ti(NMe_2)Cl_2$ and the fluorenyl potassium carbene complex **3.6** in d_6-benzene, in the triclinic space group P-1 with a = 8.3495(6) Å, b = 10.7139(13) Å, c = 16.8282(19) Å, α = 73.535(9)°, β =

86.508(7)°, γ = 71.966(7)°, V = 1372.1(2) Å^3, and D_{calcd} = 1.324 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6276 unique reflections (R_{int} = 4.11%) converged to a final R_1 = 4.84% (I > 2(I)) and Rw^2 = 10.81%.

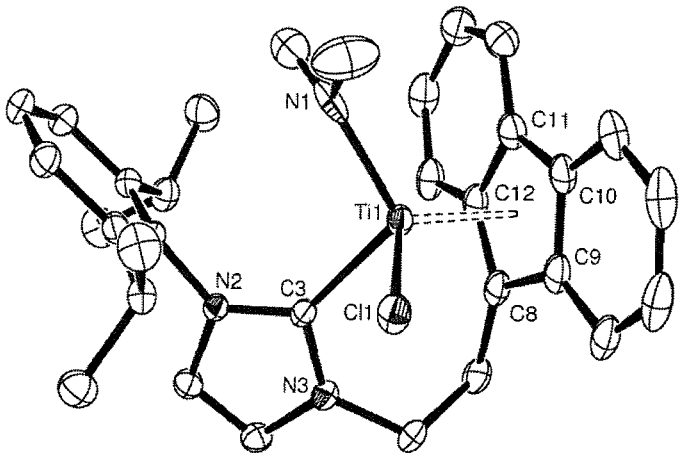
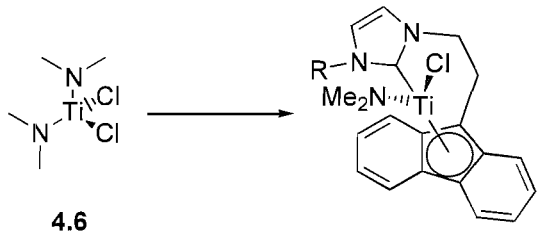


Figure 4.5 ORTEP representation of complex the titanium complex **4.7** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(3)-Ti(1) 2.221(2); N(1)-Ti(1) 1.984(2); C(3)-N(2) 1.372(3); C(8)-Ti(1) 2.382(2); C(9)-Ti(1) 2.437(2); C(10)-Ti(1) 2.431(2); C(11)-Ti(1) 2.471(2); C(12)-Ti(1) 2.442(2); C(3)-N(3) 1.365(3); N(3)-C(3)-Ti(1) 123.49(14); N(2)-C(3)-Ti(1) 133.84(14).

The structure comprises one tetrahedral Ti(III) centre coordinated by the chelate fluorenyl-NHC (binding through the fluorenyl and the NHC), one dimethylamido group, and one chloride. The Ti-C(fluorene) bond distances (Ti-C8 to C12 in the range 2.383-2.471 Å) support a symmetrically coordinated η^5- fluorenyl ring; comparable metrical data, albeit with some slip distortion, have been reported for the only other Ti(III) fluorenyl complex that has been structurally characterised.[7] The Ti-$C_{carbene}$ (2.221 Å) is in the range observed previously (2.192- 2.210 Å). The plane of the imidazol-2-ylidene ring lies 3.9° from the vector of the Ti-$C_{carbene}$ bond.

From the X-ray structure of the yellow-brown crystals it was apparent that the following transformation had taken place, to give the first example of a transition metal complex containing a carbene linked to a cyclopentadienyl type moiety bound in a bidentate mode **4.7**, Scheme 4.1.



4.6 **4.7**

Scheme 4.1 Synthesis of a titanium (III) complex. Reaction conditions 1 eq. fluorenyl potassium carbene complex, benzene, RT.

There were also colourless crystals in the mixture the X-ray structure of these was also determined:

The spiro-imidazolium salt **4.9**, Figure 4.7, was crystallised, from the reaction of $Ti(NMe_2)Cl_2$ and the fluorenyl potassium carbene complex **3.6** in benzene, in the triclinic space group P-1 with a = 8.345(4) Å, b = 10.774(5) Å, c = 16.130(7) Å, α = 103.08(4)°, β = 98.84(4)°, γ = 104.81(3)°, V = 1330.8(10) Å^3, and D_{calcd} = 1.233 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 4231 unique reflections (R_{int} = 14.09%) converged to a final R_1 = 7.66% (I > 2(I)) and Rw^2 = 13.00%. Half a molecule of benzene was present in the asymmetric unit.

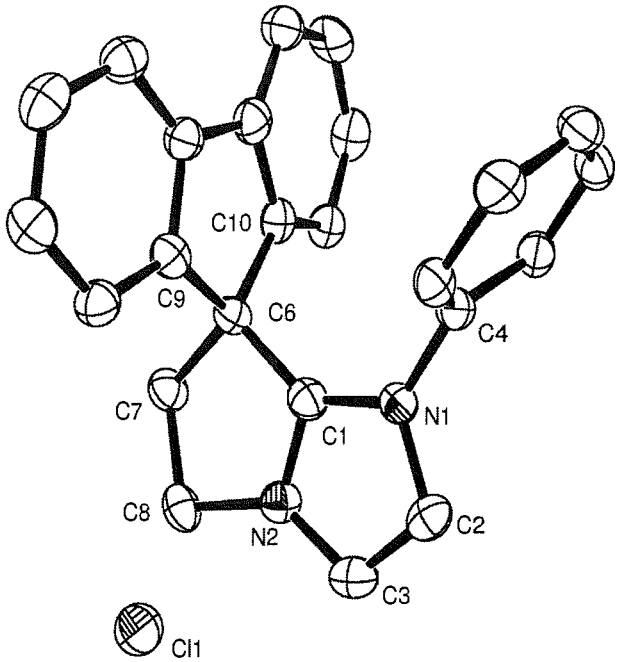
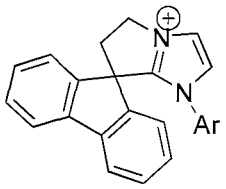


Figure 4.6 ORTEP representation of complex **4.9** showing 50% probability ellipsoids. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: N(1)-C(1) 1.341(5); N(1)-C(4) 1.456(5); N(2)-C(1) 1.335(5); C(1)-C(6) 1.501(6); N(1)-C(2) 1.401(5); C(2)-C(3) 1.340(6); N(2)-C(3) 1.382(5); N(2)-C(8) 1.474(5); C(8)-C(7) 1.535(6); C(7)-C(6) 1.575(5); C(9)-C(6) 1.537(6); C(10)-C(6) 1.526(6); N(2)-C(1)-N(1) 107.8(4); N(2)-C(1)-C(6) 113.2(4); C(1)-C(6)-C(10) 114.9(3); C(1)-C(6)-C(9) 113.9(3); C(10)-C(6)-C(9) 102.2(3); C(1)-C(6)-C(7) 99.3(3); C(10)-C(6)-C(7) 113.7(3); C(9)-C(6)-C(7) 113.5(3); N(1)-C(1)-C(6) 139.0(4).

The X-ray structure showed that the spiro imidazolium salt **4.9** shown in Figure 4.7 was present in the reaction mixture. It could be envisaged that this compound is produced by a reductive elimination of the ligand from the metal centre because the imidazol-2-ylidene carbon is now directly linked to the fluorenyl bridge head carbon.



Ar = 2,6-diisopropylphenyl

4.9

Figure 4.7 Spiro-imidazolium salt **4.9** isolated from the reaction of $Ti(NMe_2)Cl_2$ and the fluorenyl potassium carbene complex.

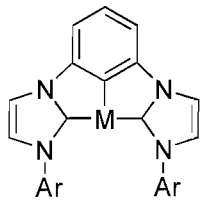
The mechanism of the reduction of the metal centre is not yet fully understood. It is plausible that the ligand is acting as the reducing agent; this conclusion is supported by the isolation from the reaction mixture by fractional crystallisation and crystallographic characterisation of the spiro imidazolium salt **4.9** shown in Figure 4.6. Normally a 2 electron reduction would be expected from a reductive elimination but careful electron counting indicates that the ligand must give up one electron in order to form the spiro compound. It is therefore likely that this electron is responsible for the reduction of the metal centre. This abnormal one electron reduction is because the NHC is acting as a neutral two electron donor and the cyclopentadienyl moiety is acting as a anionic two electron donor, if considered as η^2. In a normal reductive elimination such as bromine elimination, each donor acts as a two electron anionic donor.

Unfortunately, attempts to purify the complex were unsuccessful and the titanium complex **4.7** could not be separated from the spiro-cyclic imidazolium salt **4.9** or other organic or organometallic impurities present. This complex mixture and the paramagnetic nature of the complex meant that other spectroscopic methods such as NMR proved fruitless for analysing the product. NMR spectra were broad and contained many peaks for the impurities; electrospray mass spectroscopy did not give the desired peaks as the spectra were dominated by the peaks for the spiro-imidazolium salts present.

4.2.3 Zirconium Complexes

In 2002, Erker reported $ZrCl_4(NHC)_2$ complexes,[8] similar to the titanium complexes reported by Hermann as discussed previously, Figure 4.1.[1] Structural studies in these complexes showed that invariably the complexes adopt a trans-geometry. The relative conformation of the NHC rings was studied also by DFT methods.

There are two examples in the literature of zirconium complexes containing an NHC ligand functionalised with an anionic pendant. In 2004, Fryzuk reported a bis amide NHC pincer tridentate complex of zirconium.[9] In 2005, Holis reported a bis-NHC functionalised phenyl ligand in a CCC coordination **4.10**, Figure 4.8.[10]



Ar = 2,6-diisopropylphenyl

4.10

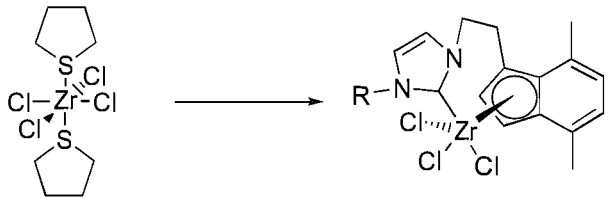
Figure 4.8 A CCC pincer ligand.

The pincer ligand **4.5** reported by Danopoulos described earlier also forms zirconium complexes.[6]

Fröhlich also reported zirconocene complexes containing NHC ligands,[2] which were discussed in chapter 1. Our aim was to synthesise zirconium complexes with the ligand in its bidentate mode.

4.2.4 Synthesis of Zirconium Complexes

$ZrCl_4.(THT)_2$ **4.11** was reacted with the dimethylindenyl potassium carbene complex **3.13b** to give the expected bidentate carbene complex. In this case there was no reduction of the metal centre; this is likely to be due to the fact that more energy is required to produce the less stable Zr(III) oxidation state. The complex was rather insoluble in polar organic solvents in which it was reasonably stable and it could only be dissolved in DCM, hot toluene or THF. The complex could be crystallised from DCM and ether to give X-ray quality crystals. Slow decomposition in DCM solution was observed, but the compound was found to be stable enough for crystallisation and NMR analysis if carried out expeditiously.



4.11 4.12

Scheme 4.2 Synthesis of a bidentate zirconium complex. Reagents and conditions: dimethylindenyl potassium carbene complex, THF, -78 °C – RT.

The zirconium complex **4.12** was crystallised from DCM layered with ether in the triclinic space group P-1 with a = 9.5873(5) Å, b = 9.7036(6) Å, c = 16.7862(11) Å, α = 96.636(3)°, β = 93.590(4)°, γ = 119.315(3)°, V = 1339.67(14) Å^3, and D_{calcd} = 1.475 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 4711 unique reflections (R_{int} = 9.53%) converged to a final R_1 = 9.60% (I > 2(I)) and Rw^2 = 18.86%.

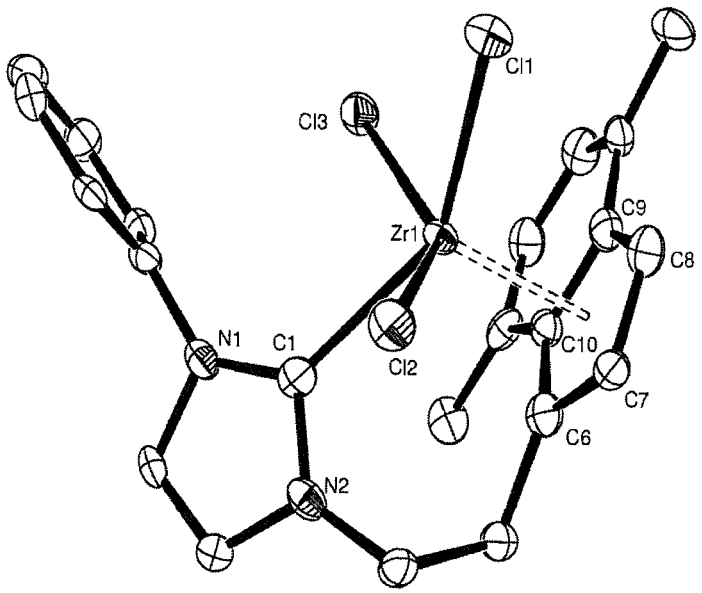


Figure 4.9 ORTEP representation of complex **4.12** showing 50% probability ellipsoids. H atoms and *iso*-propyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Zr(1)-Cl(1) 2.441(9); Zr(1)-Cl(1) 2.480 (2); Zr(1)-Cl(2) 2.458 (2); Zr(1)-Cl(3) 2.413 (2); C(6)-Zr(1) 2.531(8); C(7)-Zr(1) 2.489(8); C(8)-Zr(1) 2.440(9); C(9)-Zr(1) 2.514(9); C(10)-Zr(1) 2.579(8); N(1)-C(1)-N(2) 105.4 (7); N(1)-C(1)-Zr(1) 122.5 (6); C(1)-Zr(1)-Cl(1) 145.6 (2); C(1)-Zr(1)-Cl(2) 80.9 (2); C(1)-Zr(1)-Cl(3) 84.3 (2)

The zirconium complex **4.12** adopts a distorted trigonal bipyramidal geometry assuming that the centre of the cyclopentadienyl ring of the indenyl group occupies one coordination site. The chloride atoms lie on one face in a fac- type arrangement. The indene adopts an η^5 coordination, indicating a lack of strain in the chelate. The THT groups have been displaced, indicating that the carbene is strongly bound to the metal centre through the chelate effect. The plane of the imidazol-2-ylidene ring lies 2.5° from the Zr-$C_{carbene}$ vector.

The lack of solubility of the zirconium complex **4.12** led to the NMR spectra having to be collected in d_2-DCM this was not ideal even though the compound decomposes slowly in DCM. The $C_{carbene}$ signal is not seen in the ^{13}C NMR spectra. Any attempts to increase the pulse delay time in order to observe the slowly relaxing carbene carbon signal, resulted in decomposition and no observation of the carbene signal.

4.3 Group 5 Complexes

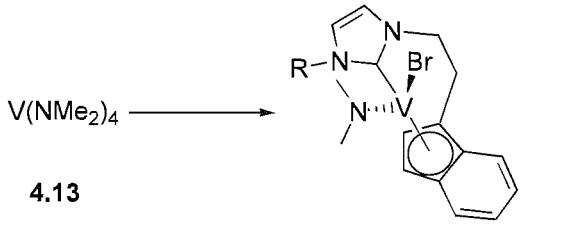
4.3.1 Vanadium Complexes

In 2003, Abernethy reported a VCl_3O(NHC) complex.[11] This was one of the first examples of NHC vanadium complexes. In 2006, both Danopoulos[6] and Gibson[12] reported bis-NHC functionalised pyridyl pincer complexes of vanadium. Prior to this thesis there were no examples in the literature of vanadium NHC complexes containing NHC ligands with pendent anionic groups.

4.3.2 Synthesis of Vanadium Complexes

The reaction of VCl_4 with the potassium fluorenyl **3.6** and indenyl NHC complexes **3.24** to give the bidentate complexes was attempted; unfortunately no products could be isolated or identified in these reactions.

Reaction of the imidazolium salts with $V(NMe_2)_4$ **4.13** could result in the double deprotonation of the imidazolium salts and the formation of the bidentate vanadium complex. The aminolysis of $V(NMe_2)_4$ by the indenyl functionalised imidazolium salt **2.19e** in toluene was also accompanied by reduction to V(III), Scheme 4.3 The red-brown crystalline product, **4.14**, was isolated in moderate yields and characterised by X-ray crystallographic methods. Again further characterisation was hampered by the paramagnetic nature of the complex and the impurities in the reaction.



R = 2,6-diisopropylphenyl

4.14

Scheme 4.3 Synthesis of the first vanadium complex **4.14** containing the bidentate NHC – indenyl ligand. Reagents and conditions: imidazolium salt, toluene, room temperature, overnight.

The vanadium complex **4.14** was crystallised from THF layered with toluene in the triclinic space group P-1 with a = 8.208(4) Å, b = 9.877(6) Å, c = 17.305(10) Å, α = 100.63(8)°, β = 97.83(4)°, γ = 105.38(5)°, V = 1303.8(13) Å^3, and D_{calcd} = 1.387 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5819 unique reflections (Rint = 7.00%) converged to a final R_1 = 5.34% (I > 2(I)) and Rw^2 = 8.75%.

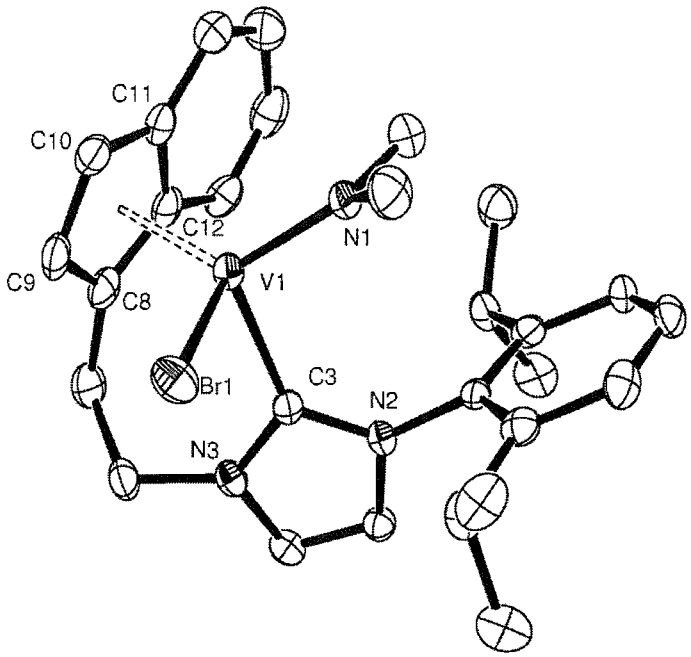


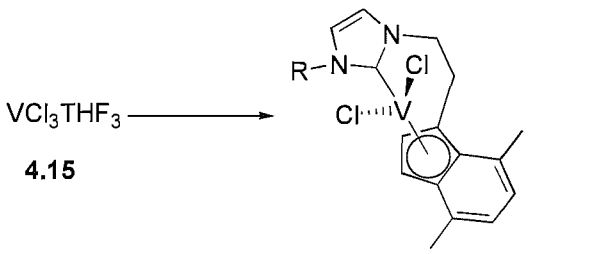
Figure 4.10 ORTEP representation of the vanadium complex **4.14** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: V(1)-N(1) 1.885(3); V(1)-C(3) 2.185(3); N(3)-C(3)1.363(4); N(2)-C(3) 1.388(4); V(1)-C(10) 2.323(4); V(1)-C(9) 2.353(4); V(1)-C(8) 2.403(4); V(1)-C(11) 2.432(4); V(1)-C(12) 2.454(4); N(3)-C(3)-N(2) 103.5(3); N(2)-C(3)-V(1) 132.0(2); N(3)-C(3)-N(2) 103.5(3).

The geometry around the metal center is distorted tetrahedral; the Ind-NHC ligand is chelating through the five-membered ring of the indenyl and the NHC groups. The V-$C_{carbene}$ and V-N_{amide} bond lengths are in the range reported in the literature.[6,13] Inspection of the V-C(indenyl) distances shows a slip distortion toward C8, C9, and C10 ($\Delta = 0.114$ Å).[14] The bridgehead C atoms of the indenyl ring are strictly planar, indicating absence of strain in the chelate. The plane of the imidazol-2-ylidene ring lies 4.3° from the vector of the V-$C_{carbene}$ bond.

Again there is reduction of the metal centre; it is likely that this has occurred by the same mechanism as the titanium complex.

It was hoped that by starting with a vanadium (III) compound that the increased difficultly of reducing V(III) to V(II) would prevent further reduction of the metal centre. This would allow the isolation of a vanadium (III) complex in higher yields with less formation of impurities. $VCl_3.(THF)_3$ was reacted with the dimethylindenyl potassium

carbene **3.13b** at -78 °C in THF. After crystallisation from a saturated THF solution layered with ether, the complex was obtained as black opaque blocks suitable for X-ray crystallography.



R = 2,6-diisopropylphenyl

4.16

Scheme 4.4 Synthesis of a bidentate vanadium (III) dichloride complex. Reagents and conditions: Dimethylindenyl potassium NHC complex, THF, -78 °C – RT, overnight.

The vanadium complex **4.16** was crystallised, from THF layered with ether, in the monoclinic space group $P_{21/c}$ with a = 16.6796(8) Å, b = 10.6407(6) Å, c = 15.5939(6) Å, β = 109.735(2)°, V =2605.1(2) Å^3, and D_{calcd} = 1.324 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5880 unique reflections (R_{int} = 22.54%) converged to a final R_1 = 6.66% (I > 2(I)) and Rw^2 = 13.05%.

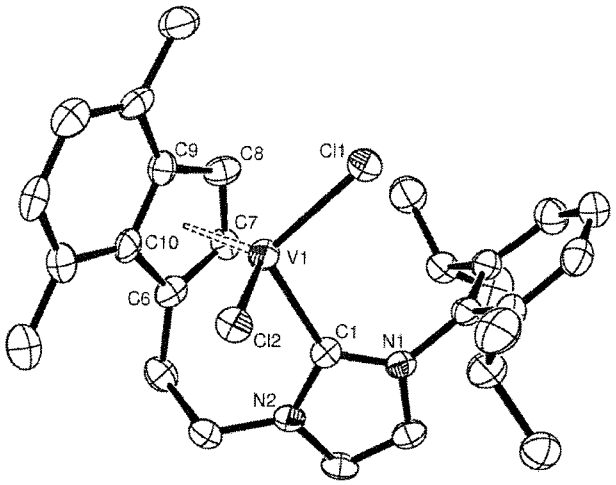


Figure 4.11 ORTEP representation of the vanadium complex **4.16** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) 1.352(6); C(1)-N(2) 1.363(5); C(1)-V(1) 2.126(5); C(6)-V(1) 2.288(5); C(7)-V(1) 2.260(5); C(8)-V(1) 2.285(5); C(9)-V(1) 2.337(5); C(10)-V(1) 2.362(5); Cl(1)-V(1) 2.2816(14); Cl(2)-V(1) 2.3189(15); N(1)-C(1)-N(2) 103.5(4); N(1)-C(1)-V(1) 133.8(3); N(2)-C(1)-V(1) 122.5(3); C(1)-V(1)-C(7) 84.55(18); C(1)-V(1)-Cl(1) 103.19(13); C(7)-V(1)-Cl(1) 114.01(12).

The complex consists of the vanadium centre with the ligand coordinated in a bidentate mode with the coordination sphere completed by two chlorides. The vanadium metal centre in this complex has adopted a tetrahedral geometry as would be expected for a 4 coordinate vanadium species. The indene ring has adopted an η^5 coordination. The bridge head atom of the indenyl ring is planar indicating no strain in the chelate. The bond length and angles are in the range of those previously observed.[5,13]

In this complex the indenyl to vanadium bond lengths are much shorter than in the previous example, this may be due to the geometry of the backbone pulling the indene closer to the metal centre or due to the metal being more electropositive due to the chlorides causing the indene to interact more strongly with the vanadium metal centre.

The plane of the imidazol-2-ylidene ring lies 4.5° from the vector of the V-$C_{carbene}$ bond indicating little strain in the ligand in this complex.

4.3.3 Niobium Complexes

In 2006 Danopoulos reported the only example of an NHC complex of niobium; in a bis-NHC pyridyl pincer complex.[6]

4.3.4 Attempted Synthesis of Niobium Complexes

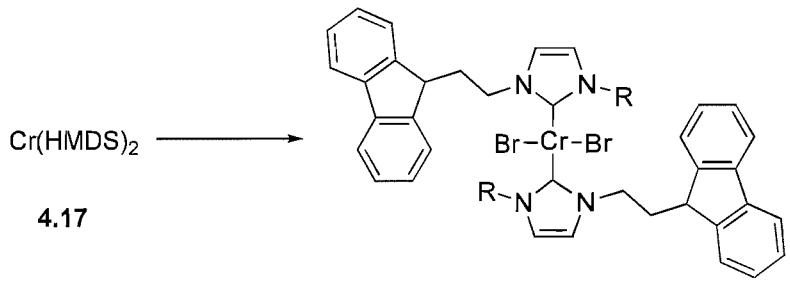
Attempts were made to synthesise niobium complexes, but unfortunately none of these were successful. The reaction of the pre-formed indenyl or fluorenyl potassium NHCs with niobium (IV) or (V) failed to give an identifiable product, as did the reaction between niobium (IV) and (V) amides with imidazolium salts.

4.4 Group 6 Complexes

4.4.1 Chromium Complexes

The first NHC chromium complex was reported in 1968, by Öfele whose synthesis made use of the acidic nature of the imidazolium salt[15] as discussed previously in chapter 1. In 1999, Tilset reported a series of chromium half-sandwich NHC complexes with various substituents on the metal centre[16], these were also discussed previously in chapter 1. Danopoulos[6] and Gibson[17] have both reported bis-NHC functionalised pyridyl pincer complexes of chromium. To date there have been no reported complexes of chromium in with the NHC is functionalised with an anionic group.

4.4.2 Synthesis of Chromium Complexes



Scheme 4.5 Synthesis of a bis NHC chromium complex. Reagents and conditions: imidazolium salt, toluene, room temperature, overnight.

Chromium bis(HMDS) **4.17** was reacted with one equivalent of the fluorenyl imidazolium salt and gave the unexpected bis carbene complex **4.18**, where two NHC moieties have been formed and the fluorenyl left protonated.

The chromium complex **4.17** was crystallised from hot toluene, in the triclinic space group P-1 with a = 10.1655(18) Å, b = 10.864(2) Å, c = 12.940(2) Å, α = 112.546(12)° β = 98.115(15)°, γ = 102.188(14)° V =1250.4(4) Å^3, and D_{calcd} = 1.398 Mg m^{-3} for Z = 1. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5757 unique reflections (R_{int} = 7.88%) converged to a final R_1 = 5.16% (I > 2(I)) and Rw^2 = 9.92%.

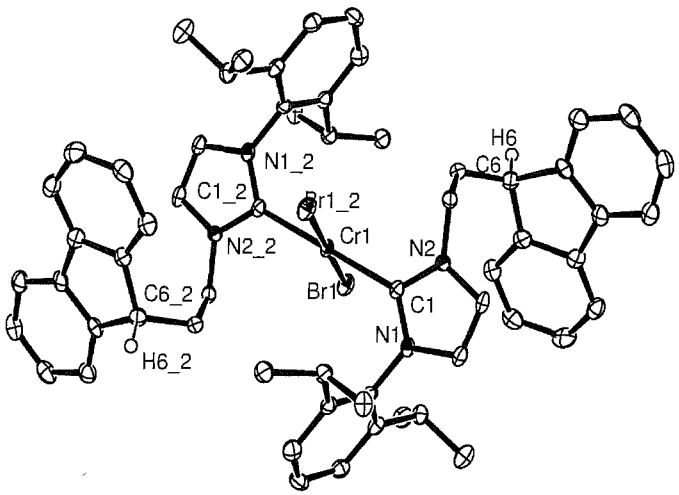


Figure 4.12 ORTEP representation of complex the chromium complex **4.17** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-Cr(1) 2.146(3); Br(1)-Cr(1) 2.4821(5); C(1)-Cr(1)-Cr(1_2) 180.000(15); Br(1)-Cr(1)-Br(1_2) 180.000(13); C(1)-Cr(1)-Br(1) 90.56 (8).

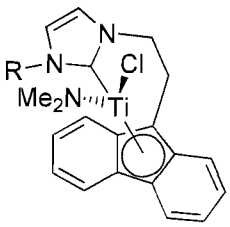
The crystal structure displays a near perfect square-planar geometry, the $C_{carbene}$-Cr-$C_{carbene}$ and Br-Cr-Br angles are exactly 180°, because the chromium is modelled as lying on a special crystallographic symmetry point, $C_{carbene}$-Cr-Br angle only slightly deviates from the perfect 90° at 90.56(8)°, this may be due to the differing sizes of R-groups each side of the imidazol-2-ylidene ring. The Br-Cr-$C_{carbene}$-N torsion angle is 70° whereas an angle of 90° would be expected to minimise the steric interaction with the bromides. The imidazole-2-ylidene rings are eclipsed, presumably lowering the steric interactions between the R-groups and the bromides. The bond angles around the tetrahedral

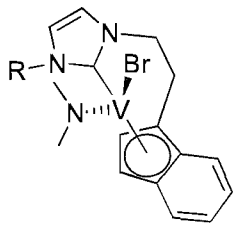
crystallographic C6 clearly indicate that the fluorenyl ring has remained protonated. The plane of the imidazol-2-ylidene ring lies 1.9° from the Cr-$C_{carbene}$ vector.

It is unclear why the bis NHC complex forms in preference to the mono carbene HMDS complex. Attempts to form the bidentate complex by heating proved unsuccessful. The reaction was repeated using two equivalents of the imidazolium salt to give the product in high yields with out contamination from unused starting materials. Elemental analysis showed this reaction proceeded cleanly and the material obtained was pure after crystallisation from hot toluene.

4.5 Conclusions

Due to the problems with reduction taking place, no high oxidation state complexes have been synthesised with the exception of Zr(IV). The reduction leads to paramagnetic complexes these make analysis by NMR impractical. In the future, it would be beneficial to investigate ways to prevent the reduction from taking place, although it may be that the complexes themselves are unstable. Both complexes **4.7** and **4.14** have been synthesised as a result of the reduction of the metal centre.

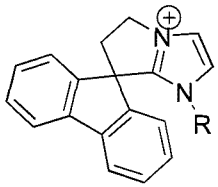




R = 2,6-diisopropylphenyl

4.7 **4.14**

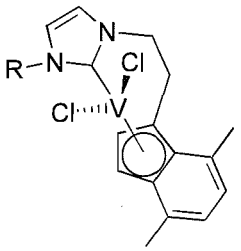
The ligand could be described as being non-innocent as with both early transition metals and the main group elements described in the previous chapter, decomposition with reduction of the metal centre appears to take place readily. It is believed the ligand undergoes a type of reductive elimination to give the spiro imidazolium salt **4.9** below.



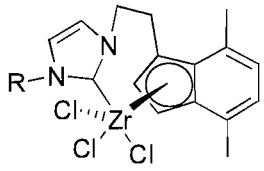
R = 2,6-diisopropylphenyl

4.9

By switching to V(III) starting materials the vanadium complexes could be obtained in higher yields because further reduction was prevented. Moving to zirconium stopped the reduction taking place, but the zirconium amides appeared to be less reactive than the titanium ones so this hampered investigation of zirconium amide complexes, only the zirconium chloride structure **4.12** could be identified.



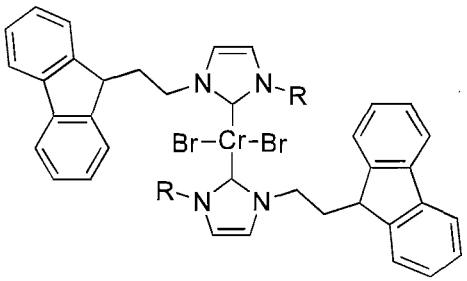
4.16



4.12

In the vanadium structures **4.14** and **4.16** the metal to indene bond lengths are very different, it is not clear why this is the case but could be envisaged to be due to the electronics or geometry of the systems.

It is interesting that in the case of chromium the bis-carbene complex **4.17** does not include any bidentate coordination.



R = 2,6-diisopropylphenyl

4.17

In the crystal structures all of the complexes display very low angles <5° between the plane of the imidazol-2-ylidene ring and the M-$C_{carbene}$ vector and the bond lengths of the NHC-M and metal to cyclopentadienyl moiety and normal indicating little strain in the complexes. This indicates that a two carbon bridge between the cyclopentadienyl moiety and the NHC ring is reasonable.

4.6 General Experimental

4.6.1 Instrumentation

Proton NMR spectra were recorded on a Bruker Avance DPX300, at 300 MHz or a Bruker Advance DPX400 spectrometers at 400 MHz. ^{13}C NMR spectra were recorded on the same spectrometers at 75 MHz and 100 MHz respectively.

Low resolution mass spectra were collected on a Micromass Platform II spectrometer. High resolution mass spectra were collected on a Bruker Apex III spectrometer.

Elemental analyses were carried out by the Department of Health and Human Sciences, London Metropolitan University. All analyses were carried out in duplicate with both results agreeing closely. Air-sensitive samples were supplied in glass tubes sealed under vacuum.

4.6.2 Solvents

Solvents were purchased from Fisher Chemicals. All solvents for moisture sensitive reactions were dried and distilled before use. Petroleum ether 40/60 was dried over sodium benzophenone ketyl, diglyme (approx 1 ml/L) was added to increase its solubility, and is referred to as petrol in the experimental. Diethyl ether was dried over sodium benzophenone ketyl and is referred to as ether in the experimental. Toluene was dried over molten sodium. THF was dried over sodium benzophenone ketyl. DCM was dried over powdered calcium hydride. Benzene was dried over sodium benzophenone ketyl and stored in an ampoule over 4 Å molecular sieves.

$CDCl_3$ was dried over 4 Å molecular sieves and stored over fresh sieves. CD_2Cl_2 was dried over calcium hydride and stored over 4 Å molecular sieves. d_8-THF was dried over NaK alloy and stored over 4 Å molecular sieves.

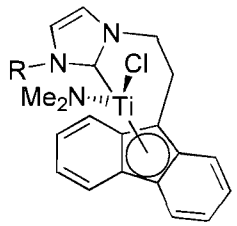
Compounds $V(NMe_2)_4$[18] and VCl_3THF_3[19] were synthesised by literature methods.

4.6.3 General

Air-sensitive reactions were carried out using standard Schlenk techniques or in a catalytically dried and deoxygenated M. Braun glovebox (<2 ppm O_2). All air-sensitive solids were stored in the glovebox. Imidazolium salts were also stored in the glovebox due to their hydroscopic nature.

4.7 Experimental

3-(2,6-Diisopropyl-phenyl)-1-[2-(fluorenyl-9-yl)-ethyl]-imidazol-2-ylidene titanium dimethylamide chloride 4.7

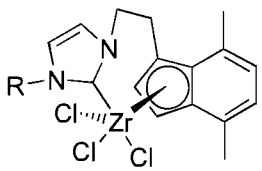


R = 2,6-diisopropylphenyl

Titanium dichloride bis(dimethylamide) (2 mmol, 4 mg) and the fluorenyl potassium NHC complex **3.6** (2 mmol, 9 mg) and d_6-benzene were combined in a glass vial then filtered through glass wool into an NMR tube. Over a period of 24h yellow-brown crystals formed in the tube. The product was not isolated as bulk material.

The X-ray structure was collected.

3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(2,5-(dimethylindenyl)-ethyl]-imidazol-2-ylidene zirconium trichloride 4.12



R = 2,6-diisopropylphenyl

$ZrCl_4(THT)_2$ (0.50 mmol, 0.200 mg) and the dimethylindene-imidazolium salt **3.13b** (0.5 mmol, 240 mg) were both dissolved in THF and combined at -78°C, and allowed to warm to room temperature and stir overnight. The volatiles were removed under vacuum and the residue dissolved in toluene and filtered through Celite. The product was crystallised from toluene/petrol at -30°C as yellow crystals (100mg, 66%).

^{1}H (CD_2Cl_2, 300 MHz): 7.49 (1H, t, J = 8 Hz, Ar); 7.48 (1H, t, J = 8 Hz); 7.28-7.25 (2H, m, Ar); 7.11 (1H, s, Ar); 7.04 (1H, s, Ar); 6.98-6.87 (1H, s, Ar); 6.84-6.82 (1H, s, Ar); 6.58 (1H, dd, J = 6, 2 Hz, indene-H); 4.98 (1H, t, J = 6 Hz, indene-H); 4.60 (1H, quin, J = 7 Hz, bridge); 4.29 (1H, quin, J = 7 Hz, bridge); 3.76-3.74 (1H, m, bridge); 3.46 (1H, m, bridge); 2.94 (1H, sept, J = 7 Hz, C*H*$(CH_3)_2$); 2.93 (1H, sept, J = 7 Hz,

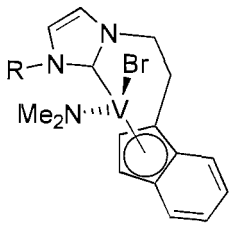
C*H*(CH_3)$_2$); 2.34 (3H, s, indene-CH_3); 2.31 (3H, s, indene-CH_3); 2.12 (6H, d, J = 7 Hz, CH(CH_3)$_2$); 1.10 (3H, d, J = 7 Hz, CH(CH_3)$_2$); 1.08 (3H, d, J = 7 Hz, CH(CH_3)$_2$).

$^{13}C\{^1H\}$ (CD_2Cl_2, 300 MHz): 144.8 (Ar); 142.7 (Ar); 142.2 (Ar) 136.7 (ArH); 136.3 (Ar); 130.9 (ArH); 129.9 (ArH); 129.4 (Ar); 128.9 (ArH); 127.7 (ArH); 127.5 (ArH); 126.4 (Ar); 123.7 (ArH); 123.7 (ArH); 123.3 (ArH); 122.8 (ArH); 47.9 (CH_2); 30.8 (CH_2); 29.3 (indene-CH_3); 27.9 (indene-CH_3); 23.6 (C*H*(CH_3)$_2$); 23.5 (C*H*(CH_3)$_2$); 23.2 (CH(C*H*$_3$)$_2$); 23.1 (CH(C*H*$_3$)$_2$); 19.2 (CH(C*H*$_3$)$_2$); 17.9 (CH(C*H*$_3$)$_2$); 17.1 (CH(C*H*$_3$)$_2$).

MS ES^+: 413.5

Calculated (%) C 56.52, H 5.59; N 4.71 Found C 56.71, H, 5.42, N 4.74

3-(2,6-Diisopropyl-phenyl)-1-[2-(1-indenyl)-ethyl]-imidazol-2-ylidene vanadium dimethylamide bromide 1.14

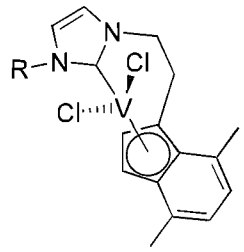


R = 2,6-diisopropylphenyl

Vanadium tetrakis(dimethylamide) (0.5 mmol) and the indene-imidazolium salt **2.19e** were both dissolved in THF and combined at -78°C, the volatiles were removed under vacuum and the product crystallised from toluene/petrol at -30°C.

The X-ray structure was collected.

3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(2,5-dimethyl)indenyl)-ethyl]-imidazol-2-ylidene vanadium dichloride 4.16



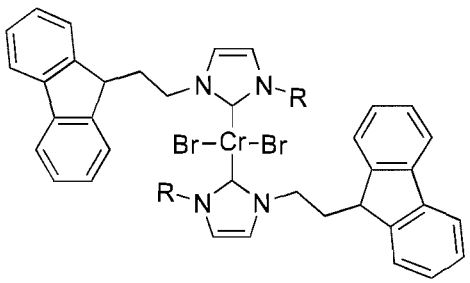
R = 2,6-diisopropylphenyl

VCl_3THF_3 (0.5 mmol, 150 mg) and the dimethylindene potassium carbene complex **3.13b** (0.5 mmol, 240 mg) were both dissolved in THF and combined at -78°C and then allowed to warm to room temperature. The volatiles were removed under vacuum and the residue dissolved in toluene. The product was crystallised from toluene/petrol.

The X-ray structure was collected.

Calculated (%) C, 64.12, H, 7.30; N, 5.34 Found C, 64.11, H, 7.25, N, 5.43.

Bis[3-(2,6-Diisopropyl-phenyl)-1-[2-(9*H*-fluoren-9-yl)-ethylimidazol-2-ylidene] chromium dibromide



R = 2,6-diisopropylphenyl

Chromium bis(silylamide) (0.26 g, 0.50 mmol) and the fluorenyl imidazolium salt were dissolved in toluene and heated to 110°C. The solid was filtered and collected and crystallised from hot THF.

The X-ray crystal structure was collected.

Calculated (%) C 68.44, H, 6.13, N, 5.32, Found C, 68.45, H, 6.20, N, 5.22.

Table 4.1 Crystallographic data for group 4 complexes

Identification code	**4.7**	**4.12**
Empirical formula	$C_{32}H_{37}ClN_3Ti$	$C_{28}H_{33}Cl_3N_2Zr$
Formula weight	547.00	595.13
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 8.3495(6) Å	a = 9.5873(5) Å
	α = 73.535(9)°.	α= 96.636(3)°.
	b = 10.7139(13) Å	b = 9.7036(6) Å
	β = 86.508(7)°.	β= 93.590(4)°.
	c = 16.8282(19) Å	c = 16.7862(11) Å
	γ = 71.966(7)°.	γ = 119.315(3)°.
Volume	1372.1(2) $Å^3$	1339.67(14) $Å^3$
Z	2	2
Density (calculated)	1.324 Mg/m^3	1.475 Mg/m^3
Absorption coefficient	0.436 mm^{-1}	0.729 mm^{-1}
F(000)	578	612
Crystal size	0.10 x 0.10 x 0.05 mm^3	0.05 x 0.05 x 0.02 mm^3
Theta range for data collection	3.25 to 27.62°.	2.92 to 25.03°.
Index ranges	-10<=h<=10	-11<=h<=11
	-13<=k<=13	-11<=k<=11
	-21<=l<=21	-19<=l<=19
Reflections collected	22627	21697
Independent reflections	6276 [R(int) = 0.0411]	4711 [R(int) = 0.0953]
Completeness to theta = 27.89°	98.8 %	99.4 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9786 and 0.9577	0.9856 and 0.9644
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F^2
Data / restraints / parameters	6276 / 0 / 340	4711 / 0 / 313
Goodness-of-fit on F2	1.088	1.238
Final R indices [I>2sigma(I)]	R_1 = 0.0484, wR^2 = 0.1081	R_1 = 0.0960, wR^2 = 0.1868
R indices (all data)	R_1 = 0.0629, wR^2 = 0.1140	R_1 = 0.1198, wR^2 = 0.1947
Largest diff. peak and hole	0.679 and -0.548 $e.Å^{-3}$	1.604 and -0.658 $e.Å^{-3}$

Table 4.2 Crystallographic data for cyclised ligand

Identification code	**4.9**
Empirical formula	$C_{33}H_{34}ClN_2$
Formula weight	494.07
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.345(4) Å
	α = 103.08(4)°.
	b = 10.774(5) Å
	β = 98.84(4)°.
	c = 16.130(7) Å
	γ = 104.81(3)°.
Volume	1330.8(10) Å3
Z	2
Density (calculated)	1.233 Mg/m^3
Absorption coefficient	0.168 mm^{-1}
F(000)	526
Crystal size	0.08 x 0.02 x 0.02 mm3
Theta range for data collection	3.07 to 24.35°.
Index ranges	-9<=h<=9
	-12<=k<=12
	-18<=l<=18
Reflections collected	15668
Independent reflections	4231 [R(int) = 0.1409]
Completeness to theta = 27.89°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9966 and 0.9867
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4231 / 0 / 337
Goodness-of-fit on F2	1.025
Final R indices [I>2sigma(I)]	R_1 = 0.0766, wR^2 = 0.1300
R indices (all data)	R_1 = 0.1615, wR^2 = 0.1587
Largest diff. peak and hole	0.239 and -0.275 $e.Å^{-3}$

Table 4.3 Crystallographic data for vanadium complexes

Identification code	**4.14**	**4.16**
Empirical formula	$C_{28}H_{35}BrN_3V$	$C_{28}H_{33}Cl_2N_2V$
Formula weight	544.44	519.40
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/C
Unit cell dimensions	a = 8.208(4) Å	a = 16.6796(8) Å
	α = 100.63(8)°.	α = 90°.
	b = 9.877(6) Å	b = 10.6407(6) Å
	β = 97.83(4)°.	β = 109.735(2)°.
	c = 17.305(10) Å	c = 15.5939(6) Å
	γ = 105.38(5)°.	γ = 90°.
Volume	1303.8(13) $Å^3$	2605.1(2) $Å^3$
Z	2	4
Density (calculated)	1.387 Mg/m^3	1.324 Mg/m^3
Absorption coefficient	1.933 mm^{-1}	0.605 mm^{-1}
F(000)	564	1088
Crystal size	0.10 x 0.05 x 0.01 mm3	0.12 x 0.12 x 0.08 mm3
Theta range for data collection	3.64 to 27.42°.	2.91 to 27.57°.
Index ranges	-10<=h<=10	-21<=h<=21
	-12<=k<=12	-13<=k<=13
	-22<=l<=22	-20<=l<=20
Reflections collected	18939	45116
Independent reflections	5819 [R(int) = 0.0700]	5880 [R(int) = 0.2254]
Completeness to theta = 27.89°	97.5 %	98.1 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9809 and 0.8302	0.9532 and 0.9310
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5819 / 0 / 304	5880 / 0 / 304
Goodness-of-fit on F2	1.019	0.926
Final R indices [I>2sigma(I)]	R_1 = 0.0534, wR^2 = 0.0875	R_1 = 0.0666, wR^2 = 0.1305
R indices (all data)	R_1 = 0.0977, wR^2 = 0.0988	R_1 = 0.2185, wR^2 = 0.1867
Largest diff. peak and hole	0.378 and -0.528 $e.Å^{-3}$	0.562 and -0.510 $e.Å^{-3}$

Table 4.4 Crystallographic data for chromium complex

Identification code	**4.18**
Empirical formula	$C_{60}H_{64}Br_2CrN_4$
Formula weight	1052.97
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	p-1
Unit cell dimensions	a = 10.1655(18) Å
	α = 112.546(12)°.
	b = 10.864(2) Å
	β = 98.115(15)°.
	c = 12.940(2) Å
	γ = 102.188(14)°.
Volume	1250.4(4) $Å^3$
Z	1
Density (calculated)	1.398 Mg/m^3
Absorption coefficient	1.870 mm^{-1}
F(000)	546
Crystal size	0.20 x 0.20 x 0.20 mm3
Theta range for data collection	3.11 to 27.61°.
Index ranges	-13<=h<=13
	-14<=k<=14
	-16<=l<=16
Reflections collected	21108
Independent reflections	5757 [R(int) = 0.0788]
Completeness to theta = 27.89°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7061 and 0.7061
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5757 / 0 / 309
Goodness-of-fit on F2	1.021
Final R indices [I>2sigma(I)]	R_1 = 0.0516, wR^2 = 0.0992
R indices (all data)	R_1 = 0.0905, wR^2 = 0.1110
Largest diff. peak and hole	0.727 and -0.516 $e.Å^{-3}$

4.8 References

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Chapter 5

Late Transition Metal Complexes with *N*-Heterocyclic Carbene Ligands Functionalised with Cyclopentadienyl Type Donors

5 Late Transition Metal Complexes

5.1 Aims

Our initial aim was to find methods to synthesise a range of late transition metal, namely groups 8, 9 and 10, complexes containing the ligands derived from the imidazolium salts discussed previously, in chapter 2. The existence of two C-H acidic sites of different pK_a (i.e. at the C2 of the imidazolium salt and the cyclopentadiene ring) raises the question of selective mono- or double-deprotonation which may lead to different binding modes of the deprotonated entity to a transition metal (monodentate, chelate bidentate or bridging).

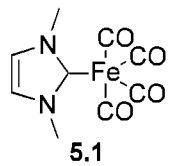
The complexes could potentially be synthesised by both ligand transfer from the potassium indenyl- or fluorenyl- NHC complexes or the silver complexes, or by methods such as alcoholysis reactions.

One of our initial aims was that some of these complexes could be tested for catalytic activity such as oligomerisation or polymerisation of ethylene or similar olefins.

5.2 Group 8 Complexes

5.2.1 Iron Complexes

There are only limited reports of iron NHC complexes. Öfele reported the reaction of a free NHC with iron pentacarbonyl, releasing CO to give the iron NHC complex **5.1**.[1]



5.1

Figure 5.1 An iron NHC complex reported by Öfele.

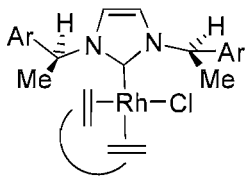
5.2.2 Attempted Synthesis of Iron Complexes

Attempts were made to synthesise iron complexes of the fluorenyl and indenyl NHCs. The reactions of $Fe(HMDS)_2$ with the imidazolium salts and $FeCl_2$ with the preformed fluorenyl or indenyl potassium carbenes were investigated. No identifiable products could be isolated.

5.3 Group 9 Complexes

5.3.1 Rhodium and Iridium Complexes

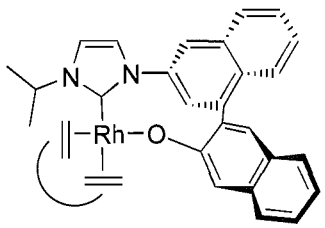
As with the other precious group metals there is currently intense research into rhodium and iridium NHC complexes because of their potential to be used as catalysts. The first rhodium NHC complexes were reported in 1996 by Herrmann.[2] Not long after in 1997, Hermann reported chiral NHC complexes of rhodium such as **5.2**.[3]



5.2

Figure 5.2 A chiral rhodium NHC complex reported by Hermann.

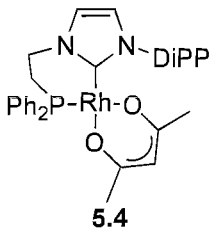
There are examples of rhodium and iridium NHC complexes in which the NHC has been further functionalised. Crabtree reported a ligand based on BINAM, in which an NHC is functionalised with a biphenyl moiety further functionalised with an anionic oxo group, this complex **5.3** is useful for ketone hydrosilylation reactions.[4]



5.3

Figure 5.3 A rhodium BINAM-functionalised NHC complex, reported by Crabtree.

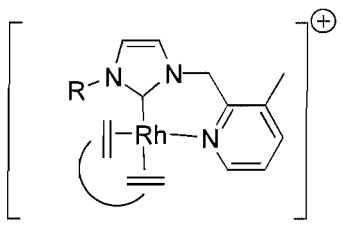
Also reported by our group and others are rhodium NHC complexes where the NHC is functionalised with a phosphine to give the bidentate phosphine NHC complexes such as **5.4**.[5,6]



5.4

Figure 5.4 A phosphine NHC complex reported by our group.

Our group reported of rhodium complexes such as **5.5** containing NHCs functionalised with pyridyl groups. Peris also reported pyridyl functionalised NHC complexes of rhodium and iridium and their use in various catalytic reactions.[7]



R = 2,6-diisopropylphenyl

5.5

Figure 5.5 A rhodium pyridyl NHC complex previously reported by our group.

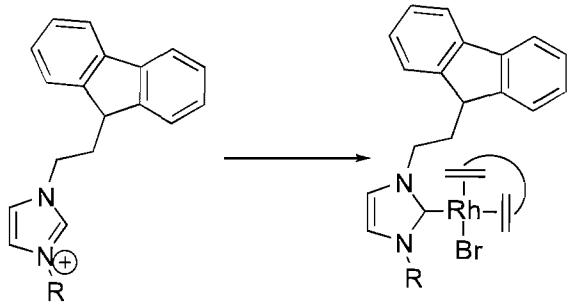
Nolan reported rhodium and iridium complexes in which two NHCs are present and both have been C-H activated, treatment of these complexes with a tetrafluoroborate salt leads to the 'unprecedented' 14 electron anionic species being synthesised.[8] In 2001, Burgess reported the synthesis of chiral oxazole functionalised NHC complexes of iridium and their use as aryl alkene hydrogenation catalysts.[9] In 2003, Crabtree reported the use of silver transmetalation reagents to synthesise rhodium and iridium NHC complexes.[10]

There have been a number of reports about rhodium half sandwich complexes, these are discussed in Chapter 1 on page 22.

5.3.2 Synthesis of Rhodium Complexes

A series of rhodium COD bromide NHC complexes were synthesised. The imidazolium salt precursors were reacted with rhodium COD methoxide to give the corresponding rhodium COD NHC bromide complexes. The isolated complexes were air-stable, yellow to red materials.

The fluorenyl rhodium NHC complex **5.10** was synthesised by the reaction of the fluorenyl imidazolium salt **2.10a** with rhodium COD methoxide dimer. The reaction proceeded cleanly in high yields.



R = 2,6-diisopropylphenyl

2.10a **5.10**

Scheme 5.1 Synthesis of a rhodium carbene complex. Reagents and conditions: $[Rh(COD)OMe]_2$, toluene, -78 °C – RT, overnight.

The rhodium NHC complex **5.10** was crystallised from a saturated DCM solution layered with ether in the triclinic space group *P*-1 with a = 10.313(5) Å, b = 13.442(5) Å, c = 15.119(5) Å, α = 68.598(5)°, β = 70.798(5)°, γ = 86.647(5)°. V = 1838.3(13) Å^3 and D_{calcd} = 1.416 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 8420 unique reflections (Rint = 4.71%) converged to a final R_1 = 6.27% ($I > 2(I)$) and Rw^2 = 14.58%.

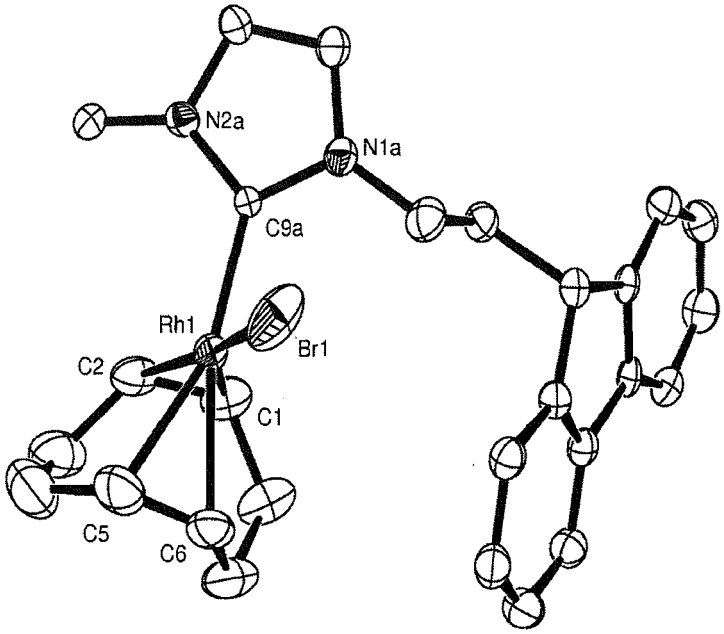


Figure 5.6 ORTEP representation of one of the independent geometries of **5.10** showing 50% probability ellipsoids. H atoms and the 2,6-diisopropylphenyl ring, except the ipso carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-C(2) 1.374(8); C(5)-C(6) 1.370(8); C(1)-Rh(1) 2.095(5); C(2)-Rh(1) 2.120(5); C(5)-Rh(1) 2.178(5); C(6)-Rh(1) 2.221(5); C(9A)-N(2A) 1.4200 C(9A)-N(1A) 1.4200; C(9A)-Rh(1) 2.000(5); Br(1)-Rh(1) 2.5088(10); N(2A)-C(9A)-N(1A) 108.0; N(2A)-C(9A)-Rh(1) 125.1(4); N(1A)-C(9A)-Rh(1) 126.7(4); C(9A)-Rh(1)-C(1) 97.6(2); C(9A)-Rh(1)-C(9B) 12.69(18); C(1)-Rh(1)-C(9B) 85.1(2); C(9A)-Rh(1)-C(2) 99.3(2); C(1)-Rh(1)-C(2) 38.0(2); C(9B)-Rh(1)-C(2) 88.05(19); C(9A)-Rh(1)-C(5) 156.8(2); C(1)-Rh(1)-C(5) 97.4(2); C(9B)-Rh(1)-C(5) 159.9(2).

There were some difficulties in modelling this structure as the electron density map displayed a large amount of splitting during the modelling process. The NHC ligand was finally modelled as two parts in equal occupancy. The phenyl ring has been modelled as common to both ligand geometries; the angle between the two orientations of the imidazole ring is about 9°. The two positions of fluorenyl ring also lay in much the same position, and have been modelled as being in the same plane. In one orientation, the plane of the imidazol-2-ylidene ring lies only 5.4° from the Rh-$C_{carbene}$ vector whilst in the other orientation it lies as much as 27.7° away. There is also one molecule of THF present in the asymmetric unit which has also been modelled as split into two equal parts. Due to the

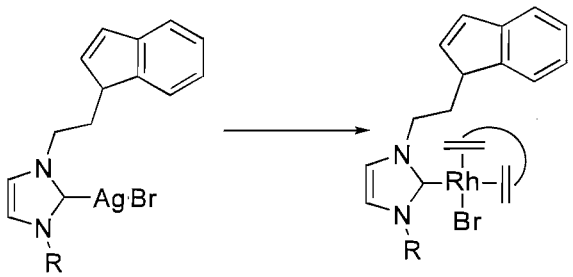
splitting in the molecule, a number of the bond lengths had to be constrained to give a stable model of the NHC ligand.

The complex has adopted a square planar geometry. The NHC occupies one coordination site, a bromide occupies another, and the COD ligand occupies two, assuming each double bond as one site.

The bond lengths and angles are consistent with what has been reported previously.[6]

The analogous rhodium indenyl NHC complex **5.11** was synthesised by reaction of the silver carbene with rhodium COD chloride dimer, Scheme 5.2. The silver was displaced and after filtration and careful crystallisation gave the desired compound.

The same compound **5.11** was also synthesised from rhodium COD methoxide and the imidazolium salt. It was found that the methoxide route gave cleaner products than the silver carbene; the reason for this is still unclear.



R = 2,6-diisopropylphenyl

3.24a **5.11**

Scheme 5.2 Synthesis of a rhodium carbene by ligand transfer form a silver carbene complex. Reagents and conditions: Toluene, $[Rh(COD)Br]_2$, overnight, reflux.

The rhodium indenyl NHC complex **5.11** was crystallised from a saturated THF solution in the orthorhombic space group P_{212121} with a = 11.795(4) Å, b = 11.853(3) Å c = 21.599(5) Å. V = 3019.7(15) Å^3 and D_{calcd} = 1.455 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6733 unique reflections (Rint = 15.00%) converged to a final R_1 = 7.83% ($I > 2(I)$) and Rw^2 = 12.19%.

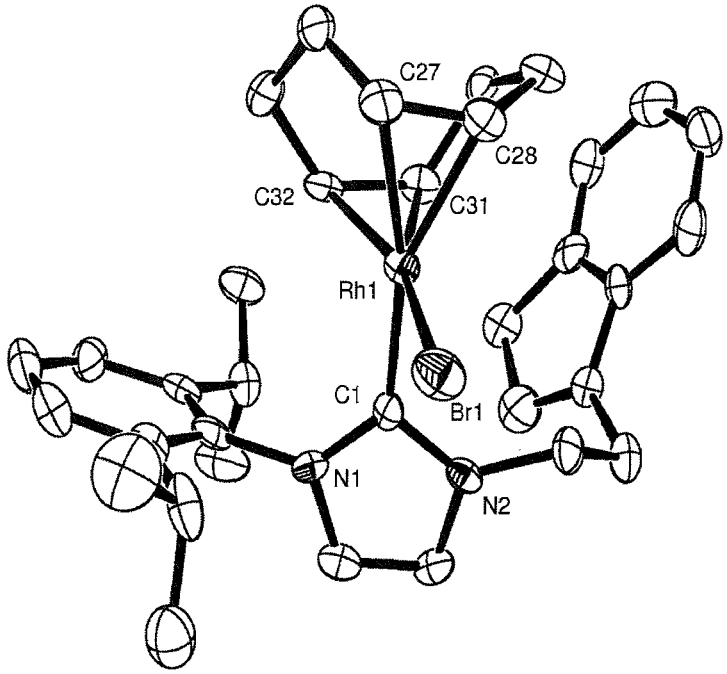
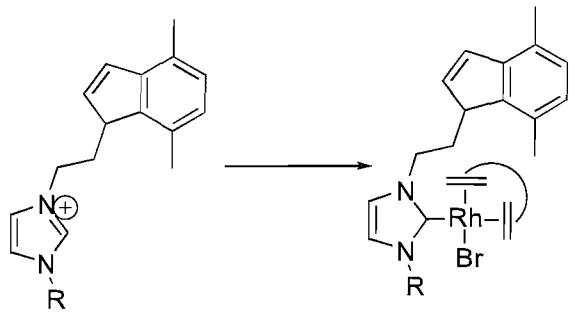


Figure 5.7 ORTEP representation of the rhodium NHC complex **5.11** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Rh(1)-C(1) 2.041(9); Rh(1)-C(32) 2.098(9); Rh(1)-C(31) 2.124(8); Rh(1)-C(28) 2.170(9); Rh(1)-C(27) 2.210(10); Rh(1)-Br(1) 2.5069(13); N(2)-C(1) 1.367(11); N(1)-C(1) 1.369(10); C(27)-C(28) 1.382(14); C(31)-C(32) 1.386(12); C(1)-Rh(1)-C(32) 93.8(3); C(1)-Rh(1)-C(31) 93.4(3); C(1)-Rh(1)-C(28) 155.6(4); C(32)-Rh(1)-C(28) 96.9(4); C(31)-Rh(1)-C(28) 81.7(4); C(1)-Rh(1)-C(27) 167.6(4); C(32)-Rh(1)-C(27) 81.3(4); C(31)-Rh(1)-C(27) 89.7(4); C(1)-Rh(1)-Br(1) 88.3(2); C(32)-Rh(1)-Br(1) 158.8(3); C(31)-Rh(1)-Br(1) 162.6(3); C(28)-Rh(1)-Br(1) 89.6(3); C(27)-Rh(1)-Br(1) 92.3(3).

The geometry of the crystal structure is broadly similar to that of the fluorenyl analogue **5.10**. The plane of the imidazol-2-ylidene ring lies only 6.3° from the Rh-$C_{carbene}$ vector. In this case the structure was modelled in the usual fashion as there was no splitting present. Again, as before the bond lengths and angles are in the range previously reported.[6]

The dimethylindenyl substituted imidazolium salt reacted with $[Rh(COD)OMe]_2$ in an analogous fashion to the other imidazolium salts. As expected the rhodium NHC complex **5.12** was obtained in good yields.



R = 2,6-diisopropylphenyl

2.27 **5.12**

Scheme 5.3 Synthesis of rhodium complex **5.12**. Reagents and conditions: $[Rh(COD)OMe]_2$, Toluene, -78 °C-RT, overnight.

The rhodium NHC complex **5.12** was crystallised from a saturated THF solution layered with ether in the triclinic space group P-1 with. a = 8.2436(2) Å, b = 8.5687(3) Å, c = 22.8614(8) Å, α = 81.819(2)°, β = 85.004(2)°, γ = 82.286(2)°. V = 1580.15(9) Å^3 and D_{calcd} = 1.449 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 7288 unique reflections (Rint = 9.55%) converged to a final R_1 = 5.46% ($I > 2(I)$) and Rw^2 = 23.29%.

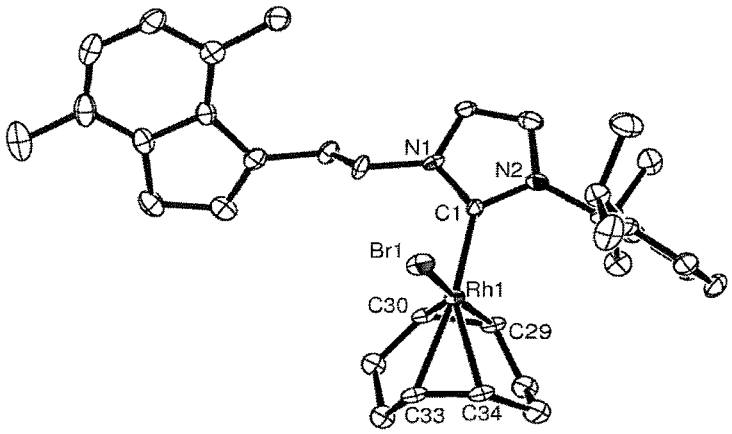


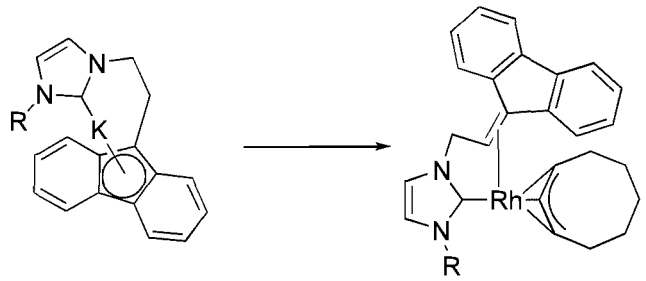
Figure 5.8 ORTEP representation of complex **5.12** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) 1.337(11); C(1)-N(2) 1.366(12); C(1)-Rh(1) 2.025(9); C(29)-C(30) 1.460(14); C(33)-C(34) 1.362(15); C(29)-Rh(1) 2.149(10); C(30)-Rh(1) 2.102(10); C(33)-Rh(1) 2.236(10); C(34)-Rh(1) 2.176(9); Br(1)-Rh(1) 2.5018(12); N(1)-C(1)-N(2) 104.3(8); N(1)-C(1)-Rh(1) 128.4(7); N(2)-C(1)-Rh(1) 127.3(7); C(1)-Rh(1)-C(30) 92.0(4); C(1)-Rh(1)-C(29) 89.7(4); C(1)-Rh(1)-C(34) 153.6(4); C(30)-Rh(1)-C(34) 98.3(4); C(29)-Rh(1)-C(34) 82.9(4); C(1)-Rh(1)-C(33) 170.0(4); C(30)-Rh(1)-C(33) 81.2(4); C(29)-Rh(1)-C(33) 89.7(4); C(1)-Rh(1)-Br(1) 90.3(3); C(30)-Rh(1)-Br(1) 147.6(3); C(29)-Rh(1)-Br(1) 172.3(3); C(34)-Rh(1)-Br(1) 93.7(3); C(33)-Rh(1)-Br(1) 91.6(3).

The geometry of this molecule is similar to the previous two rhodium NHC structures discussed here. Again the bond lengths and angles agree with those reported previously.[6] The plane of the imidazol-2-ylidene ring lies only 0.7° from the Rh-$C_{carbene}$ vector.

In the X-ray structure of the fluorenyl analogue of the NHC complexes one of the orientations of the ligand places the plane of the imidazol-2-ylidene ring 27° away from the Rh-$C_{carbene}$ vector this shows a large discrepancy from the other orientation and other Rh NHC complexes described. It is possible this may be due to some effect in the solid state such as packing pushing the ring away, or indicate some inadequacies in the model. It was not possible to model the rhodium metal centre as split into two partially occupied positions without the model becoming unstable. This may have a bearing on this large angle between the imidazol-2-ylidene ring and the Rh-$C_{carbene}$

It could be envisaged that these monodentate NHC complexes could be reliably synthesised for a wide range of substitution patterns.

Since our aim was to synthesise a bidentate rhodium complex, rhodium COD chloride dimer was reacted with the fluorenyl potassium NHC complex. An unexpected C-H activation took place in order to produce the fulvene-allyl type structure **5.13** deduced by the X-ray crystal structure determination. It could be envisaged that this compound is obtained because the bridge has become C-H activated to give a fulvene-rhodium hydride complex, followed by hydride transfer to the COD moiety to give the allyl type ligand. This unexpected activation has implications for potential catalytic applications. If the bridge is unstable, it may lead to degradation of catalysts.



R = 2,6-diisopropylphenyl

3.6 **5.13**

Scheme 5.4 Synthesis of fulvene carbene complex. Reagents and conditions: $(RhCODCl)_2$, THF, - 78 °C – RT.

The CH-activated rhodium complex **5.13** was crystallised from a saturated THF solution layered with ether in the triclinic space group P-1 with. a = 9.5366(5) Å, b = 10.3587(5) Å, c = 17.5823(9) Å, α = 85.455(2)°, β = 88.949(2)°, γ = 63.153(2)°. V = 1534.62(13) $Å^3$ and D_{calcd} = 1.365 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 7053 unique reflections (R_{int} = 6.83%) converged to a final R_1 = 3.92% ($I > 2(I)$) and Rw^2 = 7.57%.

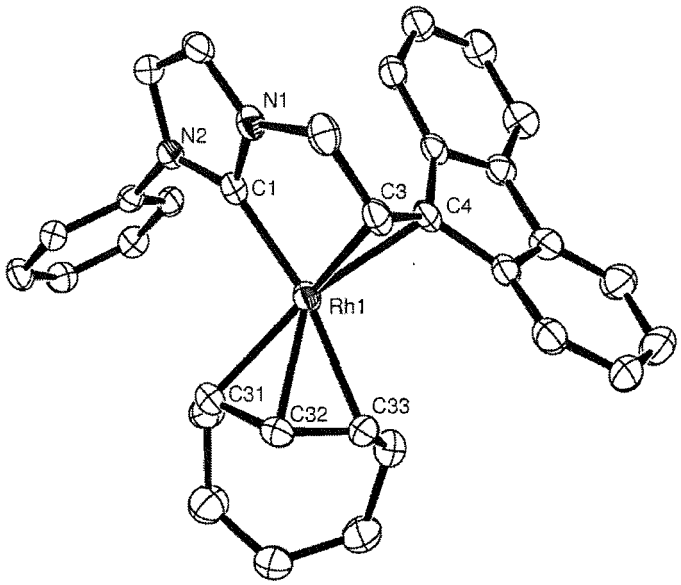
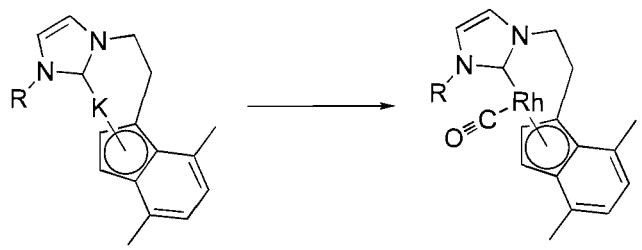


Figure 5.9 ORTEP representation of a C-H activated rhodium complex **5.13** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Rh(1)-C(1) 2.017 (3); Rh(1)-C(3) 2.082 (3); Rh(1)-C(4) 2.238 (2); Rh(1)-C(31) 2.179 (3); Rh(1)-C(32) 2.125 (3); Rh(1)-C(33) 2.214 (3); C(1)-Rh(1)-C(3) 80.66 (10); C(1)-Rh(1)-C(4) 92.10 (10); C1-Rh(1)-C(32) 130.79 (10); N(1)-C(1)-N(2) 130.4 (2).

The plane of the imidazol-2-ylidene ring lies only 1.8° from the Rh-$C_{carbene}$ vector. However, there is a large distortion in the angles around the $C_{carbene}$ atom with rotation in the plane of the imidazol-2-ylidene ring of about 20°. The Rh-$C_{carbene}$ bond length agrees with that previously seen.[6] The Rh-C_{allyl} bond lengths bond lengths agree with those already reported.[11]

It was hoped that by replacing the COD ligand with something less reactive or prone to C-H activation that the desired bidentate complex could be formed with out C-H activation taking place. The dimethyl-indenyl potassium carbene complex was reacted with rhodium carbonyl chloride to give the desired bidentate complex. This was the first example of a late transition metal complex containing a bidentate carbene – cyclopentadienyl type moiety.



R = 2,6-diisopropylphenyl

3.13b **5.14**

Scheme 5.5 Synthesis of a bidentate rhodium carbonyl complex **5.14**. Reagents and conditions: $[Rh(CO)_2Cl]_2$, THF, - 78°C – RT, overnight.

The bidentate rhodium complex **5.14** was crystallised from a saturated THF solution layered with ether in the triclinic space group P-1 with. a = 10.4658(7) Å, b = 11.8571(9) Å, c = 13.2432(8) Å, α = 103.269(3)°, β = 103.291(4)°, γ = 114.368(3)°. V = 1355.87(16) Å^3 and D_{calcd} = 1.294 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6244 unique reflections (Rint = 8.67%) converged to a final R_1 = 5.46% ($I > 2(I)$) and Rw^2 = 11.31%.

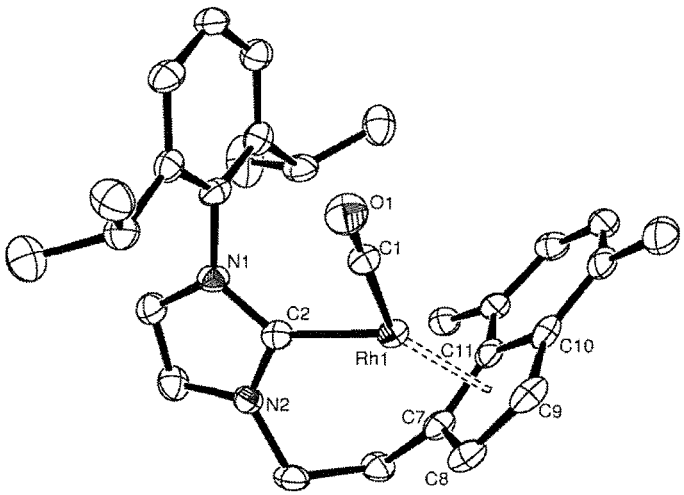


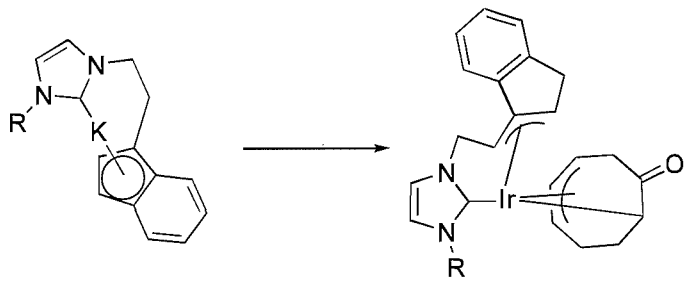
Figure 5.10 ORTEP representation of complex **5.14** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-O(1) 1.157(4); C(1)-Rh(1) 1.833(4); C(2)-N(2) 1.368(5); C(2)-N(1) 1.372(5); C(2)-Rh(1) 1.990(4); C(7)-Rh(1) 2.210(4); C(8)-Rh(1) 2.251(4); C(9)-Rh(1) 2.261(4); C(10)-Rh(1) 2.388(4); C(11)-Rh(1) 2.383(4); O(1)-C(1)-Rh(1) 175.7(4); N(2)-C(2)-N(1) 103.2(3); N(2)-C(2)-Rh(1) 123.3(3); N(1)-C(2)-Rh(1) 133.5(3); C(1)-Rh(1)-C(2) 96.64(15).

The rhodium metal centre has adopted an η^3 allyl type coordination with the indenyl ring. The rhodium has adopted the typical square planar geometry for a four coordinated rhodium complex with allyl counting as two sites of coordination and the CO and NHC as the remaining two. Within error, the Rh-$C_{carbene}$ bond length, 1.990(4), is comparable to what has been seen before in the most closely related structures, 2.001(2).[12]

The plane of the imidazol-2-ylidene ring lies only 2.6° from the Rh-$C_{carbene}$ vector.

5.3.3 Synthesis of Iridium Complexes

The extension of the Rh chemistry to the heavier congener Ir was undertaken. Initially attempts were made to react iridium COD chloride dimer with the dimethylindenyl potassium NHC complex. Another C-H activation reaction took place and instead of the expected compound all that could be identified in the reaction products was compound **5.15**, below, as this was fractionally crystallised from THF layered with ether. It could be envisaged that the included oxygen atom has come from either water or air due to the extended time of crystallisation attempts. Unfortunately, this material was not obtained as bulk material.



R = 2,6-diisopropylphenyl

3.13a **5.15**

Scheme 5.6 Synthesis of a CH-activated iridium complex **5.15**. Reagents and conditions: $[Ir(COD)Cl]_2$, THF, -78 °C – RT, air.

The iridium complex **5.15** was crystallised from a saturated THF solution layered with ether in the triclinic space group P-1 with a = 9.8379(3) Å, b = 11.4156(3) Å, c = 13.6134(5)Å, α = 78.068(2)°, β = 77.101(2)°, γ = 67.282(2)°. V = 1362.25(7) Å^3 and D_{calcd} = 1.665 Mg m^{-3} for Z = 2. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 6285 unique reflections (R_{int} = 6.51%) converged to a final R_1 = 3.47% ($I > 2(I)$) and Rw^2 = 8.20%.

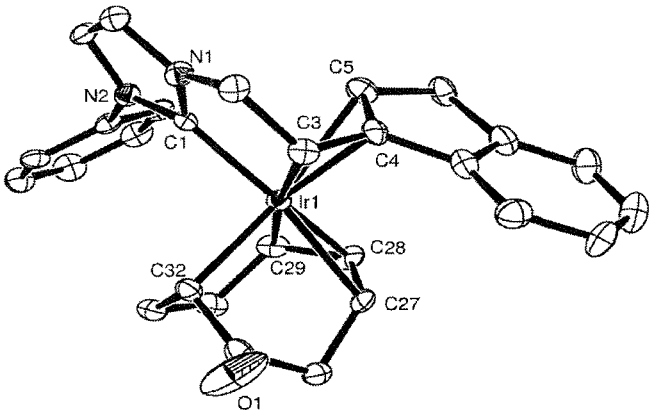
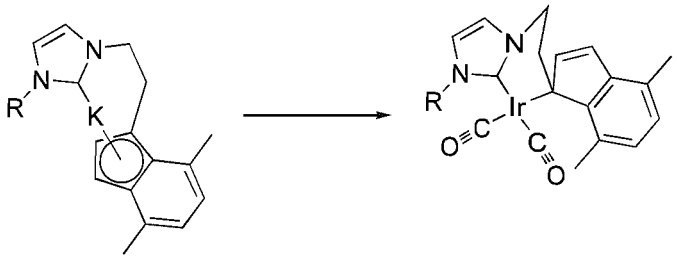


Figure 5.11 ORTEP representation of iridium complex **5.15** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) 1.358(6); C(1)-N(2) 1.361(6); C(1)-Ir(1) 2.038(5); C(3)-Ir(1) 2.180(5); C(4)-Ir(1) 2.185(5); C(3)-C(4) 1.443(6); C(4)-C(5) 1.431(7); C(5)-Ir(1) 2.338(5); C(27)-Ir(1) 2.247(5); C(28)-Ir(1) 2.127(4); C(29)-Ir(1) 2.210(5); C(32)-Ir(1) 2.125(5); C(33)-O(1) 1.215(6); N(1)-C(1)-N(2) 104.2(4); N(1)-C(1)-Ir(1) 117.3(3); N(2)-C(1)-Ir(1) 138.4(4).

The geometry of this iridium complex is based on a distorted octahedral structure. The coordination sphere contains; an NHC, two allyl moieties and an alkyl moiety. The bond lengths and angles lie within the range previously reported.[13]

The plane of the imidazol-2-ylidene ring lies only 3.5° from the Ir-$C_{carbene}$ vector.

In order to suppress the C-H activation of the ligand by Ir we tried to stabilise the lower oxidation state by a CO co-ligand. Pre-formed dimethylindenyl potassium NHC complex was reacted with $[Ir(COD)Cl]_2$ in the presence of CO to form complex **5.16** shown below. In this case the second CO has stayed bound to the iridium causing the indenyl ring to adopt an η^1 coordination mode.



3.13b **5.16**

Scheme 5.7 Synthesis of iridium complex **5.16**. Reagents and conditions: $[Ir(COD)Cl]_2$, THF, CO, -78 °C – RT, 1 hour.

Compound **5.16** was crystallised from a saturated THF solution layered with ether in the monoclinic space group $P_{21/c}$ with a = 8.3747(3) Å, b = 24.0042(16) Å, c = 12.8223(8) Å, β = 90.638(4)°. V = 2577.4(3) Å^3 and D_{calcd} = 1.664 Mg m^{-3} for Z = 4. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 5765 unique reflections (Rint = 9.07%) converged to a final R_1 = 5.59% ($I > 2(I)$) and Rw^2 = 8.29%.

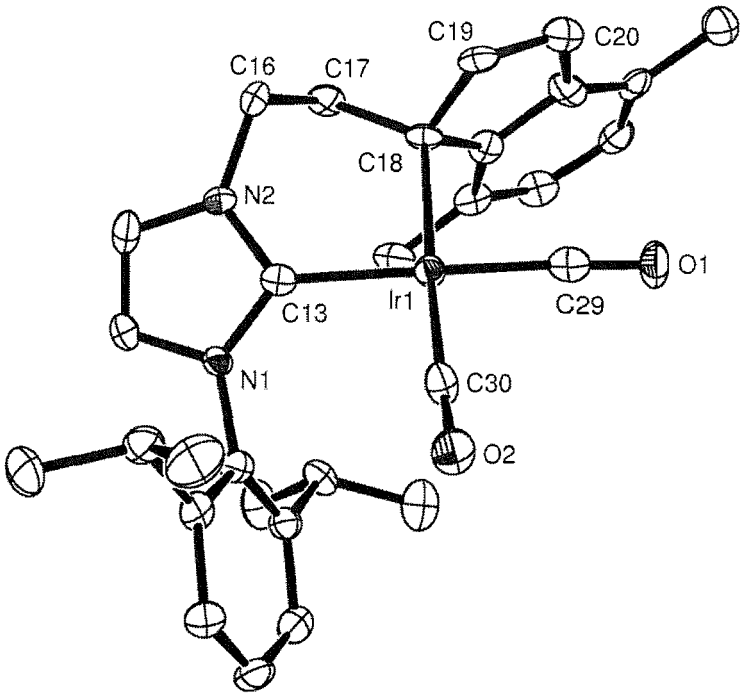


Figure 5.12 ORTEP representation of iridium complex **5.16** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(13)-N(2) 1.354(9); C(13)-N(1) 1.366(8); C(13)-Ir(1) 2.083(7); C(18)-Ir(1) 2.220(7); C(29)-O(1) 1.139(8); C(29)-Ir(1) 1.889(8); C(30)-O(2) 1.136(9); C(30)-Ir(1) 1.871(8); N(2)-C(13)-N(1) 104.2(6); N(2)-C(13)-Ir(1) 125.0(5); N(1)-C(13)-Ir(1) 130.5(5); C(19)-C(18)-C(26) 101.6(6); C(19)-C(18)-C(17) 109.9(6); C(26)-C(18)-C(17) 115.0(6); C(19)-C(18)-Ir(1) 101.5(4); C(26)-C(18)-Ir(1) 111.8(5); C(17)-C(18)-Ir(1) 115.2(5); C(30)-Ir(1)-C(29) 89.9(3); C(30)-Ir(1)-C(13) 92.4(3); C(29)-Ir(1)-C(13) 175.6(3); C(30)-Ir(1)-C(18) 174.5(3); C(29)-Ir(1)-C(18) 87.8(3); C(13)-Ir(1)-C(18) 90.2(3); O(1)-C(29)-Ir(1) 177.1(7); O(2)-C(30)-Ir(1) 175.0(7).

The iridium metal centre has adopted a typical square planar type geometry. The coordination sphere of the iridium centre contains; an NHC, two CO ligands and an η^1 indenyl ring. No crystal structures have been published containing an η^1 indene so direct comparisons cannot be made. The Ir-$C_{carbene}$ bond length is in the usual range.[13] The indenyl carbon (crystallographic C18) has the expected tetrahedral geometry. The plane of the imidazol-2-ylidene ring lies 8.5° from the Rh-$C_{carbene}$ vector

Attempts to remove one CO ligand with the aim of the indenyl increasing its hapticity to η^3 or η^5 were carried out. Heating or oxidation using amine N-oxides were unsuccessful.

5.4 Group 10 Complexes

5.4.1 Nickel Complexes

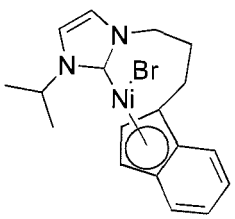
In 1993, Öfele reported the first nickel NHC complex.[1] In 1994, Arduengo reported the synthesis of low coordinate NHC complexes from nickel bis-COD and the free NHC.[14]

In 2006, Inamoto reported nickel complexes of pyridyl bis-NHC complexes of nickel.[15]

There have been reports of nickel NHC complexes functionalised with anionic groups, in 2005, Waymouth reported nickel complexes of NHCs functionalised with enolates and their use in olefin polymerisation.[16]

There have been several reports of half sandwich complexes containing nickel, these are discussed in Chapter 1 on page 19.

Recently in 2007, Shen reported a nickel complex containing an NHC functionalised with an indenyl group **5.20**.[17] This complex has a similar architecture to the compounds described later, but differs in the fact a three carbon bridge is used to link the NHC and indenyl moieties. Also the NHC is functionalised with a alkyl group not a aryl one, Shen made attempts to synthesise the aryl version but these were unsuccessful whereas our group was successful as described later. The NHC lithium indenyl complex was made in-situ and was not preformed.

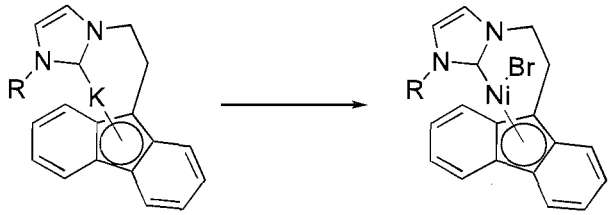


5.20

Figure 5.13 Shen's NHC indenyl nickel complex.

5.4.2 Synthesis of Nickel Complexes

$NiBr_2(DME)$ was reacted with the potassium fluorenyl carbene to give the nickel complex in which the ligand adopts a bidentate coordination mode. Compound **5.21** was crystallised by layering a saturated THF solution with ether.



R = 2,6-diisopropylphenyl

3.6 **5.21**

Scheme 5.8 Synthesis of a bidentate nickel complex **5.21**. Reaction conditions $NiBr_2DME$, THF, -78 °C – RT.

The crystal structure of **5.21** was collected in the monoclinic space group P_{21nb2} with a= 12.4781(10) Å, b = 14.7391(14) Å, c = 14.3603(13) Å, β = 104.266(5)°, V = 2559.6(4) $Å^3$ and D_{calcd} = 1.448 Mg M^{-3} for Z = 4. Data were collected at 120(2)K on a Bruker-Nonious KappaCCD diffractometer. Least squares refinement of the model based on 4508 unique reflections (R_{int} = 20.59%) converged to a final R_1 = 34.66% ($I > 2(I)$) and R_w^2 = 64.74%.

It soon became clear that this crystal system was in fact incommensurate in at least one dimension; unfortunately, crystals of a high enough quality to measure the incommensurate cell or structure could not be formed. A crude model has been determined using a commensurate cell that represents the bulk repeat unit. A number of restraints have been necessarily used to prevent the model fragmenting. Due to the nature of the crystal and the commensurate assumptions made in the solution, the thermal parameters are very large. The model can be used to show the overall structure and geometry of the complex, but the bond lengths should be treated with caution due to the large uncertainty and restrains used in the solution.

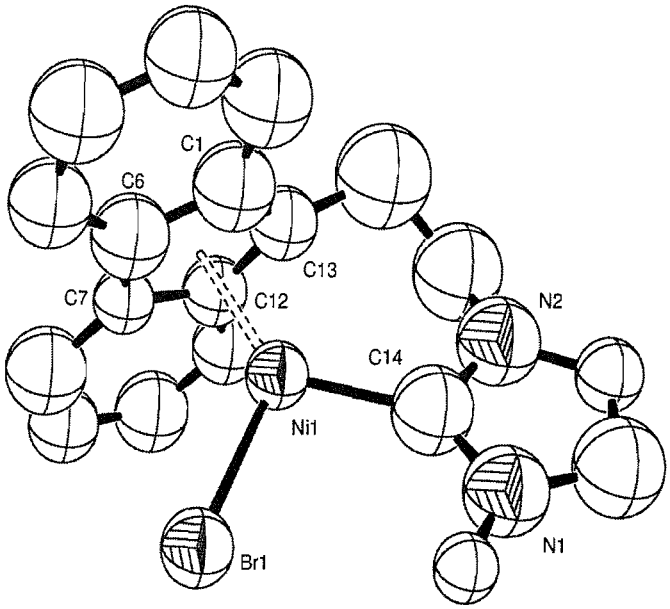


Figure 5.14 ORTEP representation of complex **5.21** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Ni(1)-C(14) 1.95(2); Ni(1)-Br(1) 2.296(7); C(1)-Ni(1) 2.178(16); C(6)-Ni(1) 2.396(19); C(7)-Ni(1) 2.38(2); C(12)-Ni(1) 2.20(2); C(13)-Ni(1) 2.052(15).

The nickel has adopted a trigonal type structure assuming the fluorenyl is taken as one coordination point at the centre of the ring. The hapticity of the fluorenyl ring lies between η^3 and η^5 but the uncertainty in the structure prevents a definite assignment. When compared to Shen's indenyl structure[17] the bond lengths to the ligands are much the same.

The complex did not prove amenable to NMR spectroscopy due to it having a slight paramagnetic nature, however elemental analysis agreed with the assignment given by the X-ray solution. It is believed that this paramagnetic element is due to the nickel having some tetrahedral, high spin electronic character. This assumption is backed-up by the fact that there is only a small energy gap between the two spin states for nickel.

Nickel indenyl complexes have previously been shown to be good polymerisation catalysts. Some initial investigations were made into the use of this nickel complex as a catalyst for ethylene oligomerisation or polymerisation.

In order for polymerisation to take place it was envisaged that this compound would need activating to remove the bromide to give the cationic complex. The complex was placed in toluene under 5 bar of ethylene and indeed no activity was seen.

Initially MAO was investigated as an activator. In this case, polymerisation activity was seen. The best results that could be achieved was a turnover number of 12.

The low activity achieved by using MAO as an activator led us to investigate other activators. $NaBPh_4$ was investigated but gave no activity. However using BPh^F_3 gave polyethylene with a turnover number of 60. Although an improvement from MAO, other activators were tested.

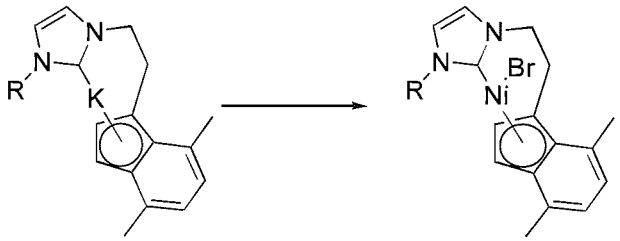
$AlEtCl_2$ was tested as an activator, although this time no polyethylene was seen, low weight oligiomers were detected. A series of experiments were conducted to see how the activity varied with temperature. Table 5.1 shows the reaction times and temperatures of the various experiments. The best conditions gave a turn over number of 79,000 which is comparable to the indenyl phosphine nickel catalyst reported recently by Zaragian. [18,19]

Table 5.1 Oligomerisation conditions and yields for the oligomerisation of ethylene.

Time min	Temp °C	Yield g / Turnover number
30	0	2.4 / 12,000
90	0	12.2 / 62,000
240	0	37.0 / 79,000
90	50	7.1 / 35,000

Shen reported the use of his nickel NHC indenyl complex as a catalyst for the polymerisation of styrene.[17] It future it may be possible to test our nickel complexes for styrene polymerisation under the same conditions.

$NiBr_2$(DME) was reacted with the potassium dimethylindene carbene to give the bidentate nickel complex, Scheme 5.9.



R = 2,6-diisopropylphenyl

3.13b **5.22**

Scheme 5.9 Synthesis of a bidentate nickel complex **5.22**. Reaction conditions $NiBr_2DME$, THF, -78 °C – RT.

Nickel compound **5.22** was crystallised from a slowly cooled saturated THF solution in the orthorhombic space group P_{cba} with a = 15.7510(14) Å, b = 14.1440(13) Å c = 22.4009(11) Å. V = 4990.5(7) Å^3 and Dcalcd = 1.427 Mg m^{-3} for Z = 8. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 2534 unique reflections (Rint = 16.68%) converged to a final R_1 = 4.80% ($I > 2(I)$) and Rw^2 = 9.43%.

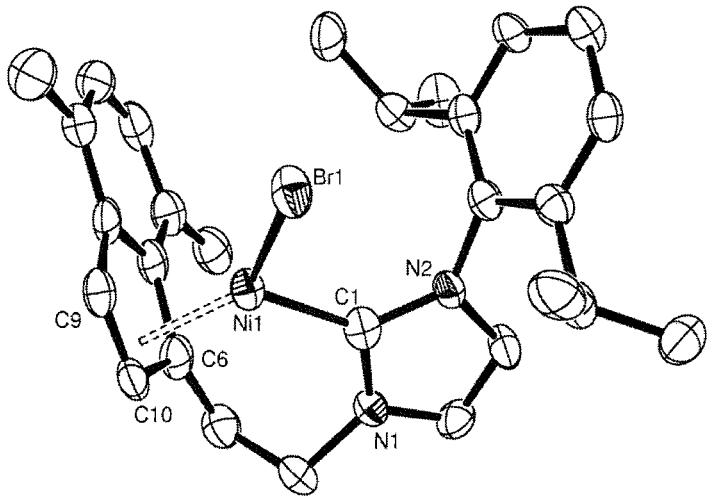


Figure 5.15 ORTEP representation of complex **5.22** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) 1.344(8); C(1)-N(2) 1.375(8); C(1)-Ni(1) 1.886(7); C(6)-Ni(1) 2.035(7); C(7)-Ni(1) 2.347(6); C(8)-Ni(1) 2.369(6); C(9)-Ni(1) 2.103(6); C(10)-Ni(1) 2.048(6); Ni(1)-Br(1) 2.3114(11); N(1)-C(1)-N(2) 103.0(5); N(1)-C(1)-Ni(1) 122.5(5); N(2)-C(1)-Ni(1) 134.5(6); C(1)-Ni(1)-Br(1) 102.4(2).

As expected, the nickel centre has adopted a triganal type structure directly analogous to the fluorenyl structure described earlier. The indenyl ring in this complex has adopted an η^3 coordination.

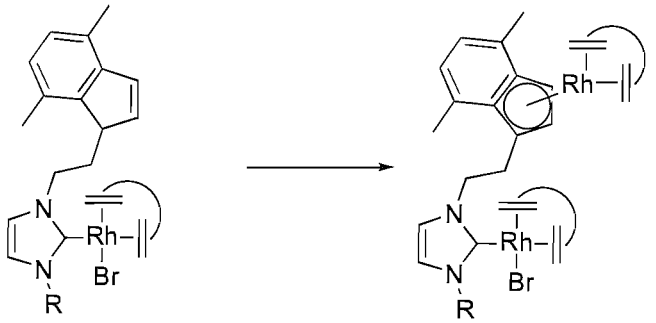
This structure is directly comparable to the structure published by Shen.[17] All the bond lengths of the coordinated species are very similar. This suggests that the number of carbons in the linker (from 2 to 3) has little effect on the strength of the coordination. The only point to be noted is that this extra carbon alters the length and torsion in the backbone so the relative geometries of the NHC and indenyl rings are different. It could be envisaged that a one carbon bridge may add strain to the complex and have an effect on the bond lengths and coordination.

The NMR spectra were sharp suggesting that this compound **2.2** was indeed diamagnetic and the compound could be partially characterised by this method, the compound was also pure by elemental analysis.

It is of note that the fluorenyl complex appears to be paramagnetic whilst the indenyl complex appears to be diamagnetic. The arrangment of the ligand system is such that it is unclear whether the geometry at the metal is distorted tetrahedral or distorted square planar, with the fluorenyl or indenyl ring occupying two of the coordination sites. The energy difference between nickel square planar and tetrahedral geometries is very small in terms of electronics; it may be that the subtle differences in the electronics cause the fluorenyl to adopt a formally tetrahedral geometry, and the indenyl a formally square planar geometry.

5.5 Bimetallic Complexes

In the first example of its kind, a novel bimetallic species **5.23** was synthesised by heating the Rh(COD)NHC complex with an equivalent of Rh(COD)OMe in toluene. Alcoholysis has taken place to give the desired bimetallic compound in low yields and isolated by fractional crystallisation. Unfortunately, the compound has resisted being isolated as bulk material.



R = 2,6-diisopropylphenyl

5.12 **5.23**

Scheme 5.10 Synthesis of a bimetallic complex. Reagents and conditions $[Rh(COD)OMe]_2$, toluene, reflux, overnight.

5.23 was crystallised from a saturated THF solution layered with ether in the monoclinic space group $P_{21/n}$ with. a = 15.539(3) Å, b = 26.596(5) Å, c = 20.236(4) Å, β = 111.73(3)°. V = 7769(3) Å^3 and D_{calcd} = 1.538 Mg m^{-3} for Z = 8. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 16317 unique reflections (Rint = 6.99%) converged to a final R_1 = 5.14% ($I > 2(I)$) and Rw^2 = 12.06%. There are two molecules in the asymmetric unit, both molecules share the same geometry.

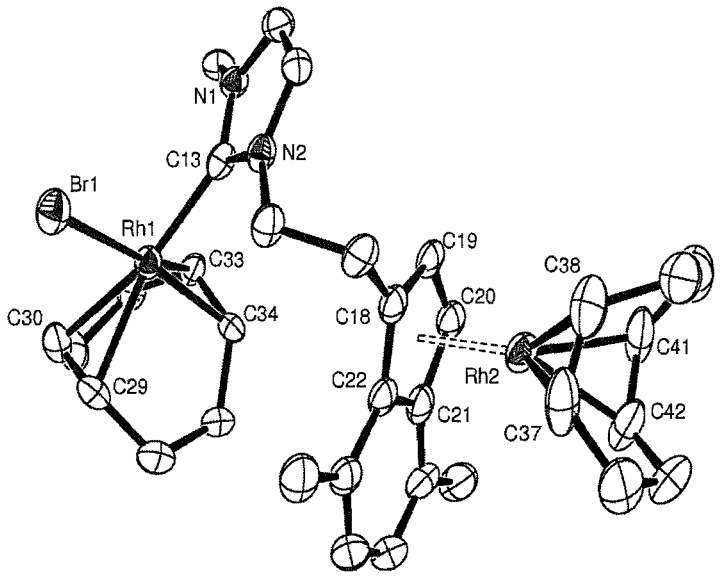


Figure 5.16 ORTEP representation of **5.23** showing 50% probability ellipsoids. H atoms and 2,6-diisopropyl ring expect the ipso-carbon are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: C(13)-Rh(1) 2.030(6); C(13)-N(1) 1.372(7); C(13)-N(2) 1.365(7); Br(1)-Rh(1) 2.5051(10); C(29)-Rh(1) 2.196(6); C(30)-Rh(1) 2.210(7); C(33)-Rh(1) 2.111(6); C(34)-Rh(1) 2.120(6); C(29)-C(30) 1.373(9); C(33)-C(34) 1.417(8); C(18)-Rh(2) 2.220(6); C(19)-Rh(2) 2.235(6); C(20)-Rh(2) 2.218(6); C(21)-Rh(2) 2.357(7); C(22)-Rh(2) 2.360(6); C(37)-Rh(2) 2.110(7); C(38)-Rh(2) 2.138(8); C(41)-Rh(2) 2.127(7); C(42)-Rh(2) 2.126(7); C(37)-C(38) 1.398(12); C(41)-C(42) 1.377(11); N(2)-C(13)-N(1) 103.0(5); N(2)-C(13)-Rh(1) 123.0(4); N(1)-C(13)-Rh(1) 133.0(4);C(13)-Rh(1)-Br(1) 86.96(16).

The structure contains two distinct rhodium centres. One centre has a coordinated NHC a bromide and a COD ligand, the geometry is square planar as seen before in the monodentate structures. The plane of the imidazol-2-ylidene ring lies 12-17° from the Rh-$C_{carbene}$ vector. The second centre has adopted a sandwich type structure in which the indenyl and COD rings each occupy one face of the rhodium centre. The indenyl has η^5 coordination, however inspection of the Rh-C(indenyl) distances shows a slip distortion toward C18, C19, and C20 ($\Delta = 0.152$ Å).[20]

5.6 Conclusions

A series of monodentate rhodium NHC complexes have been synthesised. A general method using $[Rh(COD)OMe]_2$ has been shown to be effective for a number of imidazolium salts. Silver carbenes have also been shown to give the desired products but do not work as cleanly.

It was observed that in certain situations the bridge between the NHC and cyclopentadienyl moiety may not be stable. This was seen by a C-H activation taking place in a bidentate rhodium complex.

By changing the COD ligand to CO ligands, it was possible to synthesise the bidentate complex without C-H activation.

The same was true in the case of iridium, when the COD ligand was present a C-H activated complex was isolated. When CO ligands were present, the desired bidentate complex was isolated.

A method has been found to synthesise bidentate nickel complexes. One of these complexes was investigated for catalytic activity.

It appears that in the bidentate complexes there is a slight distortion of the M-$C_{carbene}$ bond away from a symmetrical interaction with the metal, indicating there may be a very slight strain in the chelate.

It has been shown that it is possible to synthesis a bimetallic complex containing an indenyl functionalised NHC, although further work needs to be done to isolate the bulk material.

5.7 General Experimental

5.7.1 Instrumentation

Proton NMRs were recorded on a Bruker Avance DPX300, at 300 MHz or a Bruker Advance DPX400 spectrometers at 400 MHz. ^{13}C NMRs were recorded on the same spectrometers at 75 MHz and 100 MHz respectively.

Low resolution mass spectra were collected on a Micromass Platform II spectrometer. High resolution mass spectra were collected on a Bruker Apex III spectrometer.

Elemental analyses were carried out by the Department of Health and Human Sciences, London Metropolitan University. All analyses were carried out in duplicate with both results agreeing closely. Air-sensitive samples were supplied in glass tubes sealed under vacuum.

5.7.2 Solvents

Solvents were purchased from Fisher Chemicals. All solvents for moisture sensitive reactions were dried and distilled before use. Petroleum ether 40/60 was dried over sodium benzophenone ketyl, diglyme (approx 1 ml/L) was added to increase its solubility, and is referred to as petrol in the experimental. Diethyl ether was dried over sodium benzophenone ketyl and is referred to as ether in the experimental. Toluene was dried over molten sodium. THF was dried over sodium benzophenone ketyl. DCM was dried over powdered calcium hydride. Benzene was dried over sodium benzophenone ketyl and stored in an ampoule over 4 Å molecular sieves.

$CDCl_3$ was dried over 4 Å molecular sieves and stored over fresh sieves. CD_2Cl_2 was dried over calcium hydride and stored over 4 Å molecular sieves. d_8-THF was dried over NaK alloy and stored over 4 Å molecular sieves.

5.7.3 Compounds

$[Rh(CO)_2Cl]_2$, $NiBr_2DME$ was purchased from Aldrich chemicals.

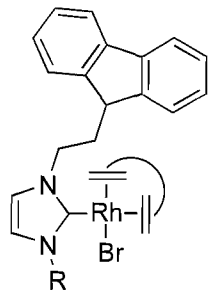
The following materials were made by literature methods: $[Rh(COD)Cl]_2$[21], $[Rh(COD)OMe]_2$[22], $[Ir(COD)Cl]_2$[23].

5.7.4 General

Air-sensitive reactions were carried out using standard Schlenk techniques or in a catalytically dried and deoxygenated M. Braun glovebox (<2 ppm O_2). All air-sensitive solids were stored in the glovebox. Imidazolium salts were also stored in the glovebox due to their hydroscopic nature.

5.8 Experimental

3-(2,6-Diisopropyl-phenyl)-1-[2-(9-9*H*-fluorenyl)-ethyl]-imidazol-2-ylidene – rhodium COD bromide 5.10



R = 2,6-diisopropylphenyl

$[Rh(COD)OMe]_2$ (0.5 mmol, 240 mg) and the fluorenyl imidazolium salt (1.0 mmol, 500 mg) were dissolved in THF and cooled to −78 °C. The solutions were combined. The reaction mixture was allowed to return to room temperature and was stirred overnight. The volatiles were removed under reduced pressure. The residue were dissolved in the minimum of THF which was then layered with ether. The product was isolated as X-ray quality crystals by filtration. Drying gave the product as a yellow crystalline material. (70%, 490 mg)

^1H (C_6D_6, 300 MHz): 7.98-7.90 (4H, m, Ar); 7.80 (1H, d, J = 6 Hz, Ar); 7.58 (1H, dd, J = 7, 2 Hz, Ar); 7.52-7.35 (5H, m, Ar); 7.32 (1H, dd, J = 7, 1 Hz, Ar); 7.23 (1H, d, J = 7 Hz, Ar); 5.08-4.90 (1H, m, COD-CH); 4.72-4.38 (3H, m, COD-CH x 3); 4.23 (1H, t, J = 6 Hz, bridge); 3.60-3.35 (1H, m, bridge); 3.18-2.90 (2H, m, C*H*$(CH_3)_2$); 2.84-2.62 (1H, m, bridge); 2.30-2.22 (1H, m, bridge); 1.80-1.42 (2H, m, COD-CH_2 x 2); 1.80-1.72 (3H, m, COD-CH_2 x 3); 1.72-1.42 (2H, m, COD-CH x 2); 1.42-1.32 (3H, m, $CH(CH_3)_2$); 1.30-1.12 (1H, m, COD-CH_2); 1.10-0.85 (9H, m, $CH(CH_3)_2$).

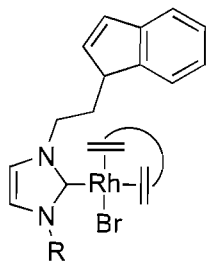
$^{13}C\{^1H\}$ (C_6D_6, 100 MHz): 146.6 (Ar); 146.4 (Ar); 146.0 (Ar); 145.3 (Ar); 140.5 (Ar); 135.4 (Ar); 129.5 (ArH); 127.2 (ArH); 127.1 (ArH); 126.9 (ArH); 125.7 (ArH); 125.5

(ArH); 125.4 (ArH); 124.4 (ArH); 123.9 (ArH); 123.1 (ArH); 121.0 (ArH); 120.0 (ArH); 49.1 (CH_2); 45.2 (Fluorenyl-C); 40.0 (CH_2); 33.7 (CH_2); 33.2 (CH_2); 30.6 (CH_2); 30.2 (CH_2); 29.2 (CH); 27.6 (CH_2); 27.0 (CH); 26.0 (CH); 25.5 (CH); 25.1 ($CH(CH_3)_2$); 23.7 ($CH(CH_3)_2$); 23.4 ($CH(CH_3)_2$); 22.4 ($CH(CH_3)_2$).

MS ES^+: 630 ($M-Br^-$).

Calculated (%) C 64.24, H 6.10, N 3.94; Found C 64.61 H, 5.80, N 4.01.

3-(2,6-Diisopropyl-phenyl)-1-[2-(3-1H-indenyl)-ethyl]-imidazol-2-ylidene –rhodium COD bromide 5.11



R = 2,6-diisopropylphenyl

1-[2-(inden-1-yl)ethyl]-3-(2,6 diisopropylphenyl)-3*H*-imidazol-1-yl silver bromide (1.0 mmol, 560 mg) and $[Rh(COD)Cl]_2$ (0.5 mmol, 250 mg) were dissolved in toluene and heated to reflux for 18 hours, the resulting solution was filtered through celite and pumped down to give the crude product. Crystallisation took place from toluene layered with petrol. (50%, 310 mg).

^1H (C_6D_6, 400 MHz): 7.48 (1H, d, J = 8 Hz, Ar); 7.36 (1H, t, J = 8 Hz, Ar); 7.27 (1H, dd, 8, 2 Hz, Ar); 7.24 (1H, t, J = 8Hz, Ar); 7.18-7.10 (2H, m, Ar); 7.07 (1H, dd, J = 8, 2 Hz, Ar); 6.87 (1H, d, J = 2 Hz, NCH); 6.67 (1H, d, J = 2 Hz, NCH); 6.12 (1H, s, indene-H); 5.54-5.47 (1H, m, indene-H); 4.77-4.72 (1H, m, indene-H); 4.68-4.64 (1H, m, bridge); 4.53-4.46 (1H, m, bridge); 3.40 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 3.23 (1H, sept, J = 7 Hz, $CH(CH_3)_2$); 3.10-3.06 (1H, m, bridge); 2.74-2.72 (1H, m, bridge); 2.01-1.96 (4H, m, COD-CH x 4); 1.61-1.38 (5H, m, COD-CH_2 x 5); 1.36-1.28 (3H, m, COD-CH_2 x 3); 1.42 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 1.00 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 0.98 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 0.86 (3H, d, J = 7 Hz, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ (C_6D_6, 100 MHz): 146.9 (Ar); 144.3 (Ar); 143.7 (Ar); 143.2 (Ar); 129.2 (ArH); 128.7 (ArH); 125.3 (Ar); 123.9 (ArH); 123.5 (ArH); 122.9 (ArH); 121.9 (ArH); 119.3 (ArH); 118.0 (ArH); 95.9 (indene-CH); 66.9 (COD); 66.8 (indene-C); 66.7

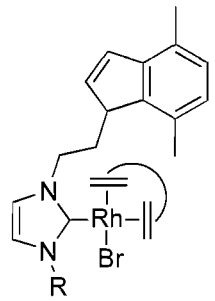
(CH_2);49.8 (CH_2); 36.9 (CH_2); 32.6 (CH_2); 30.6 (CH_2); 30.5 (CH); 29.9 (CH_2); 28.3 (CH_2); 27.8 (CH); 27.3 (CH); 27.1 (CH_2); 27.0 ($CH(CH_3)_2$); 25.4 ($CH(CH_3)_2$); 24.9 ($CH(CH_3)_2$); 22.6 ($CH(CH_3)_2$).

MS ES^+: 581 ($M-Br^-$).

HR MS ES^+: calculated 581.2385, found 581.2385, error 2.1 ppm.

Calculated (%) C 66.18, H 6.86, N 4.54; Found C 66.12 H, 6.91, N 4.56.

3-(2,6-Diisopropyl-phenyl)-1-[2-(1-(4,7-dimethyl)-1H-indenyl)-ethyl]-imidazol-2-ylidene –rhodium COD chloride 5.12



R = 2,6-diisopropylphenyl

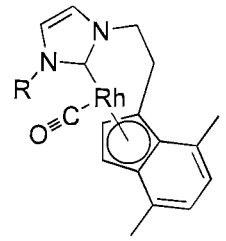
Method as above, using methoxide route. Yield 72%.

^1H (C_6D_6, 300 MHz): 7.34 (1H, d, J = 8 Hz, Ar); 7.28 (1H, dd, J = 8, 2 Hz, Ar); 7.07 (1H, dd, J = 8, 2 Hz, Ar); 6.91 (1H, d, J = 7 Hz, Ar); 6.87 (1H, d, J = 2 Hz, NCH); 6.83 (1H, d, J = 7 Hz, Ar); 6.70 (1H, d, J = 2 Hz, NHC); 6.09 (1H, s, Indene-H); 5.61-5.50 (1H, m, bridge); 4.90-4.80 (1H, m, COD); 4.78-4.69 (1H, m, COD); 4.55-4.45 (1H, m, bridge); 3.60-3.26 (4H, m, COD and C*H*($CH_3)_2$); 3.25 (3H, s, Indenyl-methyl); 3.20-3.09 (1H, m, bridge); 2.90-2.80 (1H, m, bridge); 2.60 (3H, s, indene-methyl); 1.90-1.70 (5H, m, COD); 1.60-1.20 (3H, m, COD); 1.39 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 1.02 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 1.01 (3H, d, J = 7 Hz, $CH(CH_3)_2$); 0.86 (3H, d, J = 7 Hz, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ (C_6D_6, 75 MHz): 146.9 (Ar); 144.4 (Ar); 142.5 (Ar); 141.3 (Ar); 140.7 (Ar); 134.8 (Ar); 129.7 (ArH); 128.7 (Ar); 128.6 (ArH); 127.1 (ArH); 125.2 (ArH); 123.8 (ArH); 123.6 (ArH); 122.1 (ArH); 119.3 (ArH); 95.6 (CH); 95.5 (CH); 95.4 (CH); 68.0 (CH_2); 67.6 (CH_2); 66.9 (CH_2); 50.9 (CH_2); 35.4 (CH_2); 32.3 (CH_2); 30.7 (CH_2); 30.4; (CH_2); 28.1 (CH); 27.7 (CH); 27.4 (CH); 27.3 (CH); 27.2 (CH); 24.8 (CH_2); 24.6 (CH); 23.2 (CH); 22.9 (CH); 27.8 (CH); 19.1 (CH); 17.3 (CH).

Calculated (%) C, 62.61, H, 6.86, N, 4.06; Found C, 62.60, H, 6.59, N, 3.95.

3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]-1*H*-indenyl)ethyl]-imidazol-2-ylidene rhodium carbonyl 5.14



R = 2,6-diisopropylphenyl

$[Rh(CO)_2Cl]_2$ (0.5 mmol, 190 mg) and the dimethylindenyl potassium complex (1.0 mmol, 440 mg) were dissolved in THF and cooled to -78 °C. The solution were combined. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed under reduced pressure. The residue were dissolved in toluene and filtered though Celite. The toluene solution was layered with ether, X-ray quality crystals formed which were isolated by filtration. (80%, 424 mg).

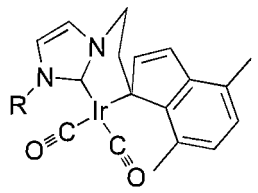
^1H (C_6D_6, 400 MHz): 7.41 (4H, m, Ar); 7.08 (1H, d, J = 7 Hz, Ar); 6.81-6.74 (1H, m, Ar); 6.49 (1H, d, J = 2 Hz, NCH); 6.28 (1H, d , J = 2 Hz, NCH); 4.92-4.80 (1H, m, bridge); 3.60-3.50 (1H, m, bridge); 3.50-3.40 (1H, m, bridge); 3.20-3.12 (1H, m, bridge); 2.50 (3H, s, indene-CH_3); 2.25 (3H, s, indene-CH_3); 2.32-2.18 (2H, m, C*H*$(CH_3)_2$); 1.44 (6H, d, J = 7 Hz, CH(C*H*$_3)_2$); 1.09 (6H, d, J = 7 Hz, C*H*$(CH_3)_2$).

$^{13}C\{^1H\}$ (C_6D_6, 100 MHz): 145.6 (Ar); 141.8 (Ar); 129.1 (Ar); 128.7 (Ar); 128.1 (ArH); 127.3 (ArH); 124.8 (ArH); 124.4 (Ar); 122.3 (Ar); 122.0 (Ar); 118.9 (ArH); 57.3 (CH_2); 49.4 (CH_2); 35.2 (indenyl-CH_3); 30.4 (indenyl-CH_3); 28.0 (*C*H$(CH_3)_2$); 27.1 (*C*H$(CH_3)_2$); 25.2 (CH(*C*H$_3)_2$); 21.7 (*C*H$(CH_3)_2$); 18.7 (*C*H$(CH_3)_2$); 16.9 (*C*H$(CH_3)_2$).

Calculated (%) C 65.91, H 6.29, N 5.31; Found C 65.41, H, 6.32, 5.41.

Ir (cm^{-1}) film from toluene: 2966, 2918, 2860, 1927 (s), 1464.

3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]indenyl)ethyl]-imidazol-2-ylidene –Iridium biscarbonyl 5.16



R = 2,6-diisopropylphenyl

Dimethylindenyl potassium NHC complex (0.5 mmol, 220 mg) and $[Ir(COD)Cl]_2$ (0.25 mmol, 176 mg) was dissolved in THF and combined at –78 °C. Carbon monoxide was bubbled through the solution as it was allowed to reach room temperature, the reaction was stirred for a further 1h whilst CO was bubbled though. The volatiles were removed and the solids re-dissolved in ether and filtered. The resulting crude product was recrystalised from ether/petrol to give the product as yellow X-ray quality crystals. Yield (85%, 274mg)

^1H (C_6D_6, 400 MHz): 7.35 (1H, t, J = 8 Hz, Ar); 7.25-7.12 (4H, m, Ar); 7.03 (1H, d, J = 5 Hz, Ar); 6.41 (1H, d, J = 2 Hz, NC*H*); 6.11 (1H, d, J = 2 Hz, NC*H*); 3.85-3.76 (1H, m, bridge); 3.50 (3H, s, indenyl-CH_3); 2.95-2.86 (1H, m, C*H*$(CH_3)_2$); 2.90 (3H, s, indenyl-CH_3); 2.70-2.60 (1H, m, C*H*$(CH_3)_2$); 1.76 (2H, m, bridge); 1.48 (1H, d, J = 7 Hz, CH(C*H*$_3)_2$); 1.38 (1H, d, J = 7 Hz, CH(C*H*$_3)_2$); 1.12 (1H, d, J = 7 Hz, CH(C*H*$_3)_2$); 1.09 (1H, d, J = 7 Hz, CH(C*H*$_3)_2$).

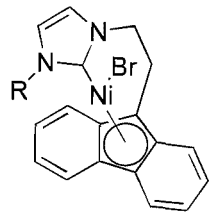
$^{13}C\{^1H\}$ (C_6D_6, 100 MHz): 145.4 (Ar); 145.0 (Ar); 135.5 (Ar); 135.0 (ArH); 129.7 (ArH); 127.5 (Ar); 126.0 (Ar); 124.3 (Ar); 123.5 (Ar); 123.2 (Ar); 123.0 (ArH); 121.8 (ArH); 120.3 (ArH); 118.7 (ArH); 51.3 (CH_2); 29.3 (CH_2); 27.4 (*C*H$(CH_3)_2$); 23.8 (indenyl-methyl); 23.8 (indenyl-methyl); 22.0 (CH(*C*H$_3)_2$); 21.7 (*C*H$(CH_3)_2$); 19.9 (*C*H$(CH_3)_2$); 17.8 (*C*H$(CH_3)_2$).

MS ES^+: 1304 ($2M^+$+MeCN-CO).

IR (film from benzene) cm^{-1}: 2963, 2866, 2023, 1956, 1923, 1657, 1616, 1457, 1411, 1259.

Calculated (%) C, 55.79, H, 5.15, N 4.34; Found C, 55.89, H, 5.35, N, 4.42.

3-(2,6-Diisopropyl-phenyl)-1-[2-(9-9*H*-fluorenyl)-ethyl]-imidazol-2-ylidene -nickel bromide (II) 5.21



R = 2,6-diisopropylphenyl

$NiBr_2DME$ (5 mmol, 1.5 g) and fluorenyl potassium NHC complex (5 mmol, 2.2 g) were dissolved in THF (10 ml) and cooled to –78 °C and combined. The resulting solution was allowed to warm to room temperature and stir overnight. The volatiles were removed under vacuum. The crude material was dissolved in toluene (20 ml) and filtered through celite. The resulting solution was concentrated to ca. 5 ml and an equal volume of petrol was added. The product crystallised in the freezer to give x-ray quality crystals. The product was recovered as a light yellow solid (87%, 2.3 g)

^1H (CD_2Cl_2, 300 MHz): The NMR spectrum consisted of a number of broad signals attributable to the ligand.

Calculated (%) C 64.55, H 5.60, N 5.02; Found C, 63.60, H, 5.70, N 5.05

Polymerisation and Oligomerisation Experiments

The required amount of nickel complex was placed in a high pressure reactor in the glove box. Toluene was then added to the catalyst. The pressure vessel was placed in an ice or oil bath at the desired temperature. The solution was saturated with ethylene by pressurising and depressurising 3 times. The activator was then injected and the vessel quickly raised to 5 bar. At the end of the reaction time the pressure was released to terminated the reaction. The conditions used are shown below:

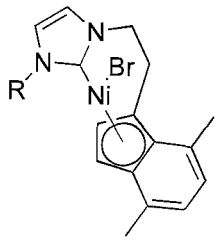
0.05mmol complex, 10 eq. MAO, 22 ml toluene, 5 bar ethylene, 2 h;

0.05mmol complex, 5 eq. $NaBPh_4$, 22 ml toluene, 5 bar ethylene, 2 h;

0.05mmol complex, 10 eq. BPh^F_3, 22 ml toluene, 5 bar ethylene, 2 h;

7μM Ni Complex, 0.5 ml 10% $AlEtCl_2$, 25ml toluene.

3-(2,6-Diisopropylphenyl)-1-[2-(1-[4,7-dimethyl]-1*H*-indenyl)ethyl]-imidazol-2-ylidene -nickel bromide (II) 5.22



R = 2,6-diisopropylphenyl

A similar method to the previous compound was followed except that the compound was crystallised by layer toluene with petrol to give x-ray quality crystals. The product was recovered as a very dark red solid (54 % yield).

^{1}H (CD_2Cl_2, 300 MHz): 7.28 (1H, t, J = 8 Hz, Ar); 7.08 (2H, d J = 2 Hz, imidazole backbone); 7.07 (1H, m, Ar); 7.00 (1H, d, J = 4 Hz, Ar); 6.80 (1H, d, J = 2Hz, imidazole backbone); 6.68 (1H, d, J = 8 Hz, Ar); 6.54 (1H, d, J = 8 Hz, Ar); 5.00 (1H, d, J = 4Hz, bridge); 4.25-4.05 (2H, m, bridge); 2.85 (1H, sept, J = 7 Hz, ipr); 2.71-2.60 (1H, m, bridge); 2.10 (1H, sept, J = 7 Hz, ipr); 2.06 (3H, s, IndMe); 2.01 (3H, s, IndMe); 1.86 (1H, dt, J = 14, 2 Hz, bridge); 1.14 (3H, d, J = 7 Hz, ipr); 1.01 (6H, d, J = 7 Hz, ipr); 0.87 (3 H, d, J = 7 Hz, ipr)

^{13}C{^{1}H} (CD_2Cl_2, 300 MHz):168.4 (Carbene); 146.3 (Ar); 145.4 (Ar); 137.12 (Ar); 129.3 (ArH); 128.7 (Ar); 128.4 (Ar); 128.0 (Ar); 127.7 (ArH); 126.8 (ArH); 126.4 (ArH); 124.3 (Ar); 123.7 (ArH); 121.9 (ArH); 101.8 (ArH); 81.8 (ArH); 78.5 (Ind); 51.0 (CH_2); 29.2 (Me); 28.6 (Me); 26.3 (CH_2); 25.7 (ipr); 25.2 (ipr); 23.2 (ipr); 23.1 (ipr); 20.8 (ipr); 18.5 (ipr).

Calculated (%) C, 62.72, H, 6.20, N, 5.22, Found C, 62.52, H, 5.94, N, 5.34.

Table 5.2 Crystallographic data for monodentate Rhodium complexes

Identification code	**5.10**	**5.11**	**5.12**
Empirical formula	$C_{38}H_{44}BrN_2Rh,C_4H_8O$	$C_{34}H_{42}BrN_2Rh$	$C_{36}H_{46}BrN_2Rh$
Formula weight	783.68	661.52	689.57
Temperature	120(2) K	120(2) K	120(2) K
Wavelength	0.71069 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	P_{212121}	P-1
Unit cell dimensions	a = 10.313(5) Å	a = 11.795(4) Å	a = 8.2436(2) Å
	α = 68.598(5)°.	α= 90°.	α= 81.819(2)°.
	b = 13.442(5) Å	b = 11.853(3) Å	b = 8.5687(3) Å
	β = 70.798(5)°.	β= 90°.	β= 85.004(2)°.
	c = 15.119(5) Å	c = 21.599(5) Å	c = 22.8614(8) Å
	γ = 86.647(5)°.	γ = 90°.	γ = 82.286(2)°.
Volume	1838.3(13) $Å^3$	3019.7(15) $Å^3$	1580.15(9) $Å^3$
Z	2	4	2
Density (calculated)	1.416 Mg/m^3	1.455 Mg/m^3	1.449 Mg/m^3
Absorption coefficient	1.586 mm^{-1}	1.914 mm^{-1}	1.832 mm^{-1}
F(000)	812	1360	712
Crystal size	0.30 x 0.20 x 0.20 mm^3	0.08 x 0.02 x 0.02 mm^3	0.20 x 0.20 x 0.08 mm^3
Theta range for data collection	2.98 to 27.70°.	3.08 to 27.45°.	2.47 to 27.74°.
Index ranges	-13<=h<=13,	-15<=h<=12,	-10<=h<=10,
	-17<=k<=17,	-15<=k<=14,	-11<=k<=11,
	-19<=l<=19	-27<=l<=22	-29<=l<=29
Reflections collected	34069	17562	32381
Independent reflections	8458 [R(int) = 0.0471]	6733 [R(int) = 0.1500]	7288 [R(int) = 0.0647]
Completeness to theta = 27.50°	99.6 %	99.6 %	99.4 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7421 and 0.6476	0.9627 and 0.8620	0.8673 and 0.7108
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8458 / 1340 / 445	6733 / 444 / 347	7288 / 0 / 331
Goodness-of-fit on F2	1.036	0.973	1.171
Final R indices [I>2sigma(I)]	$R_1 = 0.0611$, $wR^2 = 0.1416$	$R_1 = 0.0783$, $wR^2 = 0.1219$	$R_1 = 0.0955$, $wR^2 = 0.2329$
R indices (all data)	$R_1 = 0.0849$, $wR^2 = 0.1546$	$R_1 = 0.1802$, $wR^2 = 0.1520$	$R_1 = 0.1168$, $wR^2 = 0.2427$
Largest diff. peak and hole	2.107 and -1.856 $e.Å^{-3}$	0.890 and -1.108 $e.Å^{-3}$	2.349 and -2.062 $e.Å^{-3}$

Table 5.3 Crystallographic data for bidentate Rhodium Complexes

Identification code	**5.13**	**5.14**
Empirical formula	$C_{38}H_{43}N_2Rh$	$C_{29}H_{33}N_2ORh$
Formula weight	630.65	528.48
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 9.5366(5) Å	a = 10.4658(7) Å
	α= 82.455(2)°.	α= 103.269(3)°.
	b = 10.3587(5) Å	b = 11.8571(9) Å
	β= 88.949(2)°.	β= 103.291(4)°.
	c = 17.5823(9) Å	c = 13.2432(8) Å
	γ = 63.153(2)°.	γ = 114.368(3)°.
Volume	1534.62(13) $Å^3$	1355.87(16) $Å^3$
Z	2	2
Density (calculated)	1.365 Mg/m^3	1.294 Mg/m^3
Absorption coefficient	0.586 mm^{-1}	0.651 mm^{-1}
F(000)	660	548
Crystal size	0.15 x 0.15 x 0.10 mm^3	0.10 x 0.10 x 0.04 mm^3
Theta range for data collection	3.23 to 27.61°.	3.32 to 27.64°.
Index ranges	-12<=h<=12,	-13<=h<=13,
	-13<=k<=13,	-15<=k<=15,
	-22<=l<=22	-17<=l<=17
Reflections collected	46366	26187
Independent reflections	7053 [R(int) = 0.0683]	6244 [R(int) = 0.0867]
Completeness to theta = 27.61°	98.8 %	98.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9438 and 0.9173	0.9744 and 0.9321
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7053 / 0 / 374	6244 / 0 / 304
Goodness-of-fit on F^2	1.028	1.043
Final R indices [I>2sigma(I)]	R_1 = 0.0392, wR^2 = 0.0757	R_1 = 0.0546, wR^2 = 0.1131
R indices (all data)	R_1 = 0.0638, wR^2 = 0.0833	R_1 = 0.0865, wR^2 = 0.1241
Largest diff. peak and hole	0.833 and -0.566 $e.Å^{-3}$	0.526 and -0.720 $e.Å^{-3}$

Table 5.4 Crystallographic data for iridium complexes.

Identification code	**5.15**	**5.16**
Empirical formula	$C_{34}H_{38}IrN_2O$	$C_{30}H_{33}IrN_2O_2$
Formula weight	682.86	645.78
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P_{21/c}$
Unit cell dimensions	a = 9.8379(3) Å	a = 8.3743(3) Å
	α= 78.068(2)°.	α= 90°.
	b = 11.4156(3) Å	b = 24.0042(16) Å
	β= 77.101(2)°.	β= 90.638(4)°.
	c = 13.6134(5) Å	c = 12.8223(8) Å
	γ = 67.282(2)°.	γ = 90°.
Volume	1362.25(7) $Å^3$	2577.4(3) $Å^3$
Z	2	4
Density (calculated)	1.665 Mg/m^3	1.664 Mg/m^3
Absorption coefficient	4.931 mm^{-1}	5.210 mm^{-1}
F(000)	682	1280
Crystal size	0.05 x 0.05 x 0.02 mm^3	0.16 x 0.04 x 0.01 mm^3
Theta range for data collection	2.95 to 27.81°.	3.00 to 27.57°.
Index ranges	-12<=h<=12,	-10<=h<=10,
	-14<=k<=14,	-31<=k<=28,
	-17<=l<=17	-16<=l<=16
Reflections collected	25077	25444
Independent reflections	6285 [R(int) = 0.0651]	5765 [R(int) = 0.0907]
Completeness to theta = 27.81°	97.4 %	96.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9078 and 0.7906	0.9497 and 0.4894
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6285 / 0 / 343	5765 / 0 / 322
Goodness-of-fit on F^2	1.141	1.069
Final R indices [I>2sigma(I)]	R_1 = 0.0347, wR^2 = 0.0820	R_1 = 0.0559, wR^2 = 0.0829
R indices (all data)	R_1 = 0.0466, wR^2 = 0.0864	R_1 = 0.0940, wR^2 = 0.0932
Largest diff. peak and hole	6.652 and -3.496 $e.Å^{-3}$	1.308 and -1.225 $e.Å^{-3}$

Table 5.5 Crystallographic data for nickel complexes.

Identification code	**5.21**	**5.22**
Empirical formula	$C_{30}H_{31}BrN_2Ni$	$C_{28}H_{33}BrN_2Ni$
Formula weight	558.19	536.18
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	? - incommensurate	Orthorhombic
Space group	? - incommensurate	P_{bca}
Unit cell dimensions	a = 12.4781(10) Å	a = 15.7510(14) Å
	α= 90°.	α= 90°.
	b = 14.7391(14) Å	b = 14.1440(13) Å
	β= 104.266(5)°.	β= 90°.
	c = 14.3603(13) Å	c = 22.4009(11) Å
	γ = 90°.	γ = 90°.
Volume	2559.6(4) $Å^3$	4990.5(7) $Å^3$
Z	4	8
Density (calculated)	1.448 Mg/m^3	1.427 Mg/m^3
Absorption coefficient	2.340 mm^{-1}	2.397 mm^{-1}
F(000)	1152	2224
Crystal size	0.05 x 0.02 x 0.02 mm^3	0.07 x 0.07 x 0.02 mm^3
Theta range for data collection	2.93 to 25.03°.	4.03 to 20.71°.
Index ranges	-14<=h<=14,	-15<=h<=15,
	-17<=k<=17,	-14<=k<=13,
	-17<=l<=16	-22<=l<=21
Reflections collected	24308	20755
Independent reflections	4508 [R(int) = 0.2059]	2534 [R(int) = 0.1668]
Completeness to theta = 25.00°	99.8 %	98.5 %
Max. and min. transmission	0.9547 and 0.8920	0.9536 and 0.8502
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4508 / 63 / 91	2534 / 0 / 295
Goodness-of-fit on F^2	2.219	1.080
Final R indices [I>2sigma(I)]	R_1 = 0.3466, wR^2 = 0.6474	R_1 = 0.0480, wR^2 = 0.0943
R indices (all data)	R_1 = 0.4463, wR^2 = 0.6926	R_1 = 0.0756, wR^2 = 0.1060
Largest diff. peak and hole	6.652 and -3.496 $e.Å^{-3}$	0.404 and -0.445 $e.Å^{-3}$

Table 5.6 Crystallographic data for bimetallic structure.

Identification code	**5.23**
Empirical formula	$C_{44}H_{57}BrN_2Rh_2$
Formula weight	899.65
Temperature	120(2) K
Wavelength	0.6905 Å
Crystal system	Monoclinic
Space group	$P_{21/n}$
Unit cell dimensions	a = 15.539(3) Å
	α= 90°.
	b = 26.596(5) Å
	β= 111.73(3)°.
	c = 20.236(4) Å
	γ = 90°.
Volume	7769(3) $Å^3$
Z	8
Density (calculated)	1.538 Mg/m^3
Absorption coefficient	1.911 mm^{-1}
F(000)	3680
Crystal size	0.10 x 0.10 x 0.03 mm^3
Theta range for data collection	2.30 to 26.67°.
Index ranges	-19<=h<=19
	-33<=k<=33
	-25<=l<=25
Reflections collected	63459
Independent reflections	16317 [R(int) = 0.0699]
Completeness to theta = 26.67°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9449 and 0.8319
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16317 / 0 / 895
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R_1 = 0.0514, wR^2 = 0.1206
R indices (all data)	R_1 = 0.0972, wR^2 = 0.1470
Largest diff. peak and hole	2.496 and -1.508 $e.Å^{-3}$

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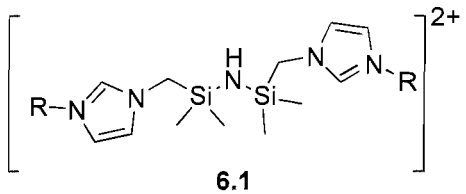
Chapter 6

Towards the Synthesis of a Silazane Functionalised NHC Pincer Ligand

6 Silazane Functionalised NHC Pincer Ligand

6.1 Aims

Our aim was to synthesise a 'CNC' type pincer ligand in which the bridgehead N atom is an anionic amido group. This would be the NHC analogue of linear tridentate PNP ligands successfully employed by Fryzuk[1], Edwards[2], Caulton[3], Liang[4] and others. To achieve this, an amide functionalised ligand with two NHCs of the type shown in Figure 6.1 was targeted. A silazane was chosen over an alkyl functionalised amine because of the ease of availability of starting materials, the chloro- functionalised silazane starting material had already been synthesised.

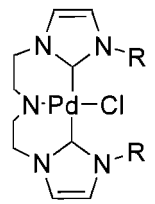


6.1

Figure 6.1 Target of pincer imidazolium salt synthesis.

The ligand precursor **6.1**, potentially offers a number of binding modes. As well as mono-NHC, bi-NHC and tri- dentate, CNC, modes, the central amine moiety could act as a neutral amine donor or be further deprotonated to act as an anionic amide donor. This could be envisaged to have an effect on binding strength and hence complex properties.

Whilst this work was in progress, Douthwaite reported an amido bis-NHC ligand and complexes thereof **6.2**.[5] Douthwaite's ligand did not contain silicon but had a two carbon bridge linking the amide to the carbene. However, the basic architecture of the ligand is the same.

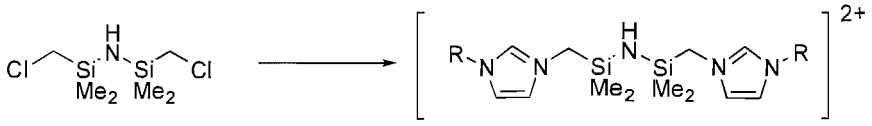


6.2

Figure 6.2 Douthwaite's amido bis-NHC ligand in a palladium complex.

6.2 Synthesis of the Imidazolium Salts

In order to synthesise the desired NHC ligand the appropriate imidazolium salts were required. The general synthetic strategy for the formation of these salts involves quaternisation of a substituted imidazole by alkyl-halides.



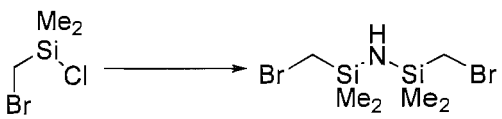
6.3 **6.4**

R = 2,6-diisopropylphenyl

Scheme 6.1 Synthesis of a silazane imidazolium salt. Reagents and conditions: 2,6-diisopropylimidazole, dioxane, 100 °C, 1 week.

Initial attempts were made to synthesise the desired imidazolium salt, **6.4**, by reacting bis(chloromethyldimethyl)silazane **6.3** with 2,6-diisopropylphenylimidazole. After dissolving the reactants in dioxane and heating to 110 °C for one week, only low yields of the imidazolium salt could be isolated. A catalytic amount of potassium iodide was added, it was hoped that halide exchange may take place forming the more reactive iodide, this did not improve the yield. Reactions were carried-out under microwave irradiation, but these failed to reduce the reaction times. The reaction was also attempted as a melt, so that the temperature could be increased, but this gave a large number of unidentified products, possibly due to decomposition.

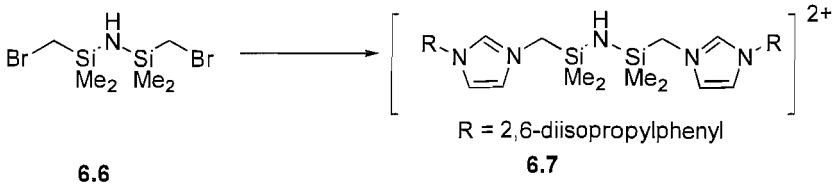
It was thought that the bromo-analogue **6.6** might give better yields in the reaction to form the imidazolium salt, as alkyl bromides are in general more reactive than the chlorides. The starting silazane was not commercially available and had to be synthesised. Bromomethyldimethylsilane **6.5** was reacted with anhydrous ammonia gave the intermediate **6.6** in 50% yield.[6]



6.5 **6.6**

Scheme 6.2 Synthesis of a bromosilazane. Reagents and conditions: Anhydrous ammonia, -78 °C – RT, 30 mins.

This compound **6.6** was then reacted with 2,6-diisopropylimidazole by heating in dioxane overnight to give the desired product in 85% yield. As envisaged, the bromo-analogue was much more reactive than the chloro compound. These silazane imidazolium salts were extremely air-sensitive and had to be handled under inert-atmospheres are all times.



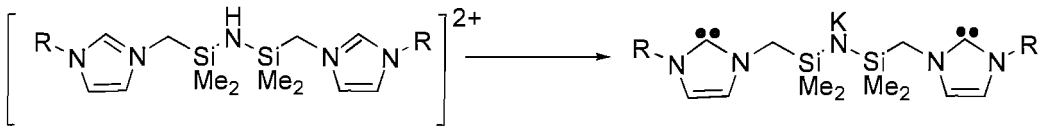
6.6 **6.7**

Scheme 6.3 Alternative synthesis of the silazane salt **6.7**. Reagents and conditions: 2,6-diisopropylimidazole, dioxane, 100 °C, 1 week.

6.3 Attempted Deprotonation of the Silazane Functionalised Salt

Our aim was to be able to deprotonate the imidazolium salts in order to give the free bis-NHC or bis NHC amide complex. Attempts to deprotonate **6.7** using n-butyllithium were unsuccessful, ^{1}H NMR spectroscopy indicated that a large number of reaction products were present; the desired compound could not be identified.

Deprotonation of **6.7** with three eq. of potassium hydride, Scheme 6.4, gave a solid material. ^{1}H NMR spectroscopy indicated that the desired product **6.8** was present in the reaction mixture. The residues were highly insoluble; the only solvent that would dissolve the compound was pyridine, the compounds decomposed quickly so only a crude ^{1}H NMR spectrum could be obtained. Due to the insolubility of the compound, it could not easily be separated from the potassium bromide or other reaction products formed. An attempt to separate the desired compound by sublimation resulted in decomposition.

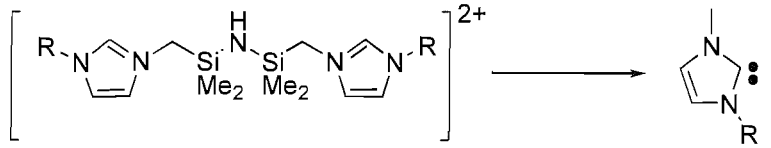


6.7 **6.8**

Scheme 6.4 Attempted synthesis of potassium NHC complex.

It was believed that the potassium amide formed when three equivalents of base were used that was causing the insolubility, as the rest of the molecule is non-polar in nature and would be expected to be extremely soluble in most solvents. When the bromide

salt **6.7** was deprotonated with 2 eq. of KHMDS in THF only one product could be identified, this was the undesired product **6.9**, Scheme 6.5.

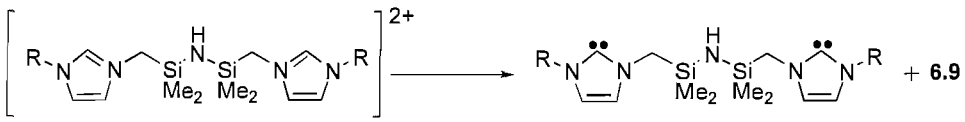


R = 2,6-diisopropylphenyl

6.7 **6.9**

Scheme 6.5 Formation of an undesired product. Reagents and conditions: 3 eq. KHMDS, THF, -78 °C – RT, overnight.

When **6.7** was deprotonated in ether it appeared that a mixture of both the desired product **6.10** and the by-product **6.9** were obtained, as observed by ^{1}H NMR spectroscopy.



R = 2,6-diisopropylphenyl

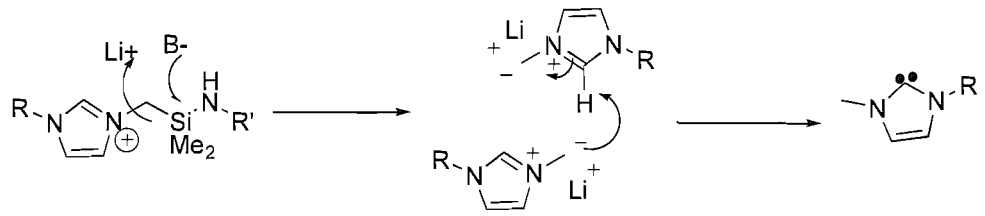
6.7 **6.10**

Scheme 6.6 Products form the reaction in ether. Reagents and conditions: 2 eq. KHMDS, ether, -78 °C – RT, overnight.

Experiments were conducted to investigate the reaction conditions for increasing the yield of **6.10**. The reaction that produced the highest proportion of **6.10**, ca. 3:2 compared to **6.9**, used ether as the solvent together with rapid warming from –78°C to RT, however the yield was very low, ca.20%, the remaining isolated material being **6.9**.

An attempt was made to synthesise an authentic sample of **6.9** in order to confirm the structure. The imidazolium salt precursor has been synthesised but unfortunately, the deprotonation to form the free carbene failed with the reaction giving a mixture of products.

It is plausible that the by-product **6.9** of the deprotonation reaction is formed by a mechanism in which the silyl group acts as a leaving group.



6.7 R = 2,6-diisopropylphenyl **6.9**

Scheme 6.7 Plausible mechanism for the formation of the by-product **6.9**.

The occurrence of this unknown and unexpected rearrangement upon attempted deprotonation of **6.7** hampered further efforts towards development of the metal chemistry of this monoamido-bis-carbene ligand.

Attempts were made to use metal amides to perform an in-situ deprotonation but these met with no success.

6.4 Conclusions

It was shown that by using the bromo- analogue of the silazane that the imidazolium salts could be synthesised in high yields. The chloro analogue gave the desired products but in lower yields.

An unexpected reaction took place during the deprotonation of the imidazolium salts. Cleavage of the silicon to carbon bond was observed resulting in decomposition of the products. The deprotonated form of the salts could not be isolated. In-situ deprotonation with basic metal complexes also failed.

Douthwaite has shown that a ligand with a similar architecture formed complexes[5], which suggests if the cleavage of the Si-C bond could be prevented then this ligand should form complexes in a similar fashion.

The possibility of deprotonation by a co-ordinated base like M-NR_2 was briefly investigated, but further investigation may be possible in the future.

6.5 General Experimental

6.5.1 Instrumentation

Proton NMRs were recorded on a Bruker Avance DPX300, at 300 MHz or a Bruker Advance DPX400 spectrometers at 400 MHz. ^{13}C NMRs were recorded on the same spectrometers at 75 MHz and 100 MHz respectively.

Low resolution mass spectra were collected on a Micromass Platform II spectrometer. High resolution mass spectra were collected on a Bruker Apex III spectrometer.

Elemental analyses were carried out by the Department of Health and Human Sciences, London Metropolitan University. All analyses were carried out in duplicate with both results agreeing closely. Air-sensitive samples were supplied in glass tubes sealed under vacuum.

6.5.2 Solvents

Solvents were purchased from Fisher Chemicals. All solvents for moisture sensitive reactions were dried and distilled before use. Petroleum ether 40/60 was dried over sodium benzophenone ketyl, diglyme (approx 1 ml/L) was added to increase its solubility, and is referred to as petrol in the experimental. Diethyl ether was dried over sodium benzophenone ketyl and is referred to as ether in the experimental. Toluene was dried over molten sodium. THF was dried over sodium benzophenone ketyl. DCM was dried over powdered calcium hydride. Benzene was dried over sodium benzophenone ketyl and stored in an ampoule over 4 Å molecular sieves.

$CDCl_3$ was dried over 4 Å molecular sieves and stored over fresh sieves. CD_2Cl_2 was dried over calcium hydride and stored over 4 Å molecular sieves. d_8-THF was dried over NaK alloy and stored over 4 Å molecular sieves.

6.5.3 Compounds

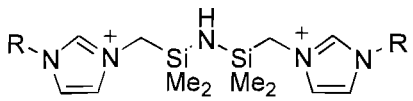
2,6-diisopropylphenylimidazole[7] and 1,3-Bis(bromomethyl)-1,1,3,3-tetramethyldisilazane[6] were synthesised by literature methods.

1,3-Bis(bromomethyl)-1,1,3,3-tetramethyldisilazane was purchased from Aldrich chemicals.

6.5.4 General

Air-sensitive reactions were carried out using standard Schlenk techniques or in a catalytically dried and deoxygenated M. Braun glovebox (<2 ppm O_2). All air-sensitive solids were stored in the glovebox. Imidazolium salts were also stored in the glovebox due to their hydroscopic nature.

Bis-[(3-(2,6-diisopropylphenyl)-1-methyl-3*H*-imidazol-1-ium)dimethyl]silazane dichloride



$2Cl^-$

R = 2,6-diisopropylphenyl

2,6-Diisopropylphenylimidazole (2.6 g, 11 mmol) was dissolved in dioxane (30 ml) and added to bis-(chloromethyl)tetramethylsilazane (1.3 g, 5.0 mmol). The solution was stirred at 110 °C under partial vacuum in an ampoule overnight to give a yellow solution containing an off white solid. The resulting suspension was dried, and then washed with ether (3 x 20 ml), dissolved in DCM (25 ml) and precipitated with ether (20 ml).

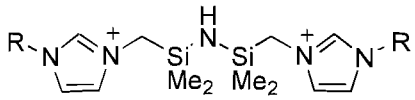
NMR (^{1}H, $CDCl_3$) 10.30 (2H, s, NC*H*N), 8.65 (2H, s, *H*CCH), 7.45 (2H, t, J = 7.5 Hz, Ar*H*), 7.22 (4H, d, J = 7.5 Hz, Ar*H*), 7.15 (2H, s, *H*CCH), 4.38 (4H, s, CH_2), 3.87 (1H, s, N*H*) 2.45 (4H, sept, J = 6.3 Hz, Me_2CH) 1.14 (12H, d, J = 6.3 Hz, CH(CH_3)$_2$, 0.80 (12H, d, J = 6.3 Hz, Me_2CH), 0.12 (12H, s, SiMe_2)

NMR (^{13}C{^{1}H}, $CDCl_3$) 145.5 (imid-*C*H), 137.5 (N*C*H), 131.7 (N*C*H), 130.6 (Ar), 125.5 (Ar), 124.6 (ArH), 123.4 (ArH), 42.7 (NCH_2) 28.71 (CHMe_2), 24.3 (*C*HMe_2), 22.9 (CHMe_2), –0.2 (SiMe_2).

MS (ES^+) 317.1(hydrolysed M^+)

MP (sealed tube) – 155 °C

Bis-[(3-(2,6-diisopropylphenyl)-1-methyl-3*H*-imidazol-1-ium)dimethyl]silazane dibromide



$2Br^-$

R = 2,6-diisopropylphenyl

Bis(bromomethyldimethyl)silazane (1.25 g, 4.0 mmol) was placed in a Schlenk and 2,6-diisopropyl imidazole (2.3 g, 10 mmol) in dioxane (30 ml) was added. The reaction was then heated to 110°°C under partial vacuum for 3 days. The volatiles were removed and the resulting solid was washed twice with ether (30 ml), dissolved in the minimum of DCM (20 ml) and precipitated with ether (100 ml). The supernatant was then removed by filtration, giving a white powder (2.6 g, 85%)

NMR (^{1}H, $CDCl_3$) 10.13 (2H,s, NC*H*N), 8.51 (2H, s, *H*CCH), 7.46 (2H, t, J = 7.5 Hz, Ar*H*), 7.24 (4H, d, J = 7.5 Hz, Ar*H*), 7.06 (2H, s, *H*CCH), 4.47 (4H, s CH_2), 3.64 (1H, s, N*H*), 2.23 (4H, septet, J = 7.0 Hz, ^{i}PrC*H*), 1.16 (12H, d, J = 7.0 Hz, CH(CH_3)$_2$), 1.09 (12H, d, J = 7 Hz, CH(CH_3)$_2$), 0.18 (12H, s, SiCH_3)

NMR (^{13}C{^{1}H}, $CDCl_3$) 145.6 (Imid-*C*H), 137.1 (N*C*H), 132.0 (N*C*H), 130.5 (Ar), 125.4 (Ar), 124.8 (ArH), 123.6 (ArH), 42.9 (NCH_2), 28.9 (*C*HMe$_2$) 24.7 (CH(CH_3)$_2$), 24.7 (CH*Me*$_2$), -0.0 (SiCH_3)

MP (sealed tube) 149 °C

6.6 References

1 MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 1112.

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3 Ingleson, M. J .; Pink, M .; Huffman, J. C .; Fan, H .; Caulton, K. G *Organometallics* **2006**, *25*, 1112.

4 Liang,, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, H.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399.

5 Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.,* **2004,** 698.

6 Bayer AG *Patent GB1058711* **1963**.

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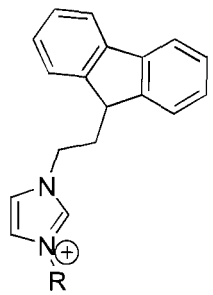
Chapter 7

Conclusions and Further Work

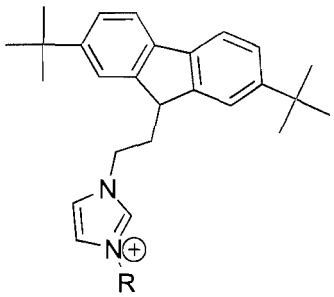
7 Conclusions

7.1 Imidazolium Salts

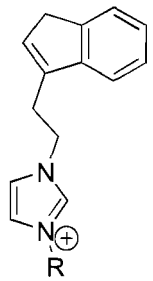
A method for the synthesis of substituted–, **2.17a-b**, and unsubstituted-, **2.10a-b**, fluorenyl functionalised imidazolium salts has been developed; this method is applicable to both aryl- and alkyl- substituted imidazoles. Indenyl functionalised imidazolium salts, **2.19a-e** and **2.27** have also been synthesised. The yields are excellent and the reactions scaled up to provide 50 g quantities of product.



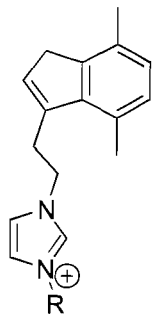
2.10a R = 2,6-di-*iso*-propylphenyl
2.10b R = mesityl



2.17a R = 2,6-di-*iso*-propylphenyl
2.17b R = mesityl



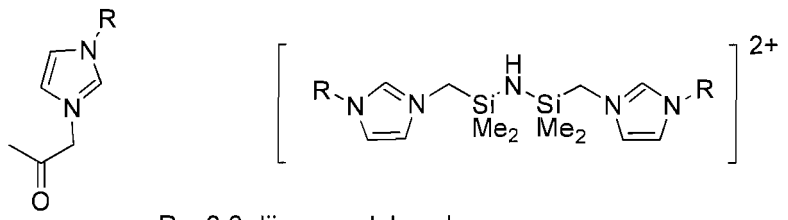
2.19a R = *tert*-butyl
2.19b R = phenyl
2.19c R = *ortho*-tolyl
2.19d R = mesityl
2.19e R = 2,6-di-*iso*-propylphenyl



2.27 R = 2,6-diisopropylphenyl

Figure 7.1 Imidazolium salts functionalised with indenyl and fluorenyl groups synthesised.

Methods were developed leading to novel ketone functionalised imidazolium salts **2.46** in extremely good yields. Novel silazane imidazolium salts **6.4** were also synthesised.



R = 2,6-diisopropylphenyl

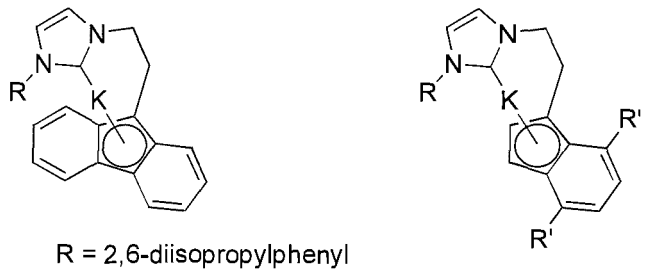
2.46 **6.4**

Figure 7.2 Ketone and silazane imidazolium salts.

Attempts to synthesise cyclopentadienyl substituted imidazolium salts using various routes were not successful. This is an area for future research bearing in mind the versatility and wide scope of cyclopentadienyl chemistry.

7.2 Main Group Complexes

A method has been developed to doubly deprotonate the fluorenyl and indenyl imidazolium salts to give the indenyl, **3.6**, or fluorenyl, **3.13a-b**, potassium NHC complexes in good yields.



R = 2,6-diisopropylphenyl

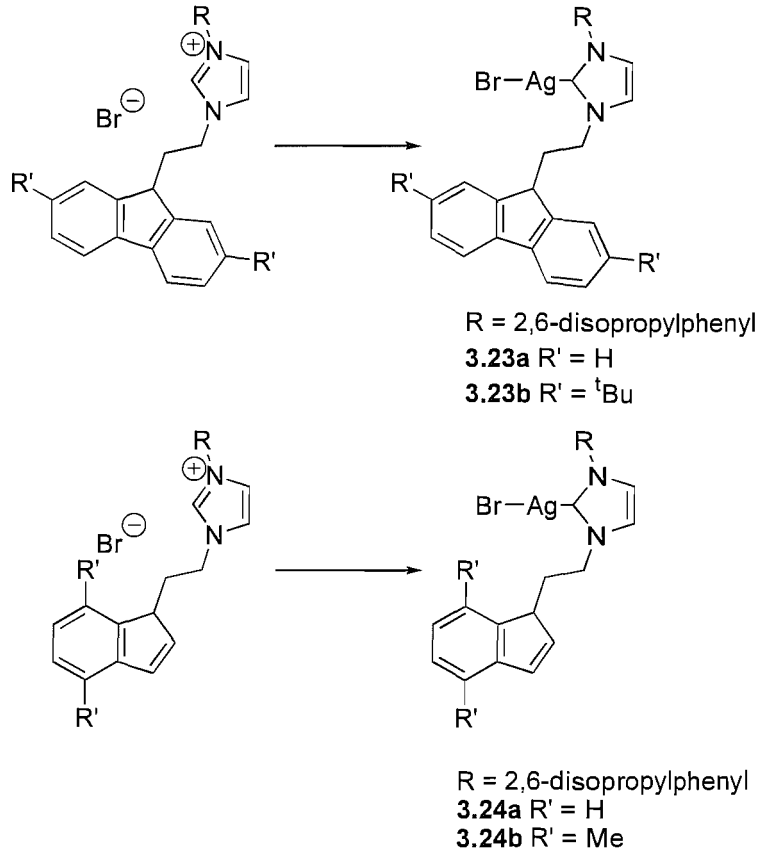
3.6

3.13a R' = H
3.13b R' = Methyl

Figure 7.3 Selected indenyl and fluorenyl potassium complexes.

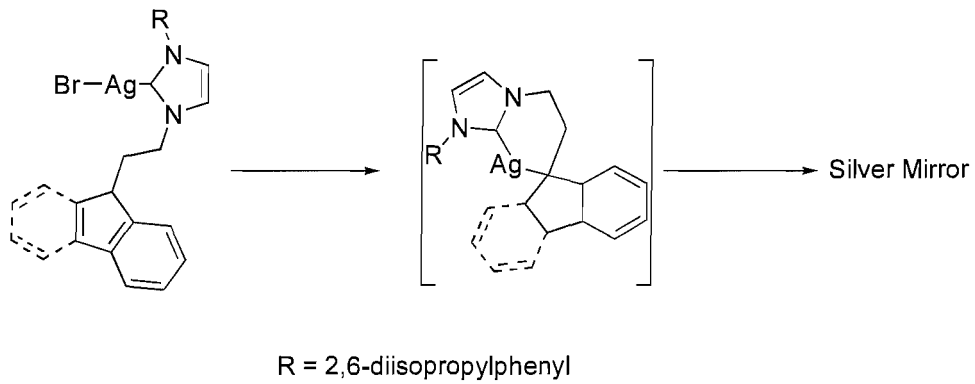
Attempts were made to isolate the mono-deprotonated neutral NHCs but the attendant decomposition and the solubility characteristics of the desired product and the by-products made this impossible.

It has been shown that the monodentate silver carbene complexes, **3.23a-b** and **3.24a-b**, of the indenyl and fluorenyl NHCs can be synthesised from Ag_2O and the imidazolium salts using standard methods.[1] It has also been shown these silver NHCs can be used as sources of NHCs in order to generate late transition metal complexes.



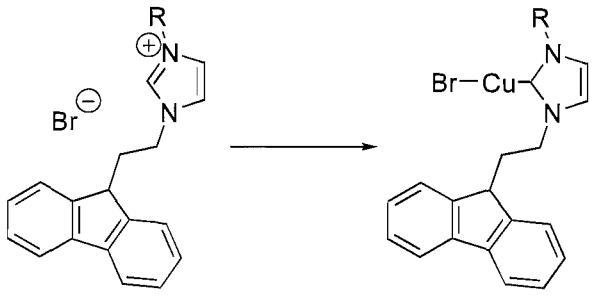
Scheme 7.1 Synthesis of silver carbene complexes.

However, attempts to synthesise the bidentate complexes resulted in decomposition releasing elemental silver, Scheme 7.2.

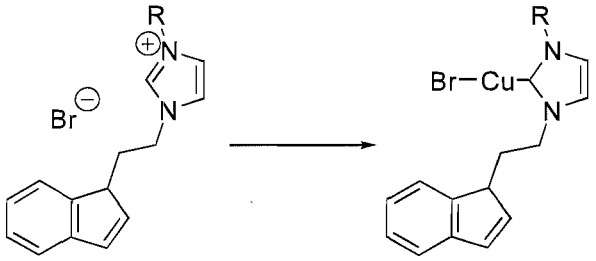


Scheme 7.2 Formation of a silver mirror.

A novel method has been found to synthesise monodentate copper complexes **3.21** and **3.22** using $[CuHMDS]_4$. This new method has wide scope.



3.21



3.22

R = 2,6-diisopropylphenyl

Scheme 7.3 Synthesis of copper carbene complexes form the imidazolium salts.

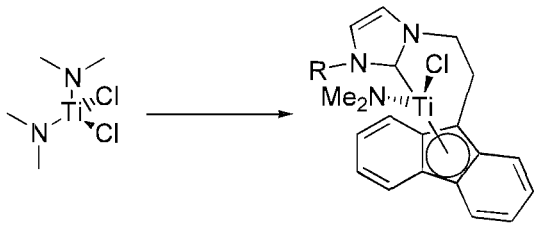
Attempts to synthesise the bidentate complexes resulted in decomposition and the release of elemental copper.

This decomposition caused problems for the synthesis of many of the main group metals, further work could be done to investigate whether this can be prevented.

Monodentate thallium and zinc complexes have also been synthesised.

7.3 Early Transition Metal Complexes

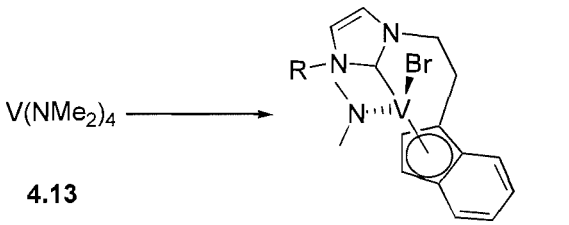
A number of bidentate early transition metal complexes have been synthesised. $TiCl_2(NMe_2)_2$ was reacted with the fluorenyl potassium NHC complex to give the bidentate Ti (III) species **4.7**, whilst $V(NMe_2)_4$ was reacted with the indenyl substituted imidazolium salt to give the V (III) bidentate species **4.14**.



4.6 **4.7**

R = 2,6-diisopropylphenyl

Scheme 7.4 Synthesis of a titanium (III) complex.



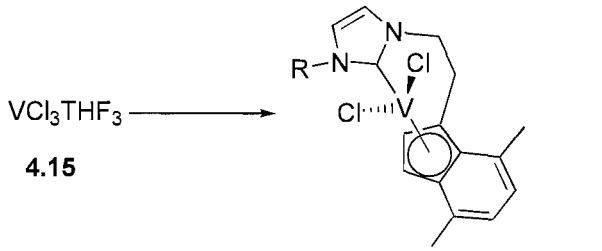
4.13 **4.14**

R = 2,6-diisopropylphenyl

Scheme 7.5 Synthesis of the first vanadium complex **4.14** containing the bidentate NHC – indenyl ligand.

In the synthesis of both of these complexes there was accompanying the aminolysis/substitution reactions. Work could be done to investigate this further.

Salt elimination strategies led to the V(III) complex **4.16** from **4.15** in a good yield. No reduction of the V (III) was seen.

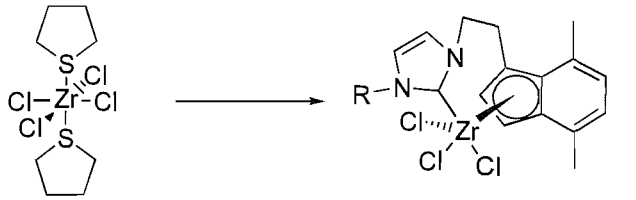


4.15 **4.16**

R = 2,6-diisopropylphenyl

Scheme 7.6 Synthesis of a bidentate vanadium (III) dichloride complex.

Similarly $ZrCl_4(THT)_2$ was reacted with the dimethylindenyl potassium NHC complex to give the bidentate zirconium (IV) complex **4.12**.



4.11

R = 2,6-diisopropylphenyl

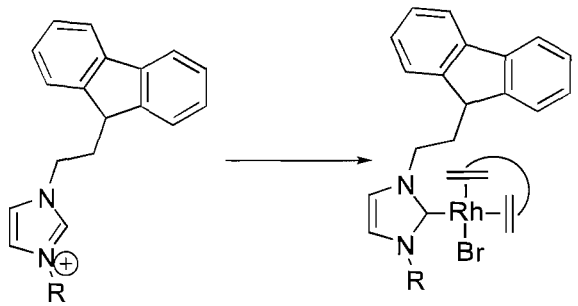
4.12

Scheme 7.7 Synthesis of a bidentate zirconium complex.

The investigation into the chemistry of the first row high-oxidation state early transition metals was complicated by the accompanying reduction of the metal centre. This gave rise to paramagnetic species that were difficult to characterise. This problem was overcome by starting with metal centres in a lower oxidation sate. This gave cleaner reactions so that the products could more readily be characterised. It is believed that these reductions took place with a similar mechanism to the decomposition of the main group bidentate complexes.

7.4 Late Transition Metal Complexes

A series of monodentate rhodium NHC complexes such as **5.10** were synthesised, these could be accessed from both the silver carbene and by reacting Rh(COD)OMe with the imidazolium salts.

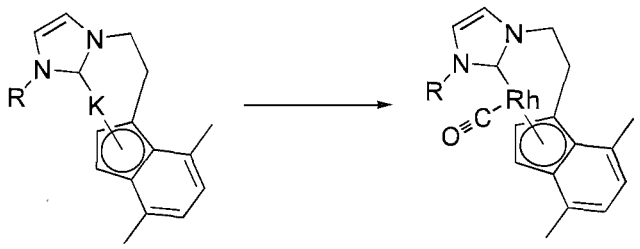


R = 2,6-diisopropylphenyl

2.10a **5.10**

Scheme 7.8 Synthesis of a rhodium carbene complex.

$[Rh(CO)_2Cl]_2$ was reacted with the indenyl potassium NHC complex **3.6** this gave the bidentate rhodium CO complex **5.14**. The first example of a late transition metal with an indenyl functionalised NHC in its bidentate form.

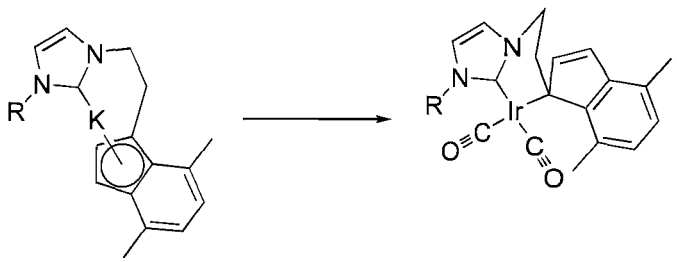


R = 2,6-diisopropylphenyl

3.13b **5.14**

Scheme 7.9 Synthesis of a bidentate rhodium carbonyl complex **5.14**.

$[Ir(COD)Cl]_2$ was reacted with the indenyl potassium NHC complex **3.6** in the presence of CO. A bidentate complex was obtained, but the complex contained two CO ligands and the indenyl ligand had adopted an η^1 coordination mode. Attempts to remove this 'extra' CO were unsuccessful.



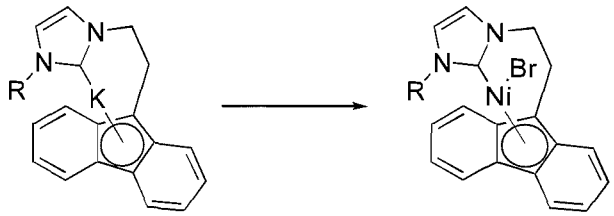
R = 2,6-diisopropylphenyl

3.13b **5.16**

Scheme 7.10 Synthesis of iridium complex **5.16**.

Further work could be done in order to find a reliable method for either the removal of the 'extra' CO or a method found for synthesising the complex with only one CO present analogous to **5.14**. The choice of an appropriate starting material is difficult in this case.

Nickel complexes with the ligand in its bidentate form such as **5.21** have been synthesised. The fluorenyl analogue showed activity for the oligomerisation of ethylene.



R = 2,6-diisopropylphenyl

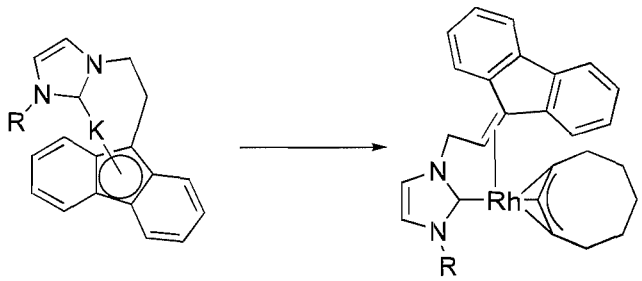
3.6 **5.21**

Scheme 7.11 Synthesis of a bidentate nickel complex **5.21**.

Further research could be directed towards the study of catalytic properties of these complexes, and also the possibility of synthesising a catalytically more active cationic complex.

Unlike the early transition metals, the late transition metals were not subject to reduction reactions but did show the added complication of C-H activation taking place within the complexes.

$[Rh(COD)Cl]_2$ was reacted with the fluorenyl potassium NHC complex **3.6**, the desired bidentate complex was not obtained, the complex had undergone a CH type activation in order to give the fulvene type complex **5.13** shown.

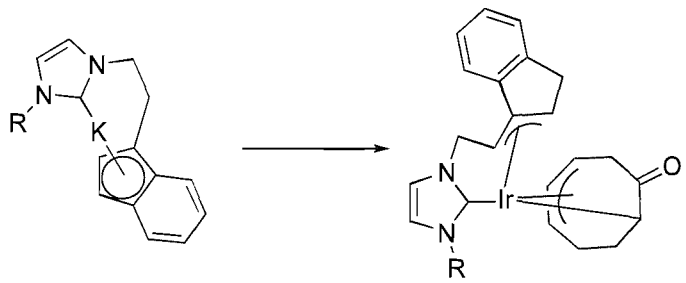


R = 2,6-diisopropylphenyl

3.6 **5.13**

Scheme 7.12 Synthesis of fulvene carbene complex.

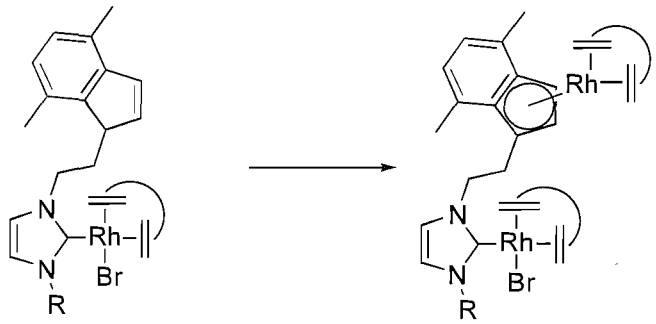
A similar reaction was carried out with $[Ir(COD)Cl]_2$ in this case a similar CH activation occurred, the only product that could be identified was an oxygen adduct **5.15** that is envisaged to have been formed after serendipitous exposure to air.



3.13a **5.15**

Scheme 7.13 Synthesis of a CH-activated iridium complex **5.15**.

A bimetallic compound **5.23** has been successfully synthesised. A possibility of future research could be to investigate the rational synthesis of these bimetallic structures with different metals to make homobimetallic structures with metals such as iridium or heterobimetallic structures with different metals. The bimetallic structures offer the possibility multimetallic catalysts.



5.12 **5.23**

Scheme 7.14 Synthesis of a bimetallic complex.

Methods have now been found to synthesise a large variety of complexes with many different metals and interesting properties of these complexes have been discovered such as reductions and C-H activations. This initial work has opened a number of avenues for further research.

7.5 Future Work

It is clear that this area of research has many possibilities for the future and there are a number of different directions that it could take.

The imidazolium salt synthesis could be further expanded to look at different substitution patterns on the cyclopentadieneyl type moiety and the imidazole. An

interesting area would be to investigate the effect of the length of the bridge between the imidazolium ring and the cyclopentadiene on its coordination properties and the properties of the catalysts derived from it. Three carbon bridges have already been shown to be viable[2], one carbon bridges deserve some attention, although these may prove harder to synthesise. Bromomethylindene is known but is more complex to synthesise than bromoethylindene.[3]

A second area that stands out for investigation is the substitution patterns on the indenyl or fluorenyl ring. Investigations could take place as to how sterics of these alkyl groups affect the nature of complexes formed.

Further attention could be given to the synthesis of cyclopentadienyl substituted imidazolium salts, as our attempts to synthesise these have so far been unsuccessful. It may be possible to find new retro-synthetic routes or take advantage of new methods in the literature for synthesising cyclopentadienyl compounds when it is published.

A feature of the ligand that deserves further attention and research is its apparent ability to reduce metal centres. If the reasons for this ability could be identified then it may be possible to alter the ligand in such a way that this is prevented.

Further attention should be paid to the early and mid transition metal complexes to further expand the range of complexes that can be made, either by exploring other metals or investigating different ligand sets on known complexes. More investigation could be carried out in to why these metals are so easily reduced.

In the area of late metals further attention could be given to the synthesis of other bidentate metal complexes including platinum and palladium as no work has yet been conducted in this area. The iridium complex with its η^1 indenyl ligand deserves attention, methods could be found to synthesise the η^5 analogue.

Further research should be done on the catalytic properties of the nickel complex. Following Shen's publication the complex could be tested for styrene polymerisation and directly compared to Shen's results. The catalytic properties of other metal complexes could also be investigated.

Bimetallic compounds also deserve some attention it has been shown in principle these can be synthesised, but work needs to be done to ascertain the extent and breadth of bimetallic species that can be prepared.

Also worth further investigation is the deprotonation of the silazane ligand to find methods to prevent this from decomposing.

7.6 Summary

Potassium NHC complexes; main group-, early-, and late- transition metal complexes derived from novel indenyl- and fluorenyl- functionalised imidazolium salts have been synthesised. A number of methods have been developed to synthesise these compounds. Much has been learnt but there are still many areas remaining for these new ligand systems to be developed and the area will be of interest for some time to come.

7.7 References

1 Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

2 Sun, H. -M.; Hu, D. –M.; Wang, Y. –S.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2007**, *692*, 903.

3 Coutot, C. H. *Ann. Chim. Phys. (Paris, Fr.)* **1915**, *4*, 58.