UNIVERSITY OF KWAZULU-NATAL

N-HETEROCYCLIC CARBENE-IRON(II) COMPLEXES: CHEMISTRY AND APPLICATION AS TRANSFER HYDROGENATION CATALYSTS

2011

MONISOLA ITOHAN IKHILE

N-HETEROCYCLIC CARBENE-IRON(II) COMPLEXES: CHEMISTRY AND APPLICATION AS TRANSFER HYDROGENATION CATALYSTS

MONISOLA ITOHAN IKHILE

2011

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

This is a thesis in which the chapters are written as a set of discrete research papers, with an overall Introduction and final Conclusion. Where one (or all) of the chapters has already been published, typically these chapters will have been published in internationally-recognised peer-reviewed journals.

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

Supervisor:

Signed: …….. Name MD BALA …… Date: ……

Co-Supervisor:

Signed: ……. Name: VO NYAMORI ……. Date ……

ABSTRACT

In the last decade *N*-heterocyclic carbene (NHC) ligands have become important in organometallic chemistry and homogeneous catalysis, rivalling the well established phosphines. Most of the current attention to date has focused on the NHC complexes of the platinum group metals (rhodium, palladium and nickel) plus ruthenium based system, but the chemistry of NHC systems of iron which is relatively inexpensive and environmentally friendlier is considerably less developed. Thus, this project involves the design, synthesis, characterization and application in catalytic transfer hydrogenation of NHC ligands and their iron(II) complexes.

The motivation for the choice of NHC as a ligand stems from the ability to systematically tune the ligand both electronically and sterically in addition to the stability and robustness of the ligand to stabilize metal centres in various environments. In this research imidazolium based NHCs are generated. Thus, three different series of imidazolium salts were synthesized and their iron(II) complexes was obtained. All the compounds were characterized by spectroscopic and crystallographic methods. These are: (a) 1,3-dialkylimidazolium salts (b) 1,3-diarylimidazolium salts and (c) ferrocenylimidazolium salts bearing methyl and phenyl spacers between the ferrocenyl and the imidazolium moieties. A total of 20 novel compounds were synthesized and are reported in this thesis.

Furthermore, the application of the new compounds as transfer hydrogenation catalysts was investigated using 17 saturated and unsaturated ketones as substrates, in the presence of KOH as the base and 2-propanol as the hydrogen source. The dialkylated NHC iron(II) complexes showed excellent yields, and TON values of up to 200 were achieved under the optimized reaction conditions. Without complexation with iron, the 1,3-diarylimidazolium and ferrocenylimidazolium series of salts were also found to be active catalysts for the transfer hydrogenation reaction of ketones in alcoholic media. In the case of ferrocenylimidazolium salts a TON value up to 1880 was achieved. Notably, two of the unsaturated ketones were successfully converted at a high yield with a high selectivity to the corresponding saturated ketones only.

In addition, the stability of NHC ligands to moisture was investigated, since an understanding of the stability of various deprotonated NHC-based imidazolium cations to attack by moisture resulting in hydrolysis products is very important to understanding the coordination chemistry of the ligands on

to metal centres. Four novel ionic diamino aldehyde compounds were obtained by moisture attack on saturated NHC ligands. The route to the formation of the hydrolysed compounds is formulated to occur via an imidazolinium ring opening process. On the other hand the unsaturated counterparts were more stable towards hydrolysis yielding adducts with the iron(II) precursors.

Finally, the electrochemical properties of the ferrocenylimidazolium salts were investigated using cyclic voltametry. By comparing the relative shifts in the formal electrode potentials of the ferrocene/ferrocenium coupled with the ferrocenylimidazolium salts, it was easy to evaluate the influence of the substituents on the carbene containing imidazolium moiety on the electrochemical properties of the iron centres. The formal electrode potential of the ferrocenylimidazolium salts shifted to higher positive potentials as compared to ferrocene, indicating a high electron withdrawing effect of the imidazolium salts. This makes the metal centres more vulnerable to attack by nucleophiles. The electrochemical studies have enabled a structure-activity correlation to be drawn for the various ferrocenylimidazolium salts.

DECLARATIONS

DECLARATION 1 - PLAGIARISM

I, ……MONISOLA ITOHAN IKHILE……., declare that:

1. The research reported in this thesis, except where otherwise indicated, is my original research.

2. This thesis has not been submitted for any degree or examination at any other University.

3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

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DECLARATION 2 - PUBLICATIONS

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

Publication 1

Ikhile, M.I.; Bala, M.D. **1,3-Bis(1-adamantyl)imidazoliumtetrachloroiodoferrate (III);** *Acta Crystallographica Section E*, **2010**, E66, m1493.

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

Publication 2

Ikhile, M.I.; Bala, M.D. **1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazol-3-ium trilodide**; *Acta Crystallographica Section E*, **2010**, E66, o3121.

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

Publication 3

Ikhile, M.I.; Bala, M.D.; Nyamori, V.O. **A Greener Method towards the Synthesis of 1,3-diarylimidazolium tetrafluoroborates** ; *South Africa Journal of Chemistry*, **2011**, 64, 101-104.

Contributions: I synthesized all the compounds, carried out the characterization and wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. The other authors are my supervisors.

Publication 4

Ikhile, M.I.; Bala, M.D.; Nyamori, V.O. **Transition Metal-free transfer hydrogenation of ketones promoted by 1,3-diarylimidazolium salts and KOH;** manuscript submitted to *Catalysis communication*, 2011**.**

Contributions: I carried out all the catalysis testing and wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. All other authors are supervisors**.**

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Contributions: I synthesized all the compounds, carried out all the cyclic voltammetry analysis, catalysis testing and wrote the initial draft of the manuscript and carried out subsequent modifications towards publication of the paper. All other authors are my supervisors

Publication 6

Ikhile, M.I.; Bala; M.D. **Structures of *N*,*N*-Bis(tertbutyl)-*N*-Formyethylenediamine halides obtained by salt metathesis from metal precursors;** manuscript in preparation.

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

Publication 7

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Publication 8

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Signed:

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This work is dedicated to my husband and children.

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2. Ikhile, M.I.; Bala, M.D.; Nyamori, V.O. **A Greener Method towards the Synthesis of 1,3-diarylimidazolium tetrafluoroborates** ; *South Africa Journal of Chemistry*, **2011**, 64, 101-104.
3. Ikhile, M.I.; Bala, M.D. **1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazol-3-ium trilodide**; *Acta Crystallographica Section E*, **2010**, E66, o3121.
4. Ikhile, M.I.; Bala, M.D. **1,3-Bis(1-adamantyl)imidazoliumtetrachloroiodoferrate (III);** published in *Acta Crystallographica Section E*, **2010**, E66, m1493.

CONFERENCE PROCEEDINGS

1. Ikhile, M.I.; Bala, M.D.; Nyamori, V.O. **Synthesis of ferrocenylimidazolium salts as catalysts in transfer hydrogenation of ketones.** (paper presented at Catalysis Society of South Africa (CATSA) conference 13-16th November **2011**, Gauteng, South Africa)
2. Ikhile, M.I.; Bala, M.D.; Nyamori, V.O**. Synthesis and application of novel *N*-heterocyclic carbenes iron(II) complexes in catalytic transfer hydrogenation of ketones**. (paper presented at South African Chemical Institute postgraduate colloquium 15th September **2011**, UKZN Westville Campus)
3. Ikhile, M.I.; Bala, M.D. **Synthesis and catalytic activity of novel *N*-heterocyclic carbene iron(II) complexes in transfer hydrogenation of ketones** (paper presented at OMCOS 16:16th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, Jul 24-Jul 28th **2011**, Shanghai, China).
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6. Ikhile, M.I.; Bala, M.D. **Synthesis of *N*-heterocyclic carbene iron(II) complexes** (paper presented at South African Chemical Institute postgraduate colloquium **2010**, UKZN Pietermaritzburg Campus).
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CHAPTER 1

INTRODUCTION

1.1 Background

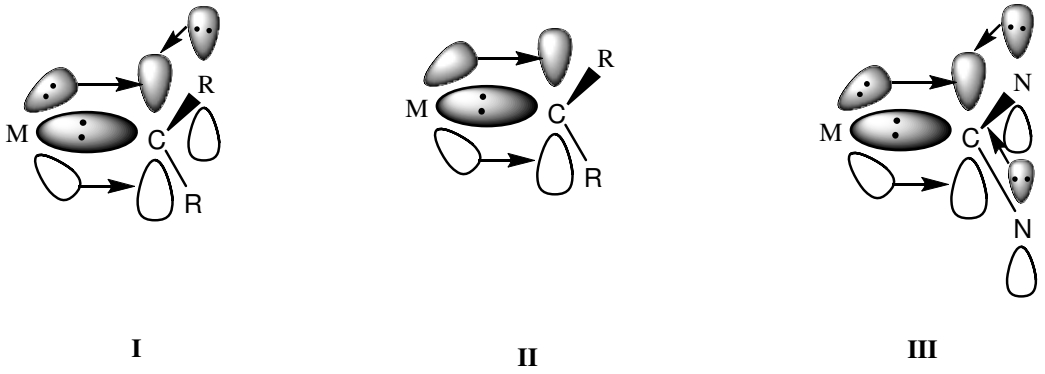
The metallation of imidazol-2-ylidenes, commonly known as *N*-heterocyclic carbenes (NHCs) which are deprotonated products of imidazolium salts was pioneered by Ofele and Wanzlick in 1968.[1] Further investigation by Lappert led to the synthesis of NHC complexes from electron rich olefins.[2] Since then, the chemistry of NHCs has remained dormant over the years because they were deemed too unstable for application in normal synthetic protocols. However, it required the isolation of the first free carbene by Arduengo and co-workers in 1991, to bring about significant renewed interest in this area.[3] Since then, the complexation of these 'new ligands' has become important to organometallic chemistry.

The ability of NHCs as ligands to bind to a variety of metal centres has been shown to equal, in fact if not exceed the binding ability of phosphines.[4] Almost all the NHC complexes of the transition metals and many main group elements have been reported.[5] NHCs bind to both hard and soft metals making them a class of very versatile ligand systems.[6] Their binding mode was believed to be primarily through σ-donation, until recent evidence suggested the occurrence of some degree of π back-donation. The use of these ligands in organometallics has greatly stimulated the development of efficient catalysts based on NHCs, with many of their metal complexes applied as highly efficient catalysts in transformations of organic compounds. Often, the activity and robustness of the NHC complexes surpass those of their corresponding phosphine counterparts. Their catalytic performance may be optimized by ligand tuning, since the electronic effect of a large number of NHC ligands have been determined and reported.[5b] In addition, their superiority over phosphine ligands include ease of preparation, low loading and high efficiency in catalysis, moderate moisture and air stability.

1.2 Types of carbenes

In principal, generally there are three types of carbene-based compounds encountered in transition metal chemistry; these are Fischer, Schrock and NHC type carbenes. Their various modes of binding are as shown in Figure 1.1.[1c] Fischer carbenes bond strongly as π acceptors to metals.

They tend to bind well with low oxidation state metals, middle and late transition metals. Their binding mode is based on σ donation from the substituent group to an empty metal d-orbital. Schrock carbenes are usually found with early transition metals. They also bind well with high oxidation state metals and are good pi-donor ligands. Unlike Fischer carbenes, they do not have π acceptor orbitals.



I **II** **III**

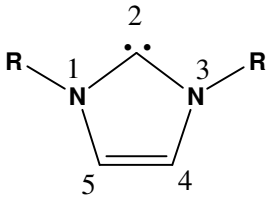
Figure 1.1 Modes of binding in Fischer **(I)**, Schrock **(II)** and NHC **(III)** carbenes.[1c]

The bonding mode in an NHC is primarily stabilized by the pi-donating *N*-substituents.[3] Hence, they are good σ-donors with a weak π-bonding to the metal. It was initially thought that the bonding mode of NHCs to the metal was principally by σ-donation. However, π-back-donation has been found to play a larger role than earlier suggested. This initial thought accounted for the reason why the bond between the carbon and metal is often represented by a single dative bond, whereas Fischer or Schrock carbenes are represented by a double bond to the metal.[7]

1.3 Types of NHCs

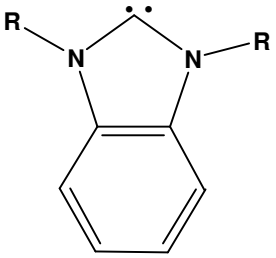
There are several types of NHCs which have been used to complex transition metals as shown in Figure 1.2.[1c] These include: the most widely studied imidazolin-2-ylidenes (**1.1**) and benzimidazol-2-ylidenes (**1.2**) which are derivatives of **1.1**, having a benzene ring fused to the backbone of the imidazole ring. Imidazolidin-2-ylidenes (**1.3**) are quite similar to **1.1** except that the backbone of the ring at positions 4 and 5 is saturated affording an electron richer NHC.[8] Tetrahyropyrimid-2-ylidenes (**1.4**) are six-membered saturated ring systems and are an extension of compound **1.3**.[9,10] 1,2,4-Triazolin-5-ylidenes (**1.5**) are composed of a five-membered ring with three nitrogen atoms at

the 1,2,4-positions with the carbenes located at the 3- and 5- positions. Both carbons of **1.5** can serve as potential donors allowing **1.5** to bond to more than one metal.[11,12] Imidazolin-4(5)-ylidenes (**1.6**) are examples of abnormal carbenes that have been reported in which the carbene carbon bonds to the metal at positions 4 or 5, instead of the usual 2-position.[13]



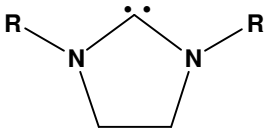
imidazolin-2-ylidenes

1.1



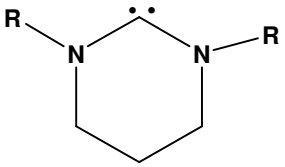
benzimidazol-2-ylidenes

1.2



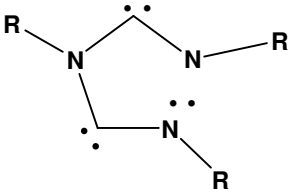
imidazolidin-2-ylidenes

1.3



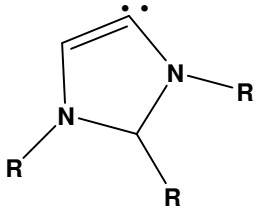
tetrahydropyrimid-2-ylidenes

1.4



1,2,4-triazolin-5-ylidenes

1.5



imidazolin-4(5)-ylidenes

1.6

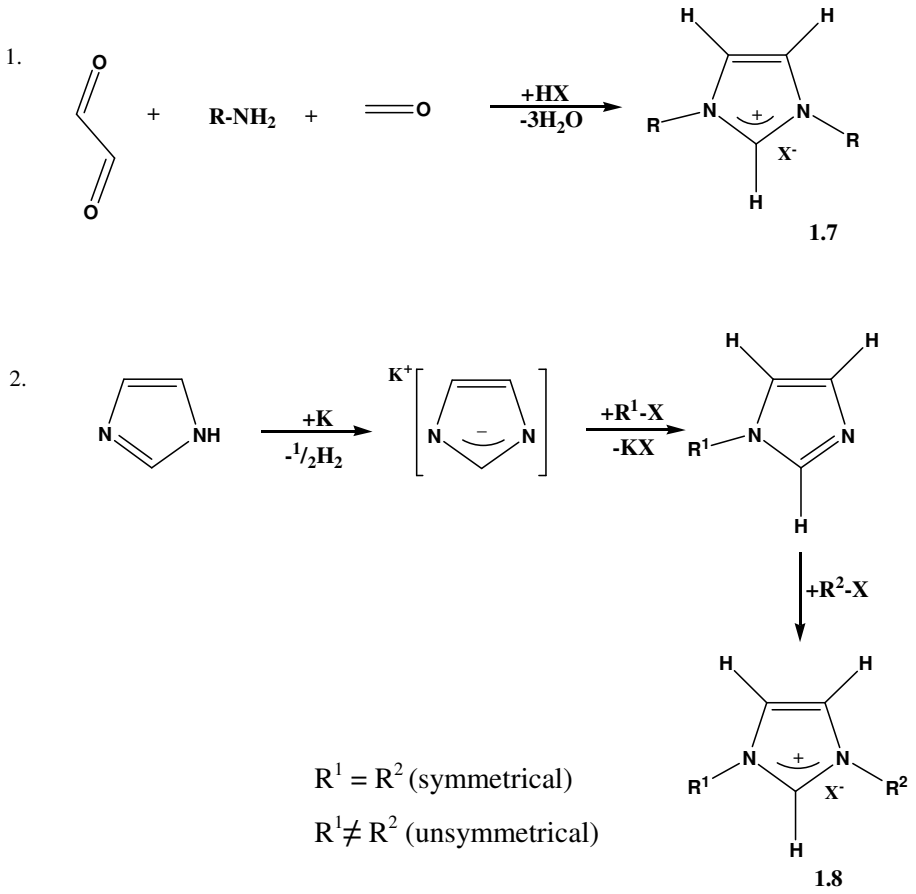
Figure 1.2 Types of NHCs.[1c]

1.4 Synthesis of NHCs

NHCs are usually prepared from azolium compounds such as imidazolium, benzimidazolium, imidazolidinium, triazolium and thiazolium salts.[5] This is achieved by deprotonation of the azolium compounds.[14,15] Another method involving the reductive desulfurization of imidazolin-, benzimidazolin- and imidazolidin-2-thiones, yielding a variety of NHCs, has also been reported.[16] Therefore, developing methods for the synthesis of imidazolium salts is of paramount important since the NHC ligands are usually obtained from them.[17]

1.5 Synthesis of imidazolium salts

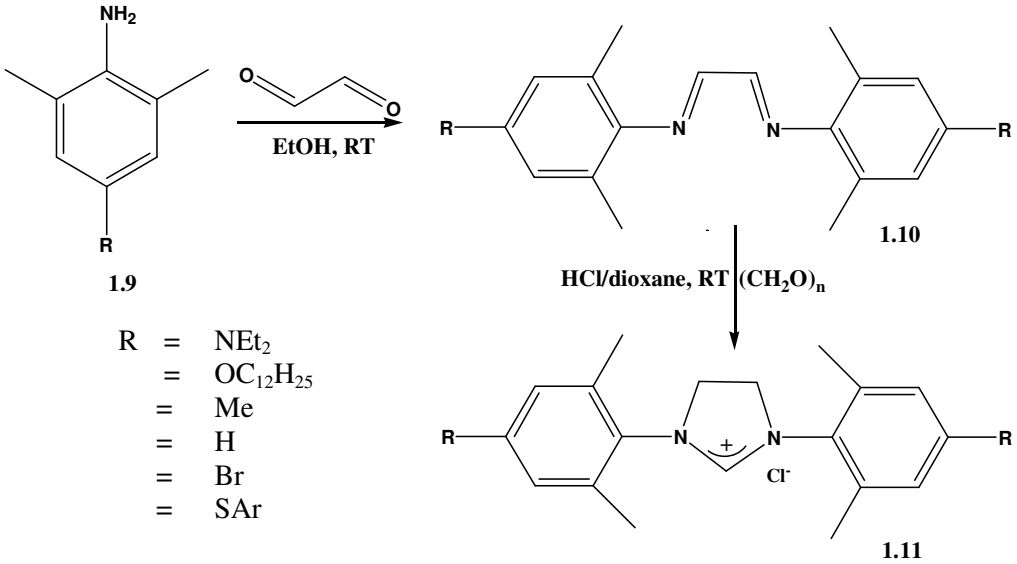
Imidazolium salts which are precursors for the synthesis of NHCs are usually synthesized *via* one of two routes: (1) one-pot synthesis by combination of a primary amine, glyoxal and formaldehyde in the presence of an acid.[18] This method is mostly suitable for making imidazolium salts **1.7**, bearing very bulky, aromatic or even very reactive *N*,*N* substituents; (2) activation of the nitrogen atom of the imidazole with an alkyl halides and subsequent reaction may lead to the formation of *N*,*N*'-disubstituted derivatives of the imidazolium salts, **1.8** (Scheme 1.1).[18,19]



Scheme 1.1 Synthesis of imidazolium salts.

Method two offers a much easier way of synthesizing unsymmetrical imidazolium salts.[16] Several other methods have been developed for the synthesis of imidazolium salts which have not been previously achieved.[20-22]

Recently, Leuthäußer *et al.*[23] have modified Arduengo's one-pot method by reacting 2,6-dimethylanilines, **1.9** (substituted at the *para*-position with various electronically diverse groups) with glyoxal to give the corresponding diimines, **1.10**. This is followed by ring closure reaction which leads to the synthesis of imidazolium salts, **1.11** as shown in Scheme 1.2. This method is more ideal for the synthesis of 1,3-diarylimidazolium salts because product purification which renders Arduengo's one-pot methods difficult is minimized.



Scheme 1.2 Synthesis of *N*,*N*'-diarylimidazolium salts.

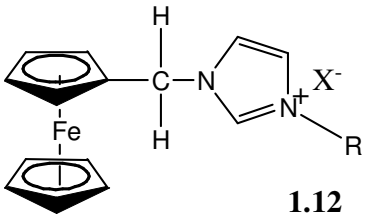
1.6 Ferrocenylimidazolium salts

Interest into ferrocene containing compounds is increasing even though it was discovered over 50 years ago.[24] This is as a result of the unique properties possessed by the ferrocene moiety which are geometric and electronic in nature.[24] These unique properties, especially the redox (electronic) property, has lead to their use in numerous industrial applications such as plastics, metallurgy, petroleum and textiles.[25] Also, ferrocenes stability towards air and moisture, in comparison to other organometallic compounds, has facilitated its use in biological applications.[26-27] Currently, ferrocene chemistry has also found wide application in immunoassays,[28-32] sensors and catalysis.[33-36]

Study of imidazolium salts containing ferrocenyl substituents is now becoming an interesting area of research due to the ferrocene moiety making it possible for the salts to be used in electrochemical

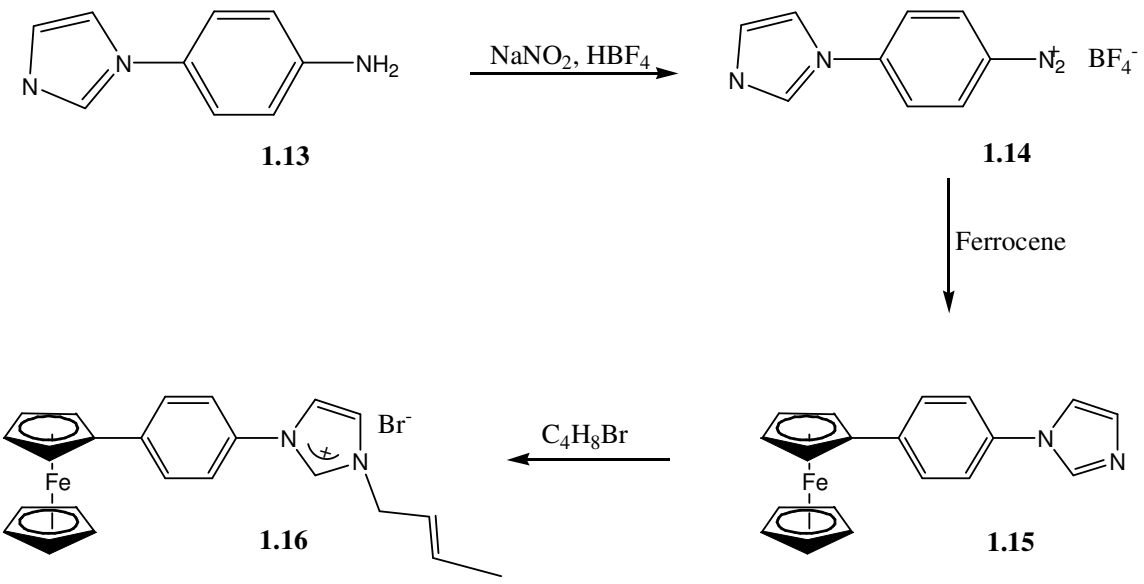
processes.[37] The reversibility of the ferrocene/ferrocenium redox (Fc/Fc^+) couple have made them useful as anion recognition species[38] making it easier to study electronic interactions in ferrocenylimidazolium salts by using cyclic voltammetry. The potential of the redox couple ferrocene/ferrocenium varies with the change in the electronic property of the substituents attached to it. The Fc/Fc^+ couple also depends on the type of spacers or linkers (e.g. alkyl or phenyl) between the ferrocenyl and the imidazolium moieties.[39]

Numerous methods exist in the literature for the synthesis of ferrocenylimidazolium salts.[40-45] Nyamori *et al*. have synthesized new ferrocenylimidazolium salts, **1.12** with methyl linkers between the two moieties having the general structure shown in Figure 1.3, by incorporating green chemistry principles of using solvent-free techniques.[46] All the new compounds were fully characterized spectroscopically. The phenyl linked ferrocenylimidazolium salts were successfully synthesized by Hovarth *et al*. using Gomberg arylation as an aryl-aryl coupling technique as shown in Scheme 1.3. This is achieved by diazotisation of a phenylimidazolium compound followed by coupling with ferrocene to afford **1.15**. Subsequent alkylation leads to ferrocenylimidazolium salts of the type **1.16**.[47]



1.12 R = CH_3, $(CH_2)_3CH_3$ or $(CH_2)_7CH_3$
X = I or Br

Figure 1.3 Ferrocenylimidazolium salt with a methyl group linking the two moieties.[46]



Scheme 1.3 Synthesis of ferrocenylphenylimidazolium salts.

1.7 Application of imidazolium salts

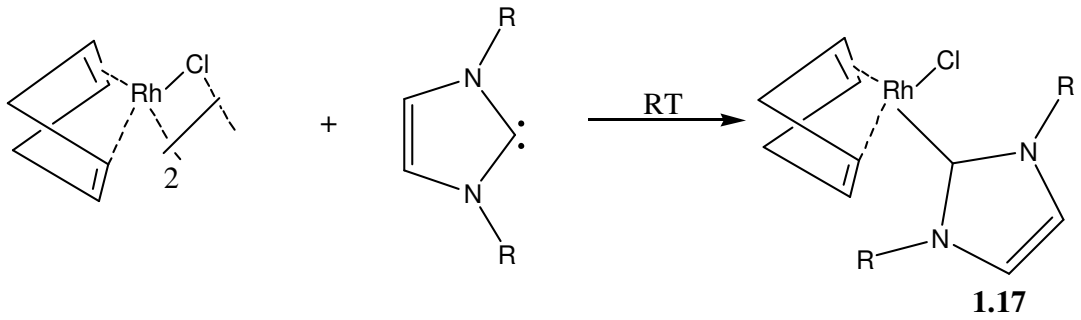
Within the last decade, imidazolium salts have received wide attention due to their numerous applications.[48-50] Their use as ionic liquids[51] and solvents for organic reaction is an advantage used in green chemistry.[52] This is because ionic imidazolium salts that are liquids at room temperature are thermally and chemically stable. They also possess high electrical conductivity, have a wide electrochemical window and a wide temperature range for applications.[53] Research has shown that their properties can be varied by changing both the cation and the nature of the counter-ion.[54] These variations of their properties have brought about the synthesis of various imidazolium salts that have found use in medicine,[55] electrochemistry,[56] nanotechnology,[57] biofuel chemistry[58] and in the petroleum industries.[51]

1.8 Synthesis of transition-metal complexes of NHC ligands

The most common routes to the synthesis of transition-metal complexes containing the NHC ligand are: (1) complexation of isolated free carbenes, (2) *in situ* deprotonation of azolium salts, (3) cleavage of electron-rich olefins and (4) transmetallation from Ag complexes.[59] The various methods are further elaborated on below.

1.8.1 Complexation of isolated free carbenes

NHC-metal complexes are usually synthesized by the deprotonation of azolium salts with a strong base to generate free carbenes which are subsequently reacted with metal precursors to generate the complex. This is by far the simplest and most direct method to the synthesis of NHC-metal complexes and has gained wide acceptability since Arduengo reported on the isolation and characterization of the first free carbene.[16] The main drawback to this method is that handling the isolated carbene is difficult due to its instability to air and moisture. The complexes are obtained by reacting the free carbene with suitable metal precursors, or by the cleavage of dimeric complexes containing bridging ligands such as halides, acetonitrile and carbon monoxide.[60-62] An example of such a process is shown in Scheme 1.4 involving the reaction of the isolated free carbene with $[(\eta^4-cod)MCl]_2$ or $[Cp^*MCl_2]_2$ (M = Rh, Ir)[59] to afford complex **1.17**. Exchanging the phosphine ligands with NHC offers another method for the synthesis of NHC-metal complexes via the free carbenes method as most phosphines are easily displaced by carbenes even at below room temperatures.[63] In addition, NHC ligands can also displace one or two carbon monoxide molecules in carbonyl complexes[64-65] e.g. $Fe(CO)_5$, $W(CO)_6$, $Ni(CO)_4$, and $Cr(CO)_6$., which can be further substituted under photolysis condition.[59]



1.17

Scheme 1.4 Cleavege of a dimeric complex by free carbenes.[59]

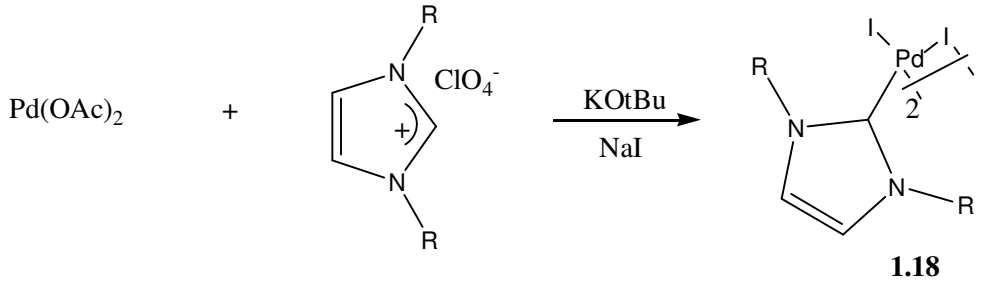
1.8.2 *In situ* deprotonation of azolium salts

The *in situ* deprotonation of azolium salts followed by complexation of the ligand to a suitable metal has the advantage of avoiding the preparation and isolation of the free NHC which has been highlighted to be unstable and difficult to handle.[59] Azolium salts can be deprotonated through various ways, which include:

(i) Deprotonation by a basic anion obtained either from the metal precursors or the azolium salts, which are usually commercially available acetate salts, acetylacetonate salts and easily prepared metal alkoxides. It must be noted that the anion itself may coordinate to the newly formed complex and, in order to avoid this incorporation, non-coordinating perchlorate, tetrafluoroborate or hexafluoroborate azolium salts are used.[59]

(ii) The introduction of an external base to deprotonate azolium salts offers synthesis of different NHC complexes as compared with the use of metal salts with basic anions.

The synthesis of a dimeric mono (NHC) complex, **1.18** which involves the use of potassium tert-butoxide as an external base with an imidazolium perchlorate and one equivalent of palladium(II) diacetate in the presence of sodium iodide, is a typical example (Scheme 1.5).[66] This dimeric mono (NHC) is a valuable precursor towards the synthesis of other NHC complexes by dimer cleavage from other ligands e.g. phosphines and NHCs.[59,67-68] Also, potassium tert-butoxide and sodium hydride are introduced as external bases in THF solution of the imidazolium salts at room temperature to generate NHCs, which are then coordinated *in situ* to e.g. $Cr(CO)_6$ or $W(CO)_6$ to yield NHC-metal complexes.[10] In addition the NHC analogous ligand of Trofimenko's tris(pyrazolyl) borate[69] was prepared by deprotonation with butyl lithium in THF, and subsequent reaction with iron(II) chloride and afforded the formation of a homoleptic hexa-(NHC) iron(III) complex.[59]



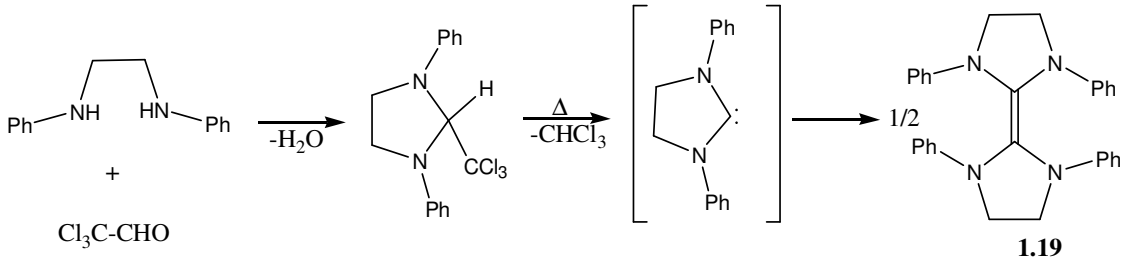
1.18

Scheme 1.5 An example of the synthesis of a dimeric mono (NHC) Pd complex.[66]

1.8.3 Cleavage of electron-rich olefins

The thermally driven cleavage by various unsaturated transition metal complexes of nucleophilic electron-rich olefins constitutes an established method for the synthesis of NHC-complexes.[2,16, 70] The electron-rich olefins, **1.19** are prepared by the dimerization of unstable NHCs (Scheme

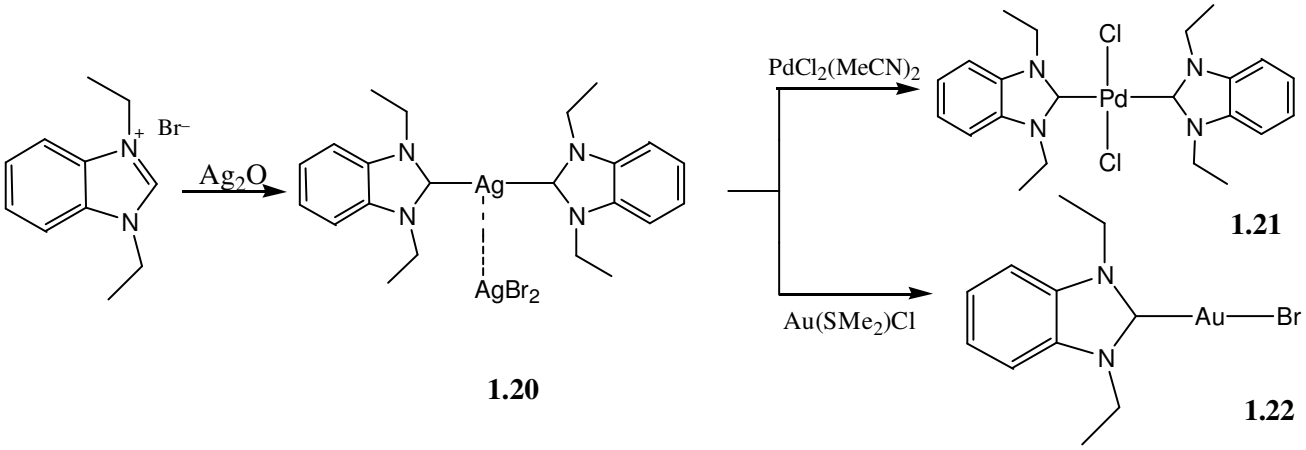
1.6).[59,71,72] Also, deprotonation of imidazolidinum salts with Grignard reagents do afford the formation of electron-rich olefins.[73] This method is highly suitable for the synthesis of NHC-complexes containing benzimidazolin-2-ylidene ligands.[16,59,74-76]



Scheme 1.6 Synthesis of electron-rich olefins.[59,71,72]

1.8.4 Transmetallation from Ag complexes

NHC-metal complexes are also synthesized by transfer of carbenes usually from Ag-NHC complexes to other metals.[16] Imidazolium salts can easily be deprotonated by using a variety of silver bases such AgOAc, Ag_2CO_3 and especially Ag_2O to obtain Ag-NHC complexes, **1.20**.[1c] As a result of lability of the Ag-carbene bond, the carbene can easily be transferred to other metals, **1.21** and **1.22** (Scheme 1.7).[77] This offers a reliable method towards the synthesis of NHC-metal complexes where other methods proved difficult or unsuccessful.[16]



Scheme 1.7 Synthesis of NHC-metal complexes by transmetallation.[1c,77]

1.9 Green chemistry

Green chemistry is the science and technology that involves the design and development of chemical products and methods that reduce or eliminate the use of toxic substances that pose risk to the environment and human health.[78] The term green chemistry was first used by the US Environmental protection Agency (EPA) during the early 1990s.[79] Since then, recognition into this new area as a culture and methodology to obtain environmentally friendly chemistry has increased. This area is getting renewed attention because of the actions of past generations, where environmental hazards have been generated by the indiscriminate use and release of various synthetic chemical wastes into the environment. Therefore, green chemists are in search for environmentally friendly chemical processes that are simple, economical and able to reduce or eliminate risk to the environment.[80] The twelve principles of green chemistry[79-81] help to show how this can be achieved.

1.9.1 Principles of green chemistry

The twelve principles of green chemistry as proposed by Anastas and Warner[81] serve as a guide for chemists in designing chemical processes with the principal aim to reduce or eliminate toxic reagents and wastes that pose a hazard to human health and the environment. Some of the principles are related to the prevention of waste, atom economy, use of less hazardous chemicals for synthesis, and the use of safer solvents and auxillaries. Determination of the atom economy of a reaction is one of the more important aspects of the application of green chemistry principles.[80] It is a concept that was developed by Barry Trost of Stanford University which evaluate the efficiency of a chemical process in a more elaborate fashion than mere calculation of yield.[79b] In line with the principles of green chemistry relevant to this study, Imrie *et al.*[82] have synthesized ferrocenylimines by means of reactions with high atom economy and also employing a solvent-free reaction, thus, eliminating the use of hazardous solvents as well.

1.10 Catalysis

General interest in catalysis is ever increasing since the word was first coined by Berzelius in 1836.[83] According to him, a catalyst is defined as something that when added to a chemical reaction speeds up the reaction and is not consumed in the process. Catalysts can be broadly classified into homogeneous or heterogeneous, based on the phase of operation. [84] When the

catalyst and the reactants are in the same phase it is referred to as homogeneous, while in heterogeneous catalysis the catalyst and the reactants occur in different phases.[84] Different types of homogeneous catalysts exist in the literature, such as the Bronsted and Lewis acids commonly utilized in organic synthesis,[85] metal ions, organic molecules including biocatalysts (enzymes, artificial enzymes) and more especially organometallic complexes.[84] In fact, organometallic compounds have found the widest application in homogeneous catalysis.[86] This is attributed to the effectiveness and especially their selectivity in comparison to heterogeneous systems.[87]

1.11 Catalytic activity of NHC iron(II) complexes

Recently, the importance of iron, highly abundant with low toxicity, has been recognized for the activation and transformation of organic/inorganic substrates.[88] Grubbs and co-workers in 2000 first reported the use of iron-NHCs in homogeneous catalysis.[89] The catalytic activity of their complexes of the type $[(NHC)_2FeX_2]$ where X = Cl or Br were investigated in atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate. Also, several NHC-based iron catalysts for polymerization reactions were developed by Gibson, Shen and co-workers.[90,91] Fe-NHCs have also found catalytic applications in C-C bond formation, cyclization reactions and transformations.[92-96] Thus, developing new Fe-NHC catalysts is a great opportunity for this emerging field.

Half-sandwich iron complexes of NHCs are known.[97-98] Recently, Tatsumi and co-workers described the activation of C-H bonds of thiophenes, furans and pyridine promoted by a coordinatively unsaturated half-sandwich iron complex containing a metallacycle derived from an NHC.[99] Also, Gao *et al*. have synthesized a novel anionic iron(II) complex $[Fe(IPr)Br_3][HIPr]C_7H_8$ which was found to be effective as a precatalyst in the cross-coupling reaction of aryl Grignard reagents with alkyl halides bearing β-hydrogens under mild reaction conditions.[100] In addition, Kandepi *et al.* have developed new iron(II) complexes containing cyclopentadienyl-functionalized NHC ligands of the general type (Cp-NHC)Fe(CO)I which acted as effective catalysts in a hydrosilylation and transfer hydrogenation reactions.[101]

1.12 Catalytic transfer hydrogenation

The reduction of multiple bonds is a fundamental and useful reaction in organic chemistry, and achieving it with relative ease and selectivity is crucial for organic chemists.[102] Achieving

reduction by the use of an organic molecule as the hydrogen donor; instead of the conventional molecular hydrogen gas is known as transfer hydrogenation.[103] Using an organic molecule as hydrogen source offers a better advantage, providing greater experimental convenience and avoidance of the risk involved with using molecular hydrogen gas which requires specialized apparatus.[102] The properties of the hydrogen donor compound utilized are important factors to consider. The hydrogen donors usually utilized are hydroaromatics, unsaturated terpenes and alcohols. These compounds normally exhibit a low oxidation potential in order to facilitate hydrogen transfer under mild conditions. The choice of the donor compounds depends on the reaction conditions and their availability. Another important factor to consider for the choice of hydrogen donor is the nature of the functional group to be reduced. Thus, alcohols are used as hydrogen donors in the reduction of carbonyl groups.[103]

1.13 Why Fe-NHC chemistry?

Catalysis has become an indispensable tool to humanity because almost all industrial products we rely on today for good livelihood will at least at one stage during the course of production come into contact with a catalyst. In this context by far the most important to both academia and industry is the role of transition metal complexes in catalysis. It is important to develop new and more efficient catalysts and also to understand the mechanisms by which the catalysts act. We decided to work with iron because it is relatively cheap and non-toxic, hence any successful catalyst based on this metal will have a lot of potential both from an economic and environmental consideration. The interest in NHC as a ligand stems from its variability (it can be easily functionalized) and its ability to stabilize the Fe metal in both its high and low oxidation states. In addition the ligand has distinct stability advantages over phospines.[104] Most of the current attention to date has focused on the NHC complexes of the platinum group metals[105] (rhodium, palladium and nickel) plus ruthenium based systems; in fact this is the theme of the 2005 Nobel Prize that was awarded in chemistry. Some of these catalysts such as the Grubb's catalyst[89] have become commercial successes and are widely used in academia and industry. However, the chemistry of NHC systems of iron is considerably less developed.[88] This observation has led to the motivation for this study.

1.14 Aims of this project

The aims of this project are to synthesize Fe-NHC compounds and investigate their catalytic activity in transfer hydrogenation of ketones. This will be achieved by:

- Synthesis of imidazolium salts and their Fe(II) complexes.
- Variation of the substituents on the imidazole ring with the following: alkyl, phenyl and ferrocenyl (both with methyl and phenyl linkers) groups and to investigate their effects on the catalytic transfer hydrogenation of ketones.
- Application of green chemistry principles, wherever possible, in the synthesis of target compounds.
- Study of the electrochemistry of the synthesized ferrocenyl imidazolium salts by cyclic voltammetry to evaluate the link between catalytic activity and electronic properties.
- Catalytic application of the synthesized compounds in transfer hydrogenation of ketones.

1.15 Highlights of the thesis

This thesis focuses on the synthesis of three different series of imidazolium salts, their iron(II) complexes and their catalytic activity in the transfer hydrogenation of ketones. As a result of the format adopted in this thesis, Chapters 2–9 will consist of a series of papers (1-8), in which the referencing style, the numbering of structures, figures, schemes, tables and general presentation vary according to the style specified by the respective journal.

In Chapter 2 (paper 1),[106] the synthesis of 1,3-dialkylimidazolium salts and their iron(II) complexes generated *in situ* is reported. The complexes were fully characterized by spectroscopic and crystallographic methods. An investigation into the catalytic activity of these novel complexes was evaluated in the catalytic transfer hydrogenation of thirteen different ketones with cyclohexanone as the model substrate and they were found to be effective for the activation of the C=O bonds to alcohols.

Furthermore, the synthesis of a second series of imidazolium salts, the 1,3-diarylimidazolium salts, are reported in Chapter 3 (paper 2),[107] with a total of four novel compounds prepared. A solvent-free approach was employed in the synthesis of diimines which are precursors towards the synthesis of the 1,3-diarylimidazolium salts. The application of these imidazolium salts synthesized in paper 2 were investigated in the metal-free transfer hydrogenation of ketones, which is reported in Chapter 4 (paper 3).[108] They were found to provide greener catalytic systems for both saturated and unsaturated ketones, resulting in selective reduction of the C=O and C=C bonds where applicable.

The catalyst efficiency was found to be comparable and in some cases even higher than some established metal-catalysed systems.

Chapter 5 (paper 4)[109] focuses on the synthesis, cyclic voltammetry and catalytic application of ferrocenylimidazolium salts in the transfer hydrogenation of ketones. Nine ferrocenylimidazolium salts containing methyl and phenyl chain linkers were synthesized and characterized by spectroscopic means and four of the compounds were also characterized by crystallographic methods. Their catalytic activity in the transfer hydrogenation of both saturated and unsaturated ketones showed good efficiency even with TON values up to 1880. Their catalytic activity was correlated with the electrochemical properties, determined by cyclic voltammetry. The influence of the chain spacers linking the ferrocenyl to the imidazolium moieties on the electrochemical properties of the salts was evaluated by comparing the relative shifts in the formal electrode potentials ($E_{1/2}$) of the ferrocene/ferrocenium group to that of the ferrocenylimidazolium salts.

Chapter 6 (paper 5)[110] evaluates the reactivity of saturated and unsaturated NHC ligands towards moisture. Two new ionic diamino compounds were synthesized and characterized by spectroscopic and crystallographic methods. The diamino compounds were formed under conditions similar to those used for deprotonation of the imidazolinium salts in order to generate free carbenes prior to complexation with metal precursors. An understanding of the stability of various deprotonated NHC-based imidazolinium cations to attack by moisture resulting in hydrolysis products is very important to understanding the coordination of the ligands on to metal centres. This chapter sheds more light on this undesirable side reaction.

Finally, Chapters 7-9 (papers 6-8)[111-113] describe X-ray structure of compounds produced in this study. Four novel compounds were obtained during various attempts to synthesize the iron(II) NHC complexes reported herein. Chapter 10 entails the summary and final conclusions relating to work described in Chapters 2-9.

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CHAPTER 2

SYNTHESIS AND CATALYTIC ACTIVITY OF NOVEL *N*-HETEROCYCLIC CARBENE IRON(II) COMPLEXES IN TRANSFER HYDROGENATION OF KETONES

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Abstract

Three novel *N*-heterocyclic carbene iron(II) complexes have been synthesized and fully characterized by spectroscopic and crystallographic methods. The complexes were then utilized as catalysts for the transfer hydrogenation of various ketones using 2-propanol as the hydrogen source and KOH as base. They were found to be catalytically active, yielding moderate to excellent conversions to the desired alcohol products. As a result, a simplified one pot system was developed using nine related 1,3-dialkylated imidazolium salts in which the complexes were generated *in situ* and catalytically tested without unnecessary purification steps. Under optimized reaction conditions, all the one pot reactions were found to provide excellent conversions similar to those based on the original isolated complexes.

Keywords

N-heterocyclic carbenes, iron precursors, imidazolium salts, transfer hydrogenation, catalyst, *in situ*, metal complex

2.1 Introduction

N-heterocyclic carbene (NHC) complexes have become important in organometallic chemistry as very active catalysts in the transformations of many organic compounds. Most of the current attention to date has focused on the NHC complexes of noble metals such as platinum [1], while the chemistry of NHC systems of iron, which is relatively inexpensive and non-toxic, is considerably less developed [2]. One of the reasons for this relates to the difficulties encountered in their

synthesis and isolation [3]. Iron(II) NHC complexes are usually prepared *via* the free carbene route [4,5]. They can also be prepared by the reaction of basic metal acetates, alkoxides, or amides with imidazolium salts [6]. Although, transmetallation of NHCs from a silver complex [7] is widely applied for the synthesis of NHC-metal complexes, no reported cases on the adaptation for the preparation of iron based NHC complexes has been recorded.

The success of Buchgraber *et al*. [8] and Mercs *et al*. [9] in the synthesis of piano-stool iron complexes have brought more interest in the synthesis of iron(II) NHC complexes. Tatsumi and co-workers have catalyzed the C-H bonds of thiophenes, furans and pyridine, using unsaturated half-sandwich NHC iron complexes [10]. The application of organometallic and coordination complexes of iron as catalysts for the reduction of carbonyl groups has been explored by several groups. Casey and co-workers, inspired by the bifunctional, ionic hydrogenation catalysis known for ruthenium, recently disclosed the catalytic activity of related iron-cyclopentadienyl complexes [11]. Their catalysts showed high activity for the hydrogenation of several ketones, aldehydes, and imines using molecular H_2 as a reducing agent and also displayed activity in transfer hydrogenation reactions by use of 2-propanol as a hydrogen source. In addition, Kandepi and co-workers have developed new Fe(II) complexes containing cyclopentadienyl-functionalised NHC ligands, which show good catalytic activity in the hydrosilylation of aldehydes and the transfer hydrogenation of ketones [12].

In line with our interest in this family of ligands, we initiated a program aimed at the evaluation of NHC-Fe systems, by developing a simple one pot protocol in which the active catalyst was generated *in situ* followed by catalytic testing. In this report both symmetrical and unsymmetrical 1,3-dialkylated imidazolium salts were utilized and the catalytic activity of the *in situ* generated complexes were tested in the transfer hydrogenation of various ketonic substrates.

2.2 Experimental

2.2.1 General procedures

All manipulations were performed using standard Schlenk techniques under an atmosphere of dry nitrogen. All solvents were dried and purified by standard procedures prior to use. Glasswares were oven dried at 110 ^{o}C. All NMR experiments were done using a 400 MHz Bruker ultrashield spectrometer and samples were dissolved in deuterated chloroform. Infrared spectra for the ligands

were recorded neat using a Perkin Elmer universal ATR Spectrum 100 FT-IR spectrophotometer, while the solution IR data for the complexes were recorded in CH_2Cl_2 on a Perkin Elmer FT-IR spectrophotometer; model RX 1. All low resolution MS samples were run on the Thermo Finnigan Linear ion trap mass spectrometer using electrospray ionization in positive mode. Accurate mass data was obtained on a Thermo Electron DFS Dual focusing magnetic sector instrument using ESI in positive mode; polyethylenimine was used as reference solution. Ligand **2.3** was purchased from Aldrich, while other ligands were synthesized according to a literature method [13]. The preparation of $CpFe(CO)_2I$ was based on a literature procedure [14]. The transfer hydrogenation reaction was monitored by GC analysis with an Agilent capillary gas chromatograph model 6820 fitted with a DB wax polyethylene column (0.25 mm in diameter, 30 m in length), a flame ionization detector and nitrogen gas was used as carrier gas at a flow rate of 2 mL/min. All reagents were purchased from Aldrich or Merck and were used as received.

2.2.2 General procedure for the synthesis of ligands 2.1-2.9

The ligands (except **2.3**) were all synthesized by adaptation of literature methods [13]. A typical and generic procedure is described. Spectroscopic and analyses data are presented. The *N*-monosubstituted azole (0.1 mmol) and dry toluene were placed in a two-neck flask and stirred until a homogeneous solution was formed; then alkyl halide (0.3 mmol) was added drop wise with continuous stirring. After addition of the alkyl halide, the mixture was stirred while heating at 40 ^oC for 24 h. The solvent was removed and dried under vacuum.

2.2.2.1 1,3-dimethylimidazolium iodide (2.1)

A brown solid. Yield 4.80 g, (98%) IR (ATR cm^{-1}): 3433, 3152, 3094, 2953, 1619, 1572, 1341, 1170, 1084, 1020, 826, 748, 617; δ_H (400 MHz, $CDCl_3$): 4.07 (6H, s, NCH_3), 7.35 (2H, s, NCH) and 9.97 ppm (1H, s, CH); δ_C (100 MHz, $CDCl_3$): 37.12 ,123.36 and 137.76 ppm.; m/z (ESI) 96.7 (M^+ - I^-). HRMS (ESI) calcd for $C_5H_9IN_2$, 97.07657 (M^+ - I^-); found, 97.07628 (M^+ - I^-)

2.2.2.2 1-methyl-3-ethylimidazolium bromide (2.2)

White solid. Yield 4.70 g (98%). IR (ATR cm^{-1}): 3065, 2975, 1670, 1571, 1467, 1172, 1101, 856, 789, 649, 789, 621, 417; δ_H (400 MHz, $CDCl_3$): 1.47 (3H, t, *J* 7.3 Hz, CH_3), 3.97 (3H, s, NCH_3), 4.32 (2H, q, NCH_2), 7.54 (2H, s, NCH) and 10.07 ppm (1H, s, CH); δ_C (100 MHz, $CDCl_3$): 15.64,

36.63, 45.18, 122.01, 123.71 and 136.73 ppm.; m/z (ESI) 111.5 (M^+ - Br^-). HRMS (ESI) calcd for $C_6H_{11}BrN_2$, 111.09222 (M^+ - Br^-); found, 111.09196 (M^+ - Br^-).

2.2.2.3 1-methyl-3-butylimidazolium bromide (2.4)

Colourless oil. Yield 1.98 g (91%). IR (ATR cm^{-1}): 3077, 2959, 1626, 1570, 1463, 1166, 1109, 752, 619, 460; δ_H (400 MHz, $CDCl_3$): 0.74 (3H, t, *J* 7.4 Hz, CH_3), 1.18 (2H, m, CH_2), 1.70 (2H, m, CH_2), 3.92 (3H, s, NCH_3), 4.14 (2H, t, NCH_2), 7.42 (1H, s, NCH), 7.53 (1H, s, NCH) and 10.03 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.41, 19.37, 32.11, 36.65, 49.72, 122.29, 123.83, 136.99 ppm; m/z (ESI) 139.4 (M^+ - Br^-) HRMS (ESI) calcd for $C_6H_{11}BrN_2$, 139.12352 (M^+ - Br^-); found, 139.12327 (M^+ - Br^-).

2.2.2.4 1-methyl-3-pentylimidazolium chloride (2.5)

Light yellowish oil. Yield 1.62 g (86%). IR (ATR cm^{-1}): 2929, 2859, 1520, 1466, 1123, 1108, 731, 662; δ_H (400 MHz, $CDCl_3$): 0.82 (3H, t, *J* 7.4 Hz, CH_3), 1.24 (4H, m, CH_2), 1.48 (2H, q, CH_2), 3.52 (2H, t, *J* 6.7 Hz, NCH_2), 3.58 (3H, s, NCH_3), 6.78 (1H, s, NCH), 6.93 (1H, s, NCH) and 7.33 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 14.05, 22.52, 28.04, 32.51, 33.29, 62.36, 125.29, 128.21, 137.73 ppm; m/z (ESI) 153.0 (M^+ - Cl^-) HRMS (ESI) calcd for $C_9H_{17}ClN_2$, 153.13917 (M^+ - Cl^-); found, 153.13877 (M^+ - Cl^-).

2.2.2.5 1,3-diethylimidazolium bromide (2.6)

Colourless oil. Yield 1.34 g (94%). IR (ATR cm^{-1}): 3426, 3066, 2977, 1562, 1448, 1350, 1229, 1164, 1083, 1032, 956, 908, 803, 753, 643; δ_H (400 MHz, $CDCl_3$): 1.40 (6H, t, *J* 7.4 Hz, CH_3), 4.38 (4H, q, NCH_2), 7.45 (2H, s, NCH) and 10.38 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 16.48, 41.96, 129.46, 136.72 ppm; m/z (ESI) 124 (M^+ - Br^-) HRMS (ESI) calcd for $C_7H_{13}BrN_2$, 125.10787 (M^+ - Br^-), found, 125.10700 (M^+ - Br^-).

2.2.2.6 1,3-dibutylimidazolium bromide (2.7)

Colourless oil**.** Yield 1.45 g (80%). IR (ATR cm^{-1}): 3401, 2959, 2874, 1649, 1510, 1462, 1280, 1107, 1080, 1025, 951, 734, 664; δ_H (400 MHz, $CDCl_3$): 0.86 (6H, t, *J* 7.4 Hz, CH_3), 1.27 (4H, m, CH_2), 1.81 (4H, m, CH_2), 4.27 (4H, m, NCH_2), 7.48 (2H, s, NCH) and 10.20 ppm (1H, s, CH), δ_C

(100 MHz, $CDCl_3$): 13.42, 19.40, 32.13, 49.74, 122.22, 136.87 ppm; m/z (ESI) 180.8 (M^+ - Br^-) HRMS (ESI) calcd for $C_{11}H_{21}BrN_2$, 181.17047 (M^+ - Br^-), found, 181.17000 (M^+ - Br^-).

2.2.2.7 1,3-dipentylimidazolium chloride (2.8)

Light yellowish oil. Yield 1.50 g (72%). IR (ATR cm^{-1}): 3291, 3113, 2956, 2929, 2860, 1509, 1465, 1457, 1377, 1284, 1229, 1108, 1078, 1056, 917, 812, 730, 695, 663, 624; δ_H (400 MHz, $CDCl_3$): 0.83 (6H, t, CH_3), 1.70 (4H, m, CH_2), 3.10 (4H, m, CH_2), 3.54 (4H, m, CH_2), 3.85 (4H, t, CH_2), 6.83 (1H, s, NCH), 6.97 (1H, s, NCH) and 7.45 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.78, 22.05, 28.54, 47.07, 62.37, 125.20, 136.88 ppm; m/z (ESI) 208.8 (M^+ - Cl^-) HRMS (ESI) calcd for $C_{13}H_{25}ClN_2$, 209.20177 (M^+ - Cl^-), found, 209.20175 (M^+ - Cl^-).

2.2.2.8 1,3-dihexylimidazolium bromide (2.9)

Light yellowish oil. Yield 2.32 g (99%). IR (ATR cm^{-1}): 3416, 2928, 2859, 1563, 1508, 1459, 1378, 1231, 1162, 1108, 1078, 1056, 917, 812, 728, 642, 562; δ_H (400 MHz, $CDCl_3$): 0.83 (6H, t, *J* 6.8 Hz, CH_3), 1.34 (4H, m, CH_2), 1.73 (4H, m, CH_2), 1.86 (4H, m, CH_2), 2.26 (4H, m, CH_2), 4.28 (4H, t, *J* 7.1 Hz, NCH_2), 7.48 (2H, s, NCH) and 10.36 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.90, 22.37, 31.07, 32.78, 41.02, 50.04, 128.19, 129.01, 137.83 ppm; m/z (ESI) 236.8 (M^+ - Br^-) HRMS (ESI) calcd for $C_{15}H_{29}BrN_2$, 237.23307 (M^+ - Br^-), found, 237.23309 (M^+ - Br^-)

2.2.3 General procedure for the synthesis of iron(II) NHCs complexes 2.10-2.12

To a suspension of the imidazolium salt (1.0 molar equiv) in dry THF (15 ml) was added KOtBu (1.2 molar equiv). After 1 h, this solution was added to a solution of [FeI(Cp)$(CO)_2$] (0.9 molar equiv) in dry toluene (40 ml). After stirring for 20 h, the formed precipitate was separated by centrifugation, washed once with dry toluene (30 ml), and then extracted with dry CH_2Cl_2 (2 x 30 ml). Evaporation of the solvent gave the crude product, which was recrystallized by slow diffusion of hexane into CH_2Cl_2 solution to give an analytically pure sample.

2.2.3.1 (η^5-C_5H_5)Fe$(CO)_2$(ImMe)I (2.10)

This complex was prepared from dimethylimidazolium iodide (0.21 g, 0.90 mmol), KOtBu (0.12 g, 1 mmol), and [CpFe$(CO)_2$I] (0.24 g, 0.8 mmol). The crude product was obtained as a brownish paste. Yield 0.12 g, (53%). IR (CH_2Cl_2, cm^{-1}): 2048, 2000. v(CO); δ_H (400 MHz, $CDCl_3$): 3.92 (6H,

s, CH_3), 5.50 (5H, s, Cp) and 7.27 ppm (2H, s, NCH), δ_C (100 MHz, $CDCl_3$): 40.65, 87.30, 127.04, 163.62, 211.37 ppm; m/z (ESI) 273.3 (M^+- I^-). HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2Fe^+$, 237.03264 (M^+ - I^-), found, 237.03256 (M^+ - I^-).

2.2.3.2 (η^5-C_5H_5)Fe(CO)$_2$(ImMeEt)I (2.11)

This complex was prepared from 1- methyl-3-ethylimidazolium bromide (0.2 g, 1.04 mmol), KOtBu (0.14 g, 1.25 mmol) and [$CpFe(CO)_2I$] (0.28 g, 0.94 mmol) to give a greenish- brown paste which was passed through a column of silica gel. The product was obtained by elution with ethyl acetate – methanol (90:10) to give a green paste. Yield 0.22 g, (57%). IR (CH_2Cl_2, cm^{-1}): 2047, 2000 v(CO); δ_H (400 MHz, $CDCl_3$):1.50 (3H, t, *J* 7.3 Hz, CH_3); 3.94 (3H, s, CH_3), 4.29 (2H, t, CH_2), 5.49 (5H, s, Cp), 7.27(1H, s, NCH) and 7.29 ppm (1H, s, NCH), δ_C (100 MHz, $CDCl_3$): 16.08, 40.71, 47.32, 87.34, 124.16, 127.68, 163.17, 211.25 ppm, m/z (ESI) 287.0 (M^+- I^-). HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2Fe^+$, 287.04829 (M^+ - I^-), found, 287.04815 (M^+ - I^-).

2.2.3.3 (η^5-C_5H_5)Fe(CO)$_2$(I^iPr)I (2.12)

This complex was prepared from 1,3-diisopropylimidazolium tetrafluoroborate (0.30 g, 1.00 mmol), KOtBu (0.14 g, 1.25 mmol) and [$CpFe(CO)_2I$] (0.37 g,1.00 mmol) to give a yellow-powder. Yield 0.31 g (57%). IR (CH_2Cl_2, cm^{-1}): 2049, 2001 v(CO); δ_H (400 MHz, $CDCl_3$):1.54 (12H, d, *J* 6.4 Hz, CH_3); 4.95 (2H, m, CH), 5.45 (5H, s, Cp) and 7.35 ppm (2H, s, NCH), δ_C (100 MHz, $CDCl_3$): 23.2, 53.5, 87.4, 122.4, 161.4, 210.8 ppm; m/z (ESI) 328.7(M^+ - I^-). HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2Fe^+$, 329.09525 (M^+ - I^-), found, 329.09476 (M^+ - I^-).

2.2.4 X-ray crystal determination of compounds 2.10, 2.11 and 2.12

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50kV, 30mA) using the APEX 2 [15] data collection software. The collection method involved ω-scans of width 0.5° and 512 x 512 bit data frames. Data reduction was carried out using the program SAINT+ [15] and face indexed absorption corrections were made using XPREP [15]. The crystal structure was solved by direct methods using SHELXTL. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their

respective parent atoms. Diagrams and publication material were generated using SHELXTL, PLATON [16] and ORTEP-3 [17]. The crystal data and experimental data for **2.10, 2.11** and **2.12** are summarized in Table 2.1.

2.2.5 General Procedure for the transfer hydrogenation of ketones

The samples were typically prepared as follows: The ketone (2.1 mmol), iron (II) NHC catalyst precursor, 0.5 mol-% and KOH (0.112 g, 10 ml, 0.2 M in propan-2-ol) were introduced into a Schlenk tube fitted with a condenser and heated at 82 ^{o}C in an inert atmosphere. The reaction was then monitored by gas chromatography, by taking aliquots at time intervals which was passed through a pad of silica and injecting 0.1 µl into the GC with a DB wax polyethylene column. The corresponding alcohol and acetone were the only products detected in all cases. The identity of the alcohols was assessed by comparison with commercially available (Aldrich Chemical Co.) pure samples. Conversions obtained were calculated from the integration values of the GC peaks which are related to residual unreacted ketone.

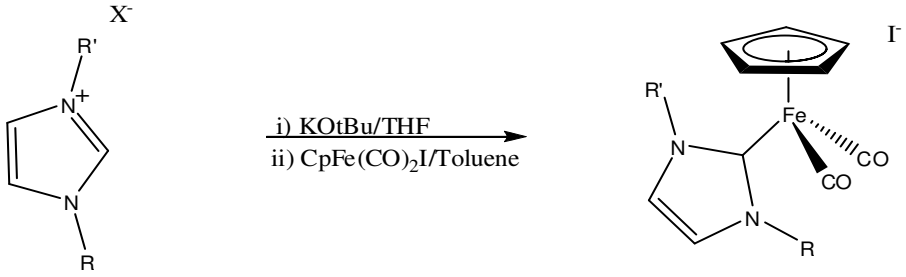
2.3 Results and Discussion

2.3.1 Synthesis and characterization

This study involves the synthesis of a series of symmetrical and unsymmetrical imidazolium based ionic salts (**2.1**-**2.9**) and generation of their piano-stool type iron(II) complexes. The ligands were synthesized by literature adopted methods [13], which involved the addition of an alkyl halide to monoalkylated imidazoles to obtain the imidazolium salts in a high yield. The formation of the imidazolium salts **2.1**-**2.9** was confirmed by ^{1}H and ^{13}C NMR spectroscopy with the appearance of a proton peak around 10.5 ppm for the proton attached to the imidazolium salt carbon atom. The mass spectrum was a source of additional evidence for the formation of the imidazolium salts **2.1**-**2.9**, showing peaks for the [M^{+} - X^{-}] ions for each of the compounds.

Metal complexes **2.10**-**2.12** were synthesized by reacting the iron(II) precursors with the corresponding NHC ligand generated *in situ* as shown in Scheme 2.1. The reaction was easily monitored by infrared spectroscopy. The shift of the CO vibrations for the complexes to higher wavenumbers (2048 and 2000 cm^{-1}) due to coordination of the nucleophilic NHC ligand as compared to those for the iron(II) precursor ($CpFe(CO)_2I$) (1996 and 2001 cm^{-1}) confirmed the

formation of the complexes. Compounds **2.10** and **2.12** were isolated as brown and yellow crystals respectively, while compound **2.11** was further purified by eluting with ethyl acetate/methanol (90:10) to give a brownish green paste which was later crystallized from a saturated solution of dichloromethane to obtained brown crystals. The compounds show good stability at room temperature in both the solid state and in solution. They can also be handled and kept in air without decomposition. The molecular structure and masses of compounds **2.10**-**2.12** were determined by ^{1}H- & ^{13}C- NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction analyses. The ^{1}H & ^{13}C NMR signals of the Cp ring appears at δ 5.45 – 5.51 ppm and δ 87.1 – 87.5 ppm respectively which correspond data found for related compounds reportedearlier [9]. The appearance of a resonance peak at around 161.5 – 164.2 ppm in the ^{13}C NMR spectrum, indicated the formation of the crucial Fe-$C_{(carbene)}$ bond [9]. The positive mode ESI spectra for compounds **2.10**-**2**.**12** show intense peaks corresponding to [M^+ - I^-] ion which further confirmed complex formation.



2.1 R = R' = CH_3 X = I

2.2 R = CH_3, R' = C_2H_5 X = Br

2.3 R = R' = $CH(CH_3)_2$ X = BF_4

2.4 R = CH_3, R' = C_4H_9 X = Br

2.5 R = CH_3 R' = C_5H_{11} X = Cl

2.6 R = R' = C_2H_5 X = Br

2.7 R = R'= C_4H_9 X = Br

2.8 R = R' = C_5H_{11} X = Cl

2.9 R = R' = C_6H_{13} X = Br

2.10 R = R' = CH_3 - (ImMe)

2.11 R = CH_3, R' = CH_2CH_3 (ImMeEt)

2.12 R = R' = $CH(CH_3)_2$, (I^iPr)

Scheme 2.1. Synthesis of NHCs iron(II) complexes

2.3.2 Molecular structures of compounds 2.10, 2.11 and 2.12

Crystals suitable for X-ray analysis for compounds **2.10** and **2.12** were obtained by slow diffusion of hexane into a saturated solution of dichloromethane at room temperature, while crystals of compound **2.11** were obtained as described above. The solid state structures of **2.10-2.12** are shown as Ortep diagrams in Figs. 2.1 – 2.3 respecively. A summary of the crystal data and refinement parameters are presented in Table 2.1, while selected bond lengths and angles are tabulated in Table 2.2. The molecular structure reveals piano-stool NHC ionic complexes with iodide as the counter anion. The bond length for the Fe-$C_{(carbene)}$ for **2.11** and **2.12** are similar and were obtained as: 1.972(2) and 1.972(8) Å respectively. These are almost similar to the same bond length for compound **2.10**, 1.969(9), which can be attributed to a slightly enhanced electron donor effect of the ethyl over a methyl substituent. These Fe-$C_{(carbene)}$ bond distances fit well in the 1.97-1.99 Å range of related monodentate piano stool iron(II) complexes [8,9] yet are significantly shorter than in tetrahedral high-spin complexes (typically 2.07-2.13 Å) [4a]. Compounds **2.10** and **2.12** have similar bond angles for CO-Fe-$C_{(carbene)}$ at 95.05(19) and 94.9(4)° respectively, which are larger than that of compound **2.11**, 91.33(10)°. This can be attributed, perhaps, to the different conformations of the ethyl substituents of the NHC ligand in the solid state.

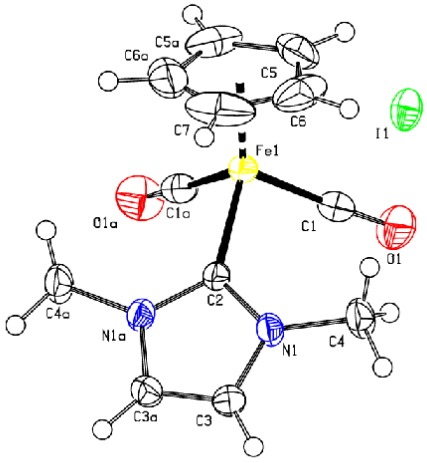


Fig. 2.1 ORTEP diagram of compound **2.10** shown at 50% probability thermal ellipsoids.

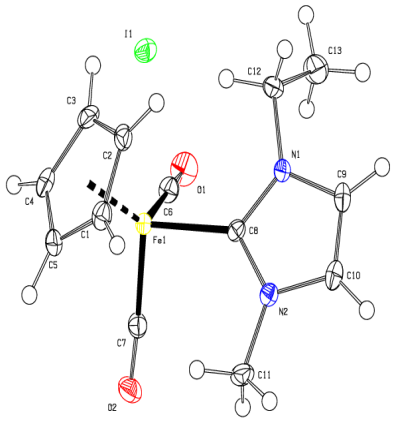


Fig 2.2. ORTEP diagram of compound **2.11** shown at 50% probability thermal ellipsoids

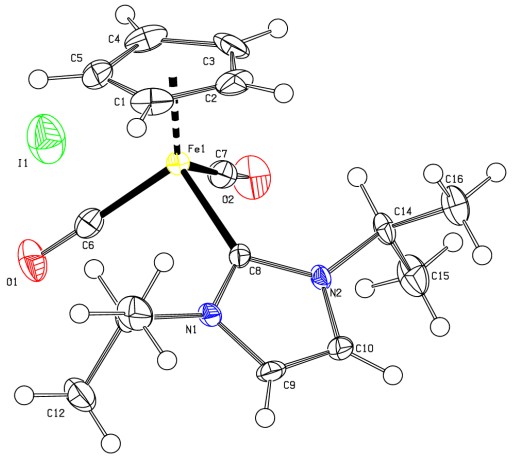


Fig. 2.3 ORTEP diagram of compound **2.12**
shown at 50% probability thermal ellipsoids

Table 2.1

Summary of the crystal data and refinement parameters of compounds **2.10**, **2.11** and **2.12**.

Compound	**2.10**	**2.11**	**2.12**
Formula	$C_{12}H_{13}FeIN_2O_2$	$C_{13}H_{15}FeIN_2O_2$	$C_{16}H_{21}FeIN_2O_2$
Formula weight	399.99	414.02	456.10
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pmn*2_1	*P*2_1/c	*P*-1
a, Å	15.1440(7)	10.0123(6)	9.0524(3)
b, Å	6.6844(3)	9.8060(6)	10.2842(3)
c, Å	14.0118(6)	15.4172(8)	10.2882(3)
α deg	90	90	89.086(2)
β, deg	90	92.1350(10)	75.128(2)
γ, deg	90	90	79.328(2)
Cell volume, $Å^3$	1418.39(11)	1512.62(15)	909.20(5)
Z	4	4	2
D_{calcd}, Mg/m^3	1.873	1.818	1.666
T, K	173(2)	100(2)	173(2)
μ, mm^{-1}	3.235	3.037	2.534

Wavelength, Å	0.71073	0.71073	0.71073
F(000)	776	808	452
Cryst size, mm^3	0.40 x 0.27 x 0.22	0.11 x 0.08 x 0.03	0.28 x 0.09 x 0.05
θ_{min},θ_{max}, deg	1.98 to 28.00	2.04 to 28.57	2.02 to 28.00
no. of reflns. collected	7328	34051	12415
No of indep. Reflns.	3399[R(int)] = 0.0370	3858 [R(int)] = 0.0475	4388[R(int)]= 0.0724
Completeness to theta	100% (28.57^o)	99.7% (28.00^o)	100% (28.00)
Absorbed correction	Integration	Semi empiricial from equivalent	Integration
Goodness-of-fit on F^2	1.026	1.026	0.964
Final R indices	0.0287, 0.0635	0.0235, 0.0495	0.0713, 0.1989
R indices (all data)	0.0328, 0.0650	0.0341, 0.0537	0.1252, 0.2281
Largestdiff.peak& hole,e. $Å^{-3}$	0.664 & -0.533	0.606 & -1.095	2.743 &-1.077

Table 2.2

Selected bond length (Å) and angle (^{o}) for compounds **2.10**, **2.11** and **2.12**.

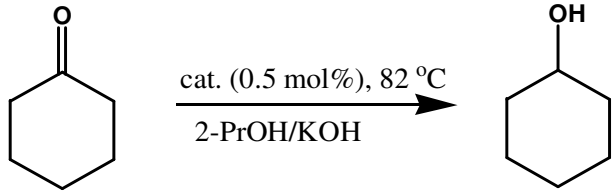
	2.10	**2.11**	**2.12**
Bond lengths			
Fe-Centroid	1.940(5)	2.108(2)	2.106(9)
Fe-C6	1.777(5) (Fe-C1a)	1.777(2)	1.779(9)
Fe-C7	1.777(5) (Fe-C1)	1.773(2)	1.787(9)
Fe-C8	1.969(6) (Fe-C2)	1.972(2)	1.972(8)
C6-O1	1.144(5) (C1a-O1a)	1.380(3)	1.133(10)
C7-O2	1.144(5) (C1-O1)	1.145(3)	1.132(11)
Bond angles			
C6-Fe-C7	93.4(3) (C1a-Fe-C1)	92.20(11)	92.70(2)
C6-Fe-C8	95.05(19) (C1a-Fe-C2)	91.33(10)	94.30(3)
C7-Fe-C8	95.05(19) (C1-Fe-C2)	96.30(10)	94.90(4)
N1-C8-N2	104.2(5) (N1a-C2-N1)	104.38(19)	104.0(6)

2.3.3 Catalytic transfer hydrogenation

The application of compounds **2.10**, **2.11** and **2.12** as catalysts were evaluated in the transfer hydrogenation of ketones. The transfer hydrogenation of cyclohexanone with propan-2-ol as hydrogen transfer agent was used as a model reaction. All the complexes were found to show activity, with best conversion obtained for compound **2.11** (Table 2.3).

Table 2.3

Catalytic Transfer Hydrogenation catalyzed by complex **2.10**, **2.11** and **2.12**.



Catalyst	Substrate	%Conversion[c]	Time (h)	TOF[b]	TON[a]
2.10	cyclohexanone	82	11	15	164
2.11	cyclohexanone	100	9	22	200
2.12	cyclohexanone	91	9	20	182

[a]Turnover number = mol product/mol catalyst
[b]Turnover frequency = mol product/ (mol catalyst x time), determined after time t
[c] Conversion was determined by GC analysis

In order to optimize the reaction, the following parameters were investigated:

- Concentration: the best results were obtained with solutions of 0.5 M concentration.
- Temperature: the optimum result was obtained at 82 °C, at room temperature no reaction occurred, and at temperatures above 100 °C, the reaction rate declined due to decomposition of the catalyst system (Fig. 2.4).
- Time: 12 h is the optimum time; the conversion tends to remain constant beyond this time as illustrated in Fig. 2.4**.**

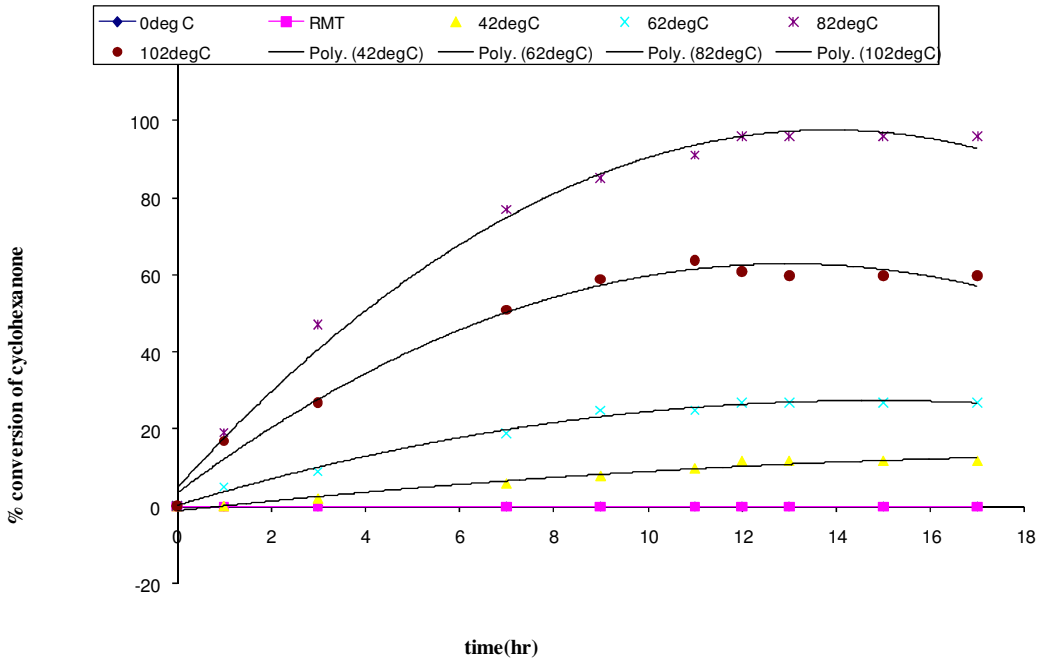


Fig. 2.4 The effect of temperature variation on the conversion of cyclohexanone over time in a one pot process based on ligand **2.3**.

We were also interested in simplifying the catalytic testing process by generating the catalyst *in situ* and testing them in the same pot without laborious and wasteful purification steps. This was achieved by using the imidazolium salts and the iron(II) precursor ($CpFe(CO)_2I$), a methodology that presents significant practical advantages for homogeneous catalysis especially given the fact that the active specie may be quite reactive and relatively unstable. Thus, in a typical experiment, freshly distilled iPrOH was added to the iron(II) precursor and the imidazolium salts (0.5 mol%) and the mixture was stirred for 1 h. This was then followed by the addition of KOH and the ketone and the reaction mixture was heated to 82 ^{o}C for 12 h. Progress of the reaction was monitored by gas chromatography.

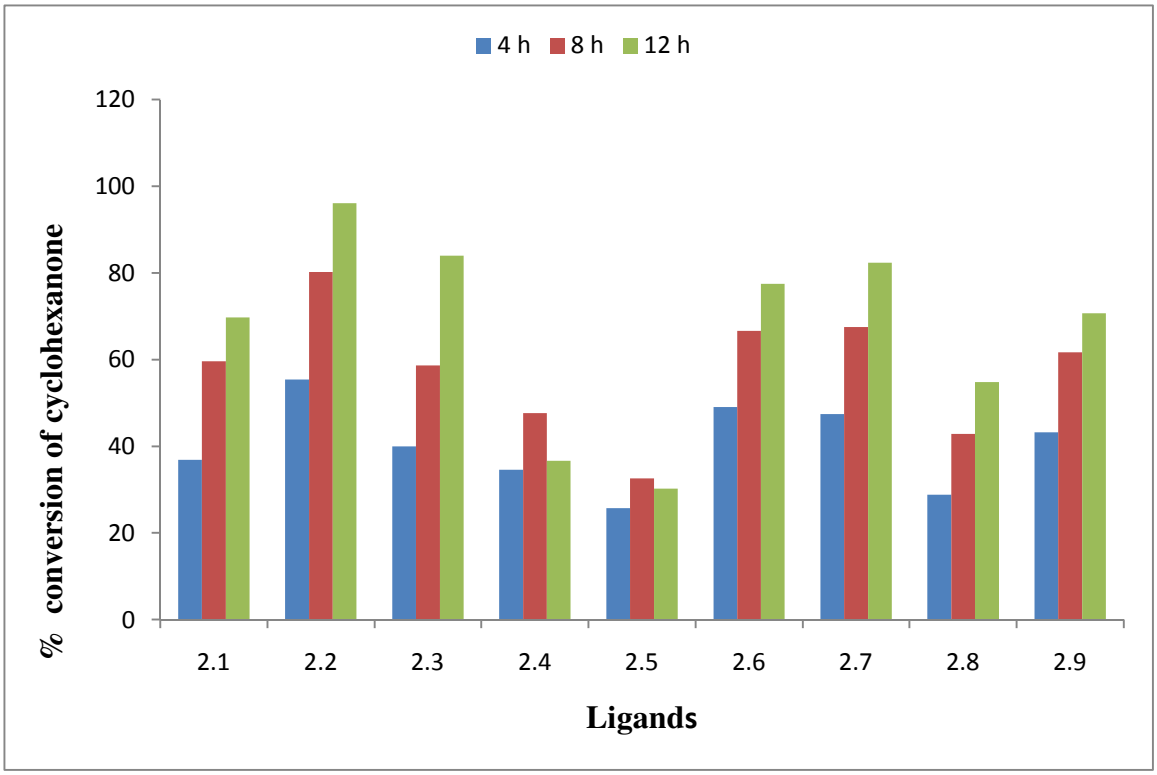


Fig 2.5 One pot conversion of cyclohexanone using imidazolium salts **2.1**-**2.9**.

In a blank test based on $CpFe(CO)_2I$ without the ligands using the optimized reaction condition obtained above (refluxing at 82 ^oC for 12 h with 0.5 mol% of the iron precursor as the catalyst), 46% conversion to cyclohexanol was recorded for the iron(II) precursor. In the absence of base (KOH), there was no reaction. When only the base (KOH, 2 mmol) without the catalyst was utilized in the transfer hydrogenation of cyclohexanone, 32% conversion was obtained after 12 h.

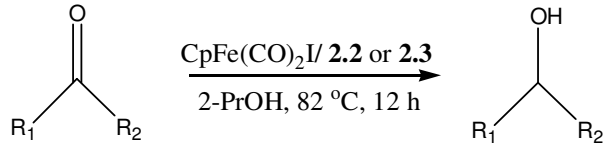
Nine different NHC ligands (**2.1**-**2.9**) were applied in *in situ* catalytic transfer hydrogenation using the optimized condition. Ligand **2.2** and **2.3** gave the best conversions after 12 h (Fig. 2.5). Interestingly the structurally unsymmetrical catalysts **2.4** and **2.5** with longer carbon chains show a decline in % conversion at any particular temperature. This can be attributed to the increase in one of the *N*-alkyl side chain over the other in ligand **2.4** and **2.5**, causes a distortion in their structure. Dong *et al*. observed that when the *N*-alkyl side chains of their imidazolium salts increases, the interaction energies between the counter anions and the cation decreases [18]. Also, there is a possibility that the ligands **2.4** and **2.5** are unstable under basic condition leading to decomposition [19].

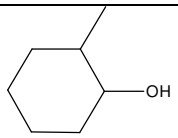
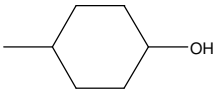
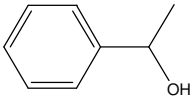
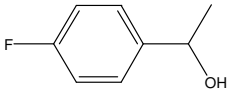
As a result of the high catalytic activity of ligands **2.2** and **2.3**, they were then employed in catalytic transfer hydrogenation of thirteen aromatic and aliphatic ketones selected to test the range and generality of the catalysis on a range of substrates that differ electronically and have a variety of steric demands. Best activity (TON up to 184) is achieved with aromatic ketones having *para*-substituents. The result showed better TON values as compared with results for iron [12] and ruthenium [20] NHC complexes published earlier. Noteworthy is the fact that changing the chlorine *para* substituted to acetophenone, with a more electron withdrawing fluorine atom causes a reduction in the % conversion (Table 2.4, entry 4 and 5). This can be attributed to the inductive effect (positive or negative) of the group *para* to the aromatic ketonic bond which is an important factor in determining the extent of the reaction.

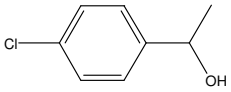
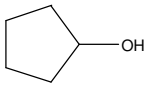
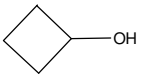
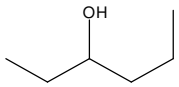
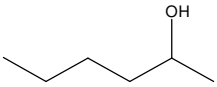
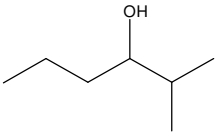
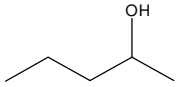
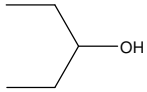
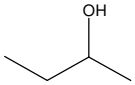
In general, catalytic activity of ligands **2.2** and **2.3** show similar trend except for a few obvious differences (Table 2.4, entry 7 and 13). In addition alkyl ketones which are usually difficult to reduce were also converted to their corresponding alcohols by this catalytic system. Ligand **2.3** gave better results, in general, in comparison to ligand **2.2**.

Table 2.4

One pot Fe- catalyzed reduction of various ketones in the presence of imidazolium salts **2.2** and **2.3**.



Entry	product	2.2 yield (%)	TON (2.2)	2.3 Yield (%)	TON (2.3)
1		28	56	45	90
2		87	174	92	184
3		55	110	68	136
4		49	98	33	66

5		83	166	89	178
6		32	64	50	100
7		17	34	100	200
8		10	20	No reaction	-
9		21	42	27	54
10		3	6	2	4
11		39	78	60	120
12		29	58	12	24
13		84	168	46	92

2.4 Conclusion

Both symmetrical and unsymmetrical 1,3-dialkylimidazolium salts have been successfully synthesized. Similarly, iron(II) complexes of the general type $[CpFe(CO)_2(NHC)]I$ were also successfully synthesized and characterized spectroscopically and by crystallography. The activity of the new complexes as catalysts generated *in situ* in a one pot reaction was tested in hydrogen transfer reactions. The results have revealed the simplicity of this method and the efficiency of the *in situ* generated catalysts in the transfer hydrogenation of fourteen ketones in the presence of 2-propanol as the hydrogen source.

Supplementary Material

Crystallographic data in cif format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 844526-844528 for compounds **2.10-2.12** respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or http:// www.ccdc.cam.ac.uk.

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CHAPTER 3

A GREENER METHOD TOWARDS THE SYNTHESIS OF 1,3-DIARYLIMIDAZOLIUM TETRAFLUOROBORATES

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Submitted by invitation to celebrate 2011 - the "International Year of Chemistry"

Abstract

A new strategic method for the synthesis of 1,3-diarylimidazolium tetrafluoroborate salts is illustrated herein. A solvent-free approach was employed in the synthesis of the diimines which are precursors in the preparation of the imidazolium salts. The reaction proceeds faster, cleaner and in a better yield than previously reported methods.

Keywords

Diimines, imidazolium salts, NHC-metal ligand precursors, solvent-free, synthesis.

3.1 Introduction

The organic compounds 1,3-diarylimidazolium tetrafluoroborates are imidazolium salts (IMSs), which have received much attention[1-,3] due to their wide applications, notably in medicine.[4] Zhao and co-workers[5] have successfully used IMSs as mild reducing agents in the production of ultrafine gold nanoparticles and as radical scavenger antioxidants to counter the damage caused by reactive oxygen species in the body. They have also found wide application in biofuel chemistry[6] and the petroleum industry,[6] as an alternative source of energy. Their use as ionic liquids[7] and as solvents[8] for many organic reactions is also an advantage. In addition, IMSs are precursors to *N*-heterocyclic carbenes (NHCs),[9] which today have become ubiquitous ligands in organometallic chemistry after the isolation of the first stable NHCs by Arduengo.[10] Numerous studies have confirmed NHC-metal complexes as highly efficient catalysts when compared to the corresponding phosphine-metal analogues.[11] From established data on the electronic and steric influence of a broad range of NHC

ligands, their catalytic performance may be systematically studied and optimized by ligand tuning.[12-17] In addition, superior properties of NHCs when compared with traditional phosphine ligands, which amongst others include: ease of preparation, non-toxicity, air and moisture stability, low loading and high efficiency in catalysis have further established the chemistry of NHC compounds.[18]

Since the deprotonation of imidazolium salts[9] has been established as the easiest and the most commonly utilised method for the synthesis of NHCs, it is therefore essential that new, simple and high yielding methods for the synthesis of the salts are developed.[19-21] Towards this effort, Arduengo and co-workers'[22] method of reacting glyoxal, formaldehyde, substituted aniline, and an acid in a one-pot synthesis, is arguably the most adopted method, but it can only be used for the synthesis of some imidazolium salts and also the product requires extensive washing to obtain an analytically pure sample, which usually resulted in low product yields.[23,24]

In an effort to improve the one-pot procedure, both the groups of Arduengo[23] and Nolan[25] have modified it so that it can be extended to more imidazolium salts especially the sterically hindered ones, in order to improve product yields and reduce tedious product purification procedures.[22] To obtain their imidazolium salts they started with glyoxal imines and used chloromethyl ether and HCl/dioxane as a source of counter-ions. In addition to obtaining a low yield, the toxicity of the reagents and long reaction times are key disadvantages of this method.[25,26]

Later on, Leuthaußer and co-workers[27] have modified Nolan's method by introducing electron withdrawing/donating groups to two of the most commonly applied NHC ligands (*N,N'*-bis(2,6-dimethylphenyl)imidazol-2-ylidene and *N,N'*-bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene); thus, allowing the systematic tuning of the electron density of the metal bonded to the NHC ligands. The diimines were obtained by reaction of the corresponding anilines and glyoxal in ethanol as the solvent, with overnight stirring. This was then followed by ring closure with HCl/dioxane to obtain their imidazolium salts. The HCl/dioxane mixture is a very hazardous/toxic and expensive counter ion source.

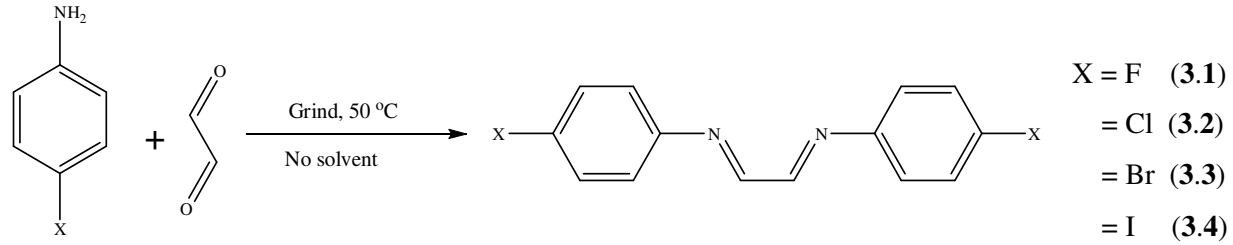
The synthesis of 1,3-diarylimidazolium salts possessing only halides substituted at the *para*-position has been reported by a few authors.[9,28] The salts were prepared by reacting glyoxal, formaldehyde, substituted aniline and an acid (in most cases HCl) as the source of counter-ions. Recently, Garden

et al.,[29] were the first to elucidate the crystal structure of 1,3-bis(4-bromophenyl)imidazolium chloride which was isolated as a dihydrate. A slight modification of Hintermann's method[30] was employed in their synthesis.

Here we report a novel method for the synthesis of 1,3-diarylimidazolium tetrafluoroborates by employing a solvent-free approach for the synthesis of the precursor diimines, which proceeds faster, cleaner and in a better yield than the aforementioned procedures. This reaction (without solvent) can be deemed 'green', is simple and occurs readily under mild conditions. To our knowledge, the solvent-free approach has not been applied before for the synthesis of diimines, which are precursors to imidazolium salts. To obtain the 1,3-diarylimidazolium tetrafluoroborates from the diimines, the ring closure reaction was conducted in the presence of a solvent due to experimental challenges encountered with the solvent-free method for this step. However, we used the milder tetrafluoroboric acid as the source of the counter-ion.

3.2 Results and Discussion

Diimines as precursors to imidazolium salts are usually prepared by heating a solution of the corresponding aniline and glyoxal in anhydrous methanol[30] or ethanol.[27] We utilized this method with dry methanol as the solvent, but did not obtain a very good yield of the desired product. This is due to the thermal and moisture sensitivity of the diimines. To overcome the problem and in keeping with the principles of green chemistry,[31] a solvent-free approach was employed in the synthesis of the diimines.[32] The compounds were synthesized via the route shown in Scheme 3.1. This involves reacting the corresponding aniline (2 equiv) with glyoxal (1 equiv) using a solvent-free reaction technique. In this method, the corresponding aniline and glyoxal mixture was ground in a mortar, placed in a flask and heated to about 50 °C to melt the mixture. This was left under vacuum until it solidified at room temperature. The reactions proceeded rapidly and were complete within a few minutes. The only exception was for compound **3.1** which took a longer time to complete. This is due to the *para* substituent on the aniline utilized in the synthesis of compound **3.1**. Fluorine being the most electronegative halide, exhibited the highest negative inductive effect on the aniline. Hence, it decreases the susceptibility to nucleophilic attack, and thus the reaction time is relatively longer when compared to other *para*-haloanilines.



Scheme 3.1 Synthesis of diimines by the solvent-free method.

This new method avoids the problem of decomposition associated with heating/reflux and the sensitivity of diimines to moisture/impurities from solvents such as methanol or ethanol, normally used in the majority of cases for their synthesis. The products (compounds **3.1**- **3.4**) were purified by minimal washing with cold anhydrous diethyl ether in order to remove unreacted aniline used in the reaction. Other solvents such as ethanol, which is considered relatively 'green', were also used in the purification of the diimines, but diethyl ether gave the best result.

The solidified melt was analysed by infrared spectroscopy to ascertain the formation of the diimines. The strong band associated with glyoxal (CO) which usually resonates around 1700 cm^{-1} was absent and was replaced by a strong absorption band at 1596 cm^{-1}, which corresponds to the normal peak region for an imine bond (C=N).[33] Further confirmation of the formation of compounds **3.1**-**3.4**, was obtained by ^{1}H and ^{13}C NMR spectroscopic analysis. The appearance of resonances at 8.34, 8.37, 8.32, 8.32 ppm in the ^{1}H NMR spectra for compounds **3.1**-**3.4** respectively**,** correspond to the imine protons (imi-H) (**Figure 3.1**). This was further confirmed by the ^{13}C NMR peak at around 159 ppm assigned to the imine carbon (imi-C) (**Figure 3.1**).

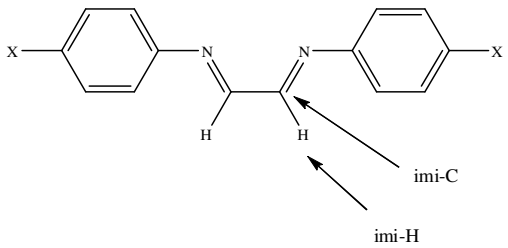
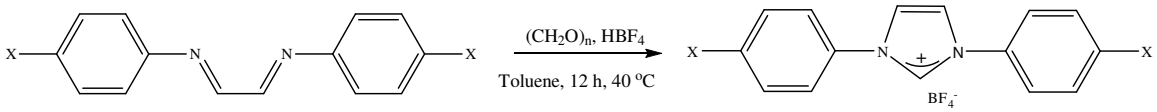


Figure 3.1 The positions of the imine proton and carbon, denoted as imi–H and imi-C, respectively.



X = F (**3.5**)
= Cl (**3.6**)
= Br (**3.7**)
= I (**3.8**)

Scheme 3.2. Synthesis of the 1,3-diaryl imidazolium tetrafluoroborates.

The reaction of the corresponding diimines (**3.1-3.4**) with paraformaldehyde and tetrafluoroboric acid (Scheme 2.1) was used as the source of counter ions in the ring closure reaction to form the corresponding 1,3-diarylimidazolium salts (**3.5**-**3.8**). Compounds **3.5**-**3.8** were found to be solids at room temperature with sharp melting points (see Experimental section for details).

^{1}H NMR analyses for compounds **3.5-3.8** (the general structure is shown on Figure 3.2**)** were performed and data for the imidazole proton (imd-H) chemical shift is recorded in Table 3.1. The gradual downfield increase of the imd-H chemical shifts may be associated with the gradual decrease in the electron withdrawing ability and hence inductive effect of the halide substituents. Thus, the chemical shift of the iodine bearing compound **3.8** has the most downfield chemical shift at 10.51 ppm for the imd-H as compared to 10.28 ppm for the fluoride bearing compound **3.5**. The use of tetrafluoroboric acid as a source of counter ions instead of the expensive HCl/dioxane[18,19] mixture leads to a reliable synthetic procedure for the synthesis of compounds **3.5**-**3.8**.

Table 3.1

The effect of variations in the *para*-halogen substituent on the imidazolium salts.

Compounds	Melting point / °C	% Yield	^{1}H-NMR (imd-H*)/ ppm
3.5	205	76	10.28
3.6	186	71	10.35
3.7	180	67	10.36
3.8	160	62	10.51

* Chemical shift of imidazole proton as indicated alongside.

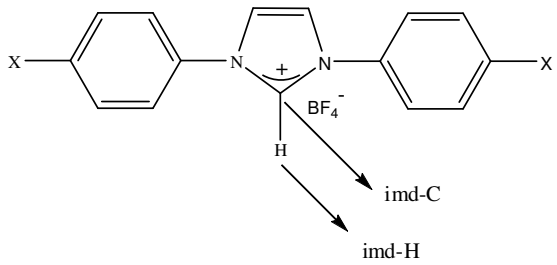


Figure 3.2 The positions of the imidazole proton and carbon, denoted as imd–H and imd-C, respectively.

3.3 Conclusion

A new synthetic strategy has been devised for the preparation of 1,3-diarylimidazolium tetrafluoroborates from diimines in excellent yields. The diimines were synthesized using solvent-free conditions and purified by solvent washing. This approach is faster, simpler and more atom economical as compared to other previously reported methods. The four novel imidazolium tetrafluoroborate salts were synthesized from starting materials that are readily available, especially the substituted aniline.

3.4 Experimental

3.4.1 General procedures

The syntheses of the 1,3-diarylimidazolium tetrafluoroborates were performed under a nitrogen atmosphere and the solvents were dried by using standard literature methods. In the case of the solvent-free reactions, grinding and all work-up procedures were done open to air. Reagents were purchased from Aldrich and were used as received. Infrared spectra were recorded with a PerkinElmer Universal ATR Spectrum 100 FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a 400 MHz Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform or deuterated dimethylsulpfoxide. Mass spectra were recorded with an Agilent Technologies, 1100 series, mass spectrometer, which was equipped with an ion trap with quadrupole analyzer and electron multiplier detector. Accurate mass data for the imidazolium salts were obtained on a Thermo Electron DFS Dual focusing magnetic sector instrument using ESI in

positive mode; polyethylenimine was used as reference solution. Melting points were recorded on a Bibby Stuart Scientific model SMP3 apparatus and were uncorrected.

3.4.2 General procedure for the synthesis of diimines

The corresponding aniline (1 equiv.) was ground in a mortar with glyoxal (0.5 equiv). The mixture was then transferred to a round-bottom flask and heated to 50 °C until it had melted and left under vacuum to solidify. It was then washed with dry cold diethyl ether to remove unreacted aniline.

3.4.2.1 1,3-Bis(4-fluorophenyl)ethylenediimine (3.1)

Starting materials used were 4-fluoro aniline (10.0 g, 90.0 mmol) and glyoxal (2.61 g, 45.0 mmol). Yield: 10.2 g; 93%, m.p. 81.6 °C; IR (ATR cm^{-1}): 3337, 3009, 2952, 1506, 1402, 1295, 1223, 1120, 1013, 1058, 987, 939, 819, 766, 612, 522; δ_H (400 MHz, $CDCl_3$): 7.11 (4H, d, *J* 8.5 Hz, Ar-H), 7.29 (4H, d, *J* 8.9 Hz, Ar-H) and 8.34 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 116.14, 122.83, 145.76, 159.01 and 163.41 ppm; m/z (ESI), **Obtained** 245.3 (M^+) **Calculated** for $C_{14}H_{10}N_2F_2$ 245.1 (M^+).

3.4.2.2 1,3-Bis(4-chlorophenyl)ethylenediimine (3.2)

Starting materials used were 4-chloro aniline (10.0 g, 78.0 mmol) and glyoxal (2.26 g, 39.0 mmol). Yield: 9.40 g, 88%; m.p. 119.7 °C; IR (ATR cm^{-1}): 3338, 3009, 2952, 1596, 1492, 1402, 1254, 1080, 988, 828, 766, 611, 522; δ_H (400 MHz, $CDCl_3$): 7.27 (4H, d, *J* 8.4 Hz, Ar-H), 7.42 (4H, d, *J* 8.6 Hz, Ar-H) and 8.37 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 122.60, 129.59, 133.81, 148.38 and 159.85 ppm; m/z (ESI), **Obtained** 277.3 (M^+) **Calculated** for $C_{14}H_{10}N_2Cl_2$ 277.2 (M^+).

3.4.2.3 1,3-Bis(4-bromophenyl)ethylenediimine (3.3)

Starting materials used were 4-bromo aniline (1.00 g, 5.80 mmol) and glyoxal (0.170 g, 2.90 mmol) Yield: 0.900 g, 85%; m.p. 120.6 °C; IR (ATR cm^{-1}): 3338, 3009, 2952, 1596, 1492, 1402, 1254, 1080, 988, 828, 766, 611, 522; δ_H (400MHz, $CDCl_3$): 7.16 (4H, d, *J* 8.6 Hz, Ar-H), 7.52 (4H, d, *J* 8.8 Hz, Ar-H) and 8.32 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 116.70, 122.91, 132.77, 148.88 and 159.94 ppm; m/z (ESI), **Obtained** 365.2 (M^+) **Calculated** for $C_{14}H_{10}N_2Br_2$ 365.4 (M^+).

3.4.2.4 1,3-Bis(4-iodophenyl)ethylenediimine (3.4)

Starting materials used were 4-iodo aniline (10.0 g, 45.7 mmol) and glyoxal (1.33 g, 22.9 mmol). Yield: 8.51 g, 81%; m.p. 157.1 °C; IR (ATR cm^{-1}): 3337, 2952, 1585, 1486, 1395, 1294, 1121, 1059, 987, 959, 8278, 766, 614, 522; δ_H (400 MHz, $CDCl_3$): 7.02 (4H, d, *J* 8.5 Hz, Ar-H), 7.74 (4H, d, *J* 8.7 Hz, Ar-H) and 8.32 ppm (2H, s, CH); δ_C (100 MHz, $CDCl_3$): 93.16, 123.12, 138.56, 149.54 and 159.98 ppm; m/z (ESI), **Obtained** 461.1 (M^+) **Calculated** for $C_{14}H_{10}N_2I_2$ 461.0 (M^+).

3.4.3 General procedures for the synthesis of imidazolium tetrafluoroborates

The diimines synthesized above were dissolved in 10 ml of toluene at 10 °C. To each of these were added 1 molar equivalent of paraformaldehyde with vigorous stirring. After 30 min, the solutions were cooled to 0 °C and an aqueous solution of HBF_4 (40%, 1.0 equiv) was added dropwise to each. The resulting solutions were stirred at room temperature for further 30 min and then heated to 40 °C for 12 h. After cooling to room temperature, diethyl ether (10 ml) was added and the slurries filtered, washed with ethyl acetate and tetrahydrofuran and vacuum dried.

3.4.3.1 1,3-Bis(4-fluorophenyl)imidazolium tetrafluoroborate (3.5)

The starting materials used were 1,3-bis(4-fluorophenyl)ethylenediimine (3.00 g, 12.3 mmol), paraformaldehyde (0.357 g, 12.3 mmol), aqueous solution of HBF_4 (40%, 12.3 mmol, 1.08 g, 0.82 ml). Light brown powder, in a .yield of 4.20 g, 75%; m.p. 204.8 °C; IR (ATR cm^{-1}): 3163, 1562, 1511, 1255, 1242, 1161, 1082, 1036, 943, 831, 751, 520; δ_H (400 MHz, [D_6]DMSO): 7.60 (4H, d, *J* 8.7 Hz, Ar-H), 7.96 (4H, d, *J* 9.0 Hz, Ar-H), 8.52 (2H, s, NCH) and 10.28 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 117.97, 122.13, 124.72, 131.13, 135.04 and 163.64 ppm; m/z (ESI): **Obtained** 257.3 (M^+ - BF_4^-) **Calculated** for $C_{15}H_{11}N_2F_2BF_4$ 257.1 (M^+ - BF_4^-); **HRMS** calculated for $C_{15}H_{11}N_2F_2BF_4$, 257.08903 (M^+ - BF_4^-), found 257.08907.

3.4.3.2 1,3-Bis(4-chlorophenyl)imidazolium tetrafluoroborate (3.6)

The starting materials used were 1,3-bis(4-chlorophenyl)ethylenediimine (2.00 g, 7.20 mmol), paraformaldehyde (0.210 g, 7.20 mmol), aqueous solution of HBF_4 (40%, 7.20 mmol, 0.630 g, 0.5 ml). Light yellow powder in a yield of 3.20 g, 76%; m.p.186.2 ◦C; IR (ATR cm^{-1}): 3326, 2957, 1590, 1491, 1401, 1295, 1122, 1059, 1015, 988, 960, 827, 617, 592, 523; δ_H (400 MHz, [D_6]DMSO): 7.82 (4H, d, *J* 8.7 Hz, Ar-H), 7.93 (4H, d, *J* 8.8 Hz, Ar-H), 8.55 (2H, s, NCH) and 10.35 ppm (1H, s, CH); δ_C (100 MHz, [D_6]DMSO): 121.94, 123.87, 130.14, 133.46, 134.60 and

135.05 ppm; m/z (ESI): **Obtained** 289.3 (M^+ - BF_4^-). **Calculated** for $C_{15}H_{11}N_2Cl_2BF_4$ 289.0 (M^+ - BF_4^-); **HRMS** calculated for $C_{15}H_{11}N_2Cl_2BF_4$, 289.02993 (M^+ - BF_4^-), found 289.05271.

3.4.3.3 1,3-Bis(4-bromophenyl)imidazolium tetrafluoroborate (3.7)

The starting materials used were 1,3-bis(4-bromophenyl)ethylenediimine (0.200 g, 0.546 mmol), paraformaldehyde (0.016 g, 0.546 mmol), aqueous solution of HBF_4 (40%, 0.546 mmol, 0.048 g, 0.034 ml). Light brown powder in a yield of 0.134 g, 67%; m.p. 180 °C; IR (ATR cm^{-1}): 3455, 3397, 3323, 3079, 2925, 1706, 1553, 1423, 1220, 1002, 821, 749, 620, 519, 435; δ_H (400 MHz, $[D_6]$DMSO): 7.87 (4H, d, *J* 8.9 Hz, Ar-H), 7.93 (4H, d, *J* 8.9 Hz, Ar-H), 8.55 (2H, s, NCH) and 10.36 ppm (1H, s, CH); δ_C (100 MHz, $[D_6]$DMSO): 121.89, 123.07, 124.07, 133.07, 133.88 and 134.94 ppm; m/z (ESI), **Obtained** 379.2 (M^+ - BF_4^-). **Calculated** for $C_{15}H_{11}N_2Br_2BF_4$ 379.1 (M^+ - BF_4^-); **HRMS** calculated for $C_{15}H_{11}N_2Br_2BF_4$, 378.92685 (M^+ - BF_4^-), found 378.92585

3.4.3.4 1,3-Bis(4-iodophenyl)imidazolium tetrafluoroborate (3.8)

The starting materials used were 1,3-bis(4-iodophenyl)ethylenediimine (0.300 g, 0.655 mmol), paraformaldehyde (0.019 g, 0.655 mmol), aqueous solution of HBF_4 (40%, 0.655 mmol, 0.058 g, 0.04 ml). Light brown powder in a yield of 0.22 g, 62%; m.p. 160 °C; IR (ATR cm^{-1}): 3327, 2954, 1588, 1486, 1399, 1295, 1122, 1015, 1059, 939, 988, 829, 767, 616, 592, 523; δ_H (400 MHz, $[D_6]$DMSO): 7.84 (4H, d, *J* 8.7 Hz, Ar-H), 8.24 (4H, d, *J* 8.7 Hz, Ar-H), 8.70 (2H, s, NCH) and 10.51 ppm (1H, s, CH); δ_C (100 MHz, $[D_6]$DMSO): 96.36, 121.78, 123.91, 134.33, 134.67 and 138.85 ppm; m/z (ESI): **Obtained** 473.2 (M^+ - BF_4^-). **Calculated** for $C_{15}H_{11}N_2I_2BF_4$ 473.1 (M^+ - BF_4^-); **HRMS** calculated for $C_{15}H_{11}N_2I_2BF_4$, 472.90062 (M^+ - BF_4^-), found 472.90014.

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CHAPTER 4

TRANSITION METAL-FREE TRANSFER HYDROGENATION OF KETONES PROMOTED BY 1,3-DIARYLIMIDAZOLIUM SALTS AND KOH

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Abstract

An efficient transition metal-free and greener catalytic system was developed for the selective transfer hydrogenation of saturated ketones to alcohols. This was achieved by the use of 1,3-diarylimidazolium salts in the presence of KOH as a promoter for the reaction. When the range of substrates was expanded to include unsaturated ketones, selective reduction of the double bond occurred. Catalyst efficiency was comparable to some established metal-catalysed systems. The current system is made green by utilizing milder aerobic reaction conditions as compared to inert atmosphere conditions required for corresponding metal-based systems.

Keywords

Ketones, Imidazolium salts, Transfer hydrogenation, Metal-free catalysts, Alcohols, Turnover numbers

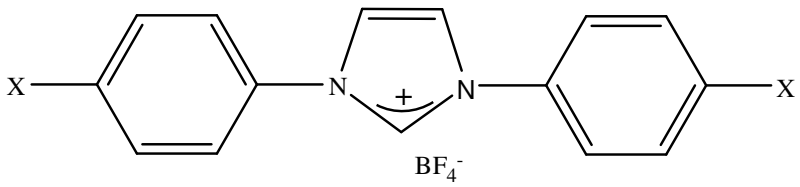
4.1 Introduction

Catalytic reduction of ketones to alcohols is important to industry because the end-products have numerous applications in the pharmaceutical, perfumery, agrochemical, bulk and fine chemical industries [1-4]. Much of the work conducted to date on the catalytic transfer hydrogenation of ketones incorporates transition metals, such as platinum [5], gold [6], iridium [7], rhodium [8] and ruthenium [9]. The metal-based catalyst systems have been found to be very effective although from a view point of sustainability they have many disadvantages. These include the fact that they are expensive and toxic to the environment especially in the homogeneous environment in which

they are most active [10]. There is therefore a need for an inexpensive and environmentally friendly catalytic system capable of matching the activities of the transition metal based systems.

Numerous applications of imidazolium salts exist in literature [11-12]. Their use as precursors [13] towards the synthesis of *N*-heterocyclic carbene ligands (NHC), which mimic and in many instances were able to completely replace phosphines [14] as ligands in organometallic reactions, has made them popular. Reasons for the superiority of NHCs over phosphines include ease of preparation, relative air and moisture stability, low loading and high efficiency in catalysis [15]. Also, the ability of NHCs to be tuned sterically and electronically has been the driving force that facilitated their use as ligands in metal complexes [16]. Thus, NHC-based complexes have been very effective in homogeneous catalysis and have found application in olefin metathesis [17], hydroformylation [18], hydrosilylation [19], epoxidation [20] and hydrogenation reactions [21]. Most of these catalysed reactions also require inert conditions, in addition to the use of heavy metals. Recently, Kadepi and co-workers [22] in their search for less expensive and environmentally friendlier catalyst systems, synthesized, iron(II) NHC complexes which were found to be very effective catalysts for the transfer hydrogenation of ketones. However, the difficulties encountered in their synthesis [23], which involved generation of reactive free carbenes prior to coordination, have greatly limited their use in catalysis [24].

As part of an ongoing search to develop a cheaper, easily accessible and a simple set-up catalyst system, the imidazolium salts **4.1**-**4.4** (Figure 4.1) were synthesized and used in a metal-free system for the transfer hydrogenation of ketones. The 1,3-diarylimidazolium tetrafluoroborates with halides substituted at the *para*-position were synthesized according to a modified procedure [13]. It is also worth noting that the application of imidazolium based ionic salts goes beyond use as precursors to make metal complexes [25]; they have been widely applied in medicine as antimicrobial agents [26]. To our knowledge, their use in a transition metal-free environment as organic catalysts for the activation of C=O and C=C bonds has not been explored.



X = F (**4.1**)
= Cl (**4.2**)
= Br (**4.3**)
= I (**4.4**)

Figure 4.1. The 1,3-diarylimidazolium salts (**4.1**-**4.4**).

4.2 Experimental

All reactions were conducted in air. Isopropanol was distilled prior to use. The ketones were purchased from Aldrich and used without further purification. All other starting materials were commercially available and used as received. The reactions were monitored by GC analysis with an Agilent capillary gas chromatograph model 6820 fitted with a DB wax polyethylene column (0.25 mm in diameter, 30 m in length), and a flame ionization detector. Nitrogen gas was used as carrier gas at a flow rate of 2 mL/min. The oven temperature for the aromatic (except 4-fluoroacetophenone) and the cyclic ketones (except cyclobutanone) was 70 ^{o}C, while for the remaining ketones the oven temperature was set at 50 ^{o}C. Samples (0.1 μl) were injected at 260 ^{o}C front inlet temperature for the aromatic (except 4-fluoroacetophenone) and the cyclic ketones (except cyclobutanone). For the remaining ketones the front inlet temperature was 180 ^{o}C.

4.2.1 Procedure for the transfer hydrogenation reactions

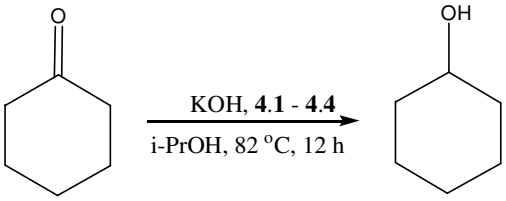
A typical procedure is described in which the 1,3-diarylimidazolium salt as catalyst (0.5 mol%) and KOH (0.112 g, 10 ml, 0.2 M in isopropanol) as promoter were placed in a round-bottomed flask followed by the addition of the respective ketones (2.1 mmol). The mixtures were refluxed at 82 °C for 12 h. The reactions were monitored by gas chromatography by taking aliquots at various time intervals. The samples were passed through a pad of silica and then injected into a GC. The identities of the products were assessed by comparison of their retention time with commercially available (Aldrich Chemical Co.) samples. The percentage conversions were obtained from integration values of GC peaks which were related to residual unreacted ketone.

4.3 Results and discussion

The current study is inspired by our general interest in the incorporation of greener procedures into catalysis; hence transfer hydrogenation under metal-free conditions was investigated. In the exploratory experiment, transfer hydrogenation of cyclohexanone was tested with the imidazolium salts **4.1**-**4.4** as catalysts and isopropanol as the hydrogen source (and solvent) in a basic KOH environment**.** A very low catalyst loading of 0.5 mol% of the 1,3-diarylimidazolium salts (Figure **4.1**) was used in an aerobic environment and later in pure water (only very low conversion of the product was obtained in water). Imidazolium salts **4.1-4.4** show high activity towards the conversion of cyclohexanone to cyclohexanol with **4.1** showing the highest substrate conversion (Table 4.1). A turnover number (TON) up to 194 was observed which is higher than some of the metal-catalysed reactions reported to date [7]. This can be attributed to the negative inductive effect introduced by the *para*-fluorine substituent of the imidazolium carbon centre. In general, the reactivity pattern can easily be attributed to the inductive effect which renders the imidazolium carbon more susceptible to attack by an electrophile such as the ketonic C=O bond, or the alkene C=C bond (observed for the unsaturated ketones).

Table 4.1

Transfer hydrogenation of cyclohexanone catalysed by imidazolium salts **4.1**-**4.4**.



Imidazolium salt	Conversion (%)[a]	TON[b]
4.1	97	194
4.2	81	162
4.3	80	160
4.4	77	154

[a]Conversion was determined by GC analysis after 10 h for **4.1** and 12 h for **4.2-4.4**.
[b]Turnover number (TON) = mol product/mol catalyst

Moderate to high conversions of the cyclohexanone to cyclohexanol were recorded as shown in Table 4.1. It was imperative to establish the role of the various components, notably the imidazolium salt, the KOH promoter and the solvent/hydrogen source in the catalytic transfer hydrogenation process. Evidence for the involvement of the carbene in facilitating reduction of the ketone is provided by the results presented in Figure 4.2. When a blank run (no KOH or salt added) was conducted, there was no reaction observed, but when only KOH was added 40% conversion of cyclohexanone to cyclohexanol was observed after 12 h reaction. This is consistent with similar reactions that have established the role of KOH in catalytic transfer hydrogenation reactions [27, 28, 29]. These reactions rely on the use of high concentrations of the base and long reaction time. Without base initiated deprotonation, the imidazolium salt **4.1** on its own initiated very negligible conversion (2%) of the ketone. However, with the base and **4.1** when combined, the conversion increases to 97% after 10 h reaction time.

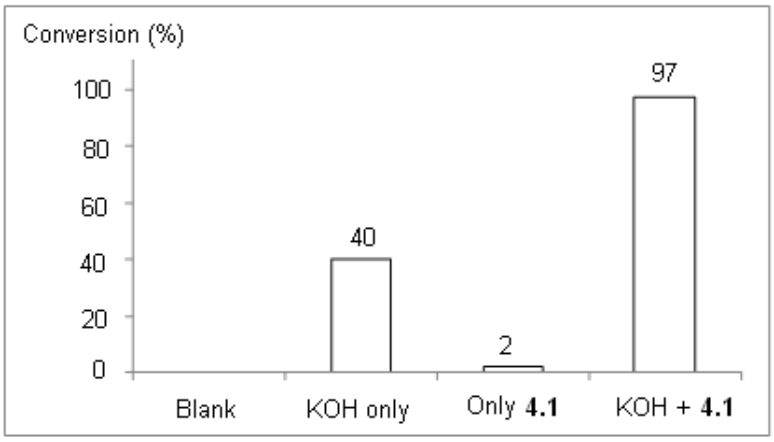
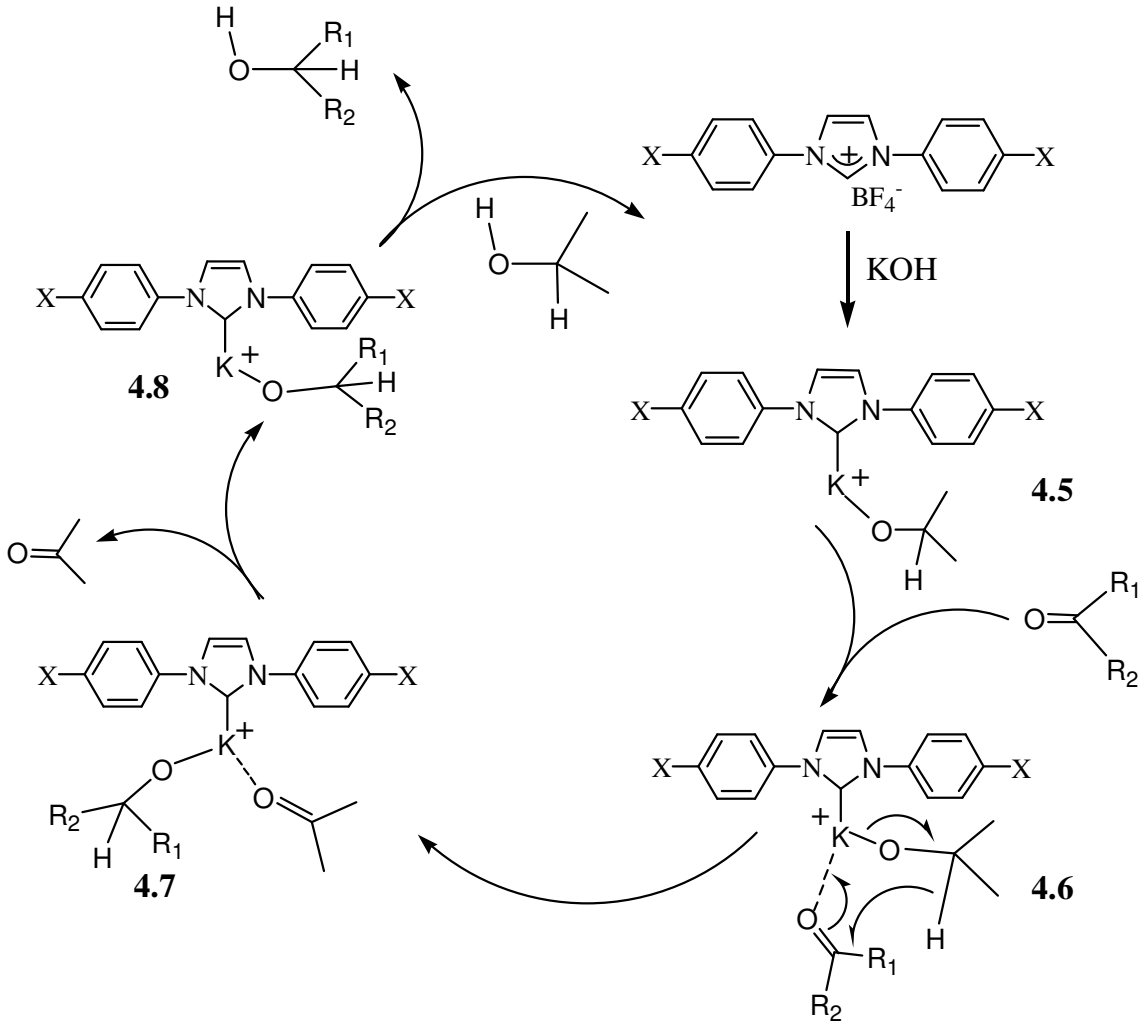


Figure 4.2. Percentage conversion of cyclohexanone to cyclohexanol by transfer hydrogenation from isopropanol in the absence or presence of one or both key (KOH & imidazolium salt **4.1**) reagents.

A plausible mechanism is proposed as shown in Scheme 4.1. This mechanism is similar to the proposed mechanism by Ouali *et al*. [28] for the base catalyzed transfer hydrogenation of ketones, which is also similar to the proposed mechanism for the hydride transfer from a metal-coordinated

alkoxide to the ketone in Meerwein-Ponndorf-Verly reduction of ketones catalysed by aluminium (III) [30].

The first step involved deprotonation of the imidazolium salt in a basic (KOH) isopropanol mixture, followed by potassium coordination to the reactive carbene specie and subsequent generation of an (NHC) potassium isopropoxide (**4.5,** Scheme 4.1). The ketone was then activated by **4.5** through coordination to the K-NHC and concerted hydrogen transfer to yield intermediate **4.6** and then rearrangement yields **4.7**. The subsequent release of acetone yields the alkoxide **4.8** which coordinates a new isopropanol moiety to yield the alcohol product.



Scheme 4.1 A plausible mechanism for the transfer hydrogenation of ketones using 1,3-diarylimidazolium salts promoted by KOH in isopropanol.

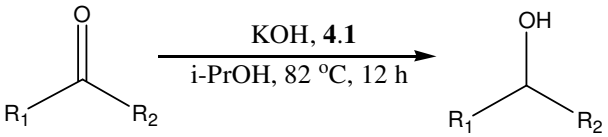
This mechanism is based on a possible interaction between the isopropanol/ketone and with the base/imidazolium salt. As observed in Figure 4.2, the marked improvement in catalytic activity obtained when both KOH and the imidazolium salt **4.1** were utilised in the reaction points to a definite involvement of the imidazolium salts. This contrasts to either situation when only KOH or imidazolium salt **4.1** was used. The coordination of the ketone to K-NHC to yield **4.6** is usually favoured by the stability of the M-O bond. For the base catalysed transfer hydrogenation a trend has been established associated with the charge density of the alkali metal thus: Li > Na > K [28]. The assumption is that the imidazolium salt contributes to a stronger K-O bond initially and also influences product elimination due to a combination of the ability of the NHC as a ligand to exhibit both high basicity and strong nucleophilicity [14].

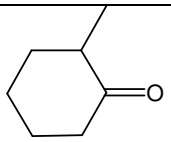
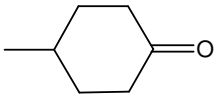
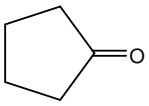
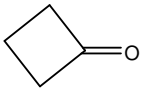
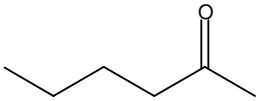
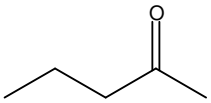
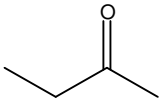
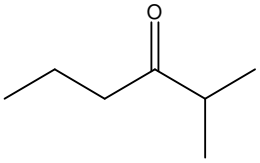
In order to understand the full extent and generality of this catalytic system, imidazolium salt **4.1** was further tested with a set of ketones chosen to explore the effects of electronic and steric variations of substrate backbone on the ketonic C=O bond. The result of this study is presented in Table 4.2. The imidazolium salt **4.1** was effective in the activation of the C=O bond in all the substrates studied. In this instance also, TON values were obtained that are in some cases comparable to or higher than those reported for Ru-catalysed transfer hydrogenation reactions [7]. The cyclic aliphatic ketones (entries 1-4) generally yielded better alcohol conversions than the acyclic components (entries 5-10) with cyclobutanone showing the best conversion of 100% after 6 h. A general trend attributable to access to the C=O bond is observed to be dependent on the size of the group α to the C=O bond, e.g. the isopropyl-containing ketone (entry 8) shows the least susceptibility to reduction. The trend may also be attributed to the relative ease of formation and stability of the carbocation, with terminal ones being less stable and more reactive towards reduction. Also, due to steric reasons, the effect of changing a substituent group from an *ortho*- to *para*-position on the phenyl group resulted in a significant increase in catalytic activity (entries 1 and 2) for the C=O group. A similar trend was also reported by Enthaler and co-workers [9], but in their case an increase in catalytic activity was observed by changing the electron-donating group from the *para*- to *ortho*-position in their system. The *ortho*-substituted ketone resulted in the least reactivity of the cyclic compounds due to a combination of steric interference of the substituent *ortho* to the reactive C=O bond and poor electronic contribution of the *ortho* methyl group. Ketones in which the reactive C=O group is β to a CH_3 (terminal) are found to be more reactive than internal C=O groups (bonded by ethyl and propyl groups). This showed that a steric rather than an electronic interaction is the dominant factor for this catalysis. When the *para*-substituted

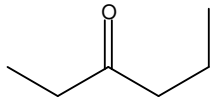
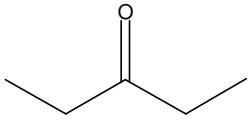
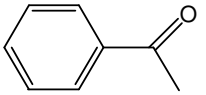
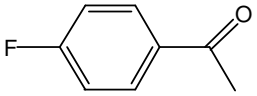
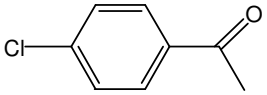
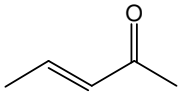
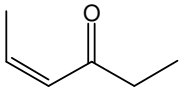
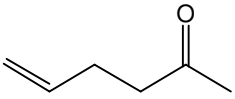
acetophenones is replaced by a substituent with a less electrophilic group (entries 12 versus 13) a significant increase in substrate conversion to product was observed. This suggests that the inductive effect (positive or negative) of the group *para* to the aromatic C=O group is an important determinant of the extent of the reaction.

Table 4.2

Transfer hydrogenation of ketones catalysed by imidazolium salt **4.1**.



Entry	Ketone	Conversion (%)[a]	TON[b]
1		27	54
2		96	192
3		37	74
4		100[c]	200
5		19	38
6		20	40
7		37	74
8		3	6

9		7	14
10		11	22
11		61	122
12		47	94
13		84	168
14[d]		55	110
15[d]		78	156
16		32	64

[a]Conversion was determined by GC analysis.
[b]Turnover number (TON) = mol product/mol catalyst.
[c]Conversion determined after 6 h.
[d]Converted into a saturated ketone.

In addition, the scope and selectivity of the catalyst system was further extended to the study of unsaturated ketones (entries 11-16). The α,β-unsaturated ketones 3-penten-2-one (entry 14) and 4-hexen-3-one (entry 15) were selectively reduced to the corresponding saturated ketones, instead of C=O reduction to the alcohols as observed in previous entries. Martin and List have also shown that the catalysed transfer hydrogenation of α,β-unsaturated ketones results in conversion to the corresponding saturated ketones with high enatioselectivity [31]. Also, Sakaguchi *et al*. [32] have reported the selectivity of their iridium-catalysed system for the transfer hydrogenation of unsaturated ketones to saturated ones. They further confirmed the preferred selectivity of their catalytic system towards reduction of the C=C double bond over the C=O bonds. On the other hand, there exist numerous examples in the literature of the reduction of the carbonyl group of α,β-unsaturated ketones to the corresponding alcohols [33]. Thus, this system is one of the few

[31,32,34] exhibiting high selectivity for the reduction of the C=C double bond in an α,β-unsaturated ketone (entries 14 and 15). For the aliphatic α,β-unsaturated ketones (entries 14 and 15), the conjugated keto-ene resonance facilitates hydrogenation of the C=C bond in preference to the C=O bond. On the other hand the unconjugated, 5-hexen-2-one (entry 16) was converted in moderate yield to the corresponding alcohol. In this instance the selectivity is in favour of the reduction of the C=O bond, which can be attributed to the ethyl spacer (between the C=C and C=O bonds) which disrupts the keto-ene conjugation and resonance stabilisation. Aromatic ketones were also converted to the corresponding alcohols even though they also contain α,β-conjugation involving the C=O bond (entries 11-13). In this case the C=C bonds form part of the phenyl ring system which, due to electron delocalization, is very stable and difficult to reduce, thus affording the preferred selective reduction of the aromatic ketones to the corresponding alcohols.

4.4 Conclusions

We have for the first time been able to successfully use 1,3-diarylimidazolium salts as catalysts in the absence of transition metals for the selective activation of the reduction of ketonic C=O and alkenyl C=C bonds. Moderate to excellent yields were obtained for various aliphatic, aromatic, cyclic and unsaturated ketones. The reaction does not require the usual inert conditions commonly associated with transition metal-based catalysis. When all the permutations are combined together, it can be concluded that the best substrate for these catalytic systems is an aromatic ketone containing electron donating *para* substituents.

Acknowledgements

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CHAPTER 5

FERROCENYLIMIDAZOLIUM SALTS AS CATALYSTS IN TRANSFER HYDROGENATION OF KETONES

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Abstract

Ferrocenylimidazolium salts with methyl and phenyl linkers to *N*-heterocyclic carbene derivatives were synthesized and characterized by spectroscopic and crystallographic methods. The influence of the chain spacers linking the ferrocenyl to the carbene moieties, on the electrochemical redox properties of the salts analysed by cyclic voltammetry, was evaluated by comparing the relative shifts in the formal electrode or peak potentials (E^0 or $E_{1/2}$) of the ferrocene/ferrocenium group to those of the ferrocenylimidazolium salts. Their effectiveness as catalysts was investigated in transfer hydrogenation of saturated and unsaturated ketones and the ferrocenylimidazolium salts were found to be very active in transforming the ketones to the corresponding alcohols. Notably, two of the unsaturated ketones (3-pent-2-one and 4-hexen-3-one) were converted in high yields to the corresponding saturated ketones. A link between the electrochemical and catalytic properties was established.

Keywords

Ferrocenylimidazolium salts; Transfer hydrogenation; Ketones; Alcohols; Formal electrode potentials

5.1 Introduction

The synthesis of ferrocenylimidazolium salts has attracted interest because of the rich chemistry and applications associated with ferrocene.[1] The functionalization of imidazolium salts with ferrocene gives them unique electronic properties, such as the ability to stabilize carbocations.[2] Also, the

powerful donor capacity of ferrocene is in principle advantageous to the additional stabilization of electron deficient carbene moiety.[3,4] This has led to its use in numerous industrial applications and especially in medicine.[5,6] Current areas of interest in ferrocene chemistry also include its use in catalysis,[7-14] as sensors,[15] and as immunoassay reagents.[14,16-21]

Furthermore, ferrocenylimidazolium salts have found usefulness in electrochemical process as molecular recognition species.[22] This is as a result of the presence of two electro-active species, i.e. the ferrocene and the imidazole in these compounds. The presence of ferrocene in ferrocenylimidazolium salts gives rise to a ferrocene/ferrocenium redox couple, the redox potential of which depends on the imidazolium ring *N*-substituents (Scheme 5.1).[11] Also, the interaction between the ferrocene and the imidazolium ring depends on the nature of the spacer or linker between the two moieties.[22] Thomas *et al.,* have synthesized novel ferrocenyl compounds for use as anion recognition molecules where they investigated the electrochemical properties of the salts by cyclic voltammetric technique.[23] Bai and co-workers also synthesized ferrocenylbenzimidazolium salts and investigated their application for anion binding of Cl^-, Br^- and I^- ions.[24] Studies by Bildstein *et al*.[25] on the electrochemical properties of ferrocenylbenzimidazolium salts, using cyclic voltammetry showed significant electronic communication between the carbene moiety and the *N*-ferrocenyl substituent. Cyclic voltammetry of iron(II) *N*-heterocyclic carbene (NHC) complexes[26,27] has also been conducted in order to establish the influence of the NHC on the catalytic activity of the iron centre. Hence, numerous examples exist in literature on the synthesis of ferrocenylimidazolium salts.[3,28-32]

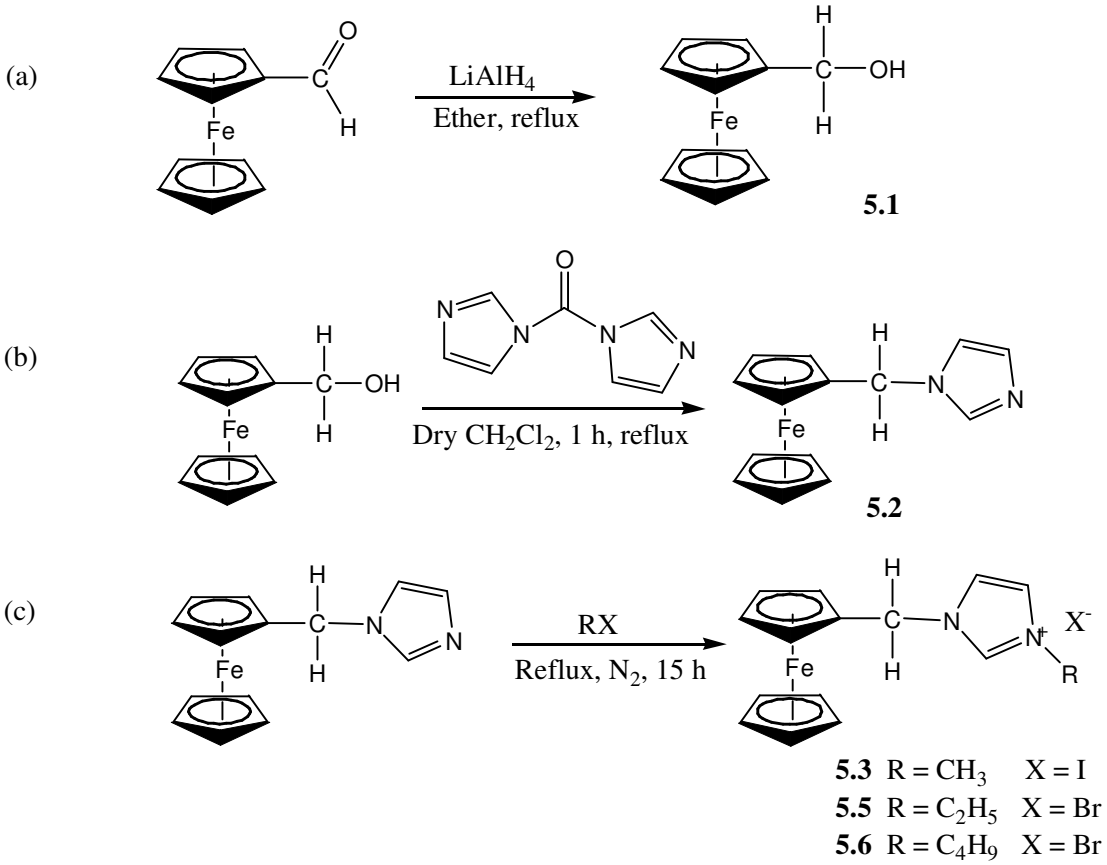
The application of ferrocenylimidazolium salts as ligand precursors in the synthesis of ferrocenyl NHC complexes is of great importance. For instance, Bildstein *et al.*[33] have synthesized metal complexes of W(0), Pd(II) and Hg(II) with ferrocenylimidazolium salts. Coleman *et al*.[1] have also synthesized and structurally characterized a palladium(II) ferrocenyl NHC complex. In addition, Seo and co-workers[34] successfully obtained chiral ferrocenylimidazolium salts which were used as precursors in the synthesis of rhodium and iridium complexes. These complexes showed moderate enantioselectivities in the transfer hydrogenation of ketones. In 2009, Jiang *et. al*. also reported good enantioselectivities for the transfer hydrogenation of ketones,[35] catalysed by Rh(I)-ferrocene-based planar chiral NHC complexes. Transfer hydrogenation of ketones to the corresponding alcohols has become an important transformation in organometallic chemistry especially in the pharmaceutical[36] and fine chemical industries.[37] Therefore, the search for inexpensive, active and

environmentally friendly catalysts is important in order to expand the scope of available routes to achieving this transformation. Hence, in this report we present the first use of ferrocenylimidazolium salts in mediating the transfer hydrogenation of ketones.

5.2 Results and discussion

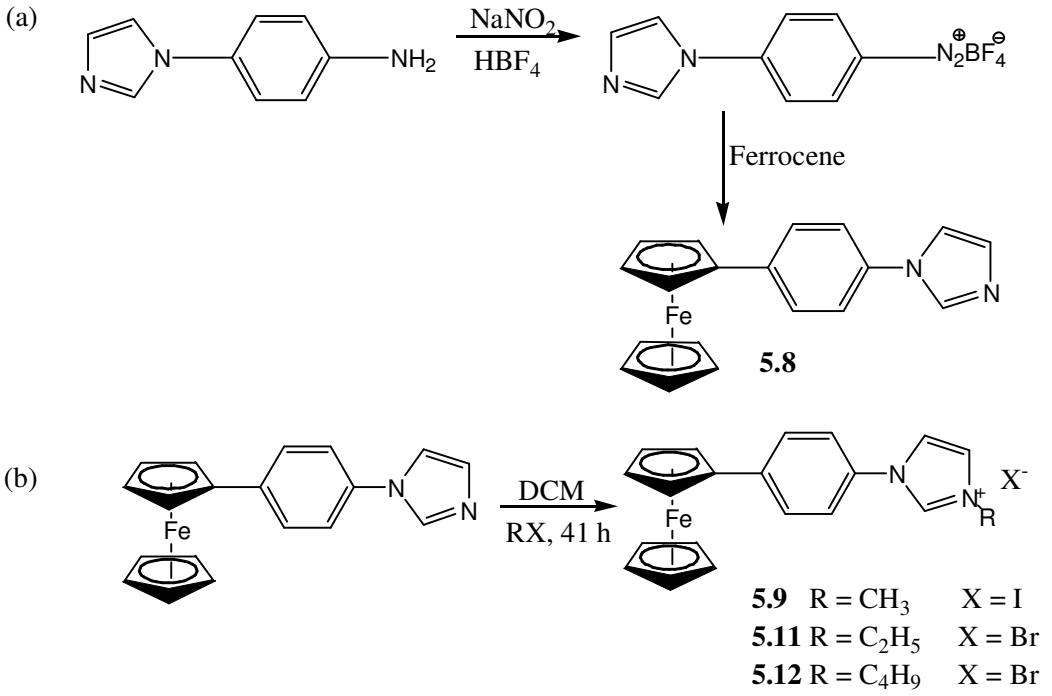
5.2.1 Synthesis

The synthesis of the two types of ferrocenyl salts, one containing a methyl and the other a phenyl linker to imidazolium were conducted via different routes. The ferrocenylmethylimidazolium salts were synthesized following an established procedure.[38] In this procedure, ferrocenylmethylimidazole, **5.2**, was prepared from ferrocenylmethanol **5.1**, which in turn was prepared by the reduction of ferrocenecarboxaldehyde with lithium aluminium hydride as shown in Scheme 5.1. The target salts (**5.3**-**5.6**) were synthesized by alkylating **5.2** with the corresponding alkylhalides and subsequent solvent washing with diethyl ether to remove unreacted ferrocenylmethylimidazole, **5.2**. Compounds **5.3**-**5.6** were obtained in relatively high yields (72-92%). Ferrocenylimidazolium salts **5.3** and **5.5** were obtained as yellow powders, while **5.6** yielded a dark brown powder. A trend was observed with decrease in the melting point of the ferrocenylimidazolium salts (**5.3**-**5.6**) as the length of the imidazolium alkyl side chain **R** increased as shown in Table 5.1, which is in agreement with literature reports.[38]

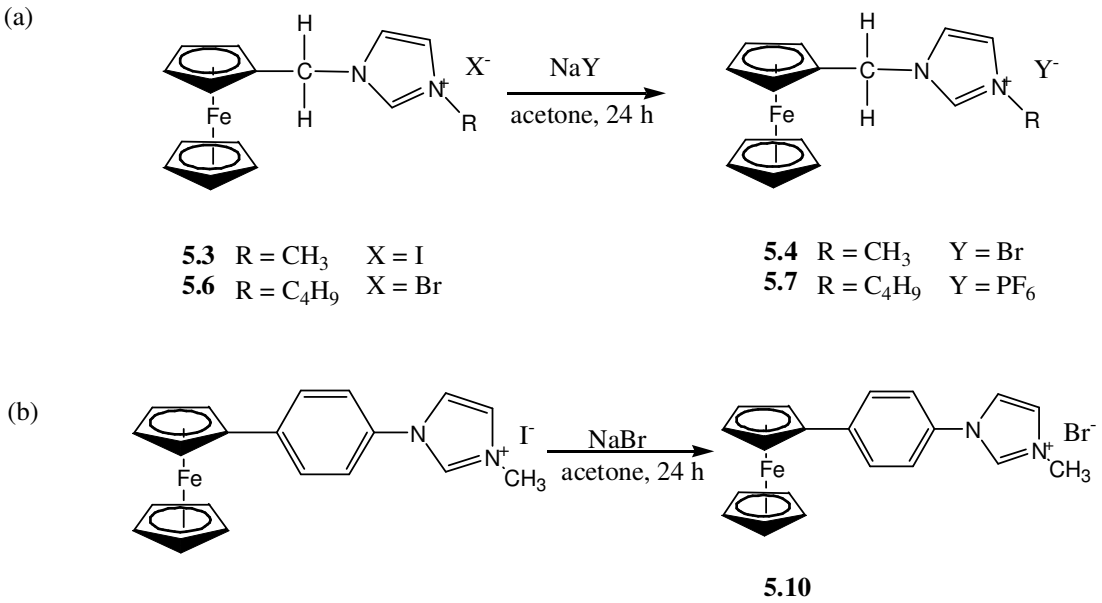


Scheme 5.1 Synthesis of ferrocenylmethylimidazolium salts.

On the other hand the synthesis of ferrocenyl salts with phenyl linkers to the imidazole was achieved by employing a Gomberg-Bachmann reaction of diazotization followed by coupling of ferrocene to afford **5**.**8** in a better yield than was reported earlier for related reactions (Scheme 5.2).[32] Compound **5**.**8** was then used as a precursor to generate target molecules **5**.**9**-**5**.**12**, by alkylating the ferrocenylphenylimidazolium salt with the corresponding alkylhalides**.** The melting points of ferrocenylphenylimidazolium salts **5.9**-**5.12**, did not follow similar trends as earlier observed for ferrocenylmethylimidazolium salts, **5.3**-**5.6**. The melting point increased as the imidazolium alkyl chain length was increased from C1-C2, and decreased from C2 to C4 (see Table 5.1, compounds **5.9**-**5.12**) Furthermore, metathesis reactions were used to obtain compounds **5**.**4**, **5**.**7** and **5**.**10** as shown in Scheme 5.3 in order to investigate the effect of changing the counter anion on the physical properties of the salts. High yields were obtained in all cases (81-96%).



Scheme 5.2 Synthesis of ferrocenylphenylimidazolium salts**.**



Scheme 5.3 Anion exchange of ferrocenylimidazolium salts.

Noteworthy, is the effect of changing the ferrocenyl linkers to the imidazolium from methyl to phenyl on the physical properties of the salts. Generally, the melting points of the ferrocenylmethylimidazolium compounds **5**.**3**-**5**.**7** were lower than those of the ferrocenylphenylimidazolium salts **5**.**10**-**5**.**12**. The only exception was observed with compounds **5**.**3** and **5**.**9**. This can be attributed to increase in molecular size of ferrocenylphenylimidazolium salts and possible pi-pi stacking interactions in **5.10-5.12** provided by the phenyl linker as compared to the methyl linker. The stronger intermolecular attractive forces, require more energy to weaken or break the attraction, leading to higher melting points as compared to the ferrocenylmethylimidazolium salts **5.3-5.7** Compound **5**.**4** was obtained as an oil**,** which may be attributed to a change in the anionic size.[38] As the anionic size increased the melting point should decrease as a result of disruption in the crystal lattice.[38,39] Increasing the length of the alkyl chain on the imidazole from methyl to ethyl (**5**.**10** and **5**.**11**), did not significantly affect the melting point of the ferrocenylphenylimidazolium salts, but when the alkyl length was further increased to butyl, a decrease in the melting point was observed, which is in agreement with the literature report.[5] This can be attributed to disruption in the crystal packing of the ferrocenylphenylimidazolium salts as the packing molecular size of the imidazolium alkyl side chain R, increased.

5.2.2 NMR and FTIR spectroscopyy Characterization

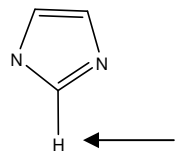
The NMR data give some indication of the level of electronic interactions between the cationic centres and the various anions. Evidence of the deshielding effect of the anion is observed from the significant shift of the imidazole protons in the neutral compounds **5**.**2** and **5**.**8,** from lower to higher resonance (^{1}H NMR spectra) as compared to the corresponding salts. This as expected is proportional to the electronegativity of the counterion (Table 5.1). Generally, the deshielding effect is more pronounced for the ferrocenylphenylimidazolium salts, showing the effect of the unsaturation in the phenyl group. A similar trend was observed for both ferrocenylalkylimidazolium and ferrocenylphenylimidazolium salts, when the alkyl length to the imidazole was increased from ethyl (**5**.**5** and **5**.**11**) to butyl (**5**.**6** and **5**.**12**). A shielding effect was observed with a slight shift to lower frequency (10.62 and 11.27 ppm) to (10.56 and 11.23 ppm), respectively due to the increased electron density from the alkyl groups.

Table 5.1

Molecular structural variations of the ferrocenylimidazolium salts **5.2-5.12.**

Compounds	**-R**	**X^-**	**Mp/^oC**	**^1H NMR/ppm[a]**
5.2	none	none	80	7.45
5.3	CH_3	I	145.5	9.96
5.4	CH_3	Br	Oil	9.97
5.5	C_2H_5	Br	92.3	10.62
5.6	C_4H_9	Br	85.5	10.56
5.7	C_4H_9	PF_6	Paste	8.62
5.8	None	None	161.5	7.84
5.9	CH_3	I	140.5	10.65
5.10	CH_3	Br	179.5	10.64
5.11	C_2H_5	Br	184.5	11.27
5.12	C_4H_9	Br	158.5	11.23

[a]chemical shift of imidazole proton



Imidazole proton

The compounds were also analysed by infrared and mass spectrometry. They all exhibited similar infrared spectra. The band observed around 1528-1573 cm^{-1} corresponds to the N-C-N stretch in imidazole.[11] The C-H and N-H stretching frequencies were observed between 2934-3079 cm^{-1} and 3300-3639 cm^{-1} respectively. The bands which are characteristic of the presence of ferrocene in a molecule[11] were observed around 820-1150 cm^{-1}. The mass spectra for all the ferrocenylimidazolium salts synthesized, showed a peak which corresponds to the molecular ions ($m/z = M^+ - X^-$).

*5.2.3 Molecular structures of compounds **5.5**, **5.7**, **5.8** and **5.9***

Four of the ferrocenylimidazolium salts synthesized were structurally analysed by X-ray diffraction studies. Crystals suitable for X-ray analysis were each obtained for compounds **5.5**, **5.7**, **5.8** and **5.9** by slow diffusion of hexane into a saturated solution in dichloromethane. The ORTEP diagrams are shown in Figures 5.1-5.5 respectively. Selected bond lengths and angles are shown in Tables 5.2

and 5.3. A Summary of the crystal data and structure refinement parameters are given in Tables 5.4 and 5.5.

Compound **5.5** crystallizes with three molecules (the ferrocenylmethylimidazolium molecule, water and bromine) in the asymmetric unit, in the monoclinic space group $P2_1/c$. The structure consists of a ferrocenyl moiety with a methyl linker to ethylimidazolium bromide and a water molecule. The bond length N1-C11 which is 1.477(3) is a shorter than similar bond length in compound **5.7** (1.484 (15)). This can be attributed to steric influence introduced by increase in alkyl length in compound **5.7** as compared to compound **5.5**.

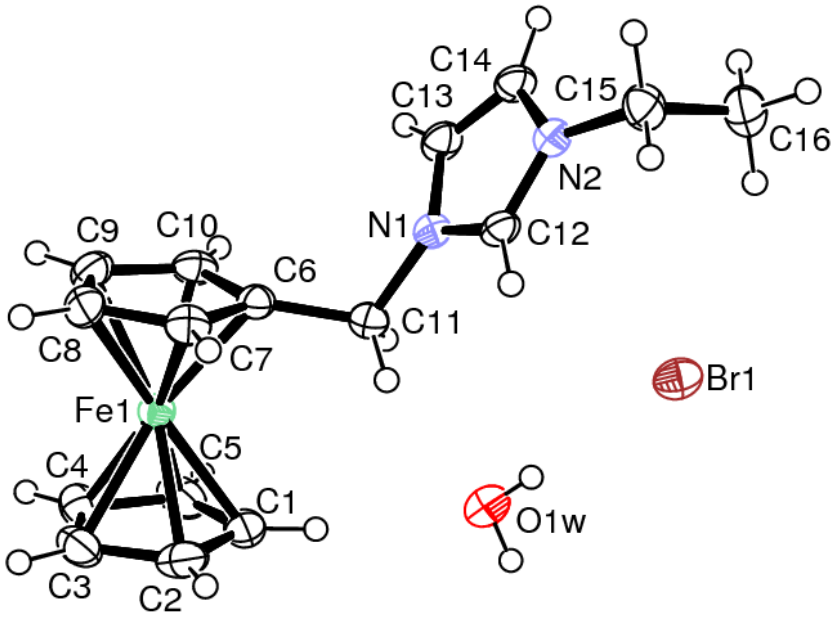


Figure 5.1 Crystal structure of compound **5.5.**

Compound **5.7** crystallizes with four molecules in the asymmetric unit, in the monoclinic space group $P2_1$. The structure consists of a ferrocenyl moiety with methyl linkers to the butylimidazolium hexafluorophosphate. An expected range for the bond lengths for N1-C11, [1.484(15) Å] and N2-C15 [1.481(17) Å] was obtained. The bond length of Fe1-C10 [2.005(13) Å] is shorter than the bond length of Fe1-C6 [2.041(13) Å], this is as a result of the influence of the methyl group substituted at C10. The bond angle for N1-C14-N2 is 107.5(12)^o is smaller than the bond angles for C14-N1-C12 [110.9(12)^o] and C14-N2-C15 [125.4(12)^o]. This is an indication of the delocalization of the positive charge of the imidazolium ring over the N1-C14-N2 angle in the

ring. The molecular packing diagram for compound **5.7** viewed along the c axis is shown in Figure 5.3. It contains four molecules in a unit cell. The molecules are packed in such a way that two molecules of the ferrocenylmethylimidazolium are in a head to tail pattern with the hexafluorophosphate ions on their opposite sides.

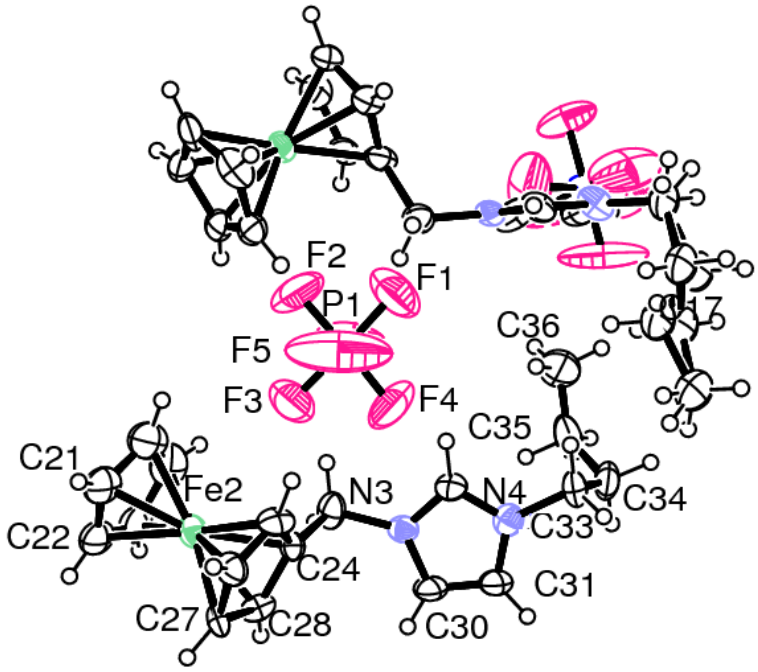


Figure 5.2 Crystal structure of compound **5.7.**

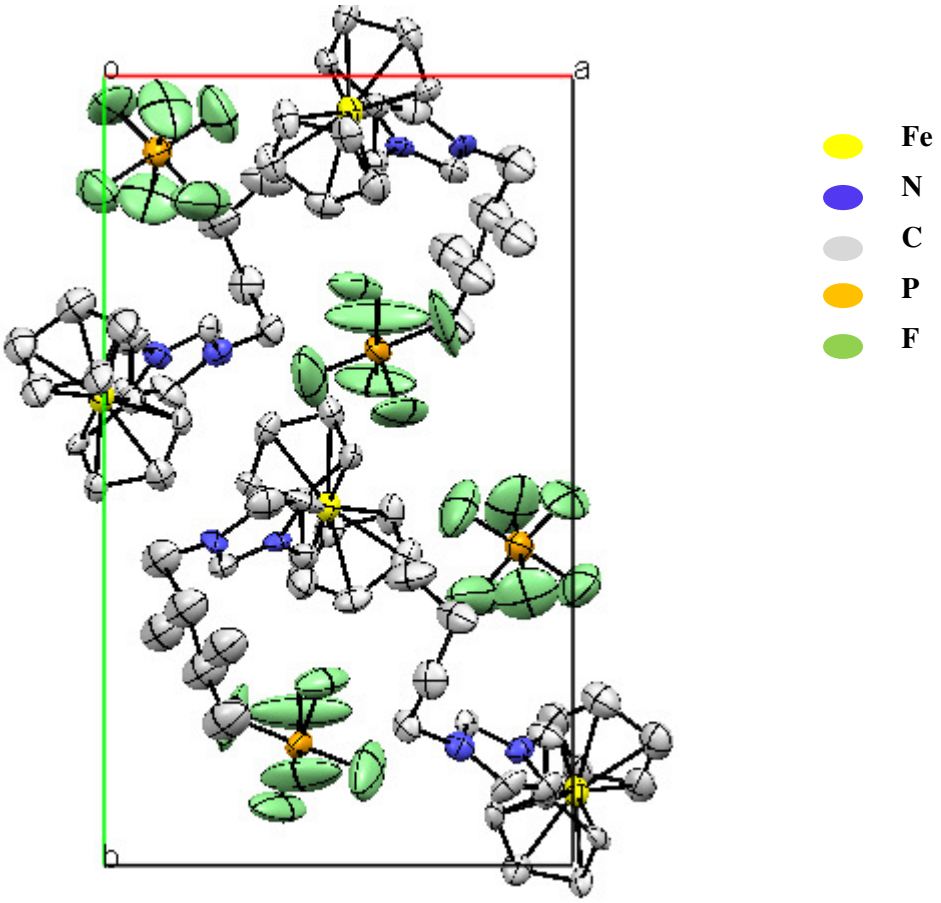


Figure 5.3 Packing diagram for compound **5.7**

The molecular structure of compound **5.8** has been previously reported.[32] They both crystallize in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The bond length N1-C14, which is 1.451(9) Å is longer than similar bond length in the structure reported earlier,[32] N5-C6 [1.425(2) Å]. The bond length C14-N1, which is 1.427(3) Å, is shorter than the similar bond length in compound **7**, N1-C11 [1.484(15) Å]. This can be attributed to the influence of a high degree of unsaturation exhibited by the phenyl ring in comparison to the methyl linker of the ferrocenyl moiety to the imidazole.

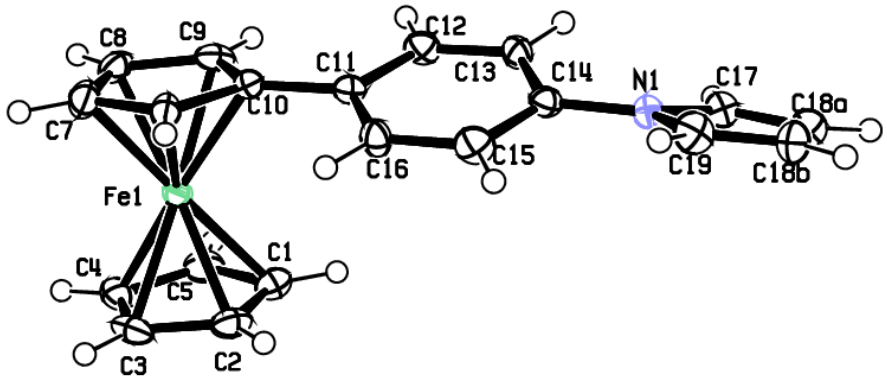


Figure 5.4 Crystal structure of compound **5.8.**

Onyancha *et. al*.[40] reported the crystal structure of compound **5.9**, during the course of this research. Compound **5.9** crystallizes in the monoclinic space group $P2_1/c$. The molecule consists of unsymmetrical ferrocenylphenylimidazolium, with iodide as the counter-anion and a water molecule. The bond length C14-N1 [1.451(9) Å] is longer than similar bond length in previously reported, C9-N1 [1.431 (4) Å] [40] and also in compound **5.8**, which is 1.427(3) Å. This is as a result of the formation of the imidazolium salts which also contribute to the shift to higher resonance of the ^{1}H NMR peak of compound **5.9** of the imidazole proton in comparison to compound **5.8**. Hydrogen bonding exists between the iodide counter-anion and the water molecule. The bond angle N2-C19-N1, 108.9(7)^o is smaller than the bond angle C20-N2-C19, 127.2(7)^o.

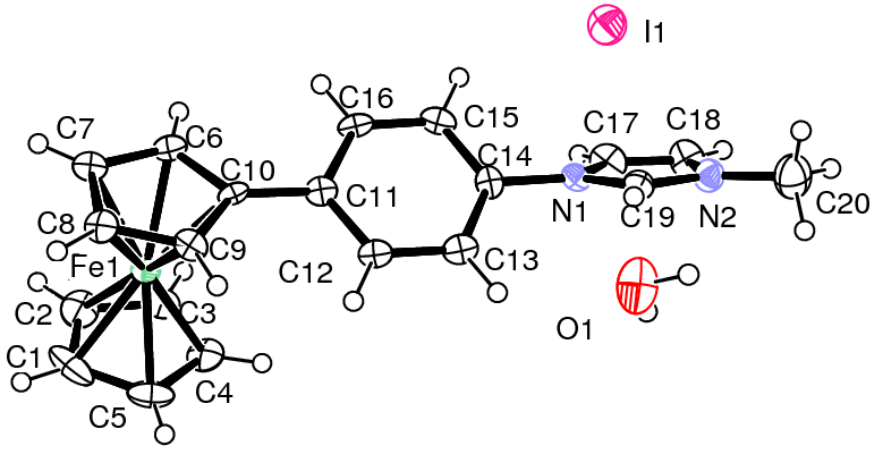


Figure 5.5 Crystal structure of compound **5.9.**

Table 5.2

Selected bond lengths (Å) and angles (°) for compounds **5.5** and **5.7**.

Compound 5.5		**Compound 5.7**	
Bond lengths		**Bond lengths**	
N1-C11	1.477(3)	N1-C11	1.484(15)
Fe1-C10	2.032(2)	Fe1-C10	2.005(13)
N2-C15	1.473(3)	N2-C15	1.481(17)
N2-C12	1.329(3)	N2-C14	1.335(16)
Fe1-C6	2.016(2)	Fe1-C6	2.041(13)
Bond angles		**Bond angles**	
N1-C12-N2	108.4(2)	N1-C14-N2	107.5(12)
C12-N1-C11	124.2(2)	C14-N1-C12	110.9(12)
C12-N2-C15	124.5(2)	C14-N2-C15	125.4(12)
C10-Fe1-C6	121.12(16)	C10-Fe1-C1	120.4(6)

Table 5.3

Selected bond lengths (Å) and angles (°) for compounds **5.8** and **5.9**.

Compound 5.8		**Compound 5.9**	
Bond lengths		**Bond lengths**	
C10-C11	1.474(3)	C14-N1	1.451(9)
Fe1-C1	2.039(2)	C11-C10	1.437(10)
Fe1-C6	2.0479(19)	Fe1-C1	2.053(8)
C14-N1	1.427(3)	N2-C19	1.332(10)
N1-C17	1.371(2)	N2-C20	1.435(11)
Bond angles		**Bond angles**	
C14-N1-C17	126.75(16)	N2-C19-N1	108.9(7)
C1-Fe1-C5	69.84(12)	C6-Fe1-C1	152.8(4)
C19-N1-C14	127.37(17)	C20-N2-C19	127.2(7)
C13-C14-N1	120.08(17)	C5-Fe1-C6	166.6(4)

Table 5.4

Summary of the crystal data of compounds **5.5** and **5.7**.

Compound	**5.5**	**5.7**
Formula	$C_{16}H_{21}BrFeN_2O$	$C_{18}H_{23}F_6FeN_2P$
Formula weight	393.11	468.20
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)C	$P2_1$
a, Å	12.8696(9)	9.7739(13)
b, Å	7.5858(5)	16.4278(19)
c, Å	16.8379(11)	12.6114(18)
α deg	90	90
β, deg	94.021(2)	93.755(5)
γ, deg	90	90
Cell volume, $Å^3$	1639.77(19)	2020.6(5)
Z	4	4
D_{calcd}, Mg/m^3	1.592	1.539
T, K	173(2)	173(2)
μ, mm^{-1}	3.356	0.885
Wavelength, Å	0.71073	0.71073
F(000)	800	960
Cryst size, mm^3	0.33 x 0.31 x 0.06	0.73 x 0.07 x 0.02
θ_{min}, θ_{max}, deg	1.59 to 28.00	1.62 to 25.00
no. of reflns. collected	3.0563	9603
No of indep. Reflns.	3952[R(int) = 0.0719]	6414[R(int) = 0.0762]
Completeness to theta	100% (28.00)	99.9% (25.00)
Absorbed correction	Integration	None
Goodness-of-fit on F^2	0.985	0.935
Final R indices	R_1 = 0.0318	R_1 = 0.0721
	wR_2 = 0.0748	wR_2 = 0.1442
R indices (all data)	R_1 = 0.0462	R_1 = 0.1815
	wR_2 = 0.0791	wR_2 = 0.1839

Table 5.5

Summary of the crystal data of compounds **5.8** and **5.9**.

Compound	**5.8**	**5.9**
Formula	$C_{19}H_{16}FeN_2$	$C_{20}H_{21}FeIN_2O$
Formula weight	328.19	488.14
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	14.9854(3)	17.2863(11)
b, Å	7.6920(2)	7.3530(5)
c, Å	12.8379(3)	16.8744(12)
α deg	90	90
β, deg	104.7110(10)	117.030(4)
γ, deg	90	90
Cell volume, $Å^3$	1431.29(6)	1910.8(2)
Z	4	4
D_{calcd}, Mg/m^3	1.523	1.697
T, K	173(2)	173(2)
μ, mm^{-1}	1.050	2.415
Wavelength, Å	0.71073	0.71073
F(000)	680	968
Cryst size, mm^3	0.58 x 0.24 x 0.02	0.54 x 0.06 x 0.01
θ_{min}, θ_{max}, deg	1.40 to 28.00	1.32 to 26.00
No. of reflns. collected	13639	16600
Completeness to theta	100% (28.00)	100.0% (26.00 °)
Absorbed correction	None	None
Goodness-of-fit on F^2	0.943	1.019
Final R indices	R_1 = 0.0335	R_1 = 0.0533
	wR_2 = 0.0840	wR_2 = 0.1306
R indices (all data)	R_1 = 0.0481	R_1 = 0.1056
	wR_2 = 0.0941	wR_2 = 0.1575

5.2.4 Cyclic voltammetric analysis

The ferrocenylimidazolium salts were analysed by cyclic voltammetry (Figs. 5.6 and 5.7). As shown in Table 5.6, the current ratio i_{pc}/i_{pa} for all the compounds was approximately equal to 1 (except for ferrocene, and compounds **5.5, 5.7** and **5.10** which gave ratios significantly different from unity), hence suggesting electrochemical reversibility for most compounds analysed**.** The formal redox potential (E^0) is usually expressed as the half wave potential, $E_{1/2}$ which is the average value between the anodic peak (E_{pa}) and the cathodic peak (E_{pc}) assuming the diffusion constants for the oxidized and reduced species are similar. For a Nernstian system, $E_{1/2}$ is independent of scan rate.[41] The peak-to-peak separation (ΔE) for all the compounds (Table 5.6) is between 0.066 – 0.089 V. The theoretical value for ΔE for a reversible process is 0.057/n V (sometimes given as 0.059/n V). However, the measured value for a reversible process is generally higher (0.07/n V is typically acceptable) due to uncompensated solution resistance and non-linear diffusion.[42] It should be noted that the fact that ΔE departs from the theoretical value of 0.057 V (or 0.059 V) for an electrochemically reversible one-electron process, does not compromise the criterion of reversibility.[41]

The influence of the imidazolium salt substituent on the ferrocenyl moiety was easily evaluated by comparing the half wave potential ($E_{1/2}$). The $E_{1/2}$ values (for compounds **5.2**-**5.12**) shifted to a more positive potential (0.482 – 0.595 V) as compared to that of ferrocene (0.436 V) as shown in Table 5.6. The voltammograms are given in Figures 5.6 and 5.7. The potentials were scanned in the anodic forward direction, denoted by the arrow (→), from -1.00 V to +1.00 V as shown in Figures 5.6 and 5.7. A reversible redox wave similar to the unsubstituted ferrocene was observed for compounds **5.2**-**5.12**. However, a shift to higher positive potential for the ferrocenylimidazolium salts was observed as compared to ferrocene. This can be attributed to the electron withdrawing ability of the imidazolium salts, which by withdrawing electrons away from the ferrocenyl centre makes oxidation difficult. The neutral ferrocenylimidazoles (**5**.**2** and **5**.**8**) have lower $E_{1/2}$ values in comparison with their ferrocenylimidazolium salt counterparts. Noteworthy, is the effect of increasing the length of the alkyl substituent on the imidazolium salts; the $E_{1/2}$ values increase to a more positive potential as the alkyl length increases. This is due to increase in positive inductive effect of the relatively longer alkyl chain.

Table 5.6

The cyclic voltammetry data of ferrocenylimidazolium salts showing the oxidation (anodic) and reduction (cathodic) peak potentials (E_{pa} and E_{pc}, respectively) and peak currents (i_{pa} and i_{pc}, respectively).

Compound	E_{pa}/V	E_{pc}/V	$E_{1/2}$/ V	ΔE ($E_{pc} - E_{pa}$) /V	i_{pc}µ/A	i_{pa}µ/A	i_{pc}/i_{pa}
Ferrocene	0.479	0.393	0.436	0.086	10.7	8.88	1.20
5.2	0.577	0.506	0.542	0.071	6.53	5.77	1.13
5.3	0.631	0.553	0.592	0.078	8.93	10.5	0.85
5.4	0.601	0.512	0.557	0.089	2.47	2.29	1.08
5.5	0.621	0.540	0.581	0.081	4.39	2.68	1.64
5.6	0.637	0.553	0.595	0.084	8.90	8.10	1.10
5.7	0.619	0.547	0.583	0.072	5.59	3.63	1.54
5.8	0.518	0.446	0.482	0.072	4.33	3.74	1.16
5.9	0.565	0.494	0.529	0.071	6.86	7.93	0.87
5.10	0.524	0.458	0.491	0.066	0.94	1.55	0.61
5.11	0.536	0.458	0.497	0.078	0.79	0.80	0.99
5.12	0.547	0.458	0.503	0.089	0.39	0.37	1.06

In addition, the data in Table 5.6 show a variation of the redox potentials of the ferrocenyl with methyl (**5**.**2**-**5**.**7**) or phenyl (**5**.**8**-**5**.**12**) linkers to the imidazolium moiety. The methyl linkers exhibited a higher formal electrode potential than the phenyl ones. This can be attributed to the delocalization of electrons in the phenyl ring, which decreases the electron-withdrawing effect of the imidazolium salts. This renders the $E_{1/2}$ value in compounds **5**.**8**-**5**.**12** less positive than those of compounds **5**.**2**-**5**.**7**. Batterjee and co-workers have reported a similar effect in which the electron potential shifted to a lesser positive potential as a result of the introduction of a double bond in their compound **II** as compared to compound **I** (from 0.317 V in **I** to 0.302 V in **II**).[43]

Furthermore, as the ionic size increases, oxidation becomes more difficult. Thus, a shift to higher positive potential was observed. This trend occurred with both the methyl (**5**.**3** and **5**.**4**) and phenyl (**5**.**9** and **5**.**10**) spacers in the ferrocenylimidazolium salts on changing their counter-ions from bromide to iodide (see Table 5.6). A possible explanation could be that as the anion size increases, there is a relatively larger charge distribution and the withdrawing ability of the imidazolium salt

increases. As a result, a lower electron density is experienced by the ferrocenyl centre, thus oxidation becomes difficult. We have in the past probed the effect of increasing the anionic size using ^{1}H NMR spectroscopy and have found that as the anionic size of the ferrocenylimidazolium salt decreases, the chemical shift of the resonances in the ^{1}H NMR spectrum shifted downfield.[38] This confirmed that the anion size has an influence on the electrostatic interaction between the imidazolium moiety and the ferrocenyl substituent.

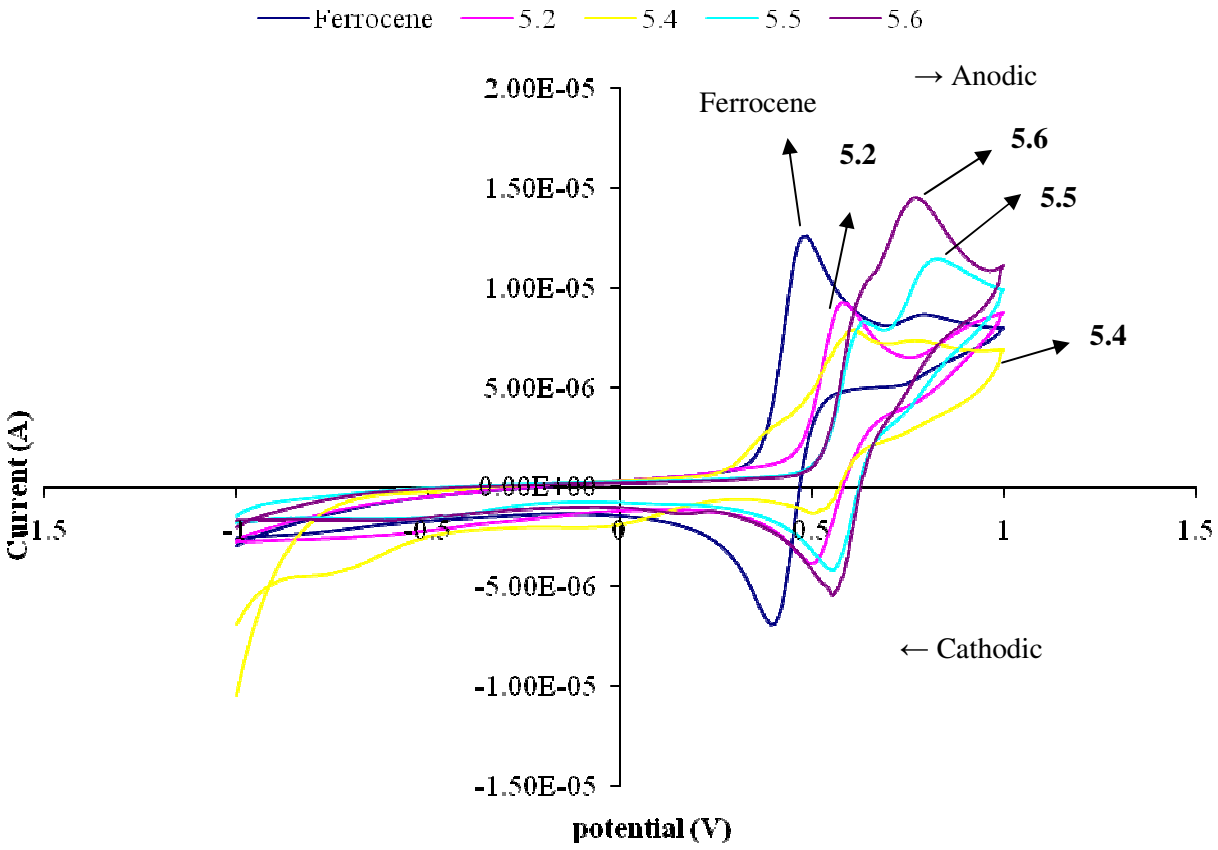


Figure 5.6 Comparison of the cyclic voltammograms of compounds **5.2**, **5.4**, **5.5** and **5.6** with that of ferrocene**.** Arrows (→ or ←) indicate the scan direction.

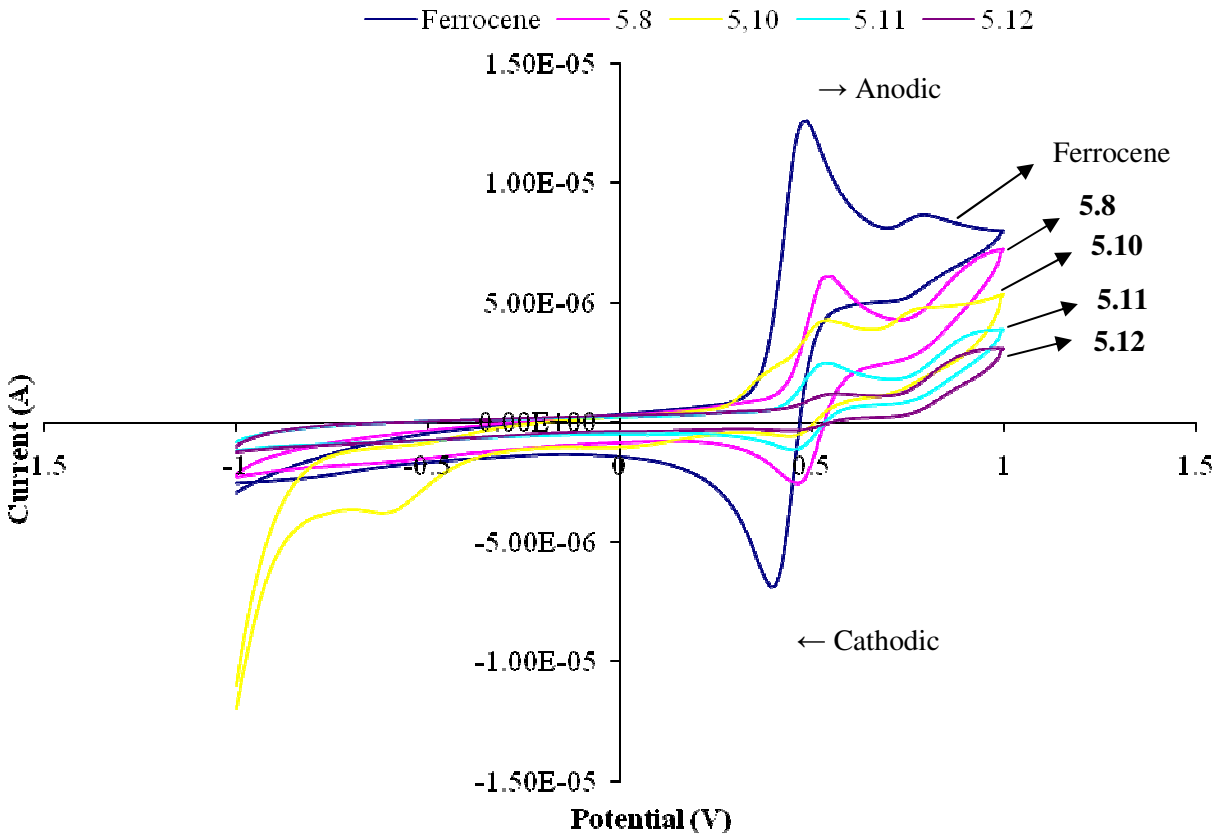


Figure 5.7 Comparison of the cyclic voltammograms of ferrocenyl compounds **5.8**, **5.10**, **5.11** and **5.12** with that of ferrocene. Arrows (→ or ←) indicate the scan direction.

5.2.5 Catalytic transfer hydrogenation

The application of the ferrocenylimidazolium salts was investigated in transfer hydrogenation of both saturated and unsaturated ketones. In an exploratory experiment, acetophenone was used as substrate and 0.05 mol% of the ferrocenylimidazolium compounds were used as catalysts. The solvent, propan-2-ol, was also the H-transfer agent and the reaction mixture was refluxed at 82 ^{o}C for 12 h. Compounds **5.2**-**5.12** showed high activity towards the conversion of acetophenone to 1-phenylethanol as shown in Table 5.7. A turnover number (TON) up to 1880 was observed, which was comparable to some data for precious metal catalysed reactions reported earlier.[44] The initial encouraging results prompted us to extend the catalytic system to other ketones in order to establish its scope and limits.

For this purpose compounds **5.6** and **5.12** were selected since they gave the highest conversion which is attributable to the shift to more positive potentials than their counterparts (see Table 5.6). They are almost similar in structure, apart from their linkers i.e. methyl and phenyl linkers of the ferrocenyl to the imidazole respectively. Table 5.8 shows the results obtained. By introducing an electron-donating group to the *ortho*-position of cyclohexanone, the % conversion obtained was drastically reduced (Table 5.8, entry 2). A better conversion was obtained, when the same electron-donating group was moved to the *para*-position. An increase in the % conversion was obtained by changing the electron-donating group from the *para*- to the *ortho*- position by Enthaler and co-workers.[45] Introduction of an electron-withdrawing group to acetophenone brought about a reduction in % conversion (entry 9), which was even more pronounced when a more electron-withdrawing group was attached to the *para*-position of acetophenone (entry 8). The cyclic aliphatic ketones gave a better % conversion than the acyclic aliphatic ketones. This can be attributed to an easy access to the C=O bond in cyclic aliphatic ketones as compare to more sterically hindered acyclic aliphatic ketones, thus making reduction difficult.

Table 5.7

Transfer hydrogenation of acetophenone catalysed bycompounds **5.2-5.12**.

Compound	Conversion (%)[a]	TOF[b]	TON[c]
5.2	63	105	1260
5.3	72	120	1440
5.4	66	110	1320
5.5	70	117	1400
5.6	80	133	1600
5.7	74	123	1480
5.8	57	95	1140

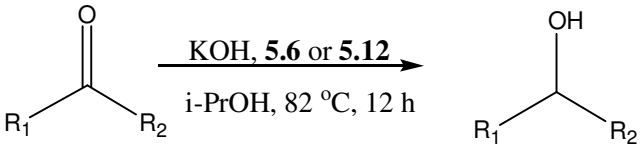
5.9	68	113	1356
5.10	61	102	1220
5.11	69	115	1380
5.12	94	157	1880

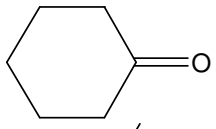
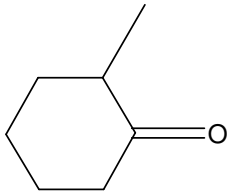
[a]Conversion was determined by GC analysis
[b]Turnover frequency (TOF) = mol product/(mol catalyst x time), determined after time t
[c]Turnover number (TON) = mol product/mol catalyst

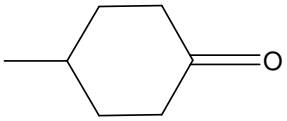
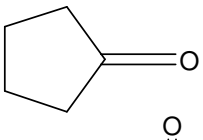
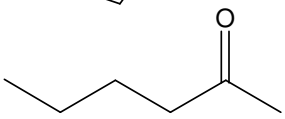
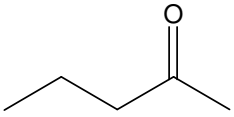
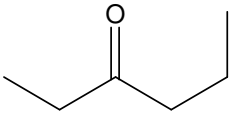
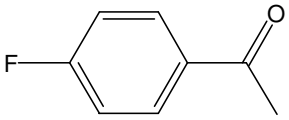
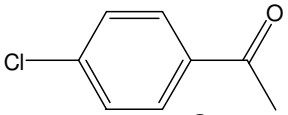
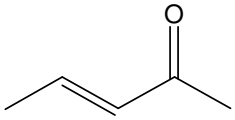
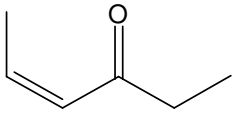
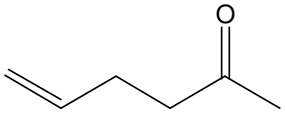
Furthermore, the investigation was extended to three aliphatic unsaturated ketones. Two of the α,β-unsaturated ketones were not converted to the corresponding alcohols, instead they were reduced to saturated ketones at high yields (entries 10 and 11). Noteworthy, 5-hexen-2-one was significantly converted to the corresponding alcohol, showing the selectivity of the catalyst system. Overall, compound **5.12** gave the best conversion in comparison to **5.6.** The high activity exhibited by **5.12** can be attributed to its molecular structure, which also contributed to the high melting point, shift to higher resonance of the imidazole carbon in the ^{1}H NMR spectrum and shift to more positive potentials in cyclic the voltammetry.

Table 5.8

Transfer hydrogenation of saturated and unsaturated ketones catalysed by compound **5.6** and **5.12**.



Entry	Ketones	%Conversion[a] (5.6)	%Conversion[a] (5.12)	TON[b] (5.6)	TON[b] (5.12)
1		76	83	1520	1660
2		50	20	1000	400

3		62	93	1240	1860
4		9	6	180	120
5		9	24	180	480
6		13	11	269	220
7		10	5	200	100
8		21	58	420	1160
9		31	62	620	1240
10[c]		68	57	1360	1140
11[c]		89	85	1780	1700
12		30	48	600	960

[a]Conversion was determined by GC analysis
[b]Turnover number (TON) = mol product/mol catalyst
[c]Converted to saturated ketone

5.3 Conclusion

The synthesis in relatively high yields of two sets of ferrocenylimidazolium salts with methyl and phenyl linkers to the imidazole was successful. All the new compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, infrared and mass spectroscopy. Four of the compounds were also analyzed by X-ray crystallography. Their electrochemical properties were studied by cyclic voltammetry. All the salts exhibited higher electrode potentials relative to that of ferrocene as a result of the electron-withdrawing effect of the imidazolium moiety on the ferrocenyl moiety. Their catalytic activities were investigated in transfer hydrogenation of both saturated and unsaturated ketones. The compounds showed high efficiency, with compound **5.12** giving the best conversion for acetophenone at a TON value of 1880. A correlation was found between the catalytic activity and the electrochemical properties of the ferrocenylimidazolium salts when investigated by cyclic voltametry. The result of the CV studies showed a direct correlation between the length of the alkyl substituent and the formal electrode potential ($E_{1/2}$) towards more positive values. Also, catalytic activity of the salts increased in the same way. This was attributed to the increase in a positive inductive effect as the alkyl length increased, thus making the ferrocenyl centres more vulnerable to attack by nucleophiles and increasing the catalytic activity.

5.4 Experimental

5.4.1 General procedures

All manipulations involving air and moisture sensitive compounds were performed using standard Schlenk techniques under an atmosphere of dry nitrogen. All solvents were dried and purified by standard procedures prior to use. Glassware were oven dried at 110 ^{o}C. All NMR experiments were done using a 400 MHZ Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform. Infrared spectra were recorded with a Perkin Elmer Universal ATR Spectrum 100 FT-IR spectrometer. Accurate mass data was obtained on a Thermo Electron DFS Dual focusing magnetic sector instrument using ESI in positive mode. Polyethylenimine was used as reference solution**.** The cyclic voltammograms were obtained with a METROHM 797 VA Computrace at a scan rate of 0.05 V s^{-1} in acetonitrile solution containing 0.1 mol $L^{-1}$of tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) as the supporting electrolyte. The $Ag/AgCl^{-}$ couple was used as the reference electrode to determine the potential with Pt working and auxiliary electrodes. The transfer hydrogenation reaction was monitored by GC analysis with an Agilent

capillary gas chromatograph with a DB wax polyethylene column (0.25 mm in diameter, 30 m in length), a flame ionization detector and nitrogen gas was used as carrier gas. All reagents and solvent were purchased from Aldrich and Merck and reagents were used as received.

*5.4.2 Synthesis of 1-(ferrocenyl)methanol (**5.1**)*

Ferrocenecarboxaldehyde (10 g, 0.047 mol) was dissolved in mimimum anhydrous diethyl ether and transferred to a pressure equalizing dropping funnel. An ethereal solution of lithium aluminium hydride, LAH (1.80 g, 0.047 mol) was prepared in a three necked round-bottomed flask. The aldehyde solution was added into the ethereal solution dropwise while stirring under a nitrogen atmosphere. The solution was maintained at reflux for 2 h (45 ^{o}C), while being monitored by TLC. After completion it was allowed to cooled, followed by the addition of 60 ml diethyl ether. Excess LAH was destroyed by dropwise addition of cold ethyl acetate, followed by addition of ice-water slurry. The organic layer was separated, washed with water (3 x 100 ml) and then dried over anhydrous magnesium sulfate before concentration using a rotary evaporator, which was later dried under vacuum to give a yellow powder. Yield 7.2 g, 96%, mp 76-78 ^{o}C; IR (ATR cm^{-1}) 3920, 3219, 2932, 1656, 1379, 1350, 1235, 1189, 987, 807, 498, 476; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29 (2H, s, CH_2), 4.25 (2H, s, C_5H_4), 4.19 (7H, s, C_5H_4, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.58, 68.51, 68.48, 68.08, 60.97; m/z (ESI): **Obtained** 215.7 (M^+) **Calculated** for $C_{11}H_{12}FeO$ 215.8. (M^+)

*5.4.3 Synthesis of 1-(ferrocenylmethyl)imidazole (**5.2**)*

Ferrocenylmethanol, **5.1** (0.5 g, 2.3 mmol) and an excess of *N*,*N*'- carbonyldiimidazole (0.52 g, 3.2 mmol) were dissolved in DCM (10 ml). The mixture was brought to reflux and the temperature maintained at 45 ^{o}C. TLC was used to monitor the reaction, which was completed after 1 h. The reaction was quenched and allowed to cool to room temperature. Then, diethyl ether (30 ml) was added to the product mixture and the mixture was allowed to stir for five minutes at room temperature. Solvent was removed in vacuo and the resulting product was subjected to column chromatography on silica gel. Diethyl ether was used to flash down any unreacted starting material. Ethyl acetate (100%) was later used to obtain the product, as yellow powder. Yield 0.32 g, 53%, mp 80 ^{o}C; IR (ATR cm^{-1}) 3392, 3117, 1638, 1509, 1437, 1237, 1218, 1102, 1077, 809, 740, 658, 479; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (1H, s, CH), 7.00 (1H, s, CH), 6.89 (1H, s, CH), 4.84 (2H, s, CH_2), 4.16 (9H, m, C_5H_4,C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.47, 129.00, 118.60, 82.51,

68.58, 68.31, 46.52; m/z (ESI): **Obtained** 267.05748 (M^+). **Calculated** for $C_{14}H_{14}N_2Fe$ 267.05847 (M^+).

*5.4.4 Synthesis of 1-(ferrocenylmethyl)-3-methylimidazolium iodide (**5.3**)*

In a two necked RB flask, methyl lodide (0.3 ml, 8.1 mmol) was added to ferrocenylmethyl imidazole (0.05 g, 0.19 mmol) and was allowed to reflux gently at 50 ^oC under an atmosphere of nitrogen for 15 h. The mixture was then allowed to cool to room temperature, washed with anhydrous diethyl ether (5 x 3 ml) until diethyl ether remained clear after washing. A yellow powder was obtained. Yield 0.056 g, 72%, mp 145.5 ^oC; IR (ATR cm^{-1}) 3173, 1566, 1331, 1243, 1331, 1174, 1150, 811, 754, 710, 619, 553, 480; ^1H NMR (400 MHz, $CDCl_3$): δ 9.92 (1H, s, CH), 7.28 (1H, s, NCH) , 7.26 (1H, s, NCH), 5.34 (2H, s, CH_2), 4.47 (2H, s, C_5H_4) 4.26 (7H, m, C_5H_4, C_5H_5), 4.04 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.96, 123.27, 121.55, 78.46, 77.30, 69.86, 69.70, 69.24, 50.05; m/z (ESI): **Obtained** 281.07350 (M^+- I). **Calculated** for $C_{15}H_{17}N_2FeI$ 281.07412 (M^+- I).

*5.4.5 Synthesis of 1-(ferrocenylmethyl)-3-methylimidazolium bromide (**5.4**)*

In a two-necked round-bottom flask was added sodium bromide (0.043 g, 0.42 mmol), to an acetone solution of 1-(Ferrocenylmethyl)-3-methylimidazolium iodide (0.1 g, 0.25 mmol). The mixture was then stirred at room temperature for 24 h. The reaction mixture was then filtered through a plug of celite, which was concentrated in vacuo to give orange oil. Yield 0.073 g, 81%; IR (ATR cm^{-1}) 3438, 3080, 1614, 1572, 1557, 1454, 1425, 1221, 1153, 1105, 1037, 1003, 822, 749, 673, 621, 543, 503, 462; ^1H NMR (400 MHz, $CDCl_3$): δ 9.97 (1H, s, CH), 7.84 (1H, s, NCH), 7.17 (1H, s, NCH), 5.33 (2H, s, CH_2), 4.43 (2H, s, C_5H_4), 4.24 (7H, s, C_5H_4, C_5H_5), 4.02 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.64, 122.83, 121.18, 78.46, 77.34, 69.87, 69.63, 69.25, 50.15; m/z (ESI): **Obtained** 281.07381 (M^+- Br^-). **Calculated** for $C_{15}H_{17}N_2FeBr$ 281.07412 (M^+- Br^-).

*5.4.6 Synthesis of 1-(ferrocenylmethyl)-3-ethylimidazolium bromide (**5.5**)*

Synthesis similar to **5.3** above using ethyl bromide (0.6 ml, 8.1 mmol), to give a yellow powder. Yield 0.06 g, 84%, 92.3 ^oC; IR (ATR cm^{-1}) 3432, 3386, 3138, 3065, 2065, 1626, 1565, 1558, 1463, 1412, 1347, 1319, 1236, 1157, 1027, 1007, 848, 807, 774, 708, 554, 506, 485, 447; ^1H NMR (400 MHz, $CDCl_3$): δ 10.62 (1H, s, CH), 7.16 (1H, s, NCH), 7.11 (1H, s, NCH), 5.34 (2H, s, CH_2), 4.42

(2H, s, C_5H_4), 4.36 (2H, q, C_5H_4,), 4.23 (7H, s, C_5H_5), 1.54 (3H, t, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.94, 120.18, 120.99, 77.58, 70.09, 69.85, 69.54, 50.16, 45.56, 15.76; m/z (ESI): **Obtained** 295.08962 (M^+- Br^-). **Calculated** for $C_{16}H_{19}N_2FeBr$ 295.08977 (M^+- Br^-).

*5.4.7 Synthesis of 1-(ferrocenylmethyl)-3-butylimidazolium bromide (**5.6**)*

Synthesis similar to **5.3** above using, butyl bromide (2.6 ml, 8.1 mmol). A dark brown powder was obtained. Yield 0.07 g, 92%; mp 85.5 ^oC; IR (ATR cm^{-1}) 3571, 3393, 3168, 2965, 1563, 1448, 1155, 1105, 812, 656, 631, 553, 478; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (1H, s, CH), 7.03 (2H, m, NCH, NCH), 5.36 (2H, s, NCH_2), 4.41 (2H, s, C_5H_4), 4.26 (9H, m, C_5H_4, C_5H_5, NCH_2), 1.87 (2H, m, CH_2), 1.36 (2H, m, CH_2), 0.95 (3H, t, *J* 0.98, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), 136.42, 120.80, 120.66, 78.83, 77.33, 69.84, 69.56, 69.30, 49.98, 32.12, 19.53, 13.44; m/z (ESI): **Obtained** 323.12104 (M^+- Br^-). **Calculated** for $C_{18}H_{23}N_2FeBr$ 323.12107 (M^+- Br^-).

*5.4.8 Synthesis of 1-(ferrocenylmethyl)-3-butylimidazolium hexafluorophosphate (**5.7**)*

In a two necked flask, sodium hexafluorophosphate (0.035 g, 0.21 mmol) was added into acetone solution of (ferrocenylmethyl)-3-butylimidazolium bromide (0.05 g, 0.13 mmol). The mixture was then stirred under a nitrogen atmosphere for 24 h at room temperature. The reaction mixture was then filtered through a plug of celite. The filtrate was then concentrated in vacuo to afford an orange-brown paste. Yield 0.1 g, 96%. IR (ATR cm^{-1}): 3639, 3167, 2934, 1562, 1448, 1154, 820, 775, 555, 501, 478; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (1H, s, CH), 7.18 (1H, s, NCH), 7.17 (1H, s, NCH), 5.15 (2H, s, NCH_2), 4.38 (2H, s, C_5H_4), 4.23 (2H, s, C_5H_4), 4.20 (5H, s, C_5H_5), 4.08 (2H, t, *J* 5.75, NCH_2), 1.82 (2H, m, CH_2), 1.32 (2H, m, CH_2), 0.93 (3H, t, *J* 0.98, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 134.49, 121.86, 121.72, 78.38, 77.35, 69.89, 69.54, 69.23, 49.97, 31.79, 19.39, 13.30; m/z (ESI): **Obtained** 323.12105 (M^+- PF_6^-). **Calculated** for $C_{18}H_{23}N_2FeBr$ 323.12107 (M^+- PF_6^-).

*5.4.9 Synthesis of 1-(4-ferrocenylphenyl)imidazole (**5.8**)*

A solution of sodium nitrite (0.088 g, 1.26 mmol) in water (2 cm^3) was added dropwise to an ice cold solution of 4-(1H-imidazol-1-yl) aniline (0.2 g, 1.26 mmol) and aqueous tetrafluoroboric acid (50%, 0.4 cm^3, 6.2 mmol) in water (4 cm^3), whereupon a yellowish precipitate was observed. After complete addition of the sodium nitrite solution, the mixture was stirred for another 5 min. This was followed by the dropwise addition of a CH_3CN and CH_2Cl_2 (1:2) 3 cm^3 solution of Ferrocene

(0.24 g, 1.26 mmol), resulting in a greenish-brown suspension. The cooling bath was removed and the mixture stirred for 1 h. Subsequently, H_2O (40 cm^3) was added and the reaction mixture extracted with CH_2Cl_2 (2 x 14 cm^3). The red organic layer was washed with dilute Na_2SO_4, the solvent was removed in vacuo, resulting in a brown residue, which was washed with n-hexane (3 x 6 cm^3) to remove residual ferrocene. A brownish-orange powder was obtained. Yield 0.12 g (30%), mp. 161.5 ^oC; IR (ATR cm^{-1}) 3096, 1660, 1531, 1488, 1302, 1249, 1103, 1055, 1031, 1002, 885, 813, 725, 655, 531, 509, 482, 456; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (1H, s, CH), 7.55 (2H, m, C_6H_4), 7.29 (3H, d, C_6H_4, NCH), 7.19 (1H, s, NCH), 4.64 (2H, t, *J* 1.6, C_5H_4), 4.35 (2H, t, *J* 1.6, C_5H_4), 4.04 (5H, s, C_5H_5), ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.24, 135.57, 135.10, 130.35, 127.24, 121.57, 118.24, 83.88, 69.73, 69.38, 66.95; **Obtained** 329.07411 (M^+). **Calculated** for $C_{19}H_{16}N_2Fe$ 329.07412 (M^+).

*5.4.10 General procedure for the preparation of complexes **5.9**, **5.11** and **5.12***

In a two neck round-bottom flask, 1-(4-ferrocenylphenyl) imidazole (1 molar equiv) was reacted with alkylhalide (5 molar equiv) in CH_2Cl_2 (15 ml). The mixture was stirred for 41 h at room temperature. After solvent removal, the mixture was treated with Et_2O (10 cm^3), filtered, washed with Et_2O (3 x 15 cm^3) and dried in vacuo. Crystals suitable for X-ray analysis was obtained by slow diffusion of hexane into a CH_2Cl_2 solution.

*5.4.11 Synthesis of 1-(3-methyl-(4-ferrocenylphenyl)imidazolium iodide (**5.9**)*

This complex was prepared from 1-(4-ferrocenylphenyl)imidazole (0.1 g, 0.3 mmol) and methyl iodide (0.1 ml, 1.5 mmol). The crude product was obtained as an orange powder (0.12 g, 86%), mp (140.5 ^oC); IR (ATR cm^{-1}) 3396, 3079, 1552, 1528, 1220, 1071, 820, 749, 620, 542, 504, 459; ^1H NMR (400 MHz, $CDCl_3$) δ 10.65 (1H, s, CH), 7.64 (4H, d, C_6H_4), 7.52 (1H, s, NCH), 7.40 (1H, s, NCH), 4.66 (2H, t, *J* 1.8, C_5H_4), 4.39 (2H, t, *J* 1.8, C_5H_4), 4.27 (3H, s, NCH_3), 4.04 (5H, s, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.15, 135.93, 131.59, 127.67, 123.99, 122.04, 120.37, 82.37, 69.88, 67.89, 66.79, 37.63; **Obtained** 343.08906 (M^+-I^-). **Calculated** for $C_{20}H_{19}N_2FeI$ 343.08977 (M^+-I^-).

*5.4.12 Synthesis of 1-(3-methyl-(4-ferrocenylphenyl)imidazolium bromide (**5.10**)*

In a two-necked round-bottom flask was added sodium bromide (0.019 g, 0.18 mmol) to an acetone solution of 1-(3-methyl-(4-ferrocenylphenyl)imidazolium iodide, **5.9** (0.05 g, 0.11 mmol). The mixture was then stirred at room temperature for 24 h. The reaction mixture was then filtered through a plug of celite, which was concentrated in vacuo to give a yellowish brown powder. Yield 0.035 g, 87%; mp 179.5 ^{o}C; IR (ATR cm^{-1}) 3452, 3397, 3079, 1706, 1553, 1423, 1220, 1003, 821, 749, 621, 519. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (1H, s, CH), 7.64 (4H, d, C_6H_4), 7.54 (1H, s, NCH), 7.45 (1H, s, NCH), 4.65 (2H, t, *J* 1.6, C_5H_4), 4.38 (2H, t, *J* 1.6, C_5H_4), 4.26 (3H, s, NCH_3), 4.04 (5H, s, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.26, 136.27, 131.73, 127.81, 124.07, 122.15, 120.45, 82.54, 70.07, 70.01, 66.95, 37.70; **Obtained** 343.08885 (M^+-Br^-). **Calculated** for $C_{20}H_{19}N_2FeBr$ 343.08977 (M^+-Br^-).

*5.4.13 Synthesis of 1-(3-ethyl-(4-ferrocenylphenyl)imidazolium bromide (**5.11**)*

This complex was prepared from 1-(4-ferrocenylphenyl)imidazole (0.056 g, 0.17 mmol) and ethyl bromide (0.06 ml, 0.85 mmol). The crude product was obtained as an orange powder (0.025 g, 64%), mp 184.5 ^{o}C; IR (ATR cm^{-1}) 3378, 3096, 1608, 1530, 1492, 1300, 1249, 1058, 885, 815, 741, 658, 531, 501, 455; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (1H, s, CH), 7.64 (4H, d, C_6H_4), 7.53 (1H, s, NCH), 7.19 (1H, s, NCH), 4.66 (2H, q, *J* 7.4, NCH_2), 4.65 (2H, t, *J* 1.6, C_5H_4), 4.38 (2H, t, *J* 1.6, C_5H_4), 4.04 (5H, s, C_5H_5), 1.67 (3H, t, *J* 7.3, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.92, 135.56, 130.36, 127.70, 121.50, 121.55, 120.05, 83.87, 69.72, 66.82, 66.58, 45.84, 15.73; **Obtained** 357.10388 (M^+-Br^-). **Calculated** for $C_{21}H_{21}N_2FeBr$ 357.10542 (M^+-Br^-).

*5.4.14 Synthesis of 1-(3-butyl-(4-ferrocenylphenyl)imidazolium bromide (**5.12**)*

This complex was prepared from 1-(4-ferrocenylphenyl)imidazole (0.024 g, 0.0732 mmol) and butyl bromide (0.04 ml, 0.366 mmol). The crude product was obtained as a brownish orange powder. Yield 0.03 g, 91%, mp 158.5 °C; IR (ATR cm^{-1}) 3076, 1527, 1304, 1057, 962, 887, 820, 885, 729, 656, 536, 507, 458; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (1H, s, CH), 7.64 (2H, m, C_6H_4), 7.53 (3H, m, C_6H_4, NCH), 7.34 (1H, s, NCH), 4.66 (4H, m, C_5H_4, NCH_2), 4.38 (2H, t, *J* 1.7, C_5H_4), 4.04 (5H, s, C_5H_5), 1.98 (2H, m, CH_2), 1.23 (2H, m, CH_2), 1.01 (3H, t, *J* 7.4, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.84, 135.84, 131.70, 127.68, 127.19, 121.65, 119.76, 115.02, 82.46, 69.84,

66.77, 65.53, 42.71, 32.27, 19.54, 13.51; **Obtained** 385.13641 (M^+-Br^-). **Calculated** for $C_{23}H_{25}N_2FeBr$ 385.13672 (M^+-Br^-).

5.4.15 General procedures for transfer hydrogenation

Ferrocenylimidazolium salts as catalyst, 0.05 mol%, ketones (2.1 mmol) and KOH (0.112 g, 10 ml, 0.2 M in propan-2-ol) were introduced into a round bottomed flask fitted with a condenser and refluxed at 82 ^oC. The reaction was monitored by gas chromatography, by taking aliquots at time intervals which was passed through a pad of silica and injecting 0.1 μl into a GC with DB wax polyethylene column. The identity of the alcohols was assessed by comparison of their retention time with commercially available (Aldrich Chemical Co) pure samples. Conversions obtained were calculated from the integration values of the GC peaks which are related to residual unreacted ketone.

5.4.16 X-ray crystal determination

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50kV, 30mA) using the APEX 2[46] data collection software. The collection method involved ω-scans of width 0.5° and 512x512 bit data frames. Data reduction was carried out using the program SAINT+[46] and face indexed absorption corrections were made using XPREP.[46] The crystal structure was solved by direct methods using SHELXTL. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL, PLATON[47] and ORTEP-3.[48] The crystal and experimental refinement data for **5.5**, **5.7, 5.8** and **5.9** are summarized in Tables 5.4 and 5.5.

Supplementary Material

Crystallographic data in cif format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 844511-844513 for compounds **5.7, 5.9 and 5.8** respectively. Copies of this information may be obtained free of charge from: The

Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or http:// www.ccdc.cam.ac.uk.

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CHAPTER 6

REACTIVITY OF *N*-HETEROCYCLIC CARBENES TOWARDS MOISTURE

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Abstract

An attack by moisture on saturated *N*-heterocyclic carbenes (NHCs) has resulted in the isolation of two new ionic diamino aldehyde compounds (**6.1** and **6.2**) as products of hydrolysis. The compounds have been analysed by spectroscopic methods. The crystal structures of the compounds are reported. Compounds **6.1** and **6.2** crystallized in the triclinic and orthorhombic systems respectively. The route to the formation of the hydrolysed compounds is formulated to occur via an imidazolinium ring-opening process. Due to the enhanced stability of the unsaturated NHCs as a result of electron delocalization, it was thus possible to synthesize an iron(II) NHC compound **6.3** under similar conditions. Compound **6.3** crystallized in the triclinic crystal system with a pseudo-octahedral piano-stool geometry.

Keywords

Iron(II) precursors, *N*-heterocyclic carbenes, deprotonation, moisture stability, hydrolysis

6.1 Introduction

The increase in the use of *N*-heterocyclic carbenes (NHCs) as precursor ligands in organometallic chemistry and homogeneous catalysis in the last few decades has highlighted the importance of both saturated and unsaturated imidazoli(ni)um salts to these important fields of science [1-3]. In addition NHCs are increasingly utilized as metal-free catalysts and as room temperature ionic liquids for use as electrolytes or green solvents [4]. The interest in NHCs as ligands stem from the ease of functionalization and this ability to stabilize metals in both high and low oxidation states [5]. Numerous advantages of NHCs in catalysis in comparison to the hitherto ubiquitous phosphine ligands have also been noted. These include tighter binding (hence limiting decomposition

reactions associated with ligand dissociation), superior thermal stability, and increased basicity [6]. Additionally, it has been shown by Grubbs that NHC-metal complexes can be easily generated *in situ* with good to high yields [6]. Most of the present studies on NHC-coordination have been focused on the complexes of the platinum group metals (rhodium, palladium and nickel) plus ruthenium based systems for metathesis. However, recently there is an increasing emphasis on the chemistry of Fe based systems as a greener and cheaper alternative to these systems [7,8].

Although the simplest of these methods for the synthesis of metal carbene complexes is the free-carbene route, since commercially available stable salts may be conveniently complexed to metal centers via this method, it has been shown that this can however easily result in the formation of diamino aldehydes through hydrolysis of the ligand in a ring opening reaction [9]. Denk *et. al.* [10] has also studied the reactivities of some stable carbenes toward hydrogen, oxygen, water and carbon monoxide. They found that the carbenes do not react with O_2 or CO but are attacked by water to give the respective hydrolysis products. Hence there is increasing evidence that a hydrolysis reaction is the main competing reaction pathway in the synthesis of metal-carbene complexes via a free-carbene route. Therefore, the synthetic chemist must be aware of the fact that the well-received and generally applied deprotonation protocol involving imidazolium salts with basic transition metal precursors might fail due to the presence of small quantities of water contained in the solvents or salts [11]. Here we present results on the reactivity of saturated NHC ligands towards trace amounts of water resulting in ring opening and formation of hydrolysis products and the successful synthesis of Fe(II) unsaturated NHC complex taking advantage of the reaction type. This study has revealed that in addition to the presence of external moisture (established by others) that the nature of the *N*-substituents on the imidizoli(ni)um ring and water of hydration from hydrate metal salts also influence the hydrolysis reaction and the nature of products obtained.

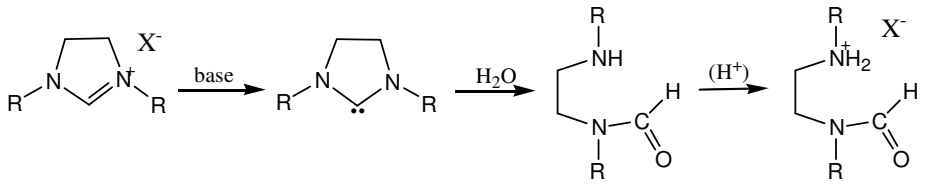
6.2 Results and discussion

NHC complexes of iron are less developed owing to the fact that their preparation has to be done from free carbenes [12-14]. Generation of free carbenes often requires special bases and harsh reaction condition [15]. Deprotonation with potassium tert-butoxide (KOtBu) and generation of the free carbenes in warm toluene [16], which was then metalated *in situ* using $FeCl_2$ and $FeI(Cp)(CO)_2$ as the iron(II) precursors, did not proceed as we expected, but rather gave **6.1** and **6.2** via the ring

opening of the imidazolinium salts forming the diamino aldehydes. Compounds **6.1** and **6.2** were isolated in moderate yields of 51 and 52 % respectively.

The novel ionic compounds **6.1** and **6.2** were characterized by IR, NMR, and LC-MS spectroscopy. IR spectroscopy showed carbonyl signals at 1669, 1657 cm^{-1} and the ^{13}C NMR spectrum give peaks at 163.76, 163.89 ppm respectively for **6.1** and **6.2**. The ESI-MS for compound **6.1** showed the molecular peak [**6.1**] – Cl^- ($C_{21}H_{29}N_2O$) at m/z 325.22737 and molecular peak for compound **6.2** was observed as [**6.2**] ($C_{27}H_{40}N_2O$) at m/z 409.32134. Further evidence for the formation and structure of compounds **6.1** and **6.2** were established by X-ray crystallography. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution. A possible route for the formation of the compounds is suggested in Scheme 6.1 [17]. The imidazolinium salt could be deprotonated in the presence of potassium KOtBu to afford the carbene. The high nucleophilicity of the naked carbene centre resulted in a subsequent insertion into an H-OH bond, leading to ring opening hydrolysis products **6.1** and **6.2**. We can only speculate on the role of the iron precursors; which may also have been involved in the redox process to accelerate the final protonation process in order to stabilize the diaminoaldehyde.

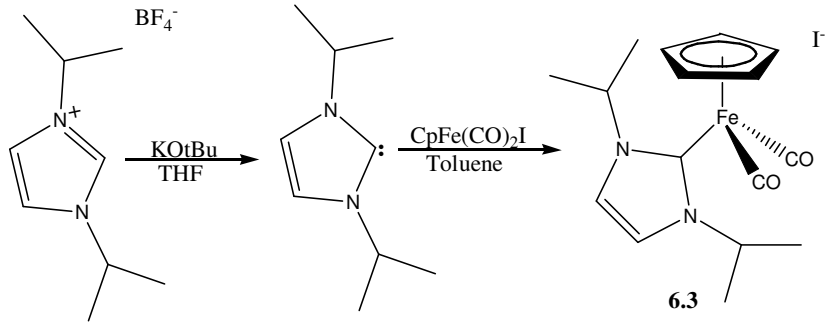
Earlier reported results of some imidazolinium salts showed by thermogravimetric analysis (TGA), that they contained ca. 1 mol H_2O [17]. This further suggested that the source of the water might be from the imidazolinium salts [10]. If all experimental precautions are taken into account, it is safe to conclude that the stability of NHCs is affected by moisture and not oxygen, which leads to the ring opening diaminoaldehyde products. Denk *et. al*. [10] further confirmed that while imidazolinylidenes are instantly hydrolyzed by moist THF or brief exposure to air, hydrolysis of the aromatically stabilized imidazolylidenes requires days to become noticeable and months to be complete. As a result of this reactivity, imidazolylidenes can be handled in air for brief periods of time, while imidazolinylidenes requires a rigorous application of the usual inert atmosphere glovebox or Schlenk techniques [18].



R = 2,4,6-trimethylphenyl X= Cl (**6.1**); R = 2,6-diisopropylphenyl (**6.2**)

Scheme 6.1: Base catalysed hydrolysis route to the formation of compounds **6.1** and **6.2**.

The reaction of unsaturated imidazolium salt with $CpFe(CO)_2I$ as the iron(II) precursor under the same condition was undertaken in order to ascertain if the reaction proceeds to give the expected product**.** This reaction proceeded as expected to generate compound **6.3** as shown in Scheme 6.2. This confirms that unsaturated NHCs are relatively more stable towards moisture and that under similar experimental conditions the generated active carbenes are able to withstand the hydrolysis reaction that is competing with complexation to a metal centre. This is also in line with the fact that the first free carbenes isolated and characterized by Arduengo that sparked renewed interest in the chemistry of NHCs were unsaturated system. This relative stability is a result of π electron delocalization in the carbene containing five membered ring which may also be further stabilised by selective ring substitution via the nitrogen atom *N*-substituents. The effectiveness of the stability due to electron delocalization is lost upon ring saturation as concluded from this study.



Scheme 6.2.: Synthesis of compound **6.3**.

The reaction leading to compound **6.3** (Scheme 6.2) was easily monitored by infrared spectroscopy. The appearance of new CO vibrations for the complex at 2047 and 2001 cm^{-1} as compared to those recorded for the iron(II) precursor, $CPFe(CO)_2I$ (1996 and 2001 cm^{-1}) points to its formation.

Compound **6.3** was isolated as yellow needle crystals that crystallized in the triclinic *P*-1 space group. The complex shows good stability at room temperature in both the solid state and in solution. It can also be handled and kept under air without decomposition. The structure and molecular weight of compound **6.3** was also determined by ^{1}H & ^{13}C NMR spectroscopic analyses and confirmed by mass spectrometry. The ^{1}H & ^{13}C NMR signals of the atoms on the Cp ring appear as singlets at δ 5.45 and 87.5 ppm respectively which corresponds to values reported for related compounds [13]. The appearance of a resonance peak at around 161.5 ppm in the ^{13}C NMR spectrum indicates formation of the Fe-C carbene bond. The positive mode ESI spectrum shows an intense peak corresponding to $[M^{+}- I^{-}]$ which further confirmed the formation of compound **6.3**.

Ortep representations for compounds **6.1, 6.2** and **6.3** are as shown in Figures 6.1, 6.3 and 6.5 respectively. Selected bond lengths and angles are collected in Table 6.1 for comparison. The crystallographic & structure refinement data are summarized in Table 6.2. The X-ray crystal structure of Compound **6.1** contains a cationic 1,4-bis(2,4,6-trimethylphenyl)diaminoaldehyde that is counterbalanced by a chloride ion. The C1-N1 bond length, 1.440(2) Å is slightly longer than those in a similar compound earlier reported [10]. The bond angle O1 – C10 – N1, 124.35(18)° is very close to that of a related structure, 124.6(3)° [16]. The torsion angle of O1 – C10 – N1 – C1 is close to 180°. The interatomic separation from Cl1 to N2 is 2.17 Å.

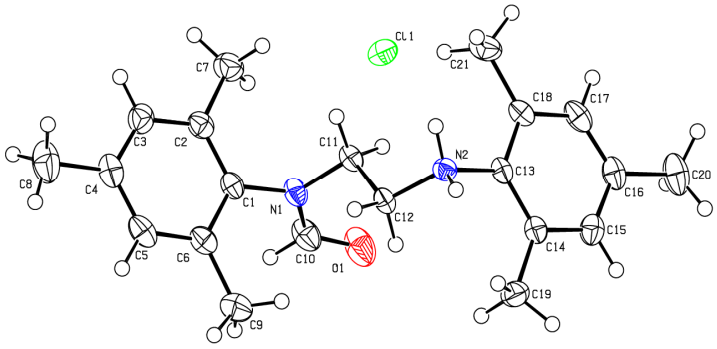


Figure 6.1 ORTEP diagram of Compound **6.1** with thermal ellipsoids shown at the 50% probability level.

The packing diagram of a unit cell of Compound **6.1** (Figure 6.2) has two cations and two anions each of which are related centrosymmetrically. The anions (Cl^{-}) are sandwiched between the

cations 1,4-bis(2,4,6-trimethylphenyl)diaminoaldehyde as viewed along *a*-axis. The anions bridge the cations via N-H…Cl intermolecular interactions. The N…Cl distance is 3.0531(14) Å, while the N-H…Cl angle is 161.4°. There exist close inter-ionic contacts between the cationic NH_2 group and the neighbouring chloride ion of the order of 3.053 Å which is 0.247 Å lower than the sum of the van der Walls radii of the atoms. This may justify the relatively higher melting point for compound **6.1** as compared to that of compound **6.2**.

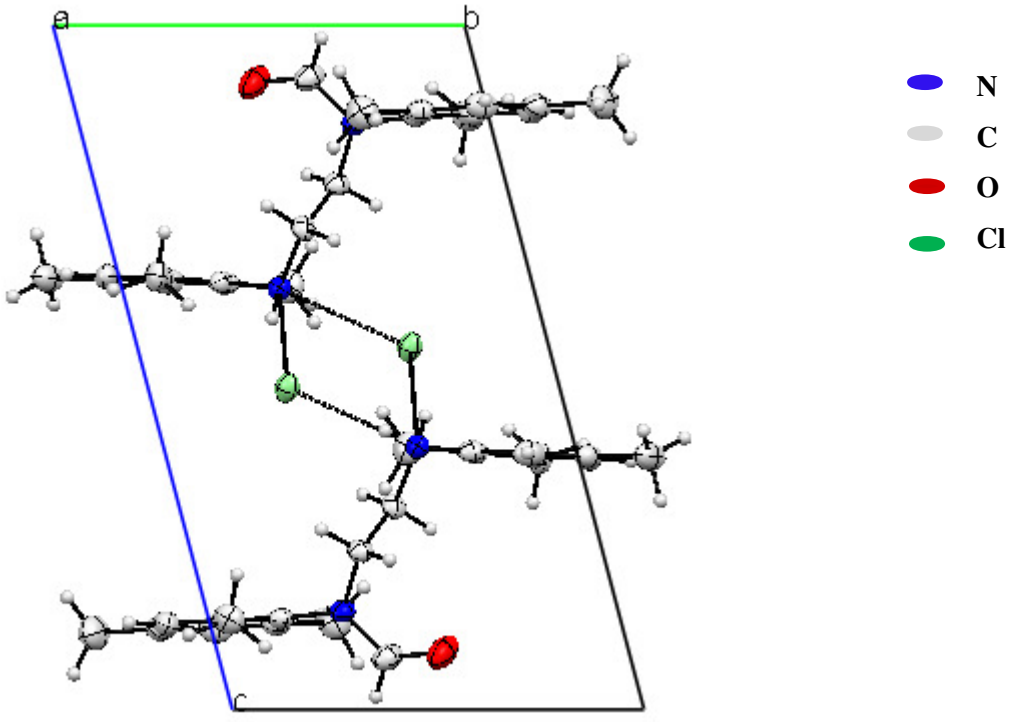


Figure 6.2 Crystal packing in a molecule of **6.1** viewed along the a-axis showing inter-atomic close contacts.

The structure of compound **6.2** is shown in Figure 6.3, which has been previously reported [17]. The bond length of C13-N1 is 1.469(3) Å a bit longer than the bond length of C14-N2, 1.464(3) Å, which can be attributed to the same hybridization of the Csp^2 atoms. The bond length of C15 – N1 is 1.338(3) Å is almost similar to the earlier reported value of 1.333(4) Å [17]. The packing diagram of compound **6.2** is shown in Figure 6.4 which is characterized by a glide plane and a two-fold screw axis that relate adjacent molecules around a centre of inversion.

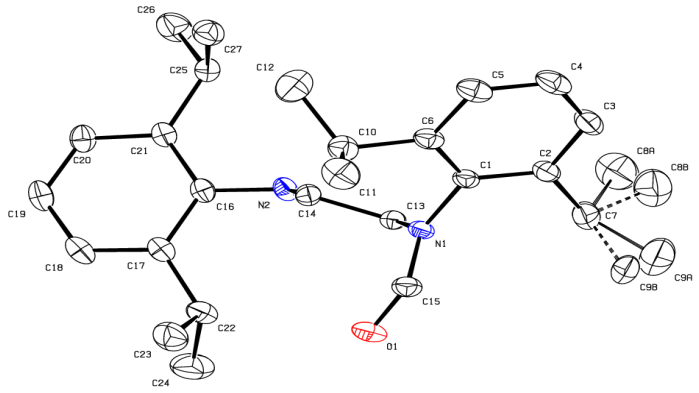


Figure 6.3 ORTEP diagram of Compound 6.**2** with thermal ellipsoids shown at the 50% probability level.

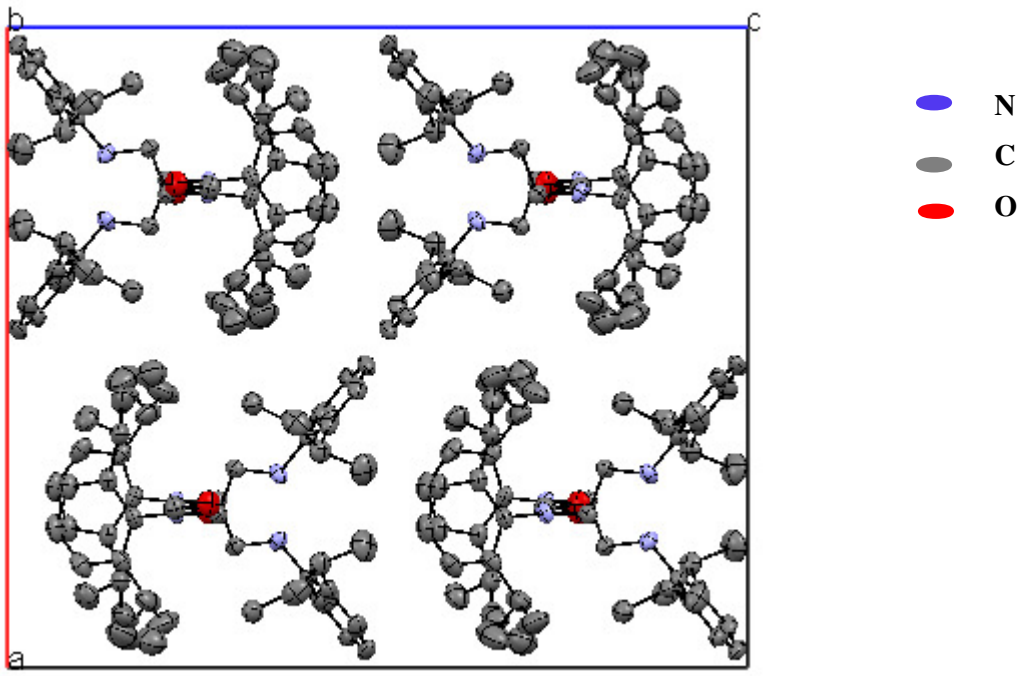


Figure 6.4 Crystal packing in a molecule of **6.2** viewed down the crystallographic *b*-axis.

The molecular structure of compound **6.3** is shown in Figure 6.5 and reveals an ionic piano-stool complex of Fe(II) bearing the NHC ligand bonded in the expected monodentate fashion with iodide as the counter anion. The geometry about the Fe(II) centre is best described as distorted octahedral

with the η^5-Cp ligand occupying three coordination sites and the two CO and NHC ligands occupying the remaining sites. Selected bond lengths and angles are presented in Tables 6.1 and crystallographic parameters for compounds **6.1-6.3** are presented in Table 6.2. The bond length for the Fe-carbene carbon is 1.972(8) Å which fits well in the 1.97-1.99 Å range of related monodentate pianostool iron(II) complexes [13,16]. Compound **6.3** packed with two molecules in a unit cell as shown in Figure 6.6 with the two molecules related through an inversion centre at ($^1/_2$, $^1/_2$, $^1/_2$).

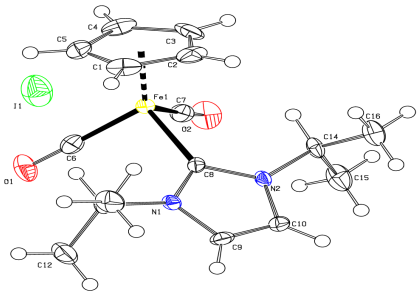


Figure 6.5 ORTEP diagram of compound **6.3** with thermal ellipsoids shown at the 50% probability level.

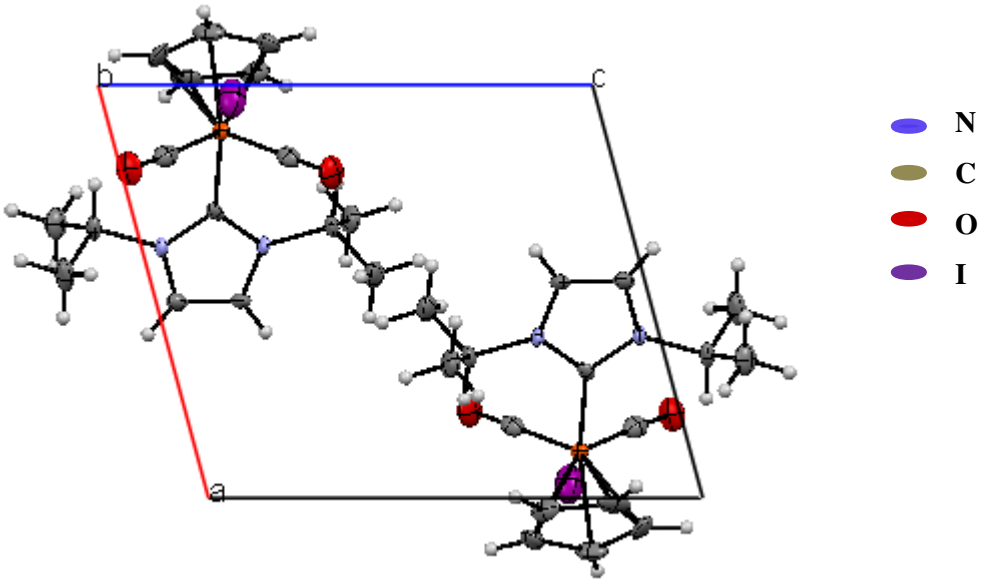


Figure 6.6 Crystal packing in a molecule of **6.3** viewed along the *b*-axis.

Table 6.1

Selected bond lengths (Å) and angles (°) for compounds **6.1**, **6.2** and **6.3**

Compound 6.1		**Compound 6.2**		**Compound 6.3**	
bond	**length**	**bond**	**length**	**bond**	**length**
C10-O1	1.227(2)	C15-O1	1.228(3)	Fe1-C7	1.787(9)
C12-N2	1.495(2)	C1-N1	1.444(3)	Fe1-C8	1.972(8)
C13-N2	1.4802(19)	C16-N2	1.422(3)	C7-O2	1.132(11)
C1-N1	1.440(2)	C13-N1	1.469(3)	Fe1-C6	1.779(9)
C10-N1	1.345(2)	C14-N2	1.464(3)	C6-O1	1.133(10)
C11-N1	1.463(2)	C15-N1	1.338(3)	C8-N2	1.359(9)
bonds	**angles**	**bonds**	**angles**	**bonds**	**angles**
O1-C10-N1	124.35(18)	O1-C15-N1	124.3(3)	O2-C7-Fe1	176.7(8)
N2-C12-C11	111.89(13)	N2-C14-C13	108.2(2)	N1-C8-N2	104.0(6)
N1-C1-C11	120.64(14)	C1-N1-C13	119.5(18)	C6-Fe1-C7	92.7(4)
N1-C11-C12	110.66(14)	C15-N1-C1	121.2(2)	C7-Fe1-C8	94.9(4)
C10-N10-C11	118.12(15)	N1-C13-C14	112.9(2)	C6-Fe1-C8	94.3(3)
C10-N1-C1	121.01(15)	C15-N1-C13	119.2(2)	O1-C6-Fe1	178.6(8)

Table 6.2

Crystallographic data & structure refinement summary for **6.1**, **6.2** and **6.3**

Compound	**6.1**	**6.2**	**6.3**
Formula	$C_{21}H_{29}ClN_2O$	$C_{27}H_{40}N_2O$	$C_{16}H_{21}FeIN_2O_2$
Formula weight	360.91	408.61	456.10
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	*P*-1	Pbca	*P*-1
a, Å	8.2516(2)	19.1817(9)	9.0524(3)
b, Å	8.8822(2)	11.8563(6)	10.2842(3)

c, Å	14.7524(4)	22.1881(12)	10.2882(3)
α deg	74.635(2)	90	89.086(2)
β, deg	86.315(2)	90	75.128(2)
γ, deg	74.635(2)	90	79.328(2)
Cell volume, $Å^3$	1006.38	5046.1(4)	909.20(5)
Z	2	8	2
D_{calcd}, Mg/m^3	1.191	1.076	1.666
T, K	173(2)	173(2)	173(2)
μ, mm^{-1}	0.201	0.065	2.534
F(000)	388	1792	452
Cryst size, mm^3	0.36 x 0.21 x 0.11	0.45 x 0.17 x 0.06	0.28 x 0.09 x 0.05
No. of reflns. collected	19610	21596	12415
Completeness to theta	100% (28.00)	100.0% (25.04)	100% (28.00)
Absorbed correction	None	None	Integration
Goodness-of-fit on F^2	0.903	1.008	0.964
Final R indices	0.0443, 0.0955	0.0531, 0.1265	0.0713, 0.1989
R indices (all data)	0.0810, 0.1073	0.1245, 0.1591	0.1252, 0.2281

6.3 Conclusion

Two ionic diamino aldehyde compounds have been synthesized by the ring opening of the imidazolinium salts in an attempt to synthesize iron(II) *N*-heterocyclic carbene complexes by reaction of the NHC ligand and Fe(II) sources. A complex of Fe(II) NHC was easily synthesized by using an unsaturated imidazolium salt. All the compounds are air stable and were fully characterized by spectroscopic and crystallographic methods.

6.4 Experimental

6.4.1 General procedures

All reactions were conducted under nitrogen using standard Schlenk techniques. All solvents were dried and purified by standard procedure prior to use. All workup procedures were done in air. Reagents were purchased from Aldrich and were used as received. The iron source, $CpFe(CO)_2I$ was synthesized according to literature methods [19]. Infrared spectra were obtained from a Perkin Elmer FT-IR spectrophotometer model 100 equipped with a universal ATR sampling accessory (neat) or Perkin Elmer FT-IR spectrophotometer, model RX 1 in CH_2Cl_2 solution. All NMR experiments were done using a 400 MHz Bruker Ultrashield spectrometer in deuterated chloroform. Accurate mass data was obtained on Thermo Electron DFS dual focusing magnetic sector instrument using ESI in positive mode, polyethylenimine was used as reference solution**.** Melting points were recorded on a Bibby Stuart Scientific model SMP3 apparatus and were uncorrected.

*6.4.2 Synthesis of N,N-bis(2,4,6-trimethylphenyl)-N-formylethylenediamine chloride (**6.1**)*

A mixture of 1,3–bis(2,4,6-trimethyl phenyl)imidazolinium chloride (0.101 g, 0.29 mmol) and potassium tert-butoxide (0.039 g, 0.35 mmol) were dissolved in 20 ml of tetrahydrofuran and stirred at room temperature for 30 mins. After evaporating the solvent, the free carbene was extracted in warm toluene (2 x 20 ml). $FeCl_2$ (0.037 g, 0.29 mmol) was added to the toluene solution and refluxed for 24 h at 90 °C. Removal of the solvent gave a residue that was purified by recrystallization from CH_2Cl_2/hexane to yield orange crystals of **6.1**. Yield 0.05g (51%), Mp 180 °C; IR (ATR) cm^{-1} 2918, 2718, 2607, 1669, 1568, 1482, 1446, 1381, 1345, 1306, 1285, 1207, 1193, 1033, 850, 781, 705, 577, 477, 425; δ_H (400 MHz, $CDCl_3$): 1.60 (6H, s, CH_3), 2.16 (12H, m, CH_3), 2.58 (2H, s, CH_2), 3.76 (2H, s, NCH_2NCHO), 6.92 (4H, s, ArH), 7.92 (2H, s, $ArC\text{-}NH_2^+$), 7.97 (1H, s, NCHO), δ_C (100 MHz, $CDCl_3$): 18.09 ($C_6H_2(CH_3)_3$), 19.35 ($C_6H_2(CH_3)_3$), 21.15 ($C_6H_2(CH_3)_3$), 23.17 ($C_6H_2(CH_3)_3$), 51.12 ($NHCH_2$), 52.08 (NCH_2), 128.27, 130.18, 134.72, 135.91, 138.54, 140.21, 145.23, 160.28 (NCHO); HRMS (ESI) calcd for $C_{21}H_{29}N_2O$ 325.22799, found, 325.22737 ($M^+ - Cl^-$).

*6.4.3 Synthesis of N,N-bis(2,6-diisopropylphenyl)-N-formylethlenediamine (**6.2**)*

A mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (0.101 g, 0.23 mmol) and potassium tert-butoxide (0.0312 g, 0.28 mmol) were dissolved in 10 ml of tetrahydrofuran and

stirred at room temperature for 30 mins, after evaporation of the solvent, the free carbene was extracted in warm toluene (2 x 20 ml). The iron source $CpFe(CO)_2I$ (0.0773 g, 0.26 mmol) was then added to the toluene solution and stirred for 24 h. The solvent was evaporated. Recrystallization from CH_2Cl_2/hexane afforded **6.2** as a yellow crystal. Yield: 0.06 g, (52%), Mp 140 °C; IR (ATR) cm^{-1}, 3379, 2962, 2868, 1657, 1590, 1486, 1458, 1341, 1299, 1191, 1054, 757, 622, 576, 429; δ_H (400 MHz, $CDCl_3$): 1.14 (24H, d, *J* = 6.8 Hz, $CH(CH_3)_2$), 2.98 (2H, d, *J* = 6.7 Hz, $NHCH_2$), 3.08 (4H, m, $CH(CH_3)_2$), 3.82 (2H, t, *J* = 7.2 Hz, CH_2NCHO), 4.06 (1H, s, NH), 7.03 (3H, m, Ar-CH), 7.20 (2H, d, *J* = 7.7 Hz, Ar-CH), 7.35 (1H, d, *J* = 7.6 Hz, Ar-CH), 8.06 (1H, s, NCHO); δ_C (100 MHz, $CDCl_3$): 23.76 ($NHC_6H_3CH(CH_3)_2$), 24.45 ($NHC_6H_3CH(CH_3)_2$, $NC_6H_3CH(CH_3)_2$), 28.00 ($NC_6H_3CH(CH_3)_2$), 28.58 ($NC_6H_3CH(CH_3)_2$), 48.98 ($NHCH_2CH_2N$), 49.09 ($NHCH_2CH_2N$), 123.79, 124.02, 124.78, 129.79, 135.73, 142.54, 143.14, 147.90, 164.16 (NCHO); HRMS (ESI) calcd for $C_{27}H_{40}N_2O$ 409.32189, found, 409.32134 (M^+).

*6.4.4 Synthesis of (η^5-C_5H_5)Fe(CO)$_2$(I^nPr)I (**6.3**)*

A mixture of the 1,3-diisopropylimidazolium tetrafluoroborate (0.30 g, 1.00 mmol) and potassium tert-butoxide (0.14 g, 1.25 mmol) were dissolved in 10 ml of tetrahydrofuran and stirred at room temperature for 30 mins, after evaporation of the solvent the free carbene was extracted in warm toluene (2 x 20 ml). [$CpFe(CO)_2I$] (0.37 g, 1.00 mmol) was then added to the toluene solution and stirred for 24 h. Evaporation of the solvent gave the crude product, which was recrystallized by slow diffusion of hexane into CH_2Cl_2 solution to give analytically pure yellow crystals. Yield 0.31 g (57%). IR (CH_2Cl_2, cm^{-1}): 2047, 2001 ν(CO); δ_H (400 MHz, $CDCl_3$):1.52 (12H, d, CH_3); 4.96 (2H, m, CH), 5.45 (5H, s, Cp), 7.38 ppm (2H, s, NCH), δ_C (100 MHz, $CDCl_3$): 24.2(CH_3), 53.7(CH), 87.5(Cp), 122.4(NCH), 161.5 (NCN), 210.9 ppm (CO); HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2Fe^+$, 329.09525 (M^+ - I), found, 329.09476 (M^+ - I).

6.4.5 X-ray structure determination

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50kV, 30mA) using the APEX 2 data collection software [20]. The collection method involved ω-scans of width 0.5° and 512x512 bit data frames. Data reduction was carried out using the program *SAINT* [21]. The crystal structure was solved by direct methods using *SHELXTL* [22]. Non-hydrogen atoms were first refined isotropically followed by anisotropic

refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL, PLATON and ORTEP-3 [23,24].

Acknowledgements

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CHAPTER 7

STRUCTURES OF *N*,*N*-BIS(TERTBUTYL)-*N*-FORMYLETHYLENEDIAMINE HALIDES OBTAINED BY SALT METATHESIS FROM METAL PRECURSORS

Monisola I. Ikhile . Muhammad D. Bala

Abstract

N,*N*-bis(tertbutyl)-*N*-formylethylenediamine iodide **7.1** and *N*,*N*-bis(tertbutyl)-*N*-formylethylenediamine chloride **7.2** were obtained in an attempt to synthesize *N*-heterocyclic carbene iron(II) complexes via the free carbene route. In the process of generating the free carbenes for subsequent coordination to the iron(II) centres, **7.1** and **7.2** were isolated as products of imidazolinium salt hydrolysis. The iron(II) precursor salts were non-innocent in these reactions as the amine salts bear counter-anions by methathesis from the respective precursors used in each case, $CpFe(CO)_2I$ and $FeCl_2$, for **7.1** and **7.2**. Compounds **7.1** and **7.2** were characterized by single crystal diffraction analysis, ^1H & ^{13}C NMR, IR spectroscopy, HRMS. The single crystal X-ray diffraction analysis reveals that compound **7.1** crystallizes in the orthorhombic P2(1)2(1)2(1) space group while compound **7.2** crystallizes in the triclinic P-1 space group. In compound **7.1**, the molecules are packed with the cations related through a centre of inversion about a pair of iodide anions while in **7.2** the smaller chloride counter anions are sandwiched between the cations. The ionic distance of the chloride ion is 2.26 Å shorter than that of the iodide ion, 2.59 Å in compound **7.1**.

Keywords

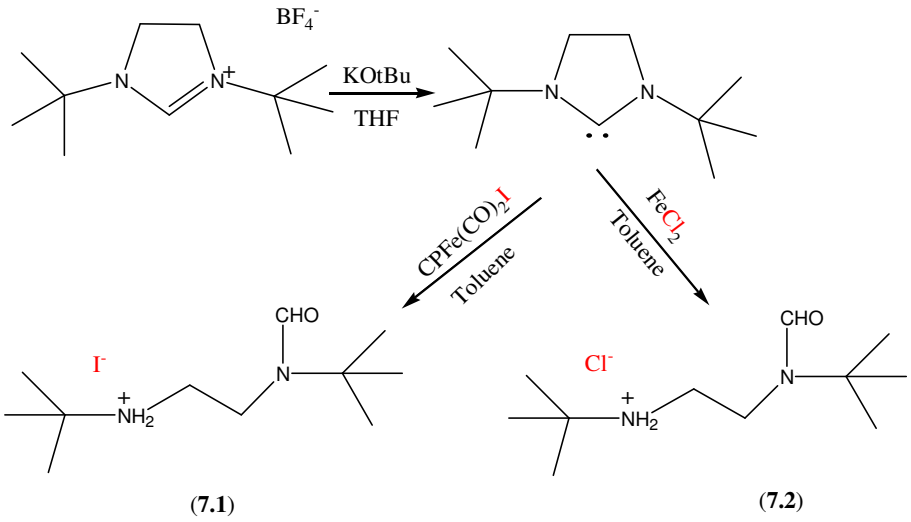
N-heterocyclic carbenes. Iron(II) precursors. Imidazolium salts. Deprotonation. Anions

Introduction

N-heterocyclic carbenes (NHC) have become important as ligands in organometallic chemistry because of their ability to stabilise a large variety of metal systems leading to extensive application as catalysts in transformations of many organic compounds [1-2]. The interest in

the ligands is also due to their unique properties including the ease of preparation and relative stability of their salts towards oxidation. Most of the current NHC complexes are focused on heavy metals such as rhodium, platinum and ruthenium [3] but the chemistry of Fe(II) NHC, which is inexpensive and environmentally friendly is less developed [4].

The title compounds were obtained as part of our work investigating the chemistry of Fe(II) NHC complexes [5-6] for application in catalysis. One of the most utilized methods for the synthesis of metal-NHC complexes is the free carbene route [7-9] which involves deprotonation of a NHC salt by a base and subsequent coordination of the free carbene on to a metal centre (Scheme 7.1). The generated free carbene is highly reactive and is susceptible to attack by any residual moisture in the reaction solvent leading for the need to conduct the reaction in highly anaerobic conditions. The stability of NHC species has been studied [10] with attention centered on the various species responsible for the decomposition of NHCs in solution. It was thus concluded that hydrolysis via attack from moisture is often the principal mode of NHC decomposition [10]. In this paper we report on the non-innocence of metal precursor salts involved in ion exchange to generate corresponding amine salts of the aldehyde generated from hydrolysis of NHCs in the presence of trace amounts of moisture.



Scheme 7.1: Synthesis of compounds **7.1** and **7.2**

Experimental

General procedures

All reactions were done under nitrogen using standard Schlenk techniques and workup procedures were done in air. Solvents were dried and purified by standard procedures prior to use. Reagents were purchased from Aldrich and were used as received. The Fe(II) precursor complex $CpFe(CO)_2I$, was synthesized according to literature method [11]. Infrared spectra were obtained from a Perkin Elmer FT-IR Spectrophotometer model 100 equipped with universal ATR sampling accessory. All NMR experiments were done using a 400 MHz Bruker Ultrashield Spectrometer in deuterated chloroform. Accurate mass data was obtained on Thermo Electron DFS dual focusing magnetic sector instrument using ESI in positive mode, polyethylenimine was used as reference solution. Melting points were recorded on a Bibby Stuart Scientific model SMP3 apparatus and were uncorrected.

*Synthesis of N,N-bis(tertbutyl)-N-formylethylenediamine iodide (**7.1**)*

For the preparation of **7.1** a suspension of 1,3-ditertbutylimidazolinium tetrafluroborate, (0.102 g, 0.38 mmol) in dry tetrahydrofuran (10 ml) was added to potassium tert-butoxide (0.0498 g, 0.45 mmol) and stirred for 1 h at room temperature. This solution was then added to a solution of $CpFe(CO)_2I$ (0.125 g, 0.41 mmol) in dry toluene (30 ml) and stirred for 24 h at room temperature. The solution was then centrifuged, the precipitate collected and washed with 10 ml of toluene. The toluene extract was combined, left standing in air to form yellowish crystals of **7.1**. (yield 0.06 g, 50%; m.p. 431 K). IR (ATR, ν): cm^{-1} 3401, 2969, 2784, 2457, 2161, 2035, 1642, 1619, 1454, 1382, 1364, 1235, 1193, 1062, 1007, 807, 768, 591, 554, 448, 420. ^1H NMR ($CDCl_3$): δ 1.40 (2 x s, 20H, NH_2, $C(CH_3)_3$), 3.13 (s, 2H, NCH_2), 3.78 (s, 2H, NCH_2), 8.36 (s, 1H, NCHO). ^{13}C ($CDCl_3$): δ 26.14 ($NH_2C(CH_3)_3$, 29.15 ($NC(CH_3)_3$), 40.23(NH_2CH_2), 43.14 (NCH_2), 57.22 ($C(CH_3)_3$, 57.37 ($C(CH_3)_3$, 164.13 (NCHO). HRMS (ESI) **calcd** for $C_{11}H_{25}IN_2O$, 201.19669 ($M^+ - I^-$) **found**, 201.19618 ($M^+ - I^-$).

*Synthesis of N,N-bis(tertbutyl)-N-formylethylenediamine chloride (**7.2**)*

For the preparation of **7.2**, 1,3-ditertbutylimidazolinium tetrafluroborate, (0.100 g, 0.37 mmol) and tert-butoxide (0.0494 g, 0.44 mmol) were mixed under nitrogen flow in 10 ml of tetrahydrofuran and stirred at room temperature for 30 mins. After evaporating the solvent, the free carbene was extracted in warm toluene (2 x 20 ml). Iron(II) choride (0.0469 g, 0.37 mmol) was then added to the toluene solution and refluxed for 24 h at 363 K. Removal of the

solvent yielded a residue that was purified by recrystallization from CH_2Cl_2/Hexane to give yellow crystalsof **7.2**. (yield 0.05 g, 54%, m.p. 468 K). IR (ATR, ν): cm^{-1} 3382, 2976, 2739, 1631, 1587, 1459, 1459, 1404, 1373, 1355, 1298, 1232, 1194, 1055, 1044, 865, 759, 587, 519, 498, 429. ^1H NMR ($CDCl_3$): δ 1.39 (m, 20H, NH_2, $C(CH_3)_3$), 3.06 (s, 2H, NCH_2), 3.79 (s, 2H, NCH_2), 8.34 (s, 1H, NCHO). ^{13}C ($CDCl_3$): δ 26.09 ($NH_2C(CH_3)_3$, 28.38 ($NC(CH_3)_3$), 39.80(NH_2CH_2), 42.10 (NCH_2), 56.81 ($C(CH_3)_3$, 57.12 ($C(CH_3)_3$, 163.39 (NCHO). HRMS (ESI) **calcd** for $C_{11}H_{25}ClN_2O$, 201.19669 (M^+ - Cl^-) **found**, 201.19575 (M^+ - Cl^-).

X-ray crystal determination

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50kV, 30mA) using the *APEX 2* [12] data collection software. The collection method involved ω-scans of width 0.5° and 512x512 bit data frames. Data reduction was carried out using the program *SAINT+* [12] and face indexed absorption corrections were made using *XPREP* [12]. The crystal structure was solved by direct methods using *SHELXTL* [13]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using *SHELXTL*, *PLATON* [14] and *ORTEP-3* [15]. The crystal data and experimental data for compounds **7.1** and **7.2** are summarized in Table 7.1. Selected structural parameters are given in Table 7.2.

Results and Discussion

The co-ordination of iron metal to NHC is less developed in organometallic chemistry, even though iron as a metal is relatively cheap, environmentally friendly and readily abundant in comparison to other transition metals usually encountered in homogeneous catalysis [4]. Reason for the poor development of the chemistry and applications of iron NHC complexes relates to difficulties usually encountered in their synthesis [16]. The most successful method for their synthesis thus far is via the free carbene method. Unfortunately, due to stability issues the generated free carbene is susceptible to attack by other electrophiles in addition to any available iron centre. In this study, a free carbene route was employed towards the synthesis of iron(II) NHC complexes, but instead afforded compounds **7.1** and **7.2** via routes shown in Scheme 7.1. The imidazolium salt, 1,3-ditertbutylimidazolinium tetrafluroborate which is the precursor for generation of the free carbene was deprotonated with a strong base KOtBu and

due to the nucleophilic nature of the carbene, it reacted with the moisture present in the solvent during the reaction or present in air during the work up process. The Fe(II) precursors ($CpFe(CO)_2I$ and $FeCl_2$) also participated in the redox process by facilitating protonation and metathesis of counterion.

The two novel compounds (**7.1** and **7.2**) were characterized by IR, ^{1}H- & ^{13}C- NMR spectroscopy and HRMS. The presence of replaceable CO ligands in the precursor salt ($CpFe(CO)_2I$) cm^{-1} for compound **7.1** means it was easy to monitor the reaction and confirm product formation by IR spectroscopy by comparing the relative shift of the CO vibrations of the intended complex with that of the precursor. Suprisingly, no CO vibrations corresponding to any metal complex was observed in the isolated product and analysis by NMR revealed an absence of resonance peak corresponding to the cyclopentadienyl (Cp) ring in the ^{1}H NMR spectrum of compound **7.1**. This indicated that there was no coordination between the Fe(II) precursor and the NHC ligand. Furthermore, IR spectroscopy showed carbonyl signals for compounds **7.1** and **7.2** at 1642 and 1631 cm^{-1} and the ^{13}C NMR spectrum showed carbonyl carbons at 164.13 and 163.39 ppm respectively which are definitely not within the ranges usually associated with metal bound CO ligands. Further evidence was obtained via high resolution MS that confirmed compound **7.1** as [**7.1**] – I^- ($C_{11}H_{25}N_2O$) at m/z 201.19618 and compound **7.2** as [**7.2**] – Cl^- ($C_{11}H_{25}N_2O$) at m/z 201.19575.

Crystals suitable for X-ray analysis for compound **7.1** was obtained in saturated toluene solution at room temperature and for compound **7.2** by slow diffusion of hexane into a saturated dichloromethane solution. For both compounds **7.1** and **7.2** the ligand precursor salt was the same, i.e. 1,3-ditertbutylimidazolinium tetrafluroborate. The crystal structural data confirmed that in both cases there was a salt metathesis reaction involving anion exchange with the respective Fe(II) precursors. The tetrafluoroborate ions are slightly sensitive to hydrolysis, than halides since they are more stable in organic solvents. [17]. Thus, for the tetrafluoroborate salts the cation becomes more reactive affording an easier displacement of BF_4^- with the respective halides from the Fe(II) precursors. This further confirmed that the Fe(II) precursors are not spectators in the hydrolysis reaction but are actually involved in a redox process.

The X-ray crystal structure of Compound **7.1** contains *N,N*-bis(tertbutyl)-*N*-formylethylenediamine and iodide ion as the counter anion as shown in Fig. 7.1, selected bond lengths and angles are shown in Table 7.2. The lone pair of electrons on N1 undergoes delocalization as suggested by the bond angles around atom N1. The bond length C1-N1,

1.504(4) Å is shorter than the bond length C7-N2, which is 1.527 Å. This can be attributed to the bond length of C11 – N1, 1.321(2) which is the intermediate between a single and double bond, thus affording a shorter bond length for C1-N1. The crystal of Compound **7.1** packed with four molecules of both the cation and anion in the asymmetric unit cell (see Fig. 7.2). The molecular packing is in a repeat of pairs such that if **A** = cation and **B** = Anion, then **AABBAA** describes the molecular arrangement in the solid state. Here each pair of the cationic **A** moiety are related through a centre of inversion about a pair of **B** anions when viewed along the *a* axis. Molecules of compound **7.1** are stabilized by intra-molecular N-H…O hydrogen bonds with a H…A separation of 1.85 Å as shown in Table 7.3. There is also a longer range inter ionic H-bond involving the iodide counterion with a separation of 2.59 Å.

The solid state structure of **7.2** is shown in Fig. 7.3. Selected bond lengths and angles are presented in Table 7.2. Almost similar bond lengths are exhibited by both compounds **7.1** and **7.2**. They both crystallized in different space groups. A typical example is the bond length C5-N1 which is 1.468(4) Å for **7.1** and 1.468(3) Å for **7.2**. This is expected as the parent moiety is the similar and its interactions with the counter ion are long range ionic contacts although the differences in electronegativity and size [18] between the chloride ion (2.26 Å) and the larger iodide (2.59 Å) will slightly influence the bond lengths and angles in the parent cation. Hence the bond angle O1-C11-N1 which is 124.3(3)° for compound **7.2** is marginally larger than the equivalent bond angle in compound **7.1** which is 124.0(3)° for instance. Compound **7.2** packed with eight molecules in a unit cell (Fig. 7.4). A chain of intermolecular hydrogen bonds was found between NH group and the neighbouring Cl atoms separated by about 2.19-2.26 Å (the H…O distance) through space. Compound **7.2** packed in such a way that two anion molecules connect via charge assisted N-H…Cl interaction, to two cation molecules which are related through an inversion centre along the c axis. The shorter and hence stronger interionic contacts in a molecule of **7.2** coupled with the higher charge concentration of the chloride counterion justify the higher melting point of this compound.

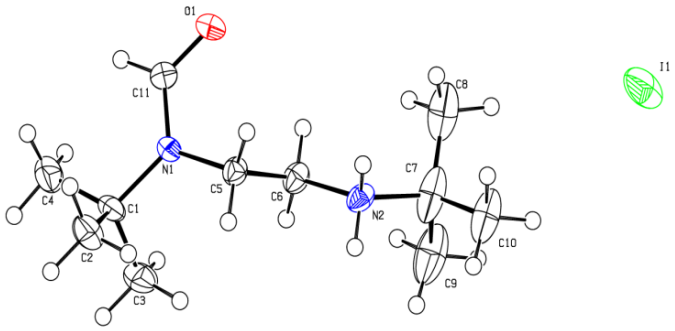


Fig. 7.1 ORTEP diagram showing 50% probability thermal ellipsoids for **7.1**

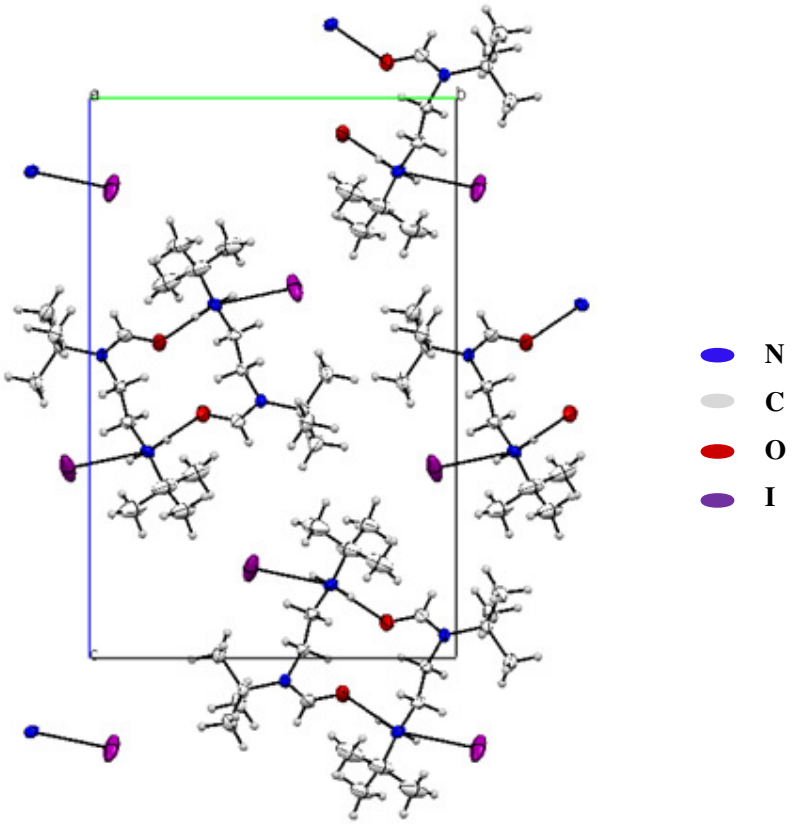


Fig 7.2 Crystal packing in a molecule of **7.1** highlighting the position of the counter-ion

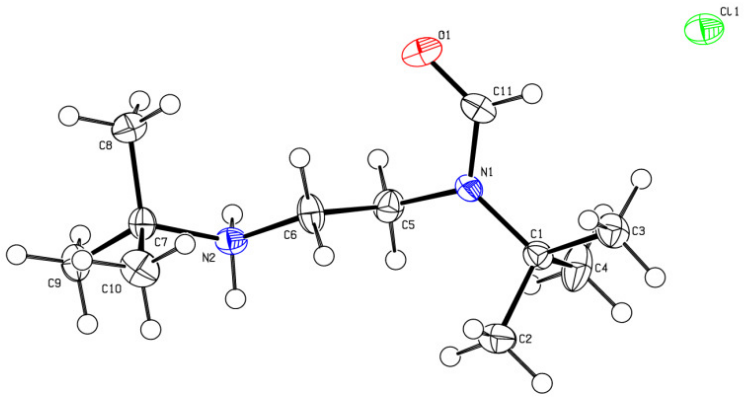


Fig. 7.3 ORTEP diagram showing 50% probability thermal ellipsoids for **7.2**

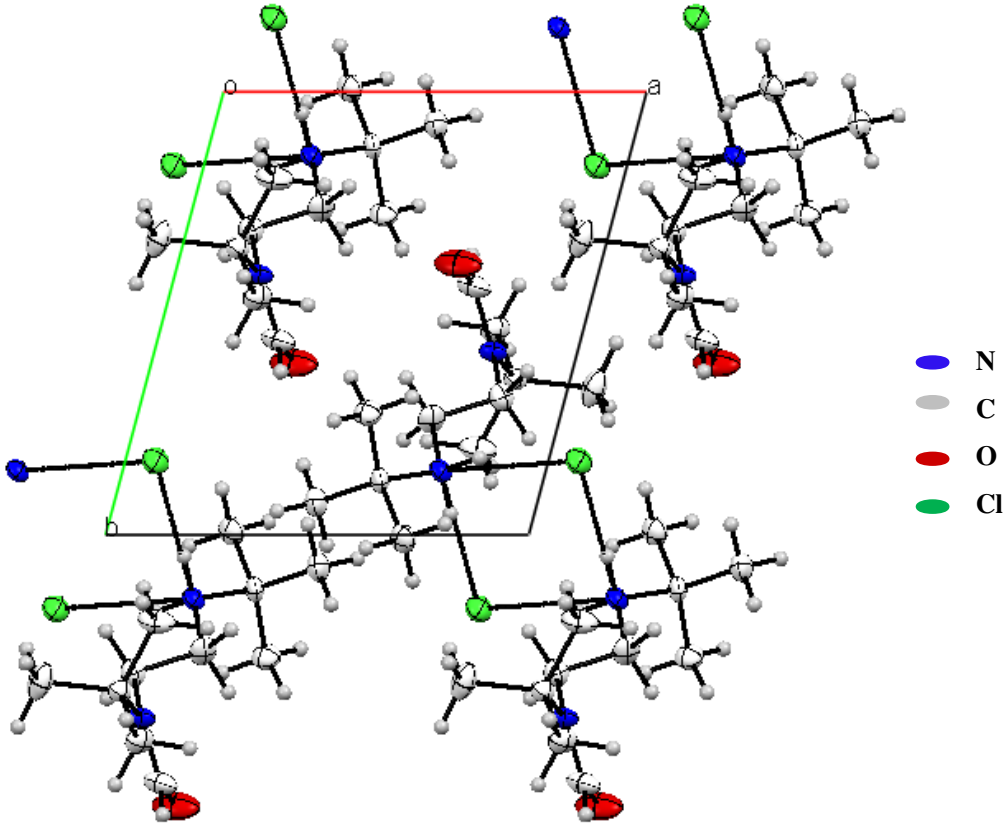


Fig. 7.4 Crystal packing in a molecule of **7.2** highlighting the position of the counter-ion.

Table 7.1 Crystallographic data, data collection and structure refinement parameters

Compound	**7.1**	**7.2**
Formula	$C_{11}H_{25}IN_2O$	$C_{11}H_{25}ClN_2O$
Formula weight	328.23	236.78
Crystal system	Orthorhombic	Triclinic
Space group	P2(1)2(1)2(1)	P-1
a/Å	6.37720(10)	8.9258(9)
b/Å	12.6670(2)	9.3102(10)
c/Å	19.3314(4)	9.7451(9)
α/°	90	108.904(3)
β/°	90	114.355(3)
γ/°	90	95.063(4)
Cell volume/A^3	1561.59(5)	674.44(12)
Z	4	2
Dcald./mg m^{-3}	1.396	1.166
T/K	173(2)	173(2)
μ/mm^{-1}	2.035	0.264
F(000)	664	260
Cryst size/mm^3	0.48 x 0.12 x 0.11	0.21 x 0.05 x 0.04
θ_{min},θ_{max}/°	1.92 to 28.00	2.39 to 25.00
No of reflns collected	23544	5474
Completeness to theta	100% (28.00)	100% (25.00)
Absorbed correction	Integration	None
Goodness of fit on F^2	1.054	0.810
Final R indices	R_1 = 0.0342, wR_2 = 0.0778	R_1 = 0.0460, wR_2 = 0.0632
R indices (all data)	R_1 = 0.0407, wR_2 = 0.0811	R_1 = 0.1359, wR_2 = 0.0818

Table 7.2 Selected structural parameters (Å and °) for compounds **7.1** and **7.2**

	7.1	**7.2**
Bond lengths		
C11-O1	1.236(5)	1.237(4)
C5-N1	1.468(4)	1.468(3)
C1-N1	1.502(4)	1.494(4)
C11-N1	1.321(4)	1.336(4)
C7-N2	1.527(5)	1.528(4)

Bond angles		
O1-C11-N1	124.0(3)	124.3(3)
C11-N1-C1	119.0(3)	124.7(3)
N2-C6-C5	107.9(3)	110.3(2)
C6-N2-C7	118.3(3)	117.1(2)
C11-N1-C5	116.3(3)	116.1(3)

Table 3 Hydrogen bond data for **7.1** and **7.2**

Compound **7.1**				
D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
N2-H2A...I1	0.92	2.59	3.481(3)	162.7
N(2)-H(2B)...O(1)#1	0.92	1.85	2.766(4)	175.1
Compound **7.2**				
D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
N(2)-H(2D)...Cl(1)#1	0.92	2.26	3.148(2)	162.8
N(2)-H(2E)...Cl(1)#2	0.92	2.19	3.104(3)	174.3

Symmetry codes: **7.1:** #1 $x-1/2, -y+5/2, -z+1$
7.2: #1 $x+1, y, z$; #2 $-x+1, -y+2, -z+1$

Conclusion

The synthesis and crystal structures of two novel ionic compounds were successfully obtained in an attempt to synthesize iron(II) *N*-heterocyclic carbene complexes. The crystal structures reveal that the hydrolysed product was obtained by deprotonation of the imidazolinium salts in order to generate the free carbenes. The two compounds have the same cation but different anions. The differences observed in their ionic distances shows the role the size and electronegativity of the counterion plays in the determination of the extent of interaction and molecular packings of the compunds.

Supplementary Material

Crystallographic data in cif format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 844546-844547 for compounds **7.1** and **7.2** respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or http:// www.ccdc.cam.ac.uk.

Acknowledgement

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CHAPTER 8

1,3-BIS(1-ADAMANTYL)IMIDAZOLIUM TETRACHLORIDOFERRATE(III)

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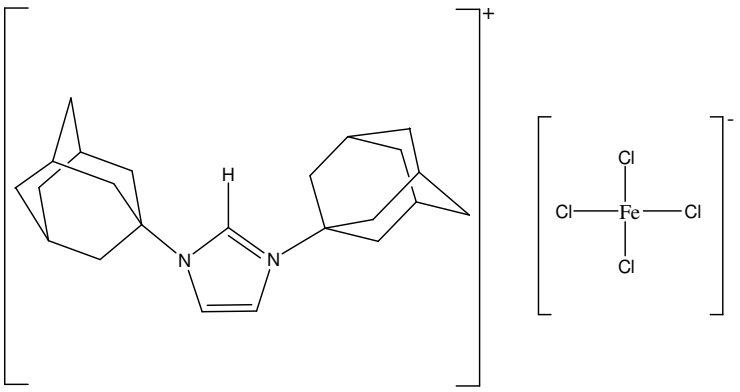
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å
R factor =0.034; wR factor = 0.089; data-to-parameter ratio = 19.5.

Abstract

The crystal structure of the title compound, $(C_{23}H_{33}N_2)$-$[FeCl_4]$, consists of 1,3-bis(1-adamantyl)imidazolium (BAIM)cations and tetrahedral tetrachloridoferrate(III) (TCF) anions. The BAIM cation possesses m symmetry, with the central imidazole ring and four C atoms of each terminal adamantyl group located on a mirror plane. The Fe and two Cl atoms of the TCF anion are also located on the mirror plane. The cyclohexane rings of the adamantyl groups adopt norma lchair conformations.

Related literature

For related structures based on the 1,3-bis(adamantyl)-imidazolium unit, see: Grossie *et al.* (2006, 2009). For a related ynthetic procedure, see: Louie & Grubbs (2000). For related *N*-heterocyclic carbene structures in general, see: Arduengo *et. al.* (1991).



Comment

The title compound (**8.1**) was obtained in an attempt to couple the *N*-heterocyclic carbene (NHC) to $FeCl_2$ using the free carbene method. The anticipated coordinated product was not obtained but a co-crystal of the ligand and $FeCl_4$ anion was isolated as **8.1**. Protonation of the NHC ligand and oxidation of the metal source observed in this process is of structural and synthetic interest.because the free carbene is commonly used for the preparation of NHC-metal complexes especially those reported by sterically demanding imidazolium salts. The structure of (**8.1**) is characterized by a symmetrical imidazolium unit and a tetrahedral iron centre with the asymmetric unit containing an independent protonated 1,3-bis(adamantyl)imidazol-2-ylidene moiety and the tetrachloridoferrate(III) and [$FeCl_4^-$]. The imidazolium moiety and the $FeCl_4^-$ anion are held together by a network Cl(1)···H(9) short distance contacts measured to be 2.904 (2) Å. In addition the molecule of (I) has a crystallographically imposed centrosymmetry and the imidazolium ring is completely planar. The cyclohexane groups of the adamantyl ligands adopt chair conformations.

Experimental

The 1,3-Bis(adamantyl)imidazol-2-ylidenium chloride (0.1 g) and potassium tert-butoxide (0.04 g) were dissolved in 20 ml of THF and stirred at room temperature for 30 min. After evaporating the solvent, the free carbene was extracted in warm toluene (2 x 20 ml). This was followed by addition of 0.034 g of $FeCl_2$ to the toluene solution and reflux for 24 h. After removal of all volatiles, the residue was purified by recrystallization from dichloromethane/hexane to give X-ray quality orange block crystals of (**8.1**).

Data collection

APEX2 (Bruker, 2005); cell refinement: SAINTPlus (Bruker, 2005); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2009) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

Crystal data and structure refinement

Empirical formula	$C_{23}\ H_{33}\ Cl_4\ Fe\ N_2$
Formula weight	535.16
Temperature	173(2) K

Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 15.3517(4) Å	α = 90°.
	b = 9.7557(3) Å	β = 90°.
	c = 16.3502(4) Å	γ = 90°.
Volume	2448.71(12) $Å^3$	
Z	4	
Density (calculated)	1.452 Mg/m^3	
Absorption coefficient	1.066 mm^{-1}	
F(000)	1116	
Crystal size	0.29 x 0.22 x 0.20 mm^3	
Theta range for data collection	1.82 to 28.00°.	
Index ranges	-20<=h<=8, -12<=k<=9, -21<=l<=20	
Reflections collected	14913	
Independent reflections	3126 [R(int) = 0.0488]	
Completeness to theta = 28.00°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.8151 and 0.7474	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3126 / 0 / 160	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0830	
R indices (all data)	R1 = 0.0489, wR2 = 0.0888	
Largest diff. peak and hole	0.759 and -0.421 $e.Å^{-3}$	

Special details

Geometry: All e.s.d.'s (except the e.s.d. in the dihedral angle between two 1.s planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotopic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving 1.s. planes.

Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C-H = 0.95 – 1.00 Å and Uiso (H) = 1.2Ueq(C)

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

Figures

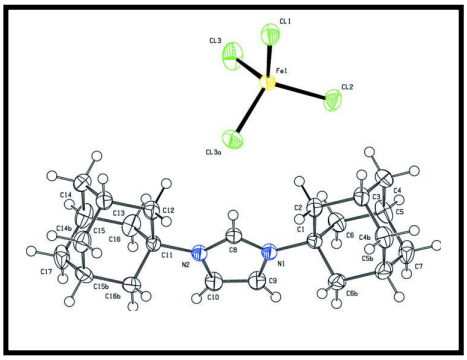


Fig. 8.1. Molecular structure of the title complex with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
C(1)	2591(1)	2500	4456(1)	24(1)
C(2)	3213(2)	2500	5179(2)	32(1)
C(3)	4157(2)	2500	4857(2)	32(1)
C(4)	4306(1)	1222(2)	4341(1)	37(1)
C(5)	3675(1)	1227(2)	3619(1)	39(1)
C(6)	2732(1)	1213(2)	3939(1)	32(1)
C(7)	3824(2)	2500	3105(2)	43(1)
C(8)	1411(2)	2500	5529(1)	25(1)
C(9)	934(2)	2500	4270(2)	32(1)
C(10)	237(2)	2500	4768(2)	33(1)

C(11)	-1(1)	2500	6322(1)	24(1)
C(12)	596(2)	2500	7072(1)	31(1)
C(13)	33(2)	2500	7848(2)	32(1)
C(14)	-533(1)	1222(2)	7856(1)	37(1)
C(15)	-1125(1)	1224(2)	7111(1)	41(1)
C(16)	-567(1)	1214(2)	6331(1)	36(1)
C(17)	-1699(2)	2500	7121(2)	46(1)
N(1)	1668(1)	2500	4753(1)	25(1)
N(2)	544(1)	2500	5563(1)	25(1)
Cl(1)	6396(1)	2500	3031(1)	42(1)
Cl(2)	6652(1)	2500	5209(1)	42(1)
Cl(3)	8179(1)	689(1)	3962(1)	53(1)
Fe(1)	7334(1)	2500	4037(1)	26(1)

Bond lengths [Å] and angles [°]

C(1)-N(1)	1.499(3)
C(1)-C(2)	1.520(3)
C(1)-C(6)	1.529(2)
C(1)-C(6)#1	1.529(2)
C(2)-C(3)	1.542(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.522(2)
C(3)-C(4)#1	1.522(2)
C(3)-H(3)	1.0000
C(4)-C(5)	1.527(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(7)	1.517(3)
C(5)-C(6)	1.540(2)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(5)#1	1.517(3)

C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(1)	1.328(3)
C(8)-N(2)	1.332(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.344(4)
C(9)-N(1)	1.376(3)
C(9)-H(9)	0.9500
C(10)-N(2)	1.383(3)
C(10)-H(10)	0.9500
C(11)-N(2)	1.496(3)
C(11)-C(16)#1	1.526(2)
C(11)-C(16)	1.526(2)
C(11)-C(12)	1.530(3)
C(12)-C(13)	1.536(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.520(2)
C(13)-C(14)#1	1.520(2)
C(13)-H(13)	1.0000
C(14)-C(15)	1.519(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(17)	1.526(3)
C(15)-C(16)	1.537(3)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(15)#1	1.526(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
Cl(1)-Fe(1)	2.1864(7)
Cl(2)-Fe(1)	2.1830(7)
Cl(3)-Fe(1)	2.1952(6)
Fe(1)-Cl(3)#1	2.1952(6)

N(1)-C(1)-C(2)	109.95(19)
N(1)-C(1)-C(6)	108.24(12)
C(2)-C(1)-C(6)	109.97(13)
N(1)-C(1)-C(6)#1	108.24(12)
C(2)-C(1)-C(6)#1	109.97(13)
C(6)-C(1)-C(6)#1	110.4(2)
C(1)-C(2)-C(3)	108.9(2)
C(1)-C(2)-H(2A)	109.9
C(3)-C(2)-H(2A)	109.9
C(1)-C(2)-H(2B)	109.9
C(3)-C(2)-H(2B)	109.9
H(2A)-C(2)-H(2B)	108.3
C(4)-C(3)-C(4)#1	109.9(2)
C(4)-C(3)-C(2)	109.30(13)
C(4)#1-C(3)-C(2)	109.30(13)
C(4)-C(3)-H(3)	109.4
C(4)#1-C(3)-H(3)	109.4
C(2)-C(3)-H(3)	109.4
C(3)-C(4)-C(5)	109.33(16)
C(3)-C(4)-H(4A)	109.8
C(5)-C(4)-H(4A)	109.8
C(3)-C(4)-H(4B)	109.8
C(5)-C(4)-H(4B)	109.8
H(4A)-C(4)-H(4B)	108.3
C(7)-C(5)-C(4)	109.56(17)
C(7)-C(5)-C(6)	109.68(17)
C(4)-C(5)-C(6)	109.52(16)
C(7)-C(5)-H(5)	109.4
C(4)-C(5)-H(5)	109.4
C(6)-C(5)-H(5)	109.4
C(1)-C(6)-C(5)	108.25(16)
C(1)-C(6)-H(6A)	110.0
C(5)-C(6)-H(6A)	110.0
C(1)-C(6)-H(6B)	110.0
C(5)-C(6)-H(6B)	110.0

H(6A)-C(6)-H(6B)	108.4
C(5)#1-C(7)-C(5)	110.0(2)
C(5)#1-C(7)-H(7A)	109.7
C(5)-C(7)-H(7A)	109.7
C(5)#1-C(7)-H(7B)	109.7
C(5)-C(7)-H(7B)	109.7
H(7A)-C(7)-H(7B)	108.2
N(1)-C(8)-N(2)	109.6(2)
N(1)-C(8)-H(8)	125.2
N(2)-C(8)-H(8)	125.2
C(10)-C(9)-N(1)	107.7(2)
C(10)-C(9)-H(9)	126.2
N(1)-C(9)-H(9)	126.2
C(9)-C(10)-N(2)	107.3(2)
C(9)-C(10)-H(10)	126.3
N(2)-C(10)-H(10)	126.3
N(2)-C(11)-C(16)#1	109.03(12)
N(2)-C(11)-C(16)	109.03(12)
C(16)#1-C(11)-C(16)	110.6(2)
N(2)-C(11)-C(12)	109.26(17)
C(16)#1-C(11)-C(12)	109.45(13)
C(16)-C(11)-C(12)	109.45(13)
C(11)-C(12)-C(13)	109.04(18)
C(11)-C(12)-H(12A)	109.9
C(13)-C(12)-H(12A)	109.9
C(11)-C(12)-H(12B)	109.9
C(13)-C(12)-H(12B)	109.9
H(12A)-C(12)-H(12B)	108.3
C(14)-C(13)-C(14)#1	110.2(2)
C(14)-C(13)-C(12)	109.17(13)
C(14)#1-C(13)-C(12)	109.17(13)
C(14)-C(13)-H(13)	109.4
C(14)#1-C(13)-H(13)	109.4
C(12)-C(13)-H(13)	109.4
C(15)-C(14)-C(13)	109.52(16)

C(15)-C(14)-H(14A)	109.8
C(13)-C(14)-H(14A)	109.8
C(15)-C(14)-H(14B)	109.8
C(13)-C(14)-H(14B)	109.8
H(14A)-C(14)-H(14B)	108.2
C(14)-C(15)-C(17)	109.78(17)
C(14)-C(15)-C(16)	109.41(16)
C(17)-C(15)-C(16)	109.65(19)
C(14)-C(15)-H(15)	109.3
C(17)-C(15)-H(15)	109.3
C(16)-C(15)-H(15)	109.3
C(11)-C(16)-C(15)	108.65(15)
C(11)-C(16)-H(16A)	110.0
C(15)-C(16)-H(16A)	110.0
C(11)-C(16)-H(16B)	110.0
C(15)-C(16)-H(16B)	110.0
H(16A)-C(16)-H(16B)	108.3
C(15)#1-C(17)-C(15)	109.3(2)
C(15)#1-C(17)-H(17A)	109.8
C(15)-C(17)-H(17A)	109.8
C(15)#1-C(17)-H(17B)	109.8
C(15)-C(17)-H(17B)	109.8
H(17A)-C(17)-H(17B)	108.3
C(8)-N(1)-C(9)	107.82(19)
C(8)-N(1)-C(1)	126.18(19)
C(9)-N(1)-C(1)	126.0(2)
C(8)-N(2)-C(10)	107.5(2)
C(8)-N(2)-C(11)	126.38(19)
C(10)-N(2)-C(11)	126.09(19)
Cl(2)-Fe(1)-Cl(1)	110.16(3)
Cl(2)-Fe(1)-Cl(3)#1	109.40(2)
Cl(1)-Fe(1)-Cl(3)#1	110.33(2)
Cl(2)-Fe(1)-Cl(3)	109.40(2)
Cl(1)-Fe(1)-Cl(3)	110.33(2)
Cl(3)#1-Fe(1)-Cl(3)	107.16(3)

Anisotropic displacement parameters

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	31(1)	22(1)	0	-3(1)	0
C(2)	23(1)	53(2)	20(1)	0	-3(1)	0
C(3)	20(1)	53(2)	22(1)	0	-3(1)	0
C(4)	25(1)	42(1)	43(1)	5(1)	-1(1)	6(1)
C(5)	26(1)	47(1)	42(1)	-17(1)	1(1)	4(1)
C(6)	26(1)	35(1)	35(1)	-8(1)	-3(1)	0(1)
C(7)	27(1)	82(2)	21(1)	0	1(1)	0
C(8)	22(1)	31(1)	22(1)	0	-4(1)	0
C(9)	26(1)	49(2)	22(1)	0	-6(1)	0
C(10)	24(1)	50(2)	25(1)	0	-6(1)	0
C(11)	21(1)	29(1)	22(1)	0	0(1)	0
C(12)	22(1)	46(2)	25(1)	0	-2(1)	0
C(13)	26(1)	46(2)	23(1)	0	-2(1)	0
C(14)	43(1)	35(1)	32(1)	7(1)	7(1)	4(1)
C(15)	40(1)	46(1)	35(1)	-5(1)	5(1)	-22(1)
C(16)	39(1)	36(1)	31(1)	-6(1)	1(1)	-12(1)
C(17)	20(1)	88(3)	29(2)	0	0(1)	0
N(1)	21(1)	33(1)	22(1)	0	-3(1)	0
N(2)	21(1)	31(1)	22(1)	0	-3(1)	0
Cl(1)	33(1)	64(1)	28(1)	0	-2(1)	0
Cl(2)	44(1)	53(1)	28(1)	0	6(1)	0
Cl(3)	50(1)	40(1)	68(1)	14(1)	16(1)	18(1)
Fe(1)	26(1)	25(1)	27(1)	0	1(1)	0

Hydrogen coordinates (x 10^4) and isotropic displacement parameters

	x	y	z	U(eq)
H(2A)	3111	1677	5521	38
H(2B)	3111	3323	5521	38
H(3)	4570	2500	5330	38

H(4A)	4211	393	4678	44
H(4B)	4914	1208	4138	44
H(5)	3778	393	3276	46
H(6A)	2318	1201	3474	38
H(6B)	2631	383	4274	38
H(7A)	4427	2500	2891	52
H(7B)	3419	2500	2634	52
H(8)	1788	2500	5990	30
H(9)	922	2500	3689	39
H(10)	-356	2500	4603	40
H(12A)	973	3323	7064	37
H(12B)	973	1677	7064	37
H(13)	419	2500	8341	38
H(14A)	-160	394	7849	44
H(14B)	-889	1202	8361	44
H(15)	-1502	388	7121	49
H(16A)	-194	386	6320	43
H(16B)	-947	1198	5842	43
H(17A)	-2087	2500	6637	55
H(17B)	-2068	2500	7618	55

Torsion angles [°]

N(1)-C(1)-C(2)-C(3)	180.0
C(6)-C(1)-C(2)-C(3)	60.91(14)
C(6)#1-C(1)-C(2)-C(3)	-60.91(14)
C(1)-C(2)-C(3)-C(4)	-60.16(14)
C(1)-C(2)-C(3)-C(4)#1	60.16(14)
C(4)#1-C(3)-C(4)-C(5)	-59.7(2)
C(2)-C(3)-C(4)-C(5)	60.3(2)
C(3)-C(4)-C(5)-C(7)	59.5(2)
C(3)-C(4)-C(5)-C(6)	-60.9(2)
N(1)-C(1)-C(6)-C(5)	178.92(16)
C(2)-C(1)-C(6)-C(5)	-61.0(2)
C(6)#1-C(1)-C(6)-C(5)	60.6(2)

C(7)-C(5)-C(6)-C(1)	-59.7(2)
C(4)-C(5)-C(6)-C(1)	60.5(2)
C(4)-C(5)-C(7)-C(5)#1	-59.9(3)
C(6)-C(5)-C(7)-C(5)#1	60.4(2)
N(1)-C(9)-C(10)-N(2)	0.0
N(2)-C(11)-C(12)-C(13)	180.0
C(16)#1-C(11)-C(12)-C(13)	60.68(13)
C(16)-C(11)-C(12)-C(13)	-60.68(13)
C(11)-C(12)-C(13)-C(14)	60.27(13)
C(11)-C(12)-C(13)-C(14)#1	-60.27(13)
C(14)#1-C(13)-C(14)-C(15)	59.3(2)
C(12)-C(13)-C(14)-C(15)	-60.6(2)
C(13)-C(14)-C(15)-C(17)	-59.4(2)
C(13)-C(14)-C(15)-C(16)	61.0(2)
N(2)-C(11)-C(16)-C(15)	-179.91(16)
C(16)#1-C(11)-C(16)-C(15)	-60.0(2)
C(12)-C(11)-C(16)-C(15)	60.6(2)
C(14)-C(15)-C(16)-C(11)	-60.7(2)
C(17)-C(15)-C(16)-C(11)	59.8(2)
C(14)-C(15)-C(17)-C(15)#1	59.7(3)
C(16)-C(15)-C(17)-C(15)#1	-60.5(3)
N(2)-C(8)-N(1)-C(9)	0.0
N(2)-C(8)-N(1)-C(1)	180.0
C(10)-C(9)-N(1)-C(8)	0.0
C(10)-C(9)-N(1)-C(1)	180.0
C(2)-C(1)-N(1)-C(8)	0.0
C(6)-C(1)-N(1)-C(8)	120.14(13)
C(6)#1-C(1)-N(1)-C(8)	-120.14(13)
C(2)-C(1)-N(1)-C(9)	180.0
C(6)-C(1)-N(1)-C(9)	-59.86(13)
C(6)#1-C(1)-N(1)-C(9)	59.86(13)
N(1)-C(8)-N(2)-C(10)	0.0
N(1)-C(8)-N(2)-C(11)	180.0
C(9)-C(10)-N(2)-C(8)	0.0
C(9)-C(10)-N(2)-C(11)	180.0

C(16)#1-C(11)-N(2)-C(8)	119.58(13)
C(16)-C(11)-N(2)-C(8)	-119.58(13)
C(12)-C(11)-N(2)-C(8)	0.0
C(16)#1-C(11)-N(2)-C(10)	-60.42(13)
C(16)-C(11)-N(2)-C(10)	60.42(13)
C(12)-C(11)-N(2)-C(10)	180.0

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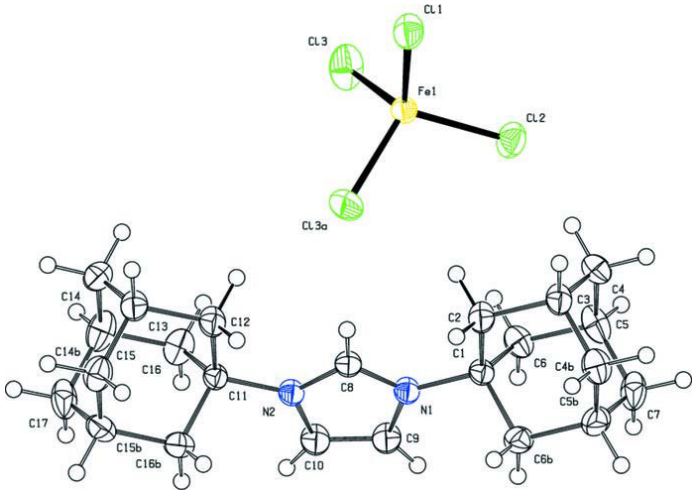
We wish to thank Dr Manuel Fernandes (University of theWitwatersrand) for data collection, and the University of KwaZulu-Natal and the NRF for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5064).

Fig. 8.1



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CHAPTER 9

1,3-BIS(2,6-DIISOPROPYLPHENYL)-4,5-DIHYDRO-1H-IMIDAZOL-3-IUM TRIIODIDE

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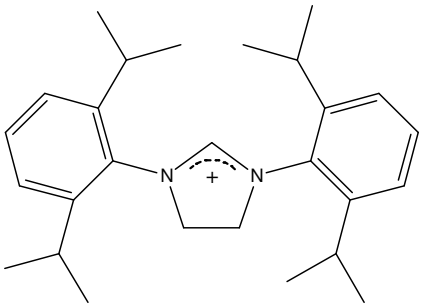
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.007 Å;
R factor = 0.039; wR factor = 0.122; data-to-parameter ratio = 24.3.

Abstract

In the crystal structure of the title compound, $C_{27}H_{39}N_2^+.I_3^-$, the imidazolidinium ring is perpendicular to a mirror plane which bisects the cation. The dihedral angle between the imidazolidinium ring and the benzene ring is 89.0 (2)°. The triiodide anion also lies on a mirror plane and is almost linear with an I—I—I bond angle of 178.309 (18)°.

Related literature

For a related structure with a 1,3-(2,6-diisopropylphenyl)-imidazolidinium unit, see: Giffin *et al*. (2010). For its synthesis,see: Llewellyn *et al.* (2006).



I_3^-

Comment

We were using a general synthetic method that involved the deprotonation of *N*-heterocyclic carbenes (NHC) salts with strong bases to generate free carbenes, followed by *in situ* metallation with an iron(II) precursors to generate iron(II) based NHC complexes. In order to obtain pianostool type compounds, η^5-$CpFe(CO)_2I$ was used as the iron(II) precursor. Piano-

stool type complexes are of interest due to their outstanding spectroscopic and structural features which has made them the subject of many elegant studies in the past. But in this instance, the title compound $C_{27}H_{39}N_2I_3$ (**9.1**) was obtained as a triiodide adduct of the protonated NHC ligand. A molecule of the cationic NHC is characterized by a bisecting mirror plane, while the triilodide counterion is symmetrical around the central iodine atom I2. The imidazolidinium ring is nearly orthogonal to the phenyl rings of the N-substituents with torsion angles N13-N1-C1-C6 close to 90°. The triilodide counterion is linear.

Experimental

To a suspension of 1,3-bis(2,6-diisopropylphenyl)imidazolidinum chloride (0.1 g) in dry THF (15 ml) was added potassium tert-butoxide (0.031 g). After 1 h, this solution was added to a solution of [η5-CpFe(CO)$_2$I] (0.07 g) in dry toluene (40 ml). After stirring for 20 h, the resulting precipitate was centrifuged and washed once with dry toluene (30 ml). The toluene extracts were combined and left standing in air to form shiny black crystals of (**9.1**).

Data collection:

APEX2 (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*

Crystal data and structure refinement

Empirical formula	$C_{27}H_{39}I_3N_2$	
Formula weight	772.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/m	
Unit cell dimensions	a = 18.0288(5) Å	α = 90°
	b = 15.4554(5) Å	β = 129.456(1)°
	c = 13.8457(6) Å	γ = 90°
Volume	2978.81(18) Å^3	
Z	4	

Density (calculated)	1.722 Mg/m^3
Absorption coefficient	3.164 mm^{-1}
F(000)	1496
Crystal size	0.39 x 0.22 x 0.14 mm^3
Theta range for data collection	1.90 to 25.99°.
Index ranges	-16<=h<=21, -19<=k<=17, -17<=l<=10
Reflections collected	10590
Independent reflections	3025 [R(int) = 0.0474]
Completeness to theta = 25.99°	99.0 %
Absorption correction	Integration
Max. and min. transmission	0.6657 and 0.3717
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3025 / 0 / 155
Goodness-of-fit on F^2	1.133
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.1024
R indices (all data)	R1 = 0.0564, wR2 = 0.1254
Largest diff. peak and hole	1.885 and -1.317 $e.Å^{-3}$

Special details

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

Refinement

Hydrogen atoms were first located in difference map and then positioned geometrically (C-H = 0.95-1.00 Å) and allowed to ride on their respective parent atoms. The highest peak and the deepest hole in the difference fourier map are located 0.87 and 0.65 Å, respectively, from atom 13.

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit s are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factor (gt) etc and is not

relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Figures

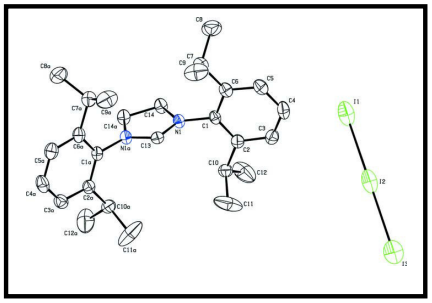


Fig. 9.1. Molecular structure of the title compound with the atom labeling scheme for non-hydrogen atoms. Ellipsoids are drawn at 50% probability level. All H atoms have been omitted.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
C(1)	3530(3)	3424(2)	2271(3)	25(1)
C(2)	3464(3)	3008(3)	3117(3)	27(1)
C(3)	3832(3)	2176(3)	3478(3)	32(1)
C(4)	4234(3)	1776(3)	3013(4)	38(1)
C(5)	4285(3)	2200(3)	2178(4)	36(1)
C(6)	3926(3)	3033(3)	1777(3)	29(1)
C(7)	4002(3)	3503(3)	879(4)	33(1)
C(8)	3652(4)	2952(4)	-246(4)	57(1)
C(9)	5023(4)	3803(4)	1556(4)	58(2)
C(10)	3021(3)	3435(3)	3630(3)	31(1)
C(11)	3787(4)	3692(5)	4980(5)	82(2)
C(12)	2255(5)	2877(4)	3461(7)	74(2)
C(13)	3642(4)	5000	2404(4)	24(1)
C(14)	2147(3)	4502(2)	778(3)	29(1)
N(1)	3154(2)	4291(2)	1873(3)	24(1)
I(1)	2458(1)	0	2774(1)	63(1)
I(2)	3495(1)	0	5434(1)	52(1)
I(3)	4512(1)	0	8170(1)	62(1)

Bond lengths [Å] and angles [°]

C(1)-C(6)	1.402(6)
C(1)-C(2)	1.406(5)
C(1)-N(1)	1.443(5)
C(2)-C(3)	1.386(5)
C(2)-C(10)	1.517(6)
C(3)-C(4)	1.383(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.382(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.389(6)
C(5)-H(5)	0.9500
C(6)-C(7)	1.519(6)
C(7)-C(9)	1.513(6)
C(7)-C(8)	1.516(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.509(6)
C(10)-C(12)	1.514(7)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-N(1)	1.301(4)
C(13)-N(1)#1	1.301(4)
C(13)-H(13)	0.9500

C(14)-N(1)	1.484(4)
C(14)-C(14)#1	1.538(7)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
I(1)-I(2)	2.8824(7)
I(2)-I(3)	2.9809(7)

C(6)-C(1)-C(2)	123.2(4)
C(6)-C(1)-N(1)	118.4(3)
C(2)-C(1)-N(1)	118.4(3)
C(3)-C(2)-C(1)	116.8(4)
C(3)-C(2)-C(10)	120.6(4)
C(1)-C(2)-C(10)	122.6(4)
C(2)-C(3)-C(4)	121.3(4)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	120.7(4)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.8(4)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	117.2(4)
C(5)-C(6)-C(7)	120.6(4)
C(1)-C(6)-C(7)	122.1(4)
C(9)-C(7)-C(6)	110.2(3)
C(9)-C(7)-C(8)	110.9(4)
C(6)-C(7)-C(8)	112.2(4)
C(9)-C(7)-H(7)	107.8
C(6)-C(7)-H(7)	107.8
C(8)-C(7)-H(7)	107.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5

H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(12)	111.7(5)
C(11)-C(10)-C(2)	110.7(4)
C(12)-C(10)-C(2)	112.3(4)
C(11)-C(10)-H(10)	107.3
C(12)-C(10)-H(10)	107.3
C(2)-C(10)-H(10)	107.3
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(1)-C(13)-N(1)#1	114.7(5)
N(1)-C(13)-H(13)	122.6
N(1)#1-C(13)-H(13)	122.6
N(1)-C(14)-C(14)#1	102.70(19)
N(1)-C(14)-H(14A)	111.2
C(14)#1-C(14)-H(14A)	111.2
N(1)-C(14)-H(14B)	111.2
C(14)#1-C(14)-H(14B)	111.2
H(14A)-C(14)-H(14B)	109.1

C(13)-N(1)-C(1)	125.5(3)
C(13)-N(1)-C(14)	109.9(3)
C(1)-N(1)-C(14)	124.5(3)
I(1)-I(2)-I(3)	178.30(2)

Anisotropic displacement parameters ($Å^2 x\ 10^3$)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(2)	20(2)	27(2)	-2(1)	13(2)	-1(2)
C(2)	22(2)	26(2)	25(2)	-2(2)	10(2)	-2(2)
C(3)	30(2)	30(2)	30(2)	3(2)	16(2)	0(2)
C(4)	35(2)	23(2)	45(2)	4(2)	20(2)	4(2)
C(5)	35(2)	31(2)	41(2)	-4(2)	24(2)	2(2)
C(6)	22(2)	26(2)	32(2)	-4(2)	15(2)	-4(2)
C(7)	31(2)	34(2)	39(2)	-2(2)	24(2)	1(2)
C(8)	67(4)	57(3)	39(2)	-11(2)	30(2)	-19(3)
C(9)	47(3)	86(4)	50(3)	-14(3)	35(2)	-28(3)
C(10)	31(2)	32(2)	27(2)	-1(2)	18(2)	1(2)
C(11)	49(3)	121(6)	43(3)	-37(3)	14(2)	20(4)
C(12)	102(5)	59(4)	118(5)	-28(4)	97(5)	-25(4)
C(13)	21(3)	27(3)	22(2)	0	13(2)	0
C(14)	19(2)	26(2)	30(2)	-1(2)	9(2)	1(2)
N(1)	19(2)	21(2)	26(1)	0(1)	11(1)	1(1)
I(1)	47(1)	39(1)	85(1)	0	33(1)	0
I(2)	33(1)	36(1)	85(1)	0	36(1)	0
I(3)	36(1)	62(1)	79(1)	0	33(1)	0

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
H(3)	3808	1875	4055	39
H(4)	4478	1204	3272	46
H(5)	4569	1917	1874	43
H(7)	3584	4028	568	40
H(8A)	3662	3296	-833	86
H(8B)	2995	2757	-661	86
H(8C)	4073	2449	28	86
H(9A)	5237	4149	2286	87
H(9B)	5050	4155	991	87
H(9C)	5444	3298	1831	87
H(10)	2701	3979	3142	37
H(11A)	4078	3171	5498	123
H(11B)	3499	4039	5258	123
H(11C)	4283	4032	5060	123
H(12A)	1761	2737	2573	111
H(12B)	1963	3192	3759	111
H(12C)	2547	2341	3942	111
H(13)	4303	5000	3121	28
H(14A)	1690	4270	882	35
H(14B)	1981	4270	-5	35

Torsion angles [°]

C(6)-C(1)-C(2)-C(3)	1.2(5)
N(1)-C(1)-C(2)-C(3)	180.0(3)
C(6)-C(1)-C(2)-C(10)	-179.1(4)
N(1)-C(1)-C(2)-C(10)	-0.3(5)
C(1)-C(2)-C(3)-C(4)	-0.6(6)
C(10)-C(2)-C(3)-C(4)	179.7(4)
C(2)-C(3)-C(4)-C(5)	0.4(6)
C(3)-C(4)-C(5)-C(6)	-0.6(6)

C(4)-C(5)-C(6)-C(1)	1.0(6)
C(4)-C(5)-C(6)-C(7)	178.8(4)
C(2)-C(1)-C(6)-C(5)	-1.4(6)
N(1)-C(1)-C(6)-C(5)	179.8(3)
C(2)-C(1)-C(6)-C(7)	-179.1(3)
N(1)-C(1)-C(6)-C(7)	2.1(5)
C(5)-C(6)-C(7)-C(9)	-74.6(5)
C(1)-C(6)-C(7)-C(9)	103.0(5)
C(5)-C(6)-C(7)-C(8)	49.4(5)
C(1)-C(6)-C(7)-C(8)	-132.9(4)
C(3)-C(2)-C(10)-C(11)	73.1(6)
C(1)-C(2)-C(10)-C(11)	-106.6(5)
C(3)-C(2)-C(10)-C(12)	-52.5(5)
C(1)-C(2)-C(10)-C(12)	127.9(5)
N(1)#1-C(13)-N(1)-C(1)	179.3(3)
N(1)#1-C(13)-N(1)-C(14)	0.1(6)
C(6)-C(1)-N(1)-C(13)	-89.2(5)
C(2)-C(1)-N(1)-C(13)	91.9(5)
C(6)-C(1)-N(1)-C(14)	89.9(4)
C(2)-C(1)-N(1)-C(14)	-89.0(4)
C(14)#1-C(14)-N(1)-C(13)	-0.1(3)
C(14)#1-C(14)-N(1)-C(1)	-179.3(3)

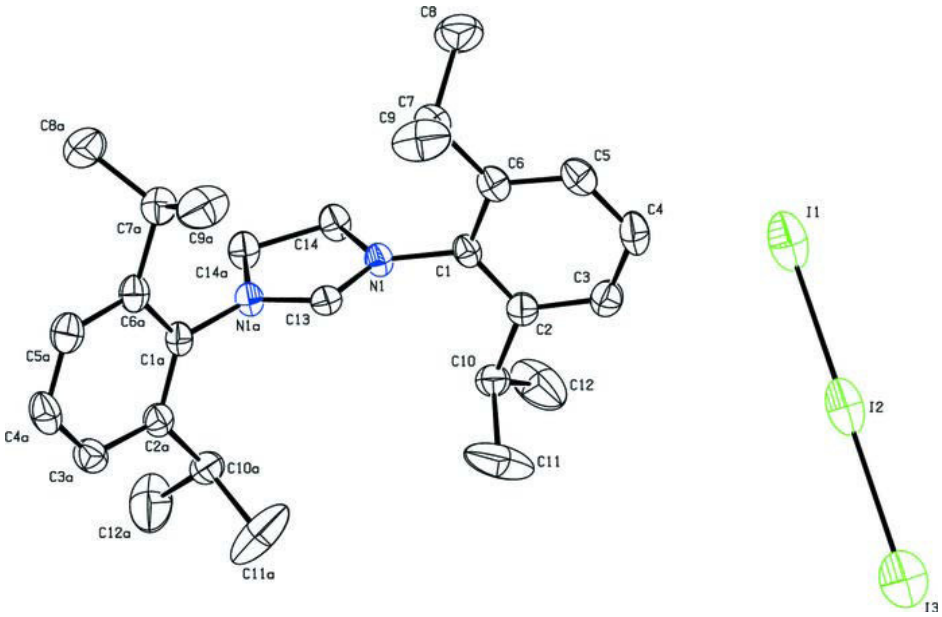
Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1,z

Acknowlegements

We wish to thank Dr Manuel Fernandes for the data collection and the University KwaZulu-Natal and the NRF for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2624).

Fig. 9.1


C8
C7
C9
C8a
C6
C5
C4
C7a
C9a
C14
C14a
N1
C1
C3
C6a
N1a
C13
C2
C5a
C1a
C10
C12
C4a
C2a
C11
C3a
C10a
C12a
C11a
I1
I2
I3

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Sheldrick, G. M. (2008). *Acta Cryst*. **A64**, 112–122.

CHAPTER 10

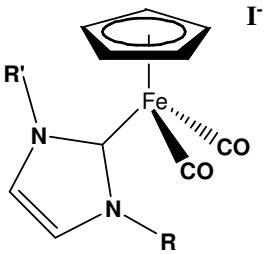
SUMMARY AND CONCLUSIONS

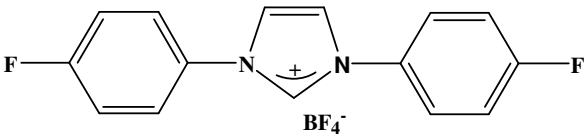
10.1 Project summary

This section will present an overview on how the project evolved and also present concluding remarks to tie the initial objectives of the project to the achieved results. In total the project is based on three different series of *N*-heterocyclic carbene (NHC) precursor salts that have been successfully synthesized. The synthesized imidazolium salts and their metal complexes are novel contributions to the emerging and growing fields that revolve around NHCs. Notable is that they have found wide application in organometallic chemistry, medicine and catalysis. All the synthesized imidazolium salts and the corresponding iron(II) NHC complexes were fully characterized by available analytical, spectroscopic and crystallographic tools and found to be of high and acceptable purity.

The first series were synthesized by addition of alkylhalide to monoalkylated imidazoles to obtain 1,3-dialkylimidazolium salts. The salts were further reacted with $CpFe(CO)_2I$ as the iron(II) precursor to give iron(II) NHC complexes of the general type $[CpFe(CO)_2NHC]^+I^-$ which were characterized spectroscopically and by X-ray crystallography. They were found to be effective as catalysts in the transfer hydrogenation of ketones, which is promising for an environmentally friendly and inexpensive catalyst system.

The second series, 1,3-diarylimidazolium salts were synthesized via a solvent-free method for the synthesis of the diamines which are the precursors used in the synthesis of the salts. The salts were also utilised as metal-free catalysts in transfer hydrogenation of ketones with excellent selectivity and conversion under a milder condition as compared to some of the metal catalysed systems. Compounds **2.11** and **2.12** (Chapter 2) which are Fe(II) NHC complexes showed almost similar catalytic activity for the transfer hydrogenation of ketones, to imidazolium salt **4.1** (Chapter 4) represented in Figure 10.1. This observation directed our attention towards the possibility of testing subsequent ligands in a metal-free fashion in order to establish the roles played by the various components of the catalyst, i.e. the metal, ligand and other additives in the catalytic process.





4.1

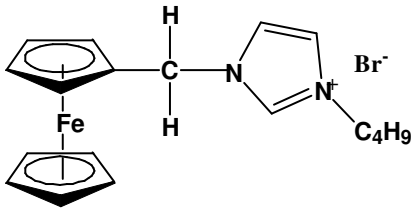
2.11 R= CH_3, R' = CH_2CH_3 (IMeEt)

2.12 R=R' = $CH(CH_3)_2$, (I^iPr)

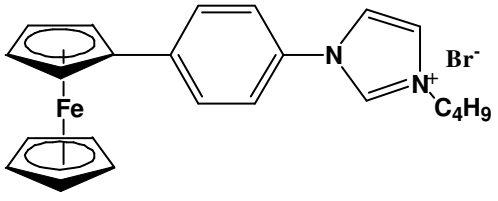
Figure 10.1 Structure of complexes **2.11**, **2.12** and imidazolium salt **4.1**

The third series, ferrocenylimidazolium salts were successfully synthesized with either an alkyl or a phenyl linker bridging the ferrocenyl to the imidazolium moieties. When tested as potential catalysts, this series of compounds also exhibited good catalytic activity for the transfer hydrogenation of ketones. Their electrochemical property when investigated by cyclic voltammetry correlated well with the catalytic activity.

A result of the high catalytic activity exhibited by the aryl imidazolium salt **4.1** prompted the investigation of the ferrocenylimidazolium salts in transfer hydrogenation of ketones, which were found to be effective in the transformation of the ketones to the corresponding alcohols. This was because the ferrocenyl moiety was anticipated to show similar electronic behavior to the aryl groups, while exhibiting unique steric properties in catalysis. Compounds **5.6** and **5.12** (Chapter 5) shown in Figure 10.2 gave the highest conversion of all the ferrocenylimidazolium salts studied with respective TON values up to 1600 and 1880 which are higher than the aryl imidazolium salt **4.1**. The two compounds both have a *N*-butyl substituent on the imidazolium moiety differentiated by the nature of the linker (methyl or phenyl) between the ferrocenyl and the imidazolium moieties.



5.6

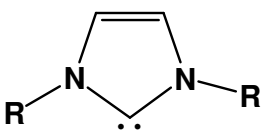


5.12

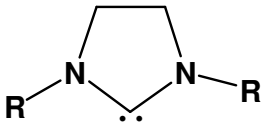
Figure 10.2 Structures of ferrocenylimidazolium salts that exhibited high catalytic activity

A correlation was established between the catalytic activity and the electrochemical properties of the ferrocenylimidazolium salts as investigated by cyclic voltametry. As the length of the alkyl substituent on the imidazolium moiety increases, the formal electrode potential ($E_{1/2}$) also increase to a more positive potential. Likewise the catalytic activity of the salts also increased. This is attributed to the increase in positive inductive effect as the length of the electron rich alkyl substituent increases, thus making the metal centres more vulnerable to attack by nucleophiles (substrates) and increasing the catalytic activity.

Also, saturated NHC (imidazolidin-2-ylidenes) were found to be more reactive towards trace amounts of water as compared to the unsaturated counterparts (imidazolin-2-ylidenes) represented in Figure 10.3. This resulted in ring opening reaction to yield novel diamino aldehyde compounds when reactions were conducted in solvents and environments containing trace amounts of moisture introduced via the solvents or hydrated iron(II) precursors with saturated NHC. The unsaturated NHC under the same condition was more resilient and yielded the expected iron(II) NHC complexes.



imidazolin-2-ylidenes



imidazolidin-2-ylidenes

Figure 10.3 General structures of unsaturated and saturated NHC ligands

10.2 Conclusions

New series of imidazolium salts which are precursors towards the synthesis of *N*-heterocyclic carbenes (NHC) were successfully synthesized. The corresponding iron(II) complexes were also obtained in fair to good yields. The saturated NHC were also found to be more reactive towards trace amounts of water in comparison to the unsaturated counterpart.

In the area of homogeneous catalysis, this work has contributed immensely to advances in the chemistry of especially environmental friendly catalysts systems based on Fe which is a cheap and readily available metal.

Finally, as a result of the promising catalytic activity of the imidazolium salts and their iron(II) derivatives in transfer hydrogenation of ketones which is a relatively simple but industrially

useful reaction, it will be interesting to expand the scope of this study along the following highlighted areas:

- Study hydrogenation reactions using other hydrogen sources such as molecular hydrogen gas as an alternative reductant, so as to compare various results to obtain the best feasible process for industrial application.
- Exploring other variants of the Fe-NHC catalyst systems. Due to the promising catalytic activity in transfer hydrogenation of ketones, synthesizing other variants of Fe-NHC complexes by variation of the substituents both electronically and sterically will serve to expand their scope of application.
- Potential areas of application of the synthesized complexes may include: oxidation reactions, hydroformylation, hydrosilylation and olefin metathesis in order to further extend the scope of the catalytic activity of the imidazolium salts and their iron(II) derivatives synthesized in this research.

SUPPORTING INFORMATION

Supporting information includes data on single crystal XRD, ^{1}H & ^{13}C NMR, IR, HR-MS, GC and CV experiments which are provided as a pdf document on compact disc accompany this thesis. The data is presented in the same order corresponding to the chapter arrangement of the thesis report. This is to keep the total volume of the printed text to a managenable and acceptable limit. Readers are encouraged to access the raw data for further information and confirmatory evidence.