THE CHEMISTRY OF IMIDAZOLIUM SALTS AND PHOSPHONIUM-BASED IONIC LIQUIDS

by

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ABSTRACT

Ionic liquids represent a new technology for use in sustainable processes as solvent replacements, in catalytic reactions and electrochemical devices. Their low vapour pressure makes them potential substitutes for highly volatile organic solvents, thus reducing the amount of pollution caused through solvent evaporation and their non-flammable nature reduces the risk of fire hazard. Perhaps the most extensively studied class of ionic liquids (ILs) is based upon the imidazolium ion and these ILs have found uses in small-scale synthesis, catalysis and more recently in industrial applications.

The reactivity of small molecules with imidazolium salts that have relevance to ILs are reported in this thesis. The imidazolium salts, a model for the imidazolium-based ionic liquids (IILs) are found to be reactive towards basic salt (silver (I) oxide), active metal (potassium), reducing agents ($NaBH_4$) and bases such as Grignard reagents. This highlights a significant pathway of decomposition for the imidazolium ion and illustrates their unsuitability as solvents for basic reactions. Phosphonium-based ionic liquids are found to be more resistant to reactive metals and strong bases than imidazolium-based ionic liquids. These results are relevant and important because other "green" solvents, such as water, carbon dioxide and alcohols are reactive with strong nucleophiles and bases. The identification of base-resistent ILs is important since it has been suggested that more than 50% of reactions are base-catalysed.

Keywords: Ionic Liquids, *N*-Heterocyclic carbenes, Grignard reagents, Borane.

DEDICATION

To my Family

My Grandmother Dewantee

For the struggles she endured in life so that I can have an education

My Father Bhismadeo

For the pride he instilled in me and the belief that I can achieve my dreams

My Mother Twolotmah

For all the love and care she gave me

My Sister Sushila

For encouraging me to come to Canada and always being the one I look up to

My Sister Vidula

For all the laughter and joy she brought into my life

My Sister Twinkle

For being the twinkle in my eye and the light in my life

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LIST OF ABBREVIATIONS

BASIL	–	Biphasic Acid Scavenging Utilising Ionic Liquids
BQ	–	*p*-Benzoquinone
Calcd	–	Calculated
cod	–	1,5-Cyclooctadiene
CP / MAS	–	Cross-Polarisation / Magic-Angle Spinning
CV	–	Cyclic Voltammetry
Dipp	–	2,6-Diisopropylphenyl
DMF	–	Dimethylformamide
DMPO	–	5,5-Dimethyl-1-pyrroline-*N*-oxide
DMSO	–	Dimethyl sulfoxide
EPR	–	Electron Paramagnetic Resonance
GIAO	–	Gauge-invariant Atomic Orbital
hcf	–	Hyperfine coupling constant
IIL	–	Imidazolium-based ionic liquid
PIL	–	Phosphonium-based ionic liquid
Mes	–	2,4,6-Trimethylphenyl
NHC	–	*N*-Heterocyclic carbene
NMR	–	Nuclear magnetic resonance
N/O	–	Not observed
RTIL	–	Room Temperature Ionic Liquid
SC	–	Solvent Cage
SCE	–	Saturated Calomel Electrode

SOMO	–	Singly occupied molecular orbital
TEMPO	–	2,2,6,6-Tetramethyl-1-piperidinyloxy
TCNE	–	Tetracyanoethylene
TGA	–	Thermogravimetric analysis
THF	–	Tetrahydrofuran
μSR	–	Muon spin resonance
μLCR	–	Muon level-crossing resonance
VOC	–	Volatile organic compounds

CHAPTER 1 : INTRODUCTION

The vast majority of industrial chemical reactions are performed either in thegas-phase with a solid catalyst or in solution, where the solvent fulfills several functions during a chemical reaction. Solvents dissolve the reactants, which facilitates collisions that must occur in order to transform the reactants to products. The solvent also provides a means of temperature control, either to increase the energy of the colliding particles so that they will react more quickly or to absorb heat that is generated during an exothermic reaction.[1] Sometimes the solvent can also mediate proton exchange. The selection of an appropriate solvent is guided by theory and experience. Generally a good solvent should meet the following criteria:

- It should dissolve the reactants.
- It should be inert to reaction conditions.
- It should have an appropriate boiling point so that the solvent does not vaporise, but can still be removed by distillation or evaporation.
- It should be easy to remove the products from the solvent.

Solvents can be classified according to their type of intermolecular interactions. There are three main groups of solvents (Figure 1-1) and they are arranged according to their weak intermolecular interactions, namely: (1) molecular liquids (solid melts giving molecules having intermolecular interactions such as dipole-dipole interaction); (2) ionic liquids (solid melts that contains only ionic interactions) and (3) atomic liquids (low melting metals like liquid mercury or liquid sodium, where there are only weak "metallic" bonds between the atoms).[2] As suggested in Figure 1-1, these solvents can be used either individually or as mixtures. It is important to note that the vast majority of chemical reactions are performed exclusively in molecular solvents and the others, for the most part, remain unexplored.

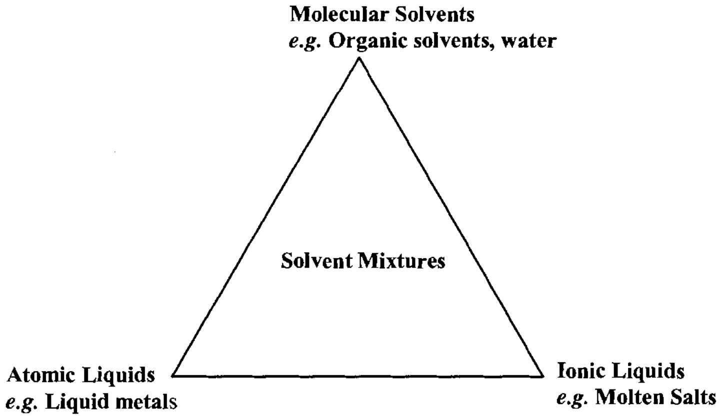

Figure 1-1: Solvent classifications.

The chemical industry is under considerable and ever increasing pressure to reduce the detrimental impact that volatile organic compounds (**VOC**s), particularly those that are toxic such as dichloromethane and those that are hazardous to handle, such as ethers, which are in addition volatile, flammable and form explosive peroxides. This pressure has led to the pursuit of more environmentally friendly technologies. The toxic and hazardous properties of many solvents, particularly chlorinated hydrocarbons, in conjunction with crucial environmental concerns, such as atmospheric emissions, contamination of water and more importantly chronic exposure, are also restricting their use. It has been recognised that using "green" solvents as alternatives to these environmentally unfriendly solvents can drastically reduce waste-solvent production and hence reduce their environmental impact.

The most prevalent of these new "green" systems include, but are not limited to water,[3, 4, 5] supercritical fluids (such as supercritical water and carbon dioxide),[6] solventless processes,[7, 8] fluorous techniques such as the use of perfluorocarbons and fluorous biphasic catalysis[9, 10] and finally ionic liquids (**ILs**).[11, 12] The link between ionic liquids and "Green" chemistry is related to the solvent properties of the ionic liquids. One of the key properties of ionic liquids is their liquid range.[a] The reputation of ionic liquids being "Green" solvents is built largely on their non-volatility because they do not create atmospheric pollutants that can result from the volatility of classic **VOCs**. Some **ILs**, such as imidazolium *bis*{(trifluoromethyl)-sulphonyl}amide salts have been recently reported by Earle *et. al.* to be distillable. These **ILs** were found to vapourise at low pressure and recondensed below the thermal decomposition point of the **ILs**.[13] Nevertheless, it was pointed out that the possibility of dealkylation and recondensation as well as the dissociation of the imidazolium cation to form the carbenes were not completely eliminated during the distillation process. The fact that some thermally stable ionic liquids can be distilled can be advantageous, since this opens up new purification methods of the **ILs**.[13]

During the last ten years, room temperature ionic liquids (RTILs) have captured the interest of chemists and engineers as novel solvents. By definition, RTILs are salts that have melting points at or below room temperature.[6] Most typically they are composed of a large organic cation and a weakly co-ordinating organic or inorganic anion such as tetrafluoroborate, hexafluorophosphate and others. The most commonly used anion in RTILs are the tetrafluoroborate and the hexafluorophosphate even though

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[a] Liquid range is the span of temperatures between the freezing point and the boiling point of a liquid.

they are found to be toxic since they release HF on hydrolysis which is toxic to the human health and eats through glass. RTILs have stimulated scientific curiosity due to their solvent properties. They have been used in research, product and process development and in a large number of innovative applications such as catalytic hydrogenation reactions.[14]

Over the last decade, chemists have designed and used a range of **IL**s that are able to dissolve a wide range of useful chemicals. These **IL**s have found applications in academic research as well as in industry. Two major chemical companies, Eastman Chemical Company and BASF have developed processes that use **IL**s on an industrial scale. Generally, it was believed that BASF was the first company to establish a commercial process that uses ionic liquids with low melting points. The idea behind the BASIL technology is to use a base, in this case 1-methylimidazole, to scavenge an acid formed during their manufacturing of alkoxyphenylphosphines. During this process the ionic liquid methylimidazolium chloride is formed. It is important to remove the acid by-product in order to prevent the decomposition of the product. However, conventional methods such as the use of amines results in the formation of solid salts, which cause problems for filtration in large scale production. Hence, during this process, which is also known as BASIL (Biphasic Acid Scavenging Utilising Ionic Liquids), the **IL**, which has a melting point of 75 °C is separated as a clear liquid from the alkoxyphenylphosphine product.[15] Eastman Chemical Company, however, as recently disclosed, has made use of **IL**s-namely ammonium and phosphonium-based ionic liquids (**PIL**s)-on an industrial scale for the last ten years, thus making them the first to commercially use an **IL** as a solvent. These **IL**s were used as solvent medium for the carbonylation reaction of methanol with a rhodium catalyst. The new solvent media were found to be more effective than a conventional solvent, which caused precipitation and loss of the rhodium catalyst. Another company that make use of **ILs** is the Novartis Pharma AG, where the **ILs** are used for headspace gas chromatography.[16] The fact that some ionic liquids have negligible vapour pressure makes them ideal for this application since they allow the detection of higher boiling point analytes.

Though **ILs** have numerous advantages over conventional solvents, it should not be taken for granted that all of them are benign to the environment. Recently, a team of scientists from the University of Pisa, tested the toxicity of a range of **ILs** on fish and found that even very low exposures of particular **ILs** could damage fish gills.[17] Some **ILs**, contrary to previous belief, have been shown to be biodegrable[18] and the toxicity of **ILs** was found to be somewhat dependent on their level of biodegradation. Hence, it is important to carry out toxicology tests on **ILs** as well as their level of biodegradation to find out which of them are more environmentally benign.

1.1 Overview of Ionic Liquids

Ionic liquids (**ILs**) are molten salts consisting of ionic species having a melting point lower than 100 °C.[19] However, this term includes an additional special definition to distinguish it from the classical definition of a molten salt. While a molten salt is generally thought to refer to a high-melting, highly viscous and corrosive medium, ionic liquids are liquids at low temperatures (<100 °C) and have relatively low viscosity. Even though some examples are known in which high temperature salt melts have been used successfully as reaction media for synthetic applications, only a liquid range below

100°C can enable the versatile substitution of conventional solvents such as dichloromethane, benzene and tetrahydrofuran.

Among the various known **ILs**, those based on imidazolium, quaternary ammonium or phosphonium salts are most commonly used because of their particular set of properties. These **ILs** exhibit a relatively wide electrochemical window,[20] good electrical conductivity, high ionic mobility[6] and a broad range of room temperature liquid compositions, negligible vapour pressure and excellent chemical and thermal stabilities.[11, 21] Due to these properties, **ILs** have been used in electrochemical technologies, as electrolytes in devices such as actuators (artificial muscles)[22] and as solvents in UV-Visible and near IR absorption spectroscopies.[23] They have also been used in clean liquid-liquid extraction processes,[24] as recyclable alternatives to aprotic solvents[6] or catalysts for organic[25, 26] and organometallic synthesis.[27] **ILs** can be used as a solvent for biocatalysis and they have advantages over conventional solvents such as ethers and dichloromethane.[28] In these latter reactions, a peptide is tethered to the **ILs** and after the reaction is complete, the by-products and the impurities are removed into the non-**IL** phase.

As mentioned before, ionic liquids are liquid at room temperature or below 100°C and in order for them to be a liquid, the cation should preferably be unsymmetrical, that is, the alkyl groups on the nitrogen atoms or the phosphorous should be of different lengths or shape. Lowering the symmetry of the cations causes a distortion from ideal close packing of the ions in the solid-state lattice, which leads to a reduction in the lattice energy and a depression of the melting points.[29] Lowering of the cation and anion symmetry also lowers the freezing point and markedly expands the liquid range of the **ILs**.[30]

ILs possess a variety of desirable properties that make them potentially useful reaction media for the chemical industry:

1. A diverse range of organic, inorganic and organometallic compounds are soluble in **ILs**. The solubility of gases[31, 32] such as O_2, benzene, nitrous oxide, ethylene, ethane and carbon monoxide is also good, which makes them attractive solvent systems for catalytic hydrogenations, carbonylations, hydroformylations and aerobic oxidations.[6]
2. Ionic liquids tend to have good thermal stability and can be liquid over a range of 300 °C.[6] This wide liquid range is a distinct advantage over traditional solvent systems that have a much narrower liquid range, for example water that has a liquid range of 100 °C or toluene of 206 °C.
3. The majority of **ILs** have low volatility. This property makes them easy to contain, use and transfer and in addition they can be used under high-vacuum conditions. This is an important feature that reduces chronic exposure to solvent vapours.
4. The polarity and hydrophilicity/lipophilicity of **ILs** can be tuned by the use of a suitable cation/anion combination. Hence, they can be tailored to be immiscible with some organic solvents and can be useful in two-phase systems. In a similar manner, hydrophobic **ILs** are suitable for use in aqueous biphasic systems. Some ionic liquids can form a triphasic system in the presence of water and particular

organic solvents, and this property can be very advantageous for extraction of the products.

5. In some extensively studied cases, the anion is weakly co-ordinating and the **ILs** can therefore be highly polar, non-coordinating solvents. This property can have a significant enhancing effect on the reactions involving cations.
6. Ionic liquids can be recycled. Recovery and recycling of the catalyst are also possible with the **ILs**, thus keeping production of waste and loss of valuable catalysts to a minimum.
7. The **ILs** cations, for example the imidazolium cations can easily be derivatised to give task-specific functionality such as metal ligating groups. These task-specific ionic liquids are very useful to control the physical properties of these new solvents.[33]

1.2 Ionic Liquids: A History

The earliest material that can be classified as an **IL** was a red oil, which was obtained in Freidel-Crafts reactions reported in the mid-19th century.[6] This red oil was much later characterised by NMR spectroscopy and found to be ethylammonium nitrate.[34] Later in 1914, the preparation of ethylammonium nitrate having a melting point of 12 °C was reported.[35] This **IL** was formed by the addition of concentrated nitric acid to ethylamine, followed by the removal of water by distillation to yield the pure salt, which was a liquid at room temperature.[36] In 1948, the first pyridinium based ionic liquids with chloroaluminate ions were developed and they were used as a bath solution for electroplating aluminum.[37]

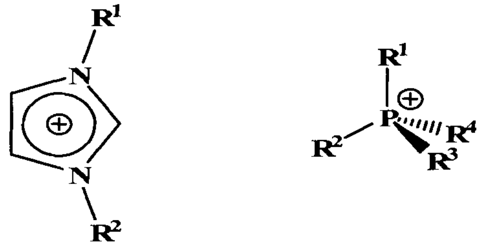
One of the first 1,3-dialkylimidazolium room temperature ionic liquids (RTILs), 1-ethyl-3-methylimidazolium tetrachloroaluminate, which was obtained through the mixing of 1-ethyl-3-methylimidazolium chloride with aluminum trichloride, was reported in 1982.[20] However, these organo-aluminate **IL**s were found to be moisture sensitive and reactive towards various organic compounds, consequently limiting their range of applications.[38]

Since then, considerable amount of research has been carried out on *N,N*-dialkylimidazolium salts and they have been great success as reaction media for many organic transformations. These ionic liquids can be finely tuned by varying the *N*-alkylimidazolium substituents and/or the anion. These materials enjoy a plethora of potential applications in various domains of the physical sciences. These members of the **IL** family are readily prepared and are now commercially available from Aldrich, Strem, Merck in Germany and EMD in the USA.

Ionic liquids containing quaternary ammonium salts have also found numerous applications and some of the quarternary ammonium salts are used as deep eutectic solvents.[11] By definition, a deep eutectic solvent is a type of ionic solvent with special properties composed of a mixture, which forms a eutectic with a melting point much lower than either of the individual components. The first generation of eutectic solvents were based on mixtures of quaternary ammonium salts with hydrogen donors such as amines and carboxylic acids. The deep eutectic phenomenon for a 2 to 1 mole ratio of choline chloride (2-hydroxyethyl-trimethylammonium chloride) and urea was first described in 2003.[15, 39] Choline chloride has a melting point of 302°C and that of urea is 133°C. The eutectic mixture, however, melts as low as -12°C. [15, 39] Compared to molecular solvents, eutectic solvents have a very low vapour pressure and are non-flammable. They share many characteristics as **IL**s but are mixtures of an ionic compound with a neutral compound. Deep eutectic solvents are cheaper to make, much less toxic and sometimes biodegradable. Deep eutectics are, however, unsuitable for reactions under basic conditions because they have active protons for example either from the carboxylic acid or from the ammonium salts that can easily be deprotonated.

Soon after the first reports on the syntheses and applications in organometallic catalysis of the air stable room temperature ionic liquids (RTILs), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMIM \cdot BF_4$), hexafluorophosphate ($BMIM \cdot PF_6$) and their analogues, in the middle of the 1990s, a renaissance of the rich chemistry of molten salts began and continues to flourish.[38] The imidazolium halogenoaluminate (III) such as 1-ethyl-3-methylimidazolium tetrachloroaluminate, [emim][$AlCl_4$] and the closely related alkylhalogenoaluminate (III) **IL**s have been by far the most widely studied.[40] 1,3-Dialkylimidazolium salts were one of the most investigated classes of **IL**s,[38, 40] but nowadays ammonium based ionic liquids and more recently **PIL**s are gaining interest since in general they are more robust, thermodynamically more stable and less reactive than imidazolium-based ionic liquids.[41]

This thesis is divided into two main sections: (1) the reactivity of imidazolium salts, a model for imidazolium-based ionic liquids (**IIL**s) and (2) reactions in phosphonium-based ionic liquids (**PIL**s). Chart 1-1 shows the structure of **IIL**s and **PIL**s.



R^1, R^2, R^3, R^4 = alkyl or aryl group

Chart 1-1: IIL (left) and PIL (right).

1.3 The Report

The chemistry of **ILs**, namely imidazolium and phosphonium-based ionic liquids as shown in Chart 1-1 plays an important role in this thesis. The imidazolium salts under investigation have high melting points (above 350°C), hence they are not classified as an **IL**. However, they are used as models to illustrate the reactivity of imidazolium-based ionic liquids with small molecules. The redox behaviour of imidazolium ions and their conjugate bases, *N*-heterocyclic carbenes are examined in Chapter 2. This study led to a new synthesis of *N*-heterocyclic carbenes by treating imidazolium ions with potassium metal. A neutral radical intermediate obtained in this reaction was studied by EPR and muonium chemistry. The synthesis of group 11 (^{13}C labelled) and group 13 complexes of *N*-heterocyclic carbenes (**NHCs**) from their imidazolium salts, with emphasis on silver halide and borane complexes are discussed in Chapter 3. The preparation and spectroscopic characterisation of these ^{13}C labelled compounds are also included. Unlike **IILs**, **PILs** are suitable media for basic reactions and this is explained in Chapter 4. A comparison between **IILs** and **PILs** is also provided, with an explanation of the persistence of the **PILs** in the presence of reactive metals and bases such as **NHCs**. Reactions under basic conditions are shown to proceed in the **PILs** and detailed in Chapter 5. Nucleophiles such as Grignard reagents are persistent in **PILs** and the fact that **PILs** can support radical and polar reactions for carbon-carbon bond formation reactions is also illustrated in this Chapter.

CHAPTER 2 : REDOX BEHAVIOUR OF IMIDAZOLIUM IONS AND *N*-HETEROCYCLIC CARBENES

Parts of this chapter were reproduced from the following journal articles:

1. Canal, J. P.; Ramnial, T.; Dickie, D. A.; Clyburne, J. A. C. "From the Reactivity of *N*-Heterocyclic Carbenes to New Chemistry in Ionic Liquids." *Chem. Commun.*, **2006,** 1809. (Reproduced by the permission of The Royal Society of Chemistry)
2. Ramnial, T.; Clyburne, J. A. C. "Imidazol-2-ylidenes and their Reactions with Simple Reagents." ACS Symposium Series no. 917, Modern Aspects of Main Group Chemistry, Chapter 19. (Reproduced with the permission from the American Chemical Society. Copyright [2005])
3. Gorodetsky, B.; Ramnial, T.; Branda, N. R.; Clyburne, J. A. C. "Electrochemical Reduction of an Imidazolium Cation: A Convenient Preparation of Imidazol-2-ylidenes and their Observation in an Ionic Liquid." *Chem. Commun.*, **2004**, *17*, 1972. (Reproduced by the permission of The Royal Society of Chemistry)
4. Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. "Reactions of *N*-Heterocyclic Carbenes (NHCs) with One Electron Oxidants: Possible Formation of a Carbene Cation Radical." *Chem. Commun.*, **2004**, *9*, 1054. (Reproduced by the permission of The Royal Society of Chemistry)

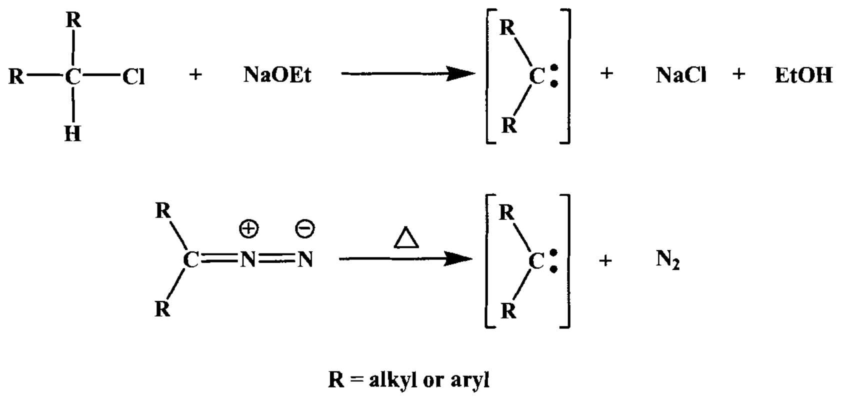
2.1 Introduction

Carbenes are two coordinate carbon compounds with no *formal charge*[42] on the carbon and posses only six valence electrons compared to the normal octet. Four of the valence electrons are involved in bonds to other atoms. The other two electrons remain on the carbon atom. These electrons may be in the same orbital (singlet state) or different orbitals (triplet state) as shown in Figure 2-1. Traditionally, carbenes were viewed as fleeting reactive intermediates that were generated *in-situ* and used in reactions such as cyclopropanation reactions or through metal complexation.[43] They are very reactive molecules and react readily with moisture from the air.

Singlet Carbene **Triplet Carbene**

Figure 2-1: Structure of a singlet carbene (left) and a triplet carbene (right).

Attempts to synthesise the simplest carbene, methylene (CH_2) were performed even before the tetravalency of carbon was established.[44] The existence of carbenes as reactive intermediates was established much later in the 1950s and the 1960s.[45, 46] They were usually synthesised by either the reaction of alkylhalides with a base or by the thermal decomposition of diazonium salts, as shown in Scheme 2-1.[43] Since then, carbenes have become well-established reactive intermediates and their high reactivity makes them versatile species for preparative, mechanistic and theoretical studies.



Scheme 2-1: ***In-situ*** **synthesis of carbenes.**

As early as 1960, Pauling[47] predicted that substituents of opposing electronic properties should stabilise singlet carbenes by preserving the electroneutrality of the carbeneic centre. The so called "push-pull" substituents include NR or OR, which are π-donating and σ-withdrawing. Since then, a considerable amount of work has been reported that bridges the gap between classical, highly reactive transient carbenes and their stable counterparts.[48]

N-Heterocyclic carbenes (**NHCs**) (Chart 2-1) became popular with the realisation that the stability of these reactive molecules could be dramatically increased by the presence of amino substituents (push-pull substituents).[43] **NHCs** contain amino groups attached to the carbeneic carbon. These amino groups have good π-donating capability and at the same time stabilise the σ-orbital by their inductive electron withdrawing nature.[49] As shown in Scheme 2-2, structures **B** and **C** show the carbene electron deficiency being reduced by the donation of two nitrogen lone pairs while the carbene lone pair is stabilised by the inductive effect of the electronegative nitrogen atoms (structure A). Arduengo[48] reported that the singlet carbenes are stabilised by the π-electron delocalisation, which was determined by X-ray data. This stabilisation has, however, been controversial and in 1996 *ab initio* calculations suggested that the singlet carbene ground state is stabilised by σ-back donation along the C-N bonds and that π-delocalisation plays only a minor role in imidazol-2-ylidene, unlike in the imidazolium cation.[50] Hence, Arduengo *et. al.* suggest that structure **B** and **C** only slightly contribute to the stabilisation of the carbene.

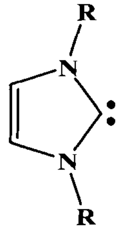
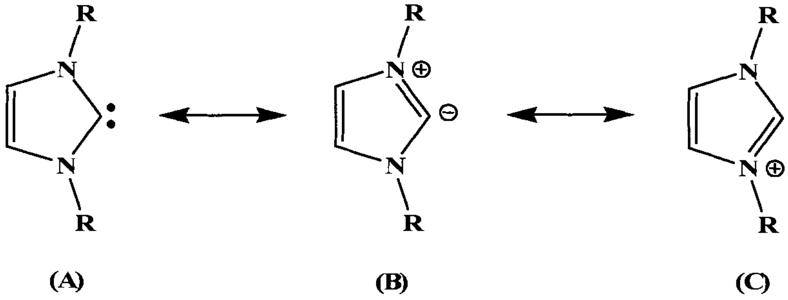

R = alkyl or aryl

Chart 2-1: Structure of an *N*-heterocyclic carbene (NHC).



R = alkyl or aryl

Scheme 2-2: Electronic stabilisation of NHCs.

NHCs are strong σ donors and have similar reactivities to their phosphine analogues. However, NHCs have come to replace phosphines in many organometallic complexes and organic reactions for several reasons:

(1) NHCs are more basic and stronger electron donors than phosphines.

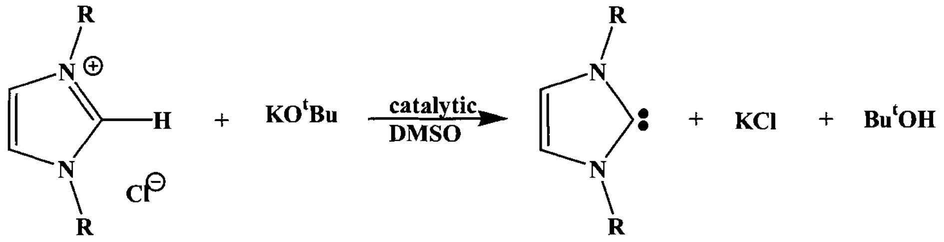
(2) They have a different steric profile than phosphines.

(3) The precursors of the **NHC**s are stable without decomposition in air and at high temperature (above 300 °C) whereas phosphines degrade at higher temperature (100 °C) and oxidise upon exposure to air to give phosphine oxides.

(4) *N*-Heterocyclic carbenes can stabilise both the low and high oxidation states metals.[51] Hence, **NHC**s are important as ligands for transition metal catalysts and have found practical applications in olefin metathesis,[52] hydrogenation, hydroformylation[53] and hydroamination.[54]

2.1.1 Standard Synthesis of NHCs

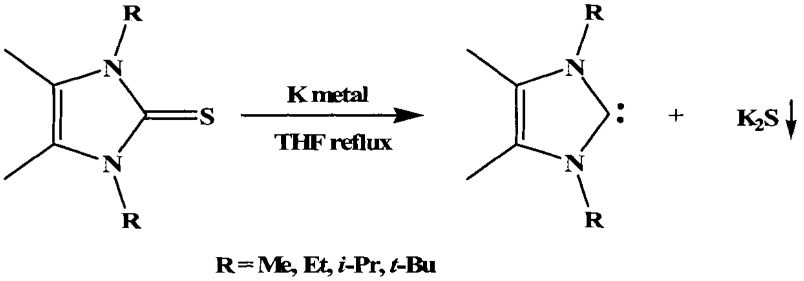
There are two principal methods for the generation of **NHC**s: (1) deprotonation of imidazolium salts, which is the most common method and (2) desulfurisation of thioureas. Imidazolium ions have a pK_a of *ca.* 24 in DMSO,[55, 56] hence they can be deprotonated using strong anionic bases such as sodium hydride (NaH) and potassium *tert*-butoxide (KO^tBu). In the original work, Arduengo *et. al.* used NaH or KH in tetrahydrofuran (THF), usually in the presence of additives like KO^tBu and catalytic amount of DMSO as shown in Scheme 2-3.[57]



R = 2,4,6-trimethylphenyl or 2,6-diisopropylphenyl

Scheme 2-3: Deprotonation of imidazolium salts using potassium *tert*-butoxide.[57]

A desulfurisation method was reported by Kuhn and Krantz in 1993 where 1,3-diisopropyl-4,5-dimethylimidazole-2-thione was treated with potassium metal to give the corresponding imidazol-2-ylidene as shown in Scheme 2-4.[58] This method has been subsequently used by Denk's group to synthesise a series of diaminocarbenes, **NHCs** (R = Me, Et, *i*-Pr, *t*-Bu).[59] The above procedure works well for the alkyl thiones but aryl substituted carbenes have not been made using this route.



Scheme 2-4: Desulfurisation of an imidazole-2-thione.

As mentioned above, the most extensively studied class of **ILs** is based upon the imidazolium ion. The relationship between an imidazolium ion and an **NHC** is the removal of a proton from the imidazolium ion. Several authors have suggested a link for the fast chemical conversion of an imidazolium ion to an **NHC** on the surface of nanoparticles through a redox process.[60] The conversion of an imidazolium ion to an **NHC** represents a simple electrolysis of the imidazolium ion, a process similar to the electrolysis reaction of water. Indeed, the imidazolium ion is the conjugate acid of the carbene as water is the conjugate acid of the hydroxide ion.[61] This relationship was also described by Breslow *et. al.*[62] who did studies on vitamin-B_1 where he explained the relationship between the thiazolium cation and thiazol-2-ylidene, the active species in biochemistry.

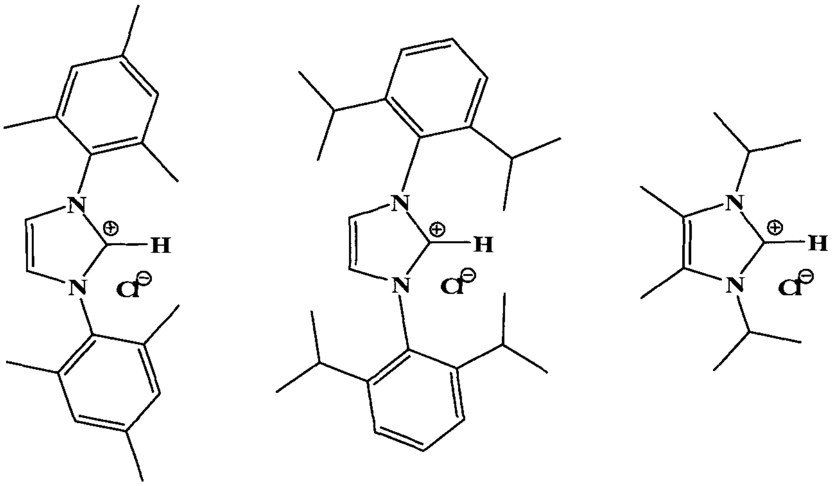
2.2 Cyclic Voltammetry of Imidazolium Ions

Cyclic voltammetric studies were performed on different imidazolium salts in order to have a better understanding of the reactivity and stability these salts and **NHCs** towards different oxidizing and reducing agents.[63] Electrochemical studies on pure **IILs** have been previously described, but the results were not conclusive due to decomposition of the imidazolium cation.[64] In this section, the electrochemical conversion of various imidazolium salts that generates their respective carbenes will be described and a new, large scale (25 g), efficient and economical method for the synthesis of important **NHCs** will also be described.

Cyclic voltammetry studies were performed on three different imidazolium salts as shown in Chart 2-2. Standard concentrations (2.0 mM) of the imidazolium salts in anhydrous dimethylformamide (DMF) with the electrolyte, tera-*n*-butylammonium hexafluorophosphate (0.1 M) were used for cyclic voltammetric studies and reported *versus* a saturated calomel electrode (SCE) at 300 mV s^{-1} with ferrocene as an internal reference (0.475 V *versus* SCE). The cyclic voltammogram (CV) of 1,3-*bis*(2,4,6-trimethylphenyl)-imidazolium chloride, [**1-H**][**Cl**] (Figure 2-2) indicated that the salt was irreversibly reduced at -2.23 V *versus* a saturated calomel electrode (SCE) at 300 mV/s.

Coulometric analysis with ferrocene as an internal standard revealed that the reduction corresponded to a single electron event implying that the species initially produced from the electrochemical reaction was likely the radical [**1-H**]$^{\bullet}$. Although this radical was not isolated, muonium chemistry and electron paramagnetic resonance (EPR) studies were used as supporting evidence for this postulated intermediate as explained in sections 2.3.3 and 2.3.4.

The CV of **[1-H]**[Cl] showed the presence of a significant peak on the return scan at -0.20 V, which corresponds to the oxidation of the new chemical species that was generated from the one electron reduction of **[1-H]**[Cl]. Interestingly, this peak occured at a similar potential as the one measured for the oxidation of 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene,[b] **NHC 1** (inset of Figure 2-2)[65] in THF, suggesting that the reduction of the imidazolium chloride produced the carbene as shown in Scheme 2-5.



[1H][Cl] [2H][Cl] [3H][Cl]

Chart 2-2: Imidazolium salts used for cyclic voltammetry studies.

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[b] Cyclic voltammetry on 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1** was performed by Brian Gorodestsky at Simon Fraser University.

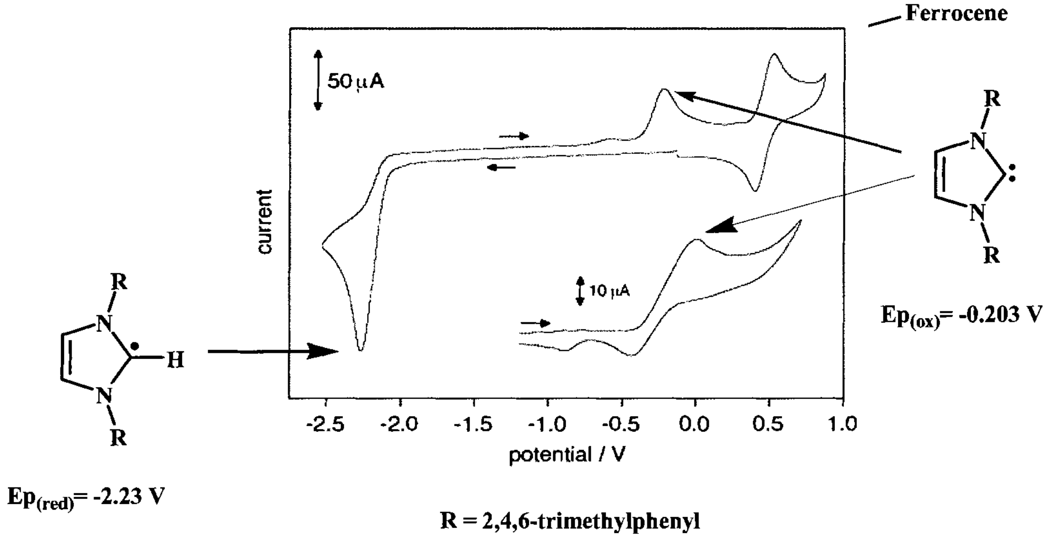
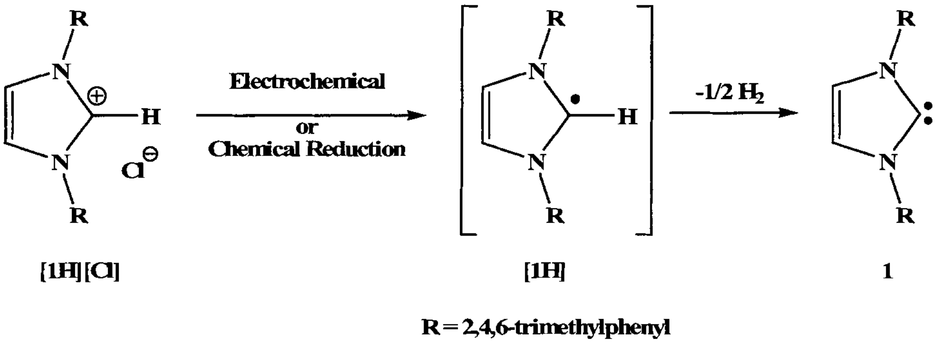


Figure 2-2: CV of [1-H][Cl] in DMF and NHC 1 in THF (inset).

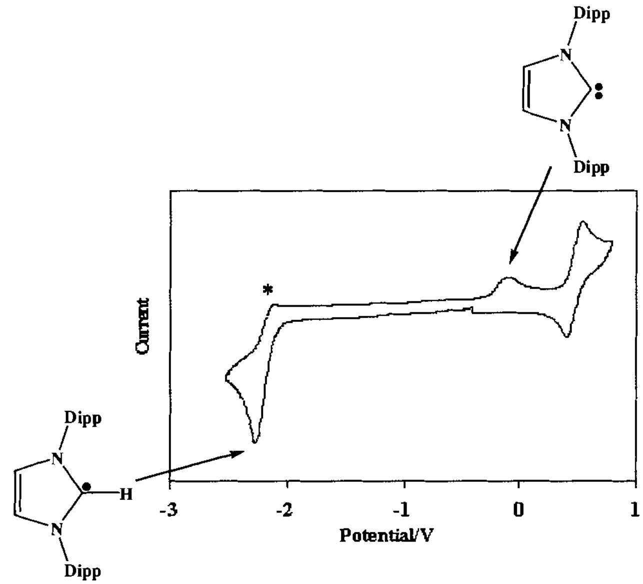


Scheme 2-5: Reduction of [1-H][Cl].

Cyclic voltammetric studies were also performed on a 2.0 mM DMF solution (electrochemical window of +1.5 V to –2.9 V) of a bulkier imidazolium salt, 1,3-*bis*(2,6-diisopropylphenyl)imidazolium chloride, **[2-H][Cl]** with tetra-*n*-butylammonium hexaflurophosphate as electrolyte (0.1 M) at a scan rate of 300 mV/s in the presence of ferrocene as internal reference (0.475 V *versus* SCE). The CV showed a reduction potential at -2.28 V as shown in Figure 2-3, which was slightly reversible probably due to steric protection, suggesting a somewhat longer lifetime for the reduction product. On the reverse scan a peak was observed at -0.094 V, which corresponds to the oxidation of the new chemical species that was generated by the one electron reduction of **[2-H][Cl]**.

Similarly, cyclic voltammetric studies on the small imidazolium salt, 1,3-diisopropyl-4,5-dimethylimidazolium chloride, **[3-H][Cl]** showed a reduction potential at -2.55 V and a peak on the reverse scan at -0.402 V. This reduction potential was somewhat higher than **[2-H][Cl]** because of the presence of the two electron donating methyl groups at $C_{4,5}$ of the imidazole ring making it more electron rich and hence harder to reduce. The stability of the **NHC**s due to the presence of the electron donating groups has been discussed by Arduengo *et. al.* and analysed by photoelectron spectroscopy.[50(a)]

The differences between the oxidation potentials (Ep_{ox} of the different chemical species formed *in-situ* by the reduction of the different imidazolium ions follows the order: Ep_{ox} **[3-H][Cl]>[1-H][Cl]>[2-H][Cl]** (not considering the negative sign) as shown in Table 2-1. Although speculative, this trend may provide physical support for qualitative observation of the three **NHC**s where the less sterically hindered **NHC 3**, is the most reactive of the three.



Dipp = 2,6-Diisopropylphenyl

Figure 2-3: CV of [2-H][Cl], * slightly reversible.

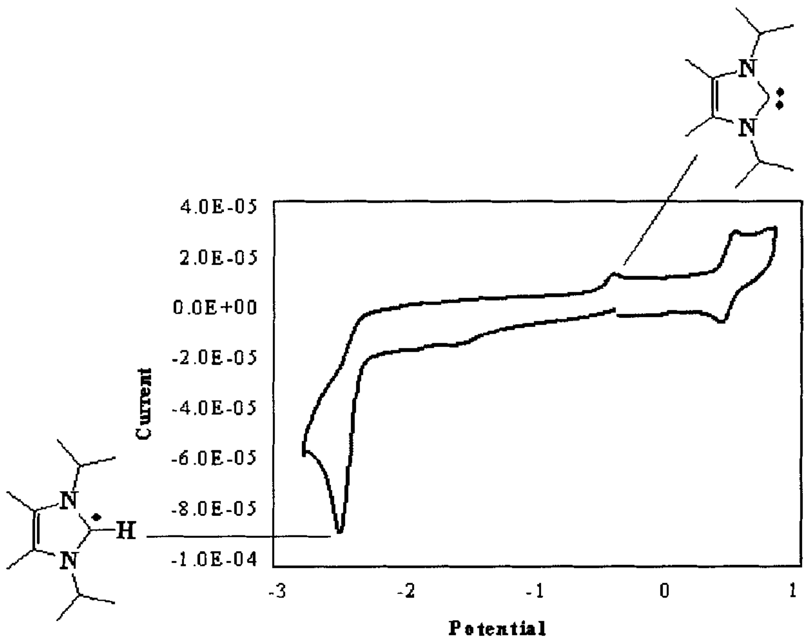


Figure 2-4: CV of [3-H][Cl].

Salts	Reduction Potential/V	Oxidation Potential/V
[1-H][Cl]	-2.23	-0.20
[2-H][Cl]	-2.28	-0.09
[3-H][Cl]	-2.55	-0.40

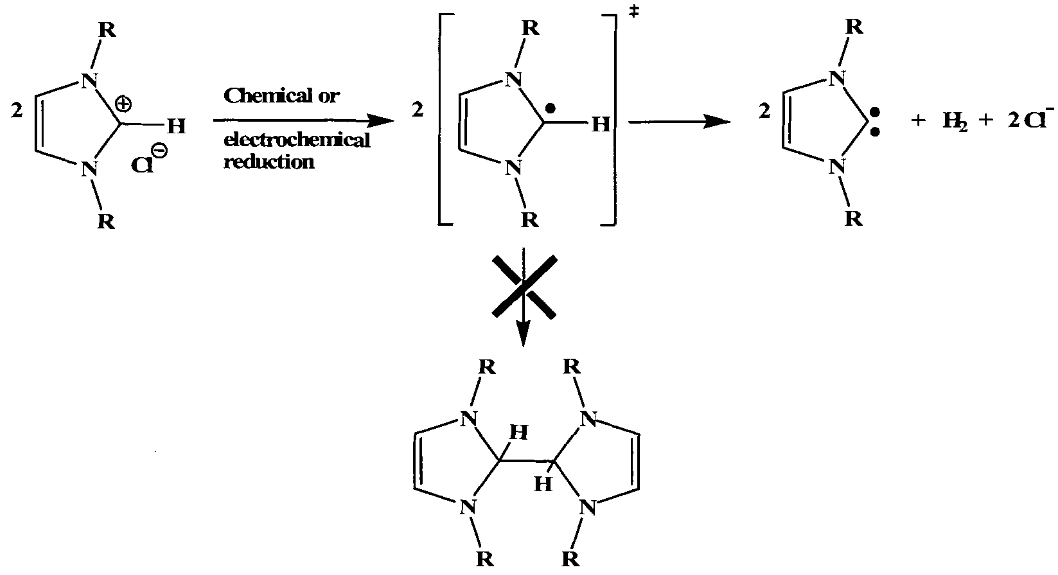
Table 2-1: Reduction and oxidation potentials of imidazolium salts in DMF.

2.2.1 Synthesis of NHCs by Reaction of Imidazolium Salts using Potassium Metal

The electrochemical reduction of the imidazolium salts to produce **NHC**s was experimentally confirmed through a large-scale reaction of the imidazolium ion (25 g) with potassium.[66] **[1-H][Cl]** was used owing to its stature to produce the most versatile and extensively used nucleophilic carbene, **NHC 1**. Potassium metal was added to a THF suspension of **[1-H][Cl]** and heated to reflux under an inert nitrogen atmosphere. A red solution was obtained over a brown precipitate and the solution was filtered through Celite. The filtrate was evaporated and the solid residue was washed with cold hexanes to give 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1** (19.g) as a white powder in 89% yield. Spectroscopic data of the product obtained were consistent with the reported **NHC 1**.[48] Traditionally, this carbene is generated *via* deprotonation of its imidazolium salt using potassium *tert*-butoxide, but the reaction involves numerous purifying steps and sometimes produces sticky materials that are often not useful for further reactions. The new method provides a fast, aprotic method to prepare large quantities of **NHC 1**.[67, 68] Reaction of **[2-H][Cl]** was also performed with elemental potassium to produce a high yield of **NHC 2**.

2.2.2 Proposed Mechanism for Electrochemical Conversion of Imidazolium Salts to NHCs

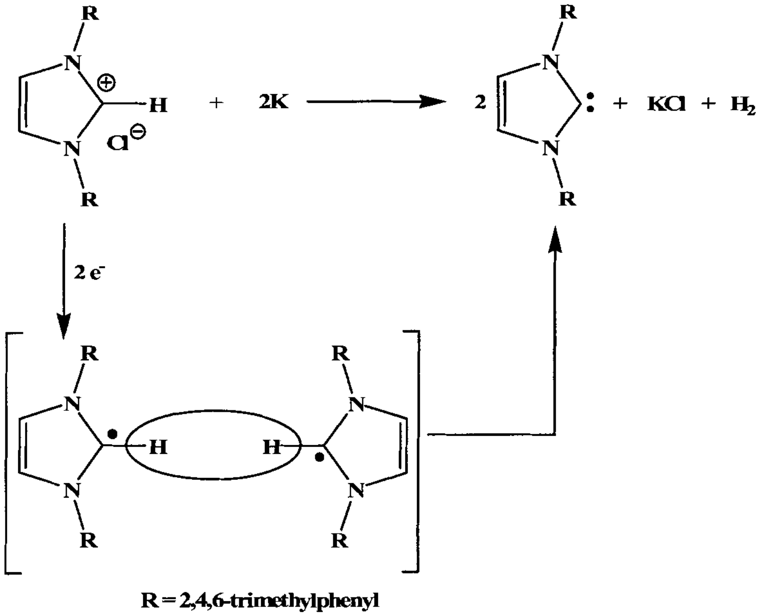
As explained before, the reduction of imidazolium salts is an one-electron process. The reaction pathway as shown in Scheme 2-6 was postulated with the assumption that the electrochemical reduction in the CV followed the same reaction mechanism that occurs during the reaction with potassium metal.



R = 2,4,6-trimethylphenyl

Scheme 2-6: Postulated mechanism for the one electron reduction of [1-H][Cl].

We propose that in the first step a neutral radical is formed. Direct evidence of this radical will be illustrated later. However, we note that this type of neutral NHC radical has been previously proposed and reported by Neta *et. al.*[69] The radical reported was produced by the irradiation of the imidazolium salt and examined by pulse radiolysis studies, UV spectroscopy and calculations. On the addition of one electron to the imidazolium ion, the aromaticity of the imidazolium cation was disrupted, which resulted in a neutral radical intermediate. This intermediate was speculated to decompose through a bimolecular reaction with another radical to form a molecule of hydrogen and free carbene as shown in Scheme 2-7 or a suface reaction. An alternate fate of this neutral radical intermediate was homocoupling to form a dimer, which has been previously suggested by Johnson *et. al.* while they studied the electrochemical reduction of the 1-butyl-3-methyl imidazolium tetrafluoroborate ionic liquid.[64] In our study, however, dimerisation of **[1-H]$^{\bullet}$** did not occur. The pathway for the formation of carbene can also be accounted for through thermodynamic arguments. The energy released in the formation of molecular hydrogen ($\Delta H_{H\text{-}H}$ = - 463 kJ/mol) is higher than that of C-C bond ($\Delta H_{C\text{-}C}$ = -348 kJ/mol). This mechanism should not be considered as the sole possibility, since a surface mechanism of potassium radical ($K^{\bullet}$) absorbing $H^{\bullet}$ cannot be ruled out.



Scheme 2-7: Proposed pathway for the reduction of [1-H][Cl] with potassium.

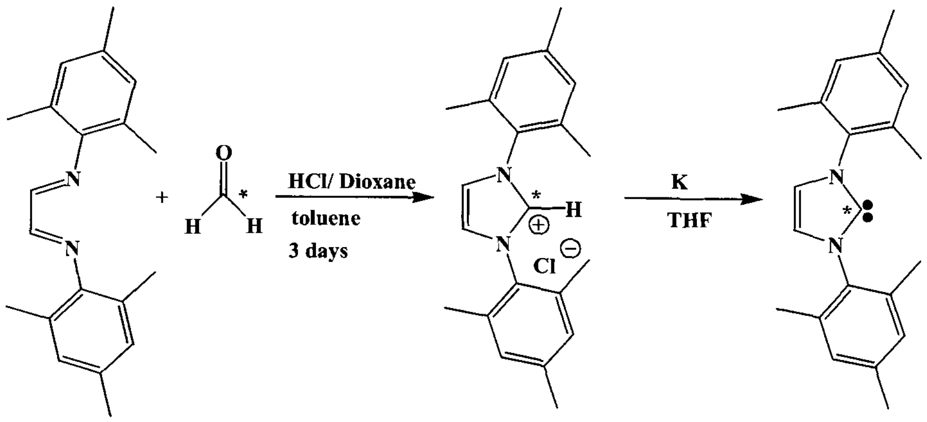
Evidence for **[1-H]**$^{\bullet}$ radical intermediate has been provided in a previous study by McKenzie *et. al.*[70] My contribution to this work was to synthesise ^{13}C labelled **[1-H][Cl]** and **[3=S]** as explained below in section 2.3.1. The carbenes from the two labelled imidazolium salts were used for muonium addition reactions as explained in section 2.3.2 and **[1-H][Cl]** was also used to synthesise and fully characterise its silver adduct. EPR techniques were also used to characterise similar radical, **[2-H]**$^{\bullet}$ as would be detailed in section 2.3.3

2.3 Synthesis of ^{13}C labelled Imidazolium Salts and Spectroscopic Studies

2.3.1 Synthesis of ^{13}C Labelled NHCs

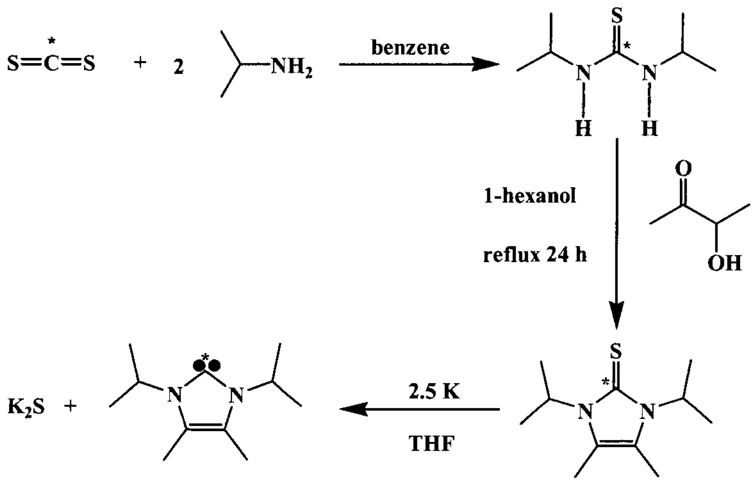
One of the major advances reported in this thesis is the synthesis of ^{13}C labelled **NHC 1** and **3**. Labelled **[1-H][Cl]** was used to prepare a monomeric silver (I) carbene complex, **[1-AgCl]**, which was fully characterised by solution and solid state ^{109}Ag and ^{13}C CP/MAS NMR spectroscopy[71] and will be discussed in chapter 3. ^{13}C labelled **NHC 3**, which required 42 trials in scaling down the reactions (tested on non-labelled material) to synthesise, was used to observe ^{13}C resonances for muon addition and muon level-crossing spectroscopy as explained in section 2.3.3.[70]

^{13}C labelled **[1-H][Cl]** was synthesised as shown in Scheme 2-8. Glyoxal-*bis*(2,4,6-trimethylphenyl)imine[57] was treated with one equivalent of ^{13}C labelled paraformaldehyde in toluene. The mixture was heated to 100°C, cooled to 40°C and then one equivalent of 4 M HCl/dioxane was added dropwise. The reaction mixture was stirred for 3 days and the white precipitate obtained was filtered and washed with cold THF to give 85 % yield of ^{13}C labelled **[1-H][Cl]**, which was further reacted with a slight excess of potassium to give ^{13}C labelled **NHC 1** in 89% yield. ^{1}H and ^{13}C NMR spectroscopy data were consistent with the reported values of the unlabelled **NHC 1**.[57]



Scheme 2-8: Synthesis of ^{13}C labelled NHC 1.

Labelled **NHC 3** was synthesised[70] as shown in Scheme 2-9 below. Two equivalents of isopropyl amine were treated with ^{13}C labelled carbon disulfide in benzene. 1,3-Diisopropylthiourea obtained from this reaction was isolated and subsequently heated to reflux in hexanol for twenty-four hours in the presence of 3-hydroxy-2-butanone. The white powder obtained was recrystallised from anhydrous ethanol to give 1,3-diisopropylthiourea, which was reacted with 2.5 equivalents of potassium metal. After the reaction was complete, the solution was filtered through Celite and the filtrate was evaporated to dryness. The white crystals obtained were purified by sublimation to give synthesised labelled **NHC 3** in 80% yield. ^{1}H and ^{13}C NMR spectroscopy data were consistent with the reported values of the unlabelled compound.[58]



Scheme 2-9: Synthesis of ^{13}C labelled NHC 3.

2.3.2 A μSR[c] study of a Neutral NHC Radical Derived from NHCs

Prior to this study, there were no reports of reactions of NHCs with radicals. Addition of a hydrogen atom to 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1**, and 1,3-di(isopropyl)-4,5-dimethylimidazol-2-ylidene, **NHC 3**, was hence studied by means of density functional calculations (B3LYP). **NHCs 1** and **3** were chosen because of their high symmetry and the ability to synthesise the ^{13}C isotopically labelled samples (see previous section). The addition of a hydrogen atom to **NHCs 1** and **3** could occur at one of the two probable sites, either at the carbeneic carbon to give **1a** and **3a** or at the alkeneic carbon to produce **1b** and **3b** as shown in Scheme 2-10.

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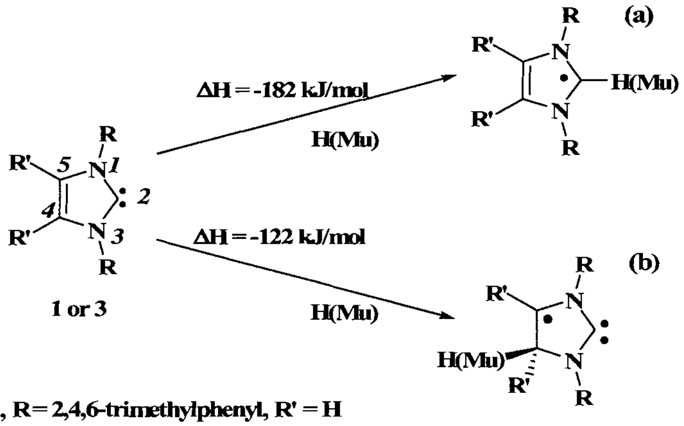
[c] I synthesised all of the carbenes including the ^{13}C labelled carbenes, which were used and analysed by Dr. I. D. McKenzie at TRIUMF (University of British Columbia). He collected and processed the relevant data.



1, R = 2,4,6-trimethylphenyl, R' = H
3, R = isopropyl, R' = methyl

Scheme 2-10: Possible reactions of NHCs with the H atom and its light "isotope", muonium, Mu.

Calculations showed the formation of **3a** to be more exothermic (60 kJ/mol) than the formation of **3b**; therefore this mode of reactivity is thermodynamically favoured. Compound **3a** was also kinetically favoured due to the absence of significant activation barrier for the addition at the carbeneic centre.[70]

The structure of **3a**, predicted by theoretical calculations, was found to be different from those calculated for the parent carbene as shown in Table 2-2. The C_2-N_1 or C_2-N_3 bonds and the N_1-C_2-N_3 angle were observed to be slightly larger for the radical than the carbene. The bond lengths and bond angles of **3a** are comparable to what Neta *et. al.* obtained from density functional calculations on a similar neutral radical.[69] The imidazole ring was no longer planar but was puckered at N_1 and N_3. The radical centre C_2 was found to be pyramidal and to our knowledge is the first reported addition reaction to a stable carbene that did not produce a planar tricoordinate carbon centre.

Bond lengths (Å)	**3**	**3a**
(N_3-C_2), (N_1-C_2)	1.377	1.430
(N_1-C_5), (N_3-C_4)	1.415	1.418
(C_4-C_5)	1.367	1.363
Bond Angles (°)		
(N_1-C_2-N_3)	102.4	104.6
(C_5-N_1-C_2), (C_2-N_3-C_4)	112.8	108.6
(N_1-C_5-C_4), (N_3-C_4-C_5)	106.0	108.5

Table 2-2: Selected bond lengths (Å) and angles (°) for NHC 3 and 3a.

Atomic hydrogen is not a common reagent for solution studies, largely because of the complications inherent in its generation. Most commonly, hydrogen atoms are produced by photolysis or radiolysis of water or other protic solvents, but this usually results in other radical species. In addition, other solvents are not compatible with imidazol-2-ylidene. Rather than using H atoms, we hence used a hydrogen atom surrogate, muonium (Mu)[72] to complement the computational studies. Muonium is a one-electron "atom" whose nucleus is the positive muon; it is chemically similar to hydrogen, but has one-ninth the mass and a lifetime of 2.2 μs. Muon spin rotation and muon level-crossing spectroscopy[72] were used to determine muon, ^{13}C and ^{14}N hyperfine coupling constants (hfcs).[73, 74]

Exposure of a ^{13}C labelled **NHC** to the muonium beam was performed at TRIUMF (Canada's national laboratory for particle and nuclear physics). Only one type of radical was observed, evident from the characteristic pair of frequencies above and below the muon Larmor frequency as shown in Figure 2-5. The muon hfcs were determined by transverse field muon spin rotation (TF-μSR) at 298 K and was observed to be 286.69 MHz for **NHC 1** and 246.43 MHz for **NHC 3**. The pair of peaks at *ca.* 73 and 320 MHz are due to a single muonated radical of **NHC 3**. Hyperfine coupling constants with the other nuclei in the radical, namely ^{13}C and ^{14}N, were observed in the μLCR spectrum with the ^{13}C resonance observable only for a sample of **NHC 3**, which contained 40% ^{13}C enrichment at C_2. The calculated hyperfine coupling constants of muonated radical of **NHC 1** and **NHC 3** were found to be in good agreement with the hyperfine coupling constants (hfcs) of **1a** and **3a**. It is interesting to note that most of the unpaired spin density was localised on the N-C_2-N region and with most concentration on the C_2 atom as shown in Figure 2-6. Given the agreement between measured and predicted hfcs, as well as the relative energies of the possible radicals, it was concluded that hydrogen and muonium atoms add exclusively to the carbeneic centre of **NHCs**.

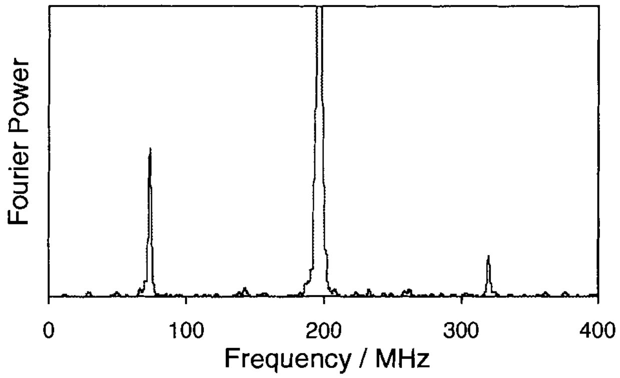


Figure 2-5: Transverse field μSR spectrum at 14.4 kG for 3 in THF at 298K. The pair of peaks at *ca.* 73 and 320 MHz are due to a single muoniated radical.

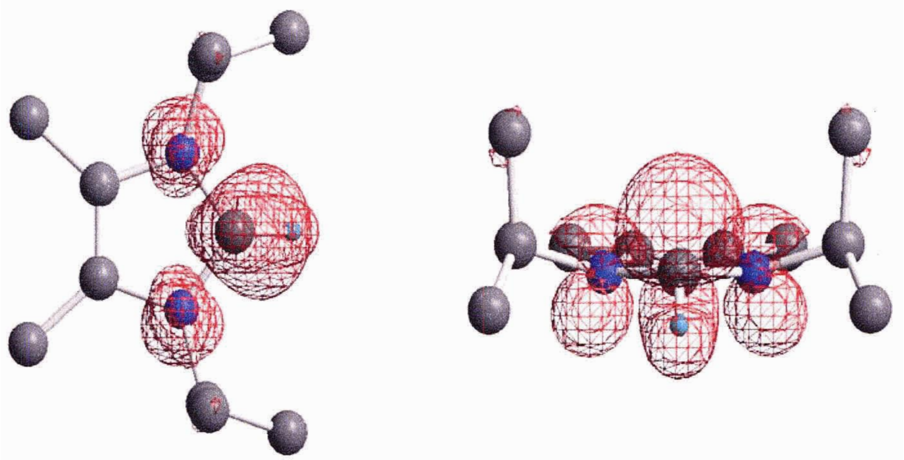


Figure 2-6: Unpaired electron spin density in 3a. For clarity, the hydrogen atoms on the alkyl substituents are not shown.

2.3.3 Electrochemical and EPR Studies of a Neutral NHC Radical

An electron paramagnetic resonance (EPR) spectroscopic study[d] was undertaken to aid the structural assignment of the radical intermediate produced during the electrolysis of **[2-H][Cl]**. As mentioned in section 2.2, the reduction of **[2-H][Cl]** was slightly reversible (Figure 2-3), suggesting that the radical formed has a somewhat longer lifetime compared to other imidazolium salts. Hence, this system was chosen to characterise the intermediate radical.

A sample of **[2-H][Cl]** was electrolysed by applying a potential of -2.3 V for five minutes in acetonitrile (1.66 mM) under an inert atmosphere referenced to a saturated calomel electrode. The acetonitrile solution was then rapidly transferred to a quartz flat-cell and the EPR spectrum was collected.

A 21 line spectrum was obtained as shown in Figure 2-7. The signal was split by the hydrogen attached at C_2 position, 2 equivalent nitrogen atoms and 2 inequivalent

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[d] The EPR studies were performed by Dr. Charles J. Walsby and the radical sample was prepared by Brian D. Gorodetsky at Simon Fraser University.

hydrogen atoms to give the 21 line spectrum. The spectrum was also simulated by using the following hyperfine coupling constants: $^{14}N(2)$ = 0.395 mT; $^{1}H(C_2)$ = 0.800 mT; $^{1}H(C_3)$ = 0.135 mT and a line width of 0.5 mT. This can be fitted to the experimental spectrum with the largest coupling occurring with the hydrogen attached to C_2 as shown in Figure 2-9. This 21 line spectrum supported the calculation performed during the μSR study, which suggested that the neutral radical is not planar but puckered at N_1 and N_3 and pyramidal at the C_2 centre making the two hydrogens at the back of the imidazole ring nonequivalent as shown in Figure 2-8.

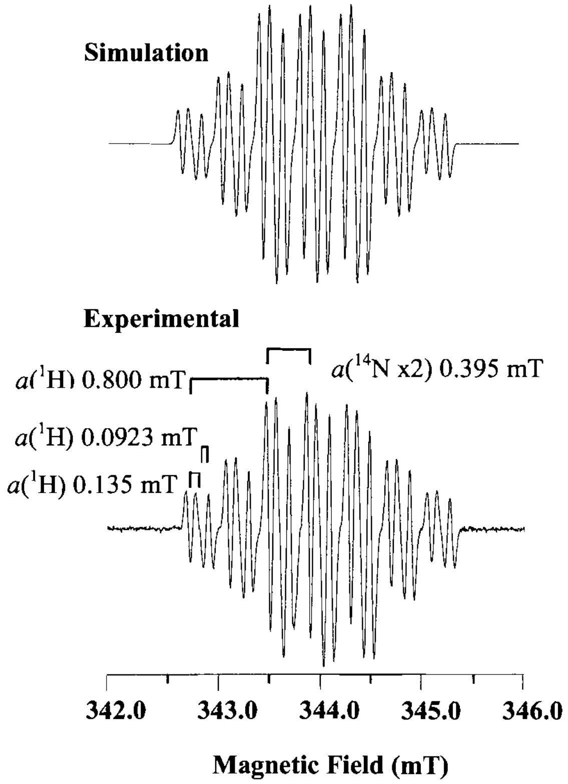

Figure 2-7: Simulated and experimental EPR spectra of [2-H]•.

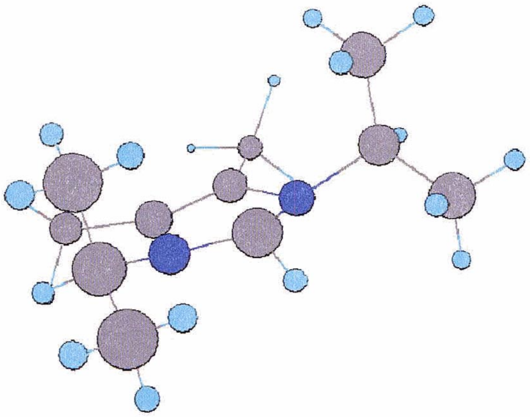

Figure 2-8: Optimised structure of [3-H]$^{\bullet}$ showing the non-planar radical centre at C2. (grey = C; royal blue = N; light blue = H)

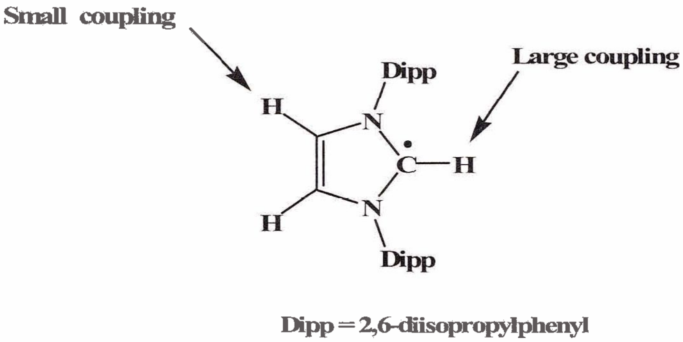

Figure 2-9: Relative magnitude of coupling between unpaired electron and hydrogens on [2-H]$^{\bullet}$ radical.

EPR spectroscopy is inherently more sensitive, that is the spectral resolution is greater than μSR since smaller splittings with the hydrogen on the phenyl groups attached to the nitrogens of the imidazole were observed in the latter case. The hyperfine couplings (mT) measured were as follows: $^{14}N = 0.395$, $^{1}H = 0.800$, $^{1}H = 0.93$ and $^{1}H = 0.137$, which implied that the species initially produced from the electrochemical reaction was **[2-H]$^{\bullet}$**. The EPR study was in accord to the μSR study described before and supports that there is a high electron density on the C$_2$-carbeneic carbon with delocalisation onto the neighbouring nitrogen atoms and minor spin density on the backbone of the imidazole. Some of the electron density was also delocalised on the 2,6-

diisopropylphenyl rings attach to the nitrogens giving some minor splittings as shown in Figure 2-10. This splitting was also resolved by simulation using the following hyperfine coupling constants: $^{1}H \times 1 = 0.135$ mT; $^{1}H \times 1 = 0.0923$ mT; $^{1}H \times 2 = 0.021$ mT; $^{1}H \times 4 = 0.015$ mT with line widths of 0.15 mT. The simulation fitted the experimental spectrum as shown in Figure 2-10.

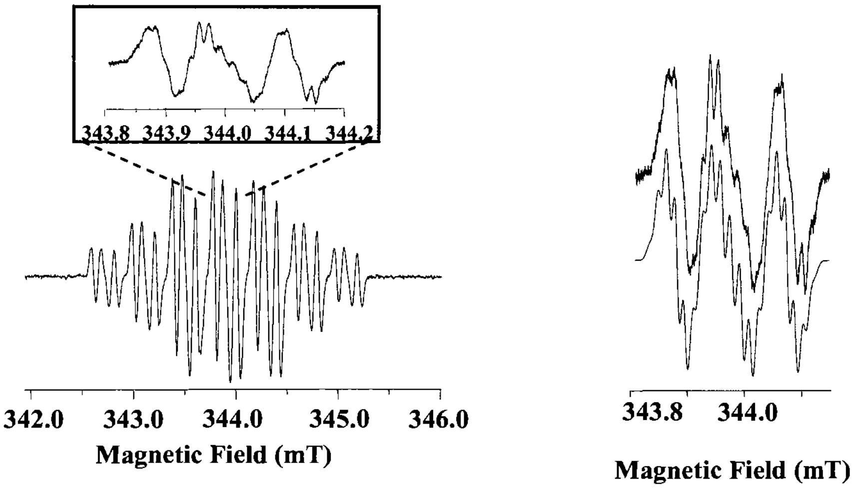

Figure 2-10: Experimental (left) and overlap of experimental and simulated spectra (right) of $[2\text{-}H]^{\bullet}$.

2.4 Single Electron Oxidation of NHCs

2.4.1 Introduction

The one electron reduction of imidazolium ions to give **NHC** was reported in section 2.2.[70] To further this study, the electrochemistry of **NHCs** was examined. The one-electron reduction of **NHCs** has been previously reported, an example being the reduction of triazol-5-ylidene.[75] Some cyclic voltammetric studies were also carried out on this particular molecule and after initial sweeps, one reversible wave for the electrochemical reduction of the carbene in the cyclic voltammetry was observed, implying that a clean one electron reduction occurred yielding the anion radical as shown in Figure 2-11. Recently, Arnold *et. al.* reported the chemically generated stable radical anion of an **NHC**, which was characterised by EPR studies.[76] He proposed that such reduction is involved in the reduction chemistry of **NHC** adducts of lanthanides with high reduction potentials.

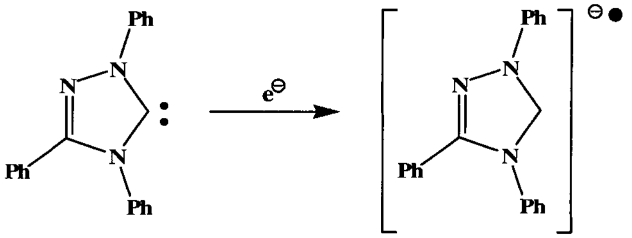

Figure 2-11: One electron reduction of triazol-5-ylidene.

To our knowledge, simple one-electron *oxidation* reactions of **NHCs** had not been reported.[e] Since **NHCs** are good *carbon-based* electron donors, their reactivity with one-electron oxidants (electron acceptors) was performed. Two different **NHCs** namely 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1** and 1,3-*bis*(isopropyl)-4,5-dimethylimidazol-2-ylidene, **NHC 3**, were used with two different oxidants namely tetracyanoethylene (**TCNE**) and ferrocenium (**CP_2Fe^+**) salts.[65]

The reactivity of **NHCs** with **TCNE** was investigated since **NHCs** are good *carbon-based* electron donors and **TCNE** is a good *carbon-based* electron acceptor.[77] **TCNE** readily forms stable salts containing **$[TCNE]^{\bullet-}$**or its π-stacked dimer **$[TCNE]_2^{2-}$**.[78] **TCNE** containing compounds have been central to the development of molecules with metallic[79] and superconducting properties.[80] The reactivity of triphenylphosphine, a comparable 2-electron donor ligand, has been previously reported with **TCNE**. A completely different molecule, a phosphoranimine as shown in Figure 2-12 was obtained through an unknown mechanism.[81] This molecule was characterised

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[e] In this context, oxidation means the *loss* of one or two electrons and not *chemical* oxidation with, for example, oxygen and sulphur.

by X-ray crystallography, NMR spectroscopy, and most relevant to this report is the IR spectroscopy. The IR spectrum of this molecule showed a strong band at 1120 cm^{-1}, charasteristic of the vibration due to the Ph-P stretch in a tetracoordinate geometry. The P-N stretching appeared at 1390 cm^{-1} as a very strong band and the C-N stretch at 2204 cm^{-1}, which can be attributed to the cyano group that is in conjugation with the P=N system. Two other CN stretches were obtained at 2262 and 2250 cm^{-1}. The TCNE stretches were different from the one observed in our study as detailed later.[81]

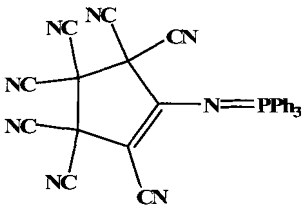
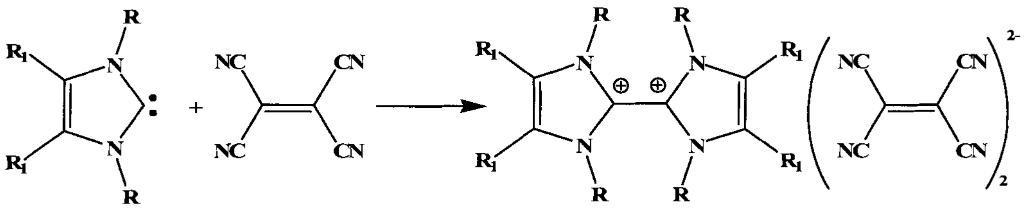


Figure 2-12: A phosphoranimine produced by the reaction of PPh_3 and TCNE.

2.4.2 Synthesis and Characterisation of two 1,2-Dications

When 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1**,[49] or 1,3-*bis*(isopropyl)-4,5-dimethylimidazol-2-ylidene, **NHC 3**,[58] were reacted with **TCNE** in THF, insoluble red materials were obtained. The air-sensitive red solids were characterised by elemental analyses, NMR and IR spectroscopy and mass spectrometry. Elemental analyses on the reaction solid products were consistent with a material containing a 1:1 ratio of **1** or **3** with **TCNE** (Scheme 2-11). The products were diamagnetic in solution and their ^1H NMR spectra exhibited signals that were downfield from the corresponding resonances of either **NHC 1** or **3**. The signals were consistent with a symmetrical imidazole fragment. The IR spectroscopic data for both compounds showed two strong ν(CN) absorptions at 2191 (s) and 2147 (s) cm^{-1} consistent with the formation of the dianion π-**(TCNE)$_2$**$^{2-}$.[82] Moreover, the deep red colour obtained on the addition of **TCNE** is consistent with the formation of π-**(TCNE)$_2$$^{2-}$** as observed previously.[83] These signals were markedly different from neutral **TCNE**,[84] which has ν(CN) absorptions at 2257 (s) and 2219 (s) cm^{-1} and from the **TCNE** stretches observed in the phospharanimine.[81] Formation of the complex anion was also supported by the ^{13}C NMR spectra, where the resonance corresponding to the ethyleneic carbon in **(TCNE)$_2$$^{2-}$** was observed at 68 ppm, upfield from that observed for **TCNE** at 110 ppm.[82]



1, R=Mes, R$_1$=H
3, R=*i*Pr, R$_1$=CH$_3$

[**1-1**]$^{2+}$, R=Mes, R$_1$=H
[**3-3**]$^{2+}$, R=*i*Pr, R$_1$=CH$_3$

Scheme 2-11: Reaction of NHCs with TCNE.

Electrospray mass spectrometry studies on the solids dissolved in THF showed distinct peaks in the positive mode at 304 and 180 amu for the products derived from **NHC 1** and **3** respectively. Under similar conditions **NHC 1** and **3** exhibited peaks at 305 and 181 amu, corresponding to the [M+H]$^{+}$ ion. Higher mass peaks were not observed. Taken in total, the spectroscopic data suggested the formation of the symmetrical dications [**1-1**]$^{2+}$ and [**3-3**]$^{2+}$. Peaks at 304.5 and 180.5 amu, anticipated due to the isotopic pattern of the dications [**1-1**]$^{2+}$ and [**3-3**]$^{2+}$ respectively were not observed, which suggested the breaking of the *C-C* bonds during volatilisation and excitation for the mass spectroscopy. The dication [**3-3**]$^{2+}$ had previously been isolated from a nucleophilic substitution reaction[19] and the ^{1}H and ^{13}C NMR spectra obtained were in agreement to the reported values.

Formation of **[1-1]**$^{2+}$ and **[3-3]**$^{2+}$ can be rationalised by the generation of the transient radical cations **[1]**$^{\bullet+}$ and **[3]**$^{\bullet+}$. Carbene radical cations have been postulated as intermediates in the electrochemical oxidation of diazo compounds[85] although no additional spectroscopic data was reported. The dimerisation of the radical cation produced the observed dicationic products. These dimers feature prominently in the chemistry of organic molecules in superacidic media.[86, 87] Other 1,2-dications, such as diphosphonium and diazonium dications have also been isolated, but interestingly none of them, to my knowledge, have been characterised by mass spectroscopy.[86] Finally, Alder *et. al.* proposed that dimerisation of **NHCs** can occur through an alternate mechanism which is proton catalysed.[88] Though similar reactions were not observed in our work as detailed later, the possibility of dimerisation cannot be ruled out and this led us to investigate the **NHC** radical cation in more detail.

In order to shed light on the structure of the putative radical cation intermediate and to understand the reasons for dimerisation of the radical cation, computational studies were performed. Gaussian 98 package of programs with the UB3LYP functional[89] were used for the computational studies.[f] The 6-31G** basis set was used to optimise the structures of **3**, **[3]**$^{\bullet+}$ and **[3-3]**$^{2+}$. The most notable feature of the radical cation was the high spin density concentrated on the carbeneic carbon as shown in Figure 2-13. The shape of the singly occupied molecular orbital (SOMO) suggested the potential of dimerisation through *C-C* σ-bond formation. Also notable was that the C-N bond length is shorter for **[3]**$^{\bullet+}$ compared to **NHC 3**. An increase in the N_1-C_2-N_2 bond angle (Table

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[f] The computational calculations were performed by Dr. I. D. McKenzie at Simon Fraser University.

2-3) was observed as expected according to Valence Shell Electron Pair Repulsion (VSEPR) theory.[90]

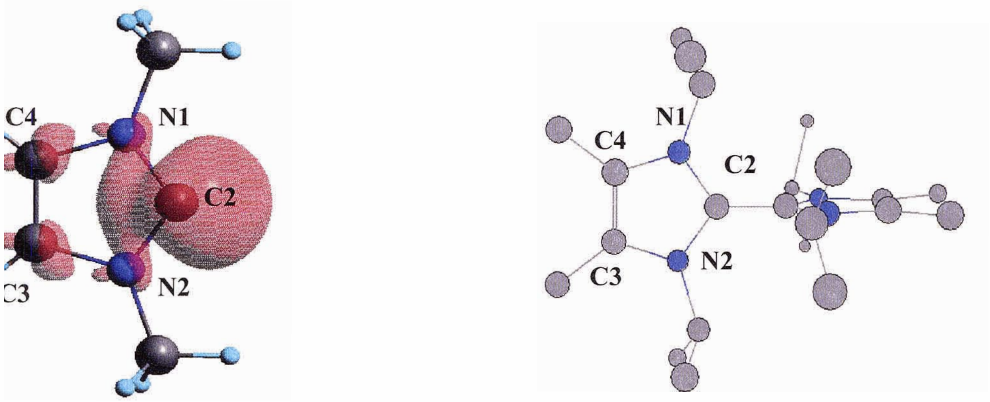
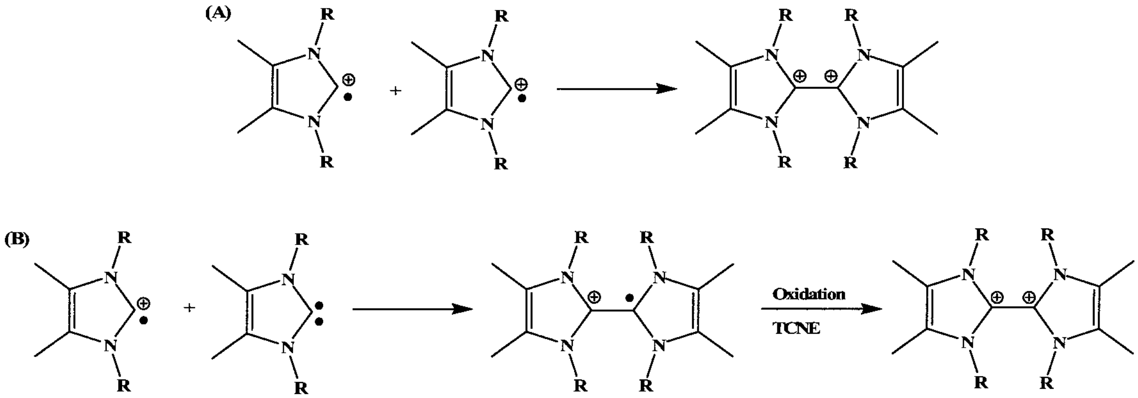


Figure 2-13: Total electron spin density of $[3]^{\bullet+}$ (left) and the calculated structure of $[3\text{-}3]^{2+}$ (right). Hydrogen atoms have been omitted for clarity.

Parameter	**3** **Calc.**	**$[3]^{\bullet+}$** **Calc.**	**$[3\text{-}3]^{2+}$** **Calc.**	**$[3\text{-}3]^{2+}$** **Exp.**[91]
C_2-N_2 (Å)	1.379	1.337	1.370	1.351(3)
N_2-C_3 (Å)	1.416	1.423	1.395	1.370(3)
C_3-C_4 (Å)	1.371	1.381	1.390	1.363(4)
C_2-C_2 (Å)	-	-	1.462	1.463(3)
N_1-C_2-N_2 (°)	102.3	111.6	107.7	108.4(2)
C_2-N_3-C_3 (°)	112.9	107.2	109.0	108.6(2)
N_2-C_3-C_4 (°)	105.9	106.9	107.1	107.4(2)
N_1-C_2-C_2-N_2 (°)	-	-	90.04	88.1

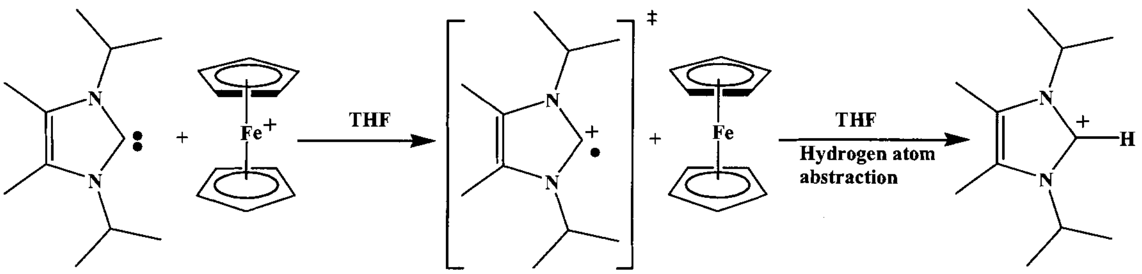
Table 2-3: Selected calculated bond lengths (Å) and angles (°) for 3, $[3]^{\bullet+}$ and $[3\text{-}3]^{2+}$.

There are at least two possible routes for the formation of **$[3\text{-}3][TCNE]_2$** as shown in Scheme 2-12. *Route A* involves dimerisation of two radical cations $[3]^{\bullet+}$. *Route B* is a stepwise process that occurs through an initial formation of the radical cation **$[3]^{\bullet+}$** followed by its reaction with **NHC 3** to produce **$[3\text{-}3]^{\bullet+}$**, which is then further oxidised to give the dication.



Scheme 2-12: Possible routes of dimerisation.

NHC 1 and **NHC 3** were also reacted with milder oxidising agents namely **[Cp$_2$Fe][PF$_6$]** and **[Cp$_2$Fe][BF$_4$]** (Scheme 2-13), which were purified and dried under vacuum before use. ^{1}H NMR spectroscopy confirmed the absence of water in the samples. Upon the combination of reactants, a slow colour change from pale yellow through dark green to reddish brown was observed. After removal of the solvent, the resulting coloured solids were washed with hexanes. When the hexanes layer was removed, an orange powder was obtained, which was identified to be ferrocene by ^{1}H NMR spectroscopy and mass spectrometry. The brown powder obtained after washing with hexanes was characterised by IR and NMR spectroscopy, mass spectrometry and elemental analysis. The principal compounds identified in the insoluble solids were the imidazolium salts **[1-H][PF$_6$]**, **[1-H][BF$_4$]**, **[3-H][PF$_6$]** and **[3-H][BF$_4$]**. A synthesis of these imidazolium species *via* protonation of **NHC**s and anion exchange reactions[94] was performed in order to confirm the identity of the compounds. Unlike the colourless reference imidazolium salts, the products identified were coloured and this might be due to the presence of a small amount of insoluble ferrocenium salts.



3 **[3-H]$^+$**

Scheme 2-13: Reaction of NHC 3 with [Cp$_2$Fe]$^+$.

The reactivity of **NHC 1** and **3** with **[Cp$_2$Fe][PF$_6$]** or **[Cp$_2$Fe][BF$_4$]** was significantly different from the reaction observed with **TCNE**. We suggest that the difference in reactivity might be because **[Cp$_2$Fe]$^+$** salts are only partially soluble in THF, thus a *heterogeneous* reaction mixture was obtained, causing the reaction proceed slowly. Another reason is that ferrocenium salts, being mild oxidising agents, react very slowly, hence when reacted with **NHC 1** and **3**, only a small amount of radical cation was initially generated thus precluding the dimerisation reaction. Alternative reactions are therefore possible, namely abstraction of hydrogen atom from other sources, such as the solvent.[92]

2.5 Conclusions

The electrochemistry of different imidazolium salts and one **NHC** was described. This study led to a new synthesis of **NHCs** by treating the imidazolium ions with potassium metal. A mechanism was proposed for the reduction of the imidazolium ions and their conversion to **NHCs**. Intermediates were identified and supported by EPR and muonium studies. Finally, oxidation of **NHCs** using strong and mild oxidising agents was also performed and it was observed that different products were obtained with different oxidising agents.

2.6 Experimental Section

2.6.1 General Procedure

[1-H][Cl],[93] **NHC 1**[93] and **NHC 3**,[58] were prepared as previously described in literature. **[1-H][PF$_6$]**, **[3-H][PF$_6$]**, **[1-H][BF$_4$]** and **[3-H][BF$_4$]** were synthesised by protonation reaction as described in literature.[94] All other chemicals were purchased from Aldrich and were used as received. Melting points were determined using a Mel-Temp apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer in five millimeters quartz tubes. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported in parts per million (ppm) reference with residual solvent peak. Infrared spectra were obtained using a Bomem MB Spectrometer with the percentage transmittance values reported in cm^{-1}. Mzi Keng Yang at Simon Fraser University obtained elemental analyses on a 1106 CHN Carlo Erba Model. Dr. David L. McGillivray carried out high resolution mass spectroscopy experiments at the University of Victoria.

All the reactions were performed in an inert atmosphere using dry solvents. All cyclic voltammetry experiments were performed using a Pine AFCBP1 bipotentiostat with a three-electrode setup using a glassy carbon disk working electrode (5 mm diameter), a platinum wire counter electrode separated from the bulk solution by a glass frit and a Ag/AgCl (in a saturated NaCl solution) reference electrode. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, which was purified by recrystallising three times from ethanol followed by drying at 110 °C under vacuum for 3 days. All glassware was flame dried and maintained under a positive pressure of dry nitrogen throughout the entire experiment. The working electrode was polished, sonicated, rinsed with ethanol and dried prior to each experiment. The dimethylformamide (DMF) was of greater than 99% purity and purchased from Aldrich in "sure-sealed" containers packaged under nitrogen. Bubbling dry nitrogen gas through the assembled system further deoxygenated the solvent. Before performing the cyclic voltammetric studies on any salts, the CV of the solvent blank was performed to make sure that there is no impurity in the solvent. All potentials were referenced to the ferrocene/ferrocenium redox couple, taken to have an $E°$ of 0.475 V *versus* saturated calomel electrode (SCE). The ferrocene used as the reference was freshly sublimed.

2.6.2 Synthesis of NHC 1 by Reacting [1-H][Cl] with Potassium Metal

A solution of **[1-H]**[**Cl**] (4.00 g, 11.73 mmol) in THF (100 mL) was treated with excess potassium metal (0.80 g, 20.47 mmol). The resulting slurry was heated to reflux for three hours under a nitrogen atmosphere to produce a red solution and a pale yellow precipitate. The mixture was filtered through Celite and the solvent evaporated under vacuum. The solid residue obtained was washed with cold hexanes to afford 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene, **NHC 1** (3.18 g, 89%) as a white powder. M.p. 154-155 °C. ^{1}H NMR (400 MHz, THF-d_8) δ (ppm) 7.01 (s, 2 H, NC*H*), 6.90 (s, 4 H, Ar-*H*), 2.25 (s, 6 H, 4-CH_3), 2.02 (s, 12 H, 2,6-CH_3). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d_8) δ (ppm) 219.4 (s, N*C*N), 139.8 (s, Ar-*C*-1), 137.7 (s, Ar *C*-4), 135.8 (s, Ar-*C*-2,6), 129.3 (s, Ar-*C*-3,5), 121.4 (s, N*CC*), 21.1 (s, 4-*C*H$_3$), 18.1 (s, 2,6-*C*H$_3$).

2.6.3 Synthesis of ^{13}C labelled [1-H][Cl]

Step 1. Glyoxal-bis(2,4,6-trimethylphenyl)imine from 2,4,6-trimethylaniline and glyoxal

2,4,6-Trimethylaniline (21.0 mL, 149.56 mmol), 40 % glyoxal in water (9.5 mL, 149.56 mmol) were added to 100 mL of ethanol followed by a few drops of 88 % formic acid to initiate the precipitation of yellow crystals from the amber solution. After stirring for 1 hour, the yellow crystals were filtered and washed with cold anhydrous ethanol and then cold ether to afford glyoxal-bis-(2,4,6-trimethylphenyl)imine (42.90 g, 98%). M.p. 158–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (s, 2 H, C*H*), 6.91 (s, 4 H, *m-H*), 2.29 (s, 6 H, *p*-CH_3), 2.16 (s, 12 H, *o*-CH_3).

*Step 2: Synthesis of ^{13}C labelled [**1-H**][Cl]*

Glyoxal-bis-(2,4,6-trimethylphenyl)imine (3.00 g, 10.30 mmol) was added to toluene (60 mL) containing ^{13}C labelled paraformaldehyde (0.31 g, 51.40 mmol). The suspension was stirred and heated to 100 °C. When the reaction reached 100 °C, it was removed from heat and allowed to cool to 40 °C. To the solution 4 M HCl in dioxane (2.0 mL, 8.00 mmol) was added, which was left to stir for 3 days. The reaction mixture was then filtered and the powder obtained was washed with cold tetrahydrofuran (THF) to afford ^{13}C labelled 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (2.99 g, 85 %). M.p. (under nitrogen atmosphere) 350-352 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.72 (s, 1 H, imidazole-H_2), 7.62 (d, 2 H, imidazole-$H_{4,5}$), 7.01 (s, 4H, *m*-H), 2.32 (2, 6 H, *p*-CH_3), 2.16 (s, 12 H, *o*-CH_3). Anal. Calcld. for $C_{20}{}^{13}CH_{25}N_2Cl$: C, 74.22; H, 7.39; N, 8.21. Found: C, 74.19; H, 7.37; N, 8.05.

*Step 3: Synthesis of ^{13}C labelled **NHC 1***

A solution of ^{13}C labelled 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (2.00 g, 5.86 mmol) in THF (100 mL) was treated with excess potassium metal (lump, 0.35 g, 8.79 mmol). The reaction mixture was heated to reflux for three hours under nitrogen to produce a red solution and a brown precipitate. The mixture was filtered through Celite, the solvent was evaporated under vacuum and the solid residue was washed with cold hexane to afford ^{13}C labelled **NHC 1** (1.59 g, 89 %) as a white powder. M.p. 154–155 °C. ^{1}H NMR (400 MHz, THF-d_8) δ (ppm) 7.02 (d, 2H, NC*H*), 6.94 (s, 4H, Ar*H*) 2.27 (s, 6H, 4-CH_3), 2.04 (s, 12H, 2,6-CH_3). ^{13}C NMR (100.61 MHz, THF-d_8) δ (ppm) 219.5 (s, N*C*N), 139.7 (s, Ar *C*-1), 137.8 (s, Ar *C*-4), 135.9(s, Ar *C*-2,6), 129.4 (s, Ar *C*-3,5), 121.4 (s, N*CC*), 21.2 (s, 4-*C*H$_3$), 18.2 (s, 2,6- *C*H$_3$). Anal. Calcld. for $C_{20}{}^{13}CH_{24}N_2$: C, 82.91; H, 7.92; N, 9.17. Found: C, 82.74; H, 7.65; N, 9.08.

2.6.4 Synthesis of 40% ^{13}C labelled NHC 3

Labeled carbon disulphide (1.00 g, 13.16 mmol) in cold benzene (3 mL) was added dropwise to isopropylamine (1.58 g, 26.32 mmol) in cold benzene (3 mL). Precipitation of a white solid occurs after stirring the solution for 1 hour which was then allowed to heat to reflux for 24 hours. The solution was filtered off and the precipitate washed with cold benzene to give white crystals of labeled 1,3-diisopropyl-thiourea (2.00 g, 12.5 mmol) in 95% yield. The labeled 1,3-diisopropyl-thiourea (2.00g, 12.5 mmol) was then mixed to unlabeled 1,3-diisopropyl-thiourea (3.00 g, 18.75 mmol) to make it 40 % ^{13}C abundant. The mixture was then dissolved in 80 mL of hexanol and to it 3-hydroxy-2-butanone (2.75 g, 31.25 mmol) was added. The reaction mixture was then heated to reflux for 24 hours and the solvent was removed under vaccuum.

Recrystalization was carried out from anhydrous ethanol to give white crystals of 1,3-diisopropyl-4,5-dimethyl-1,3-dihydro-imidazol-2-thione (4.06 g, 62 % yield). The thione (4.06 g, 19.15 mmol) was then reduced using potassium metal (1.87 g, 47.88 mmol) to give a crude sample of **NHC 3**, which was sublimed to give pure white crystals of **NHC 3** (2.76 g, 80 % yield). M.p. (under nitrogen atmosphere) 190 °C. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 3.94 (sept, 2 H, N(1,3)-C*H*(CH_3)$_2$), 1.76 (s, 6 H, $C_{4,5}$-C*H*$_3$), 1.45 (d, 12 H, $N_{1,3}$-CH(C*H*$_3$)$_2$). ^{13}C NMR (100.61 MHz, C_6D_6) δ (ppm) 205.6 (C_2), 121.5 ($C_{4,5}$), 48.9 ($N_{1,3}$-*C*H(CH_3)$_2$), 24.5 ($N_{1,3}$-CH(*C*H$_3$)$_2$), 8.9 ($C_{4,5}$-*C*H$_3$). Anal. Calcld. for $C_{10}{}^{13}CH_{20}N_2$: C, 73.42; H, 11.12; N, 15.45. Found: C, 73.39; H, 11.09; N, 15.39.

2.6.5 Reaction of NHC 1 with TCNE

To a solution of **NHC 1** (1.00 g, 3.28 mmol) in THF (20 mL), **TCNE** (0.42 g, 3.28 mmol) dissolved in THF (20 mL) was added dropwise. The solution immediately turned dark red. After stirring for 2 hours, the solvent was removed under vacuum to give a dark red solid. Recrystallisation of the solids was attempted using a variety of solvents (toluene, diethylether, dichloromethane, and tetrahydrofuran), but all attempts were unsuccessful. Isolated yield: (1.99 g, 70 %). M.p. (under nitrogen atmosphere) 115-116 °C. ^{1}H NMR (400 MHz, THF-d_8) δ (ppm) 7.30 (s, 4 H, C=C*H*), 7.15 (s, 8 H, Ar-*H*), 2.44 (s, 12 H, *p*-C*H*$_3$), 2.24 (s, 24 H, *o*-C*H*$_3$). ^{13}C {^{1}H} NMR (100.61 MHz, CD_2Cl_2) δ (ppm) 142.5 (N*C*N), 134.3 (s, Ar-*C*-1), 130.5 (s, Ar-*C-4*), 130.3 (s, Ar-*C-2,6*), 125.5 (s, Ar-*C-3,5*), 116.8 (s, N*CC*), 114.0 (TCNE, *C*≡N), 68.0 (TCNE, *C*-1), 21.1 (s, 4-*C*H$_3$), 17.6 (s, 2,6-*C*H$_3$). IR (nujol, cm^{-1}) 2147 (m), 1688 (w), 1607 (w), 1455 (s), 1229 (m), 853 (s), 723 (w). Anal. Calcd for $C_{54}H_{48}N_{12}$: C, 72.42; H, 5.59; N, 18.98. Found: C, 72.08; H, 5.69; N, 18.73. MS (EI, cation) *m/z* 304 amu (1/2 M$^+$), (Calcd. 304). MS

(LSIMS) *m/z* 304.1 amu (1/2 M^+) (Calcd. 304.1). The data was consistent with the formulation as **[1-1]**[**(TCNE)$_2$**].

2.6.6 Reaction of NHC 3 with TCNE

A stirred solution of **NHC 3** (0.25 g, 1.39 mmol) in THF (10 mL) was treated with a solution of **TCNE** (0.18 g, 1.40 mmol) in THF (20 mL) and left to stir for 2 hours. The yellow solution rapidly changed to a dark red colour. The solvent was removed under vacuum leaving a sticky dark red material. Attempts at recrystallisation from a variety of solvents (toluene, diethylether, dichloromethane, and tetrahydrofuran) were unsuccessful. Isolated yield: (0.50 g, 58%). M.p. (under nitrogen atmosphere) 160-162 °C. ^1H NMR (400 MHz, THF-d_8) δ (ppm) 4.63 (sept, 4 H, $CH(CH_3)_2$), 2.37 (s, 12 H, 4,5-CH_3), 1.58 (d, 24 H, $CH(CH_3)_2$). ^{13}C {^1H} NMR (100.61 MHz, CD_3OD) δ (ppm) 132.5 (s, *C* -4,5), 128.50 (s, N*C*N), 114.3 (s, TCNE, *C*≡N), 60.0 (TCNE, *C*-1), 52.7 (s, *C*HMe$_2$), 23.7 (s, $CH(CH_3)_2$), 9.3 (s, 4,5-CH_3). IR (nujol, cm^{-1}) 2985 (s), 2937 (s), 2195 (s), 2147 (m), 1597 (w), 1462 (s), 1376 (m), 1231 (s), 895 (s), 799 (m). Anal. Calcd for $C_{34}H_{40}N_{12}$: C, 66.21; H, 6.54; N, 27.25. Found: C, 66.17; H, 6.69; N; 27.30. MS (EI, cation) *m/z* 180 amu, (1/2 M^+) (Calcd. 180 amu). MS (LSIMS) *m/z* 180.1 (1/2 M^+), (Calcd. 180.1 amu). The data was consistent with the formulation as **[3-3]**[**TCNE**]$_2$.

2.6.7 Reaction of NHC 1 with $[Cp_2Fe]^+[PF_6]^-$

NHC 1 (0.50 g, 1.47 mmol) was dissolved in THF (20 mL) and was slowly added to ferrocenium hexafluorophosphate (0.54 g, 1.64 mmol) in THF (20 mL). (Note: Ferrocenium salts were found to be partially soluble in THF.) The yellow solution turned reddish brown very slowly over 4 h. It was stirred for 24 hours and then the solvent was removed under vacuum to give a reddish brown powder. After washing thoroughly with hexanes, a dark powder was isolated whose principle component was characterised as the imidazolium hexafluorophosphate, **[1-H][PF$_6$]**. Isolated yield: (0.47 g, 71%). M.p. (under nitrogen atmosphere) 170-172 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 9.14 (s, 1 H, C$_2$-*H*), 7.30 (s, 2 H, C=C*H*), 7.16 (s, 4 H, Ar-*H*), 2.37 (s, 6 H, *p*-C*H*$_3$), 2.18 (s, 12 H, *o*-C*H*$_3$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 142.0 (N*C*N), 139.2 (s, *C*-1), 135.4 (s, *C*-4), 132.1 (s, Ar-*C*-2,6), 130.5 (s, Ar-*C*-3,5), 126.7 (s, N*CC*), 21.2 (s, 4-*C*H$_3$), 17.8 (s, 2,6-*C*H$_3$). IR (nujol, cm^{-1}) 2951 (s), 1638 (m), 1462 (m), 1377 (m), 1226 (s), 837 (s), 739 (m). Anal. Calcld. for $C_{21}H_{25}F_6N_2P$: C, 56.00; H, 5.59; N, 6.22. Found: C, 48.95; H, 5.00; N, 6.01. MS (EI, cation) *m/z* 305.2 amu (M$^+$), (Calcd. 305.2).

2.6.8 Reaction of NHC 3 with [Cp$_2$Fe]$^+$[PF$_6$]$^-$

To a solution of **NHC 3** (0.30 g, 1.66 mmol) in THF (10 mL), ferrocenium hexafluorophosphate (0.55 g, 1.67 mmol) partially soluble in THF (10 mL) was added slowly and left to stir for 24 hours. The colour of the solution changed slowly to dark green. The solvent was removed under vacuum and then washed thoroughly with hexanes to remove any ferrocene, leaving a dark green powder whose principle component was characterised as **[3-H][PF$_6$]**. The colour of the isolated product was different from the original product due to the presence of some ferrocenium salts as impurity. Isolated yield: (0.47 g, 87%). M.p. (under nitrogen atmosphere) 154-156 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 8.48 (s, 1 H, C$_2$-*H*), 4.46 (sept, 2H, C*H*Me$_2$), 2.22 (s, 6 H, 4,5-C*H*$_3$), 1.42 (d, 12 H, CH (C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 130.4 (N*C*N), 127.4 (*C*-4,5), 51.2 (*C*HMe$_2$), 22.1 (CH(*C*H$_3$)$_2$), 7.9 (4,5- (*C*H$_3$)). IR (nujol, cm^{-1}) 3141 (s), 2951 (s), 2853 (s), 1742 (m), 1678 (m), 1608 (m), 1462 (m), 1456 (m), 1226 (m), 1162 (s), 837 (m), 739 (m), 556 (w). Anal. Calcld. for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; N, 8.59. Found: C, 39.54; H, 6.03; N, 8.77. MS (EI, cation) *m/z* 181.2 amu (M^+), (Calcd. 181.2).

2.6.9 Reaction of NHC 1 with $[Cp_2Fe]^+[BF_4]^-$

To a solution of [**1-H**][**Cl**] (0.50 g, 1.47 mmol) dissolved in THF (20 mL), a solution of ferrocenium tetrafluoroborate (0.40 g, 1.47 mmol, partially soluble in THF) was added slowly. A reddish brown solution was obtained, which was stirred for 24 hours and then the solvent was removed under vacuum to give a reddish brown powder. The powder was washed thorougly with hexanes to give a paler powder which was characterised as [**1-H**][**BF_4**]. Isolated yield: (0.49 g, 85%). M.p. (under nitrogen atmosphere) 180-182 °C. ^1H NMR (400 MHz, THF-d_8) δ (ppm) 9.04 (s, 1 H, C_2-*H*), 7.24 (s, 2 H, C=C*H*), 7.12 (s, 4 H, Ar-*H*), 2.29 (s, 6 H, *p*-CH_3), 2.07 (s, 12 H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, THF-d_8) δ (ppm) 142.0 (N*C*N), 139.1 (s, *C*-1), 135.2 (s, *C*-4), 132.0 (s, Ar-*C*-2,6), 130.3 (s, Ar-*C*-3,5), 126.2 (s, N*CC*), 21.0 (s, 4-CH_3), 17.5 (s, 2,6-*C*H_3). Anal. Calcld. for $C_{21}H_{25}BF_4N_2$: C, 64.30; H, 6.42; N, 7.14. Found: C, 63.50; H, 6.08; N, 7.52. MS (EI, cation) *m/z* 305.2 amu (M^+), (Calcd. 305.2).

2.6.10 Reaction of NHC 3 with $[Cp_2Fe]^+[BF_4]^-$

Excess ferrocenium tetrafluoroborate (0.50 g, 1.85 mmol) was added slowly to a solution of **NHC 3** (0.30 g, 1.66 mmol) in THF (10 mL). The solution was stirred for 24 hours and then filtered. A reddish green powder was obtained after removing the solvent under vacuum, which was then washed with hexanes to remove any ferrocene leaving a green powder whose principle component was characterised as the imidazolium tetrafluoroborate, **[3-H][BF$_4$]**. Isolated yield: (0.35 g, 71%). M.p. (under nitrogen atmosphere) 115-117 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 9.02 (s, 1 H, C$_2$-*H*), 4.62 (sept, 2 H, C*H*Me$_2$), 2.34 (s, 6 H, 4,5-C*H*$_3$), 1.62 (d, 12 H, CH(C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 130.3 (N*C*N), 127.2 (C-4,5), 51.0 (*C*HMe$_2$), 21.9 (CH(*C*H$_3$)$_2$), 7.8 (4,5-*C*H$_3$). IR (nujol, cm^{-1}) 3150 (s), 2952 (s), 2853 (m), 1676 (m), 1655 (m), 1460 (m), 1377 (w), 1189 (m), 1057 (m), 800 (s). Anal. Calcld. for $C_{11}H_{21}BF_4N_2$: C, 49.28; H, 7.90; N, 10.45. Found: C, 48.53; H, 7.58; N, 9.89. MS (EI, cation) *m/z* 181.2 amu (M$^+$), (Calcd. 181.2).

2.6.11 Synthesis of [1-H][PF$_6$]

[1-H][Cl] (0.30 g, 0.88 mmol) was dissolved in dichloromethane (20 mL) and to this solution silver hexafluorophosphate (0.22 g, 0.87 mmol) was added. A white precipitate was subsequently obtained and the reaction mixture was stirred for 4 hours, then filtered through Celite. The clear filtrate was dried under vacuum and the resulting white powder was characterised as **[1-H][PF$_6$]**. Isolated yield: (0.20 g, 51%). M.p. (under nitrogen atmosphere) 174-175 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 9.18 (s, 1 H, C$_2$-*H*), 7.32 (s, 2 H, C=C*H*), 7.14 (s, 4 H, Ar-*H*), 2.35 (s, 6 H, *p*-C*H*$_3$), 2.16 (s, 12 H, *o*-C*H*$_3$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 141.7 (N*C*N), 139.6 (s, *C*-1), 135.3 (s, *C*-4), 132.3 (s, Ar-*C*-2,6), 130.4 (s, Ar-*C*-3,5), 126.2 (s, N*CC*), 21.1 (s, 4-*C*H$_3$), 17.8 (s, 2,6-*C*H$_3$). IR (nujol, cm^{-1}) 2951 (s), 1638 (m), 1462 (m), 1377 (m), 1226 (s), 837 (s), 739 (m). Anal. Calcld. for $C_{21}H_{25}F_6N_2P$: C, 56.00; H, 5.59; N, 6.22. Found: C, 55.92; H, 5.49; N, 6.31. MS (EI, cation) *m/z* 305.2 amu (M$^+$), (Calcd. 305.2).

2.6.12 Synthesis of [3-H][PF$_6$]

[3-H][Cl] (0.30 g, 1.39 mmol) was dissolved in dichloromethane (20 mL) and to this solution silver hexafluorophosphate (0.35 g, 1.39 mmol) was added. A white precipitate was subsequently obtained and the reaction mixture was stirred for 24 hours, then filtered through Celite. The clear filtrate was dried under vacuum and was characterised as **[3-H][PF$_6$]**. Isolated yield: (0.32 g, 71%). M.p. (under nitrogen atmosphere) 150-154 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 8.49 (s, 1 H, C$_2$-*H*), 4.44 (sept, 2 H, C*H*Me$_2$), 2.25 (s, 6 H, 4,5-C*H*$_3$), 1.44 (d, 12 H, CH(C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 129.3 (N*C*N), 127.0 (*C*-4,5), 50.8 (*C*HMe$_2$), 22.2 (CH(*C*H$_3$)$_2$), 8.2 (4,5- *C*H$_3$). IR (nujol, cm^{-1}) 3141 (s), 2951 (s), 2853 (s), 1742 (m), 1678 (m), 1608 (m), 1462 (m), 1456 (m) 1226 (m), 1162 (s), 837 (m), 739 (m), 556 (w). Anal. Calcld. for $C_{11}H_{21}F_6N_2P$: C, 40.49; H, 6.49; N, 8.59. Found: C, 40.32; H, 6.48; N, 8.63.. MS (EI, cation) *m/z* 181.2 amu (M$^+$), (Calcd. 181.2).

2.6.13 Synthesis of [1-H][BF$_4$]

[1-H][Cl] (0.30 g, 0.88 mmol) was dissolved in dichloromethane (20 mL) and to this solution silver tetrafluoroborate (0.17 g, 0.88 mmol) was added. A dark precipitate was subsequently obtained and the reaction mixture was stirred for 4 hours, and then filtered through Celite. The clear filtrate was dried under vacuum and was characterised as **[1-H][BF$_4$]**. Isolated yield: (0.23 g, 67%). M.p. (under nitrogen atmosphere) 181-182 °C. ^{1}H NMR (400 MHz, THF-d$_8$) δ (ppm) 9.11 (s, 1H, C$_2$-*H*), 7.26 (s, 2 H, C=C*H*), 7.13 (s, 4 H, Ar-*H*), 2.30 (s, 6 H, *p*-C*H*$_3$), 2.04 (s, 12 H, *o*-C*H*$_3$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d$_8$) δ (ppm) 142.4 (N*C*N), 139.2 (s, *C*-1), 135.6 (s, *C*-4), 132.0 (s, Ar-*C*-2,6), 130.3 (s, Ar-*C*-3,5), 126.3 (s, N*C*C), 21.2 (s, 4-*C*H$_3$), 17.7 (s, 2,6-*C*H$_3$). Anal. Calcld. for

$C_{21}H_{25}BF_4N_2$: C, 64.30; H, 6.42; N, 7.14. Found: C, 64.23; H, 6.35; N, 7.09. MS (EI, cation) *m/z* 305.2 amu (M^+), (Calcd. 305.2).

2.6.14 Synthesis of [3-H][BF$_4$]

[3-H][Cl] (0.30 g, 1.39 mmol) was dissolved in dichloromethane (20 mL) and to this solution silver tetrafluoroborate (0.27 g, 1.39 mmol) was added. A dark precipitate was subsequently obtained and the reaction mixture was stirred for 24 hours and then filtered through Celite. The clear filtrate obtained was dried under vacuum and was characterised as **[3-H][BF$_4$]**. Isolated yield: (0.22 g, 59%). M.p. 114-116 °C. ^{1}H NMR (400 MHz, THF-d_8) δ (ppm) 9.04 (s, 1 H, C_2-*H*), 4.65 (sept, 2 H, C*H*Me_2), 2.32 (s, 6 H, 4,5-CH_3),1.64 (d, 12 H, CH(CH_3)$_2$). ^{13}C {^{1}H} NMR (100.61 MHz, THF-d_8) δ (ppm) 130.5 (N*C*N), 127.4 (C-4,5), 51.2 (*C*HMe_2), 21.8 (CH(*C*H_3)$_2$), 7.9 (4,5- (*C*H_3)). IR (nujol, cm^{-1}) 3150 (s), 2952 (s), 2853 (m), 1676 (m), 1655 (m), 1460 (m), 1377 (w), 1189 (m), 1057 (m), 800 (s). Anal. Calcld. for $C_{11}H_{21}BF_4N_2$: C, 49.28; H, 7.90; N, 10.45. Found: C, 49.23; H, 7.78; N, 10.36. MS (EI, cation) *m/z* 181.2 amu (M^+), (Calcd. 181.2).

CHAPTER 3 : PREPARATION OF GROUP 11 AND 13 COMPLEXES OF NHCs FROM IMIDAZOLIUM IONS

Parts of this chapter were reproduced from the following journal articles:

1. Canal, J. P.; Ramnial, T.; Dickie, D. A.; Clyburne, J. A. C. "From the Reactivity of *N*-Heterocyclic Carbenes to New Chemistry of Ionic Liquids." *Chem. Commun.*, **2006**, 1809. (Reproduced by the permission of The Royal Society of Chemistry)

2. de Fremont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; MacDonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. "Synthesis of Well-defined *N*-Heterocyclic Carbene Silver(I) Complexes." *Organometallics*, **2005**, *24*, 6301. (Reproduced with the permission from the American Chemical Society. Copyright [2005])

3. Hollmann, D.; Kennedy, A. R.; Spicer, M. D.; Ramnial, T.; Clyburne, J. A. C.; Abernethy, C. D. "Reactions of Imidazol-2-ylidene Silver (I) Chlorides with Group 4 Metal Containing Lewis Acids." *J. Organomet. Chem.*, **2005**, *690*, 5346.

4. Ramnial, T.; Clyburne, J. A. C. "Imidazol-2-ylidenes and their Reactions with Simple Reagents." ACS Symposium Series no. 917 Modern Aspects of Main Group Chemistry, Chapter 19. (Reproduced with the permission from the American Chemical Society. Copyright [2005])

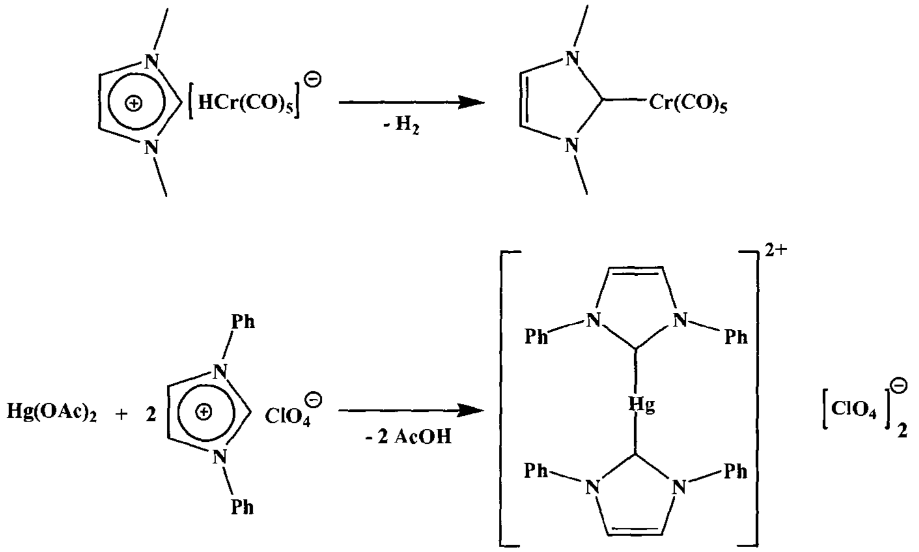
5. Chui, J. K. W.; Ramnial, T.; Clyburne, J. A. C. "*N*-Heterocyclic Carbenes: Exotic Molecules Precursors to Unusual Hydrogen Bonds." *Comments Inorg. Chem.*, **2003**, *24*, 165. (Reproduced by permission of Taylor & Francis Group.)

6. Ramnial, T.; Jong, H.; McKenzie, I. D.; Jennings, M.; Clyburne, J. A. C. "An Imidazol-2-ylidene Borane Complex Exhibiting Inter-molecular [C-$H^{\delta+}\cdots H^{\delta-}$-B] Dihydrogen Bonds." *Chem. Commun.* **2003**, 1722. (Reproduced by the permission of The Royal Society of Chemistry)

7. Ramnial, T.; Abernethy, C. D.; Spicer, M. D.; McKenzie, I. D.; Gay, I. D.; Clyburne, J. A. C. "A Monomeric Imidazol-2-ylidene-Silver (I) Chloride Complex: Synthesis, Structure and Solid State ^{109}Ag and ^{13}C CP/MAS NMR Characterisation." *Inorg. Chem.* **2003**, *42*, 1391. (Reproduced with the permission from the American Chemical Society. Copyright [2003])

3.1 Introduction: Metal Carbene Complexes

It is now more than thirty years since Öfele and Wanzlick independently published the preparation and structures of the first metal complexes containing *N*-heterocyclic carbenes (**NHCs**).[95, 96] In both reports, deprotonation of the imidazolium salts were performed with metal precursors to form the imidazol-2-ylidene complexes, as shown in Scheme 3-1. Lappert extended the methodology to complexes containing other imidazol-2-ylidene ligands.[97]



Scheme 3-1: Synthesis of first transition metal complexes of NHCs.

In 1991, Arduengo *et al.* synthesised and crystallised the first *uncomplexed N*-heterocyclic carbenes (**NHCs**) by deprotonation of 1,3-*bis*(adamantyl)imidazolium chloride.[49] The isolation of free **NHCs** provided a convenient route to metal carbene complexes.[98, 99, 100, 101, 102] Due to the presence of the two π-donor substituents at the carbeneic centre, **NHC** complexes may be classified as Fischer-type compounds. However, in contrast to the usual Fischer-type carbene complexes, **NHCs** bind to transition metals primarily through σ donation and this was believed to be the sole coordination mode until recent evidence has suggested the inclusion of some π-back-bonding.[103, 104, 105] However, the binding of **NHCs** to a metal is more complicated than anticipated and in some cases they form abnormal carbene complexes by coordinating through the $C_{4,5}$ carbon.[106] Nevertheless, *N*-heterocyclic carbenes possess some advantages over their direct analogue, the phosphine ligand, namely (1) they are stronger σ-donors, hence have a stronger interaction with the metal centres, thereby minimising ligand dissociation and enabling favourable rates for catalysis, (2) the presence of sterically encumbering groups bound to the N-atoms generate unique catalytic behaviour.[107] Hence, in contrast to "conventional" carbene ligands, the metal-carbene bond formed is somewhat longer but chemically and thermally more inert. These metal complexes have found application as catalysts for carbon-carbon bond formation reactions.[108]

Being air and moisture sensitive molecules, **NHCs** are often coordinated to metals to form air and moisture stable complexes, which can be used as carbene transfer agents. The coordination complexes of **NHCs** with late transition metals, typically those in low oxidation states, have been extensively studied; however recently there has also been an increasing interest in **NHC** complexes of early transition metal complexes in high oxidation states.[51] **NHC** complexes of late transition metals, specifically groups 8, 9 and 10, have been employed to catalyse cross-coupling reactions[109] such as Suzuki-Miyaura reactions, Heck reactions,[110] olefin metathesis[111] and hydrogenation reactions.[112] The early approach to synthesise **NHC**-metal complexes was by direct combination of a metal with the **NHC**. However, this route makes use of the highly air and moisture sensitive **NHCs**, which requires anaerobic conditions and special care in handling. This requirement led to a quest in the development of an alternative preparative method that employs air and moisture stable reagents.[106, 113]

The next section focuses on the synthesis and full characterisation of a monomeric imidazol-2-ylidene silver(I) chloride complex, which is now used as a carbene transfer agent.[114, 115] The synthesis of ionic homoleptic silver complexes is also discussed in section 3.3. Hydrogen bonding in imidazolium salts and complexes is discussed in section 3.4. The synthesis and full characterisation of an **NHC** borane complex is also described along with the analysis of the unusual dihydrogen bonding observed in the molecular structure.

3.2 NHC Silver Complexes

N-Heterocyclic metal complexes, especially those containing copper[116] and gold,[117] are known to be effective catalysts for a number of organic transformations. **NHC**-silver complexes, on the other hand are found to act as efficient catalysts for transesterification reactions, but as will be shown, the true identity of the catalytic species is uncertain.[118] Silver-**NHC** complexes are the most popular complexes used as carbene transfer agents since they can be easily prepared, usually circumventing the need to isolate free **NHC**s. Furthermore, they are quite inert towards air relative to **NHC**s.

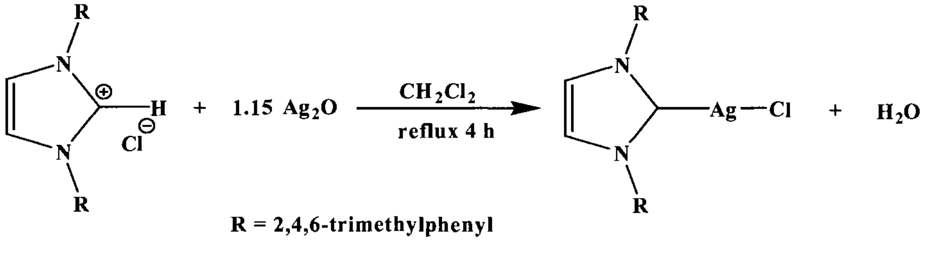
Arduengo *et. al.* were the first to structurally characterise an homoleptic, ionic **NHC**-silver complex, which was produced by the addition of a free carbene to a silver triflate salt.[119] One of the problems with this synthesis is the generation of **NHC**s, which is often difficult. This problem led to the discovery of **NHC**-silver complexes, which could be synthesised *in-situ* from imidazolium salts. Examples being the reaction of imidazolium salts with silver acetate,[120] silver oxide[106] or silver carbonate.[121]

Transmetallation reactions using **NHC**-silver complexes have also been reported for a variety of transition metals and these have been well documented in recent reviews by Arnold[114] and Lin and Vassam.[115, 122]

3.2.1 Synthesis of a Monomeric NHC Silver Chloride Complex

NHC-silver complexes are known to adopt different architectures depending on the reaction conditions employed. Most of the reported complexes are ionic homoleptic molecules with two **NHC** units bound to the silver atom in a linear fashion. [115, 118, 119, 121, 122, 123] Some polymeric and bridged structures are also known especially in the case of the presence of argentophilic interactions.[124, 125] However, monomeric **NHC**-silver halide complexes are quite rare.[122, 126, 127]

The synthesis of **NHC 1**-silver complex was achieved by reacting **[1-H][Cl]** in dichloromethane with a slight excess of Ag_2O as shown in Scheme 3-2. The mixture was heated to reflux for 4 hours[71] and was then filtered. The filtrate was concentrated on a rotary evaporator, which upon standing gave clear colourless crystals. It is interesting to note that contrary to the method described by Wang and Lin,[106] the synthesis can proceed without the exclusion of light with no deleterious effect on the yield.



Scheme 3-2: Reaction of [1-H][Cl] with Ag_2O.

3.2.2 Characterisation of a Monomeric NHC-Silver Chloride Complex

As explained above, **[1-H][Cl]** reacted with Ag_2O to give colourless crystals, which were characterised by X-ray crystallography, ^{1}H, ^{13}C, ^{109}Ag solution NMR and elemental analysis. ^{13}C and ^{109}Ag solid-state NMR spectroscopy was carried out on this compound so as to add more understanding to its structure. The coupling constants obtained from solid-state NMR are indicative of the strength of the C-N bond in case that the crystal structure is not obtained.

X-ray crystallographic studies illustrated that the clear crystals obtained were the monomeric compound, **[1-AgCl]** with a C_2 symmetry as shown in Figure 3-1. The molecular structure revealed a head to tail alignment of the complex with weak hydrogen bonding between H(1), from the back of the imidazole ring, and Cl (1). Selected bond lengths and angles are shown in Table 3-1.

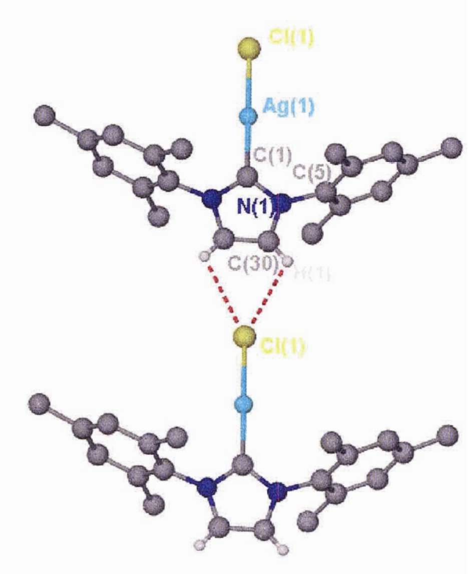
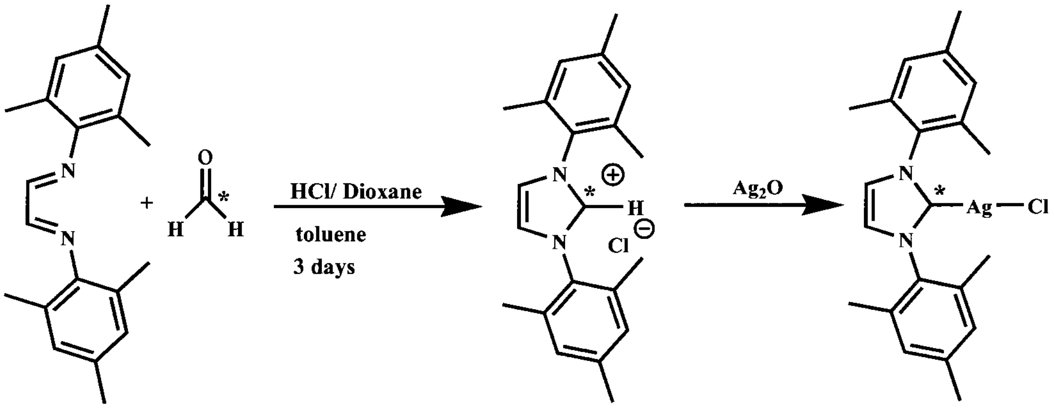


Figure 3-1: Molecular structure of [1-AgCl].

Bond Lengths (Å)			
Cl(1)-Ag(1)	2.314 (2)	N(1)-C(30)	1.386 (4)
Ag(1)-C(1)	2.056 (7)	H(1)•••Cl	2.954
C(1)-N(1)	1.357 (5)	C(1)•••Cl	3.378
N(1)-C(5)	1.438 (4)		
Bond Angles (°)			
Ag(1)-C(1)-N(5)	127.8 (2)	C(1)-N(1)-C(30)	111.5(3)
C(1)-N(1)-C(5)	121.8 (3)		

Table 3-1: Selected bond lengths (Å) and angles (°) for [1-AgCl].

The ^{1}H and ^{13}C solution NMR data were informative. **[1-H][Cl]** has a distinctive ^{1}H resonance peak at 9.7 ppm corresponding to the C_2-H, which was not observed in the ^{1}H NMR spectrum of **[1-AgCl]**. The spectrum of **[1-AgCl]** exhibited resonance peaks at 2.06 ppm and 2.34 ppm respectively for the *o*-methyl and *p*-methyl on the phenyl groups attached to the nitrogen of the imidazole ring and a singlet at 7.14 ppm corresponding to $C_{4,5}$-H resonances. These resonances also appeared in the ^{1}H NMR spectra of **[1-H][Cl]** with a slight shift in the resonance values. In the ^{13}C solution NMR spectrum, the resonance for the carbeneic carbon was not observed at natural abundance; hence ^{13}C labelled imidazolium chloride, synthesised as explained in section 2.6.3 was used. The ^{13}C labelled **[1-H][Cl]** was treated with silver oxide to synthesise ^{13}C labelled **[1-AgCl]** as shown in Scheme 3-3.



Scheme 3-3: Synthesis of ^{13}C labelled (*) [1-AgCl].

Silver has two naturally occurring isotopes, ^{107}Ag and ^{109}Ag with a natural abundance of 52% and 48%, respectively. Both isotopes are NMR active and each has a nuclear spin of ½. Given this information one would expect two doublets for the ^{13}C NMR for carbeneic carbon based on the coupling constants of each silver isotope. The ^{13}C solution NMR spectra of the ^{13}C labelled **[1-AgCl]** showed two doublets in $CDCl_3$, which were consistent with the splitting by the two, spin ½ nuclei, ^{107}Ag and ^{109}Ag as shown in Figure 3-2. The ^{13}C resonance is centred at 185 ppm, which is in the range for metal coordinated **NHCs** (170-190 pm).[119] The ^{13}C-^{107,109}Ag coupling constants were found to be large (270 Hz for ^{109}Ag-^{13}C and 234 Hz for ^{107}Ag-^{13}C) as shown in Table 3-2, some 60 Hz greater than those observed for **[1-Ag-1][CF_3SO_2]**.[119] The Ag-C bond was found to be labile, which makes this compound a good carbene transfer agent to a range of late transition metal complexes. The driving force for this reaction is the high lattice energy for the formation of silver chloride as shown in Scheme 3-4.

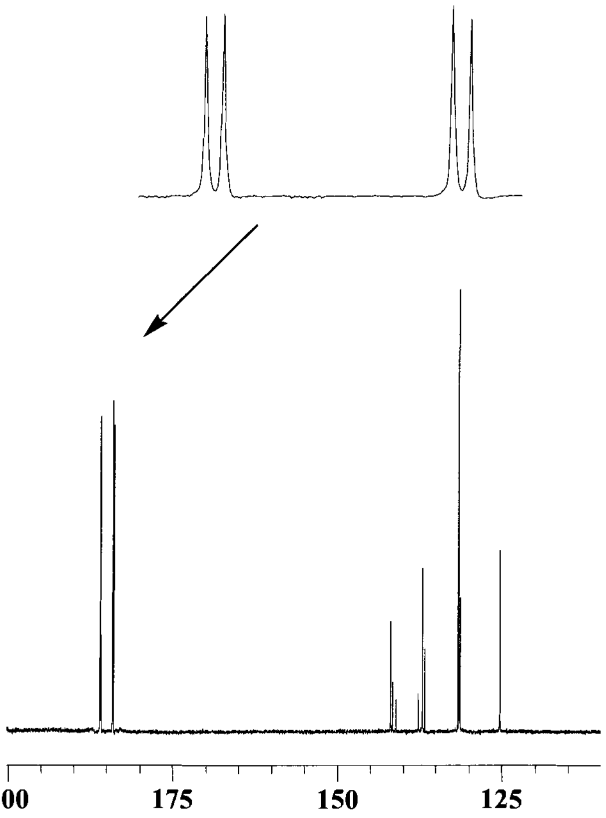
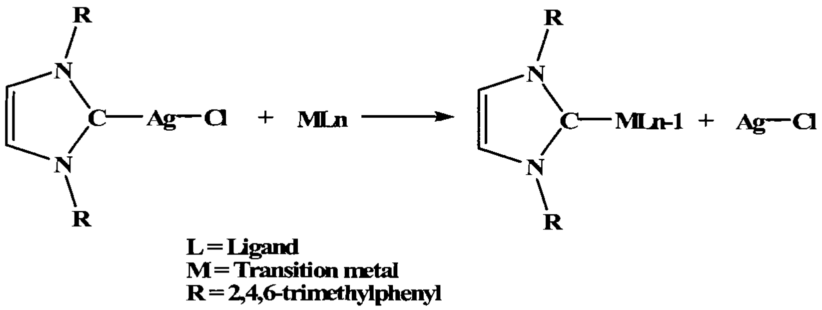


Figure 3-2: ^{13}C **solution NMR spectrum of the aromatic region of** ^{13}C **labelled [1-AgCl].**

Parameters	^{13}C resonance (ppm)	^{109}Ag resonance (ppm)	NHC 4	$[4\text{-}H]^+$
δ_{iso}	184.1(0.1)[a]	532.2(0.3)	209	136.6
δ_{11}	299(4), 295(3)[b]	1228(9)	310±20	179
δ_{22}	163(4), 163(3)	1036(58)	177±18	141
δ_{33}	88(3), 85(5)	-667(49)	82±15	92
Ω (span)	211(3), 210(3)	1895(40)		
Κ (skew)	-0.28(0.05), -0.22(0.04)	0.08(0.07)		
$\delta_{solution}$[c]	185[d]	597		

[a] $^1J_{C\text{-}Ag}$ = 250(1) Hz, (^{109}Ag-^{107}Ag); ^{13}C splitting not resolved. [b] The two components of J-split doublet.
[c] CD_2Cl_2 solution. [d] $^1J_{^{13}C\text{-}^{109}Ag}$ = 270 Hz, $^1J_{^{13}C\text{-}^{107}Ag}$ = 234 Hz.

Table 3-2: Summary of solution and solid state NMR data for labelled [1-AgCl] (^{13}C and ^{109}Ag) and NHC 4.[128]



Scheme 3-4: [1-AgCl] as a carbene transfer agent to transition metals.

As reported in a recent review,[122] the ^{109}Ag solution NMR resonances of silver **NHC** complexes have a range of δ 597 to 727 ppm.[122, 128, 129] The ^{109}Ag resonance obtained for the ^{13}C labelled **[1-AgCl]** was found to be at 597 ppm.[65] It is interesting to note that **[1-AgCl]** was found to have the lowest ^{109}Ag resonance among all silver **NHC** complexes and it set the lowest bar for the silver-**NHC** complexes. It was less downfield than expected because the molecule is somewhat symmetric. A line broadening of the ^{109}Ag resoance was observed, which was likely caused by an adjacent quadrupolar chloride nucleus.

[1-AgCl] was found to be monomeric from X-ray crystallography studies and to have a high molecular symmetry, making it ideal for solid-state CP/MAS NMR spectroscopy, which was recorded on a home-built instrument operating at 3.5 T at Simon Fraser University.[g] This instrument produces a resonance frequency of 37.55 MHz for ^{13}C nucleus and 6.95 MHz for ^{109}Ag nucleus. The ^{13}C labelled **[1-AgCl]** compound was used in order to obtain the ^{13}C solid-state NMR, which was recorded at magic angle spinning 2600 Hz, contact time of 2 ms, relaxation delay of 3s and 11146 scans. The isotropic peaks were found to be a doublet centred at 184 ppm as shown in

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[g] Dr I. Gay performed the ^{109}Ag solid-state CP/MAS NMR spectroscopy.

Figure 3-3. The peaks were broad and asymmetric due to the interaction with neighbouring ^{14}N. Further splitting was also observed due to coupling with the $^{107,109}Ag$ nuclei. The lines were, however, too broad to resolve the two isotropic splittings.

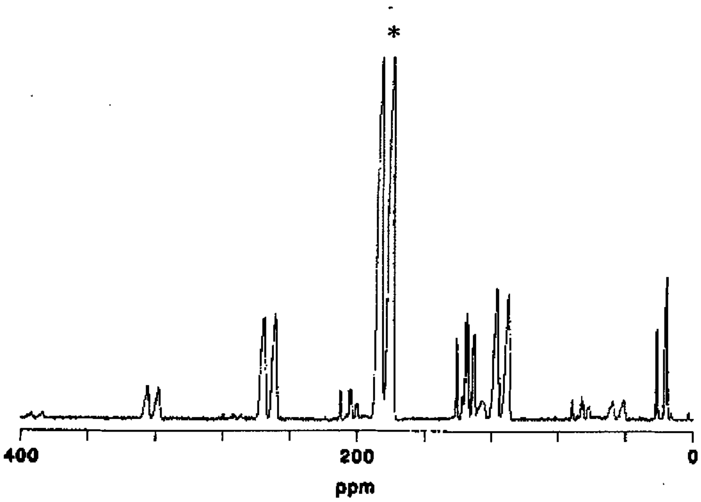

Figure 3-3: ^{13}C solid-state CP/MAS NMR spectrum of ^{13}C labelled [1-AgCl], (* ^{13}C resonance peak).

The principal values of the components of the chemical shielding tensors for the ^{13}C resonance were determined using the method where the sideband intensities for the spectra were fitted at 1400, 1700 and 2000 Hz spinning speeds, as shown above in Table 3-2.[130] Two out of three components of **[1-AgCl]** were similar to the chemical shift tensors of the free **NHC 4**, (1,3,4,5-tetramethyl-imidazol-2-ylidene) and its salt **[4-H]**$^+$ (Table 3-2). No orientation of the chemical shield tensors has been previously reported.

Silver isotopes have a low gyromagnetic ratio thus making the acquisition of ^{109}Ag CP/MAS solid-state NMR spectra difficult. However, it was possible to obtain the ^{109}Ag spectral data for **[1-AgCl]** complex in both solution and solid phases. A ^{109}Ag solid-state NMR spectrum was also recorded at a spinning speed of 2400 Hz with natural abundance of carbon. A range of spectra were run at different spinning speeds, contact time of 50 ms, a relaxation time of 5 s and 54134 scans. The resonance at 532 ppm was determined to be the centre band, as shown in Figure 3-4. A *ca.* 65 ppm difference between the isotropic chemical shift obtained in solution and solid-state NMR spectra was observed for [**1-AgCl**].

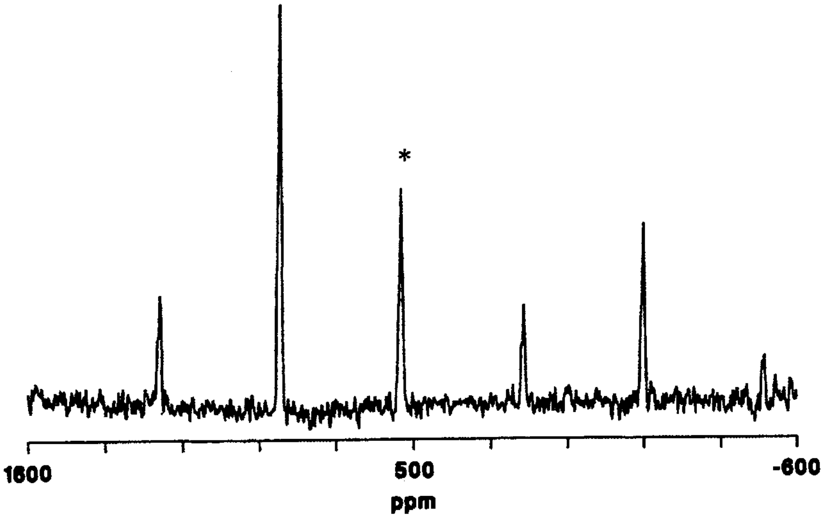

Figure 3-4: ^{109}Ag CP/MAS solid-state NMR spectrum of [1-AgCl] (* is the 532 ppm resonance peak for ^{109}Ag).

Interpretation of isotropic chemical shifts in solid-state NMR spectroscopy is one of the most successful techniques for providing structural and electronic information about a molecule. Characterisation of the anisotropy or the three-dimensional character of the chemical shielding provides a probe of the electronic environment around the nucleus of interest. Thus, the orientation of particular shielding or deshielding influences to be correlated with the molecular structure. Such an approach is especially informative when coupled with theoretical predictions of the chemical shield tensor. In order to characterise and understand the electronic nature of [**1-AgCl**], a theoretical study was performed on a simplified model, 1,3-dimethylimidazol-2-ylidene silver (I) chloride to assign the orientation of the chemical shield tensors.[h] The geometry of this molecule was optimised using the B3LYP functional[131] with the LanL2DZ basis set.[132] The calculated bond lengths for the molecule are shown in Figure 3-5 and are in good agreement with the experimental values for [**1-AgCl**] determined by X-ray crystallography (Figure 3-5). The chemical shield tensors were calculated at the same level of theory using the gauge-invariant atomic orbital (GIAO) method.[133] On the basis of these calculations, the principal directions of the chemical shield tensors for the C and Ag centres are shown in Figure 3-5. The orientation of the C chemical shield tensor is the same in [**1-AgCl**] and the free carbene, **NHC 1** with the only significant change occurring for the δ_{11} value as shown in Table 3-2.[128]

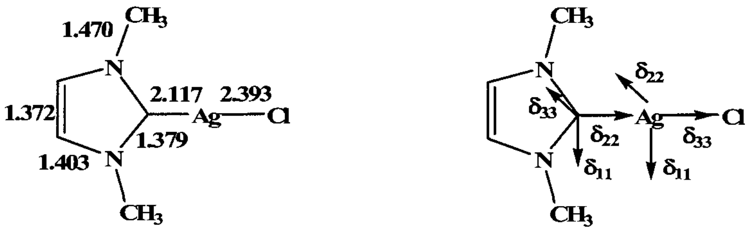

Figure 3-5: Calculated parameters (left) and structural orientation of chemical shift tensors (right) of 1,3-dimethylimidazol-2-ylidene silver (I) chloride.

3.3 Identification of Ionic Homoleptic Bis-NHC Silver Complexes

The synthesis of the monomeric [**1-AgCl**] complex was repeated in different solvents in order to improve the yield of the reaction. Three solvents, namely chloroform, acetonitrile and dimethyl sulfoxide, having different polarity, were used under similar conditions.

When the crude product of the reaction carried out in chloroform was analysed by ^{1}H NMR spectroscopy, a new set of resonances was observed. The ^{1}H NMR spectrum of

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[h] The computational calculations were performed by Dr. I. D. McKenzie at Simon Fraser University.

this product was similar to the NMR spectrum of the ionic homoleptic 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene silver (I) triflate complex, **[1-Ag-1][CF_3SO_2]**.[119] NMR spectroscopy (^1H NMR) showed two peaks at δ 1.71 and 2.42 ppm, which were assigned to the *o*-CH_3 and the *p*-CH_3 groups respectively. These values were quite different from ^1H NMR resonances in the neutral monomeric silver (I) carbene complex (δ 2.05 and 2.37 ppm, respectively). This difference is because the methyl groups on 2,4,6-trimethylphenyl group of the imidazole ring of **[1-Ag-1]**$^+$ are in the shielding cone of the other aryl group.

The monomeric **[1-AgCl]** crystals were clear wheareas the ionic **[1-Ag-1]**$^+$**[$AgCl_2$]**$^-$ were pale yellow. The **[1-Ag-1]**$^+$**[$AgCl_2$]**$^-$ crystals were picked out and x-ray crystallographic studies confirmed the side-product to be **[1-Ag-1]**$^+$**[$AgCl_2$]**$^-$.[129] The experimental data showed that the increasing polarity of the solvents led to an increase in the amount of the ionic homoleptic *bis*-**NHC**-Ag complex formed, as shown in Table 3-3. It is reasonable to suggest that polar solvents favour the formation of the ionic **[1-Ag-1]**$^+$ form better than non-polar solvents and might shift the equilibrium of {**[1-AgCl]**/**[1-Ag-1]**$^+$} towards the ionic *bis*-**NHC**-Ag complex. This observation suggests that there is a dynamic equilbrium in solution involving species such as **[1-AgCl]** and **[1-Ag-1]**$^+$ and potentially the free carbene (**NHC 1**) as shown in Scheme 3-5.

Solvent (dielectric constant)[134]	**[1-Ag-1]**$^+$**[$AgCl_2$]**$^-$	**[1-AgCl]**
Chloroform (4.2)	15%	85%
Acetonitrile (37.5)	25%	75%
Dimethyl sulphoxide (46.7)	34%	66%

Table 3-3: Product distribution of [1-Ag-1]$^+$[$AgCl_2$]$^-$ and [1-AgCl].

$$2[\mathbf{1\text{-}Ag\text{-}Cl}] \rightleftharpoons [\mathbf{1\text{-}Ag\text{-}1}]^{+}[\mathbf{AgCl_2}]^{-} \rightleftharpoons \mathbf{2\ NHC\ 1} + \mathbf{2\ AgCl}$$

Scheme 3-5: Equilbrium between neutral monomeric and homoleptic ionic silver complex.

The X-ray crystal structure of the cation (Figure 3-6) showed a two-coordinate silver (I) atom in a linear environment with a C-Ag-C angle of 180°. The Ag-C bond distances are 2.066(5) and 2.084(5) Å, while both Ag-Cl bond distances are 2.534 Å as shown in Table 3-4. All values are in good agreement with previously reported *bis*-carbene complexes.[48] There is one cation $[\mathbf{1\text{-}Ag\text{-}1}]^{+}$ and one anion $[\mathbf{AgCl_2}]^{-}$ present in the asymmetric unit. The complex is monomeric with no argentophilic interactions and no Ag-(μCl)$_2$-Ag bridging present as shown in Figure 3-6, with the minimal Ag(I)···Ag(I) distance being 6.397(4) Å and no interaction between the silver of the anion.

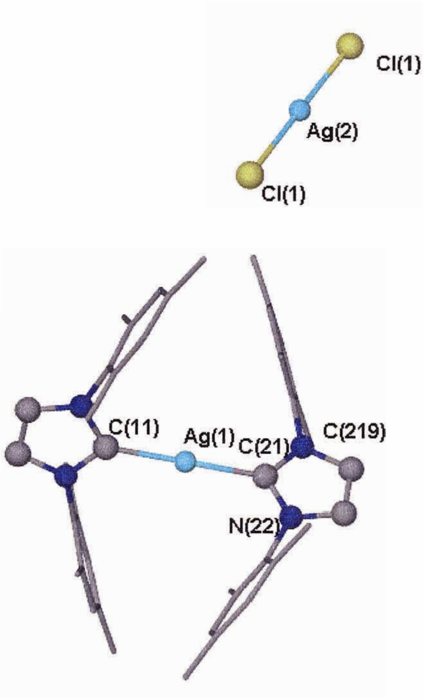


Figure 3-6: Molecular structure of $[\mathbf{1\text{-}Ag\text{-}1}]^{+}$ $[\mathbf{AgCl_2}]^{-}$. Hydrogen atoms have been omitted for clarity.

Complex	Ag-C (Å)	Ag-X (anion) (Å)	C-Ag-C (°)
[1-Ag-1]$^{+}$[AgCl$_{2}$]$^{-}$	2.066(5)	2.534(5)	180.0(1)
	2.084(5)		
[1-Ag-1]$_{2}^{+}$[Ag$_{4}$I$_{6}$]$^{2-}$	2.079(5)	2.7556(14)-2.7774(14)	172.5(2)
	2.082(5)	2.8121(14)-2.7212(12)	
		2.7468(12)-2.7751(13)	
		2.7157(13)-2.7627(14)	
		2.8507(14)-2.7025(14)	
		2.7175(14)-2.8397(14)	
		2.7052(14)-2.7627(14)	

Table 3-4: Selected bond lengths (Å) and angles (°) for [1-Ag-1]$^{+}$ complexes

The synthesis of monomeric **[1-Ag]**[**I**] was also attempted in acetonitrile in order to investigate the effect of halide and solvent polarity on the structure of the complex. The ^{1}H and ^{13}C NMR spectra of the product matched that observed for [**1-Ag-1**]$^{+}$ cation, leading to the conclusion that an ionic homoleptic *bis*-**NHC**-Ag complex was formed in acetonitrile. Zhang *et. al.* on the other hand, have reported the synthesis of a polymeric mono carbene silver (I) iodide complex, free of the *bis*-carbene, in a less polar solvent, dichloromethane. This supports that the polarity of the solvent must be the dominating factor in directing the structure adopted by an iodide silver complex to either the *mono*- or *bis*-carbene.

The X-ray structure as shown in Figure 3-7, confirmed that the silver (I) atom was surrounded by two carbon atoms in a near linear environment with a C-Ag-C bond angle of ≈180°. This observed molecule had anion disorder and the asymmetric unit had two [**1-Ag-1**]$^{+}$ cations and one **[Ag$_{4}$I$_{6}$]**$^{2-}$ anion leading to a **[1-Ag-1]**$_{2}^{+}$**[Ag$_{4}$I$_{6}$]**$^{2-}$ formulation. This complex had no argentophilic interactions and the most interesting feature of this molecule was the anion disorder with a massive octahedral anion **[Ag$_{4}$I$_{6}$]**$^{2-}$ cluster.

Interestingly, after our report of the neutral monomeric **[1-Ag][Cl]** complex, a paper by Sentman *et. al.*[118] reported the synthesis of the homoleptic ionic **$[1\text{-}Ag\text{-}1]^+[AgCl_2]^-$** complex, which was used as a carbene delivery for organometallic transformations. However, on careful analysis of their ^1H NMR data, we could clearly identify the formation of the neutral monomeric **[1-Ag][Cl]** complex instead of the what they claimed to be the ionic **$[1\text{-}Ag\text{-}1]^+[AgCl_2]^-$** complex.[71]

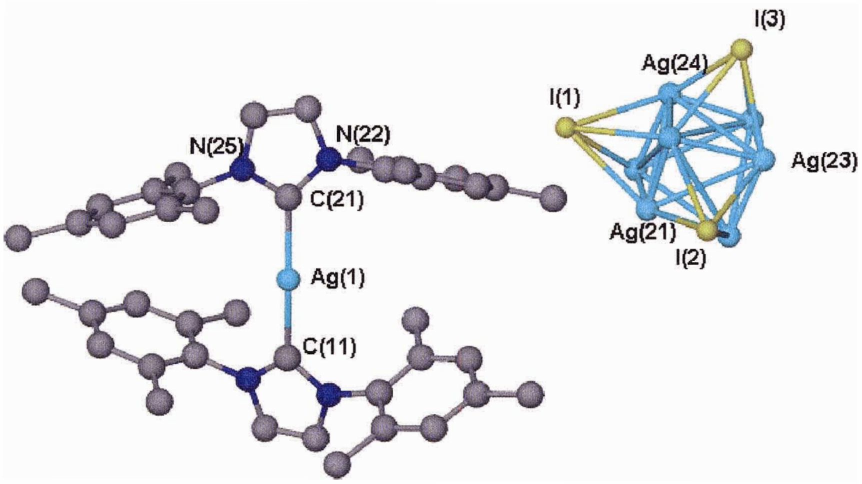


Figure 3-7: Molecular structure of $[1\text{-}Ag\text{-}1]_2\,[Ag_4I_6]$. Hydrogen atoms have been removed for clarity.

3.4 Formation of an NHC Borane Complex

3.4.1 Introduction

A hydrogen bond is a non-covalent, directional, *inter/intra*-molecular and 'weak' interaction between proton donors and acceptors. It is an ubiquitous phenomenon of significant importance across a wide spectrum of chemical systems, governing both the *structural* and the *functional* properties of inorganic, organic and biochemical systems alike. Bordering between dispersion and covalent interactions, its strength and directionality depend on the type of proton donor and acceptor pair.

By definition the term *hydrogen bond* describes a broad range of interactions where a local bond is constituted by an X-H group acting as a proton donor to A that acts as a proton acceptor group. This general description is often depicted as [X-H···A]. The dissociation energy of hydrogen bonds varies over a large range, from 0.2 to 40 kcal mol^{-1} and this broad range reflects the diverse components that contribute to the overall hydrogen bond.[135] Electrostatic attractions, covalent contributions, van der Waals interactions, charge assistance,[136] cation-π and charge transfer have all been shown to play a role in the hydrogen bond[137] and Steiner has most recently reviewed this area of chemistry.[135]

Classically, hydrogen bonds [X-H···A] are formed by strongly polar groups [X^{δ}-$H^{\delta+}$] on one side, and an acceptor, [$A^{\delta-}$] on the other. Typical hydrogen bond donors "X" include O, N, halogens or other strongly electronegative atoms. Typical acceptor groups "A" include O, N, S and halides. The association between donor and acceptor groups is often directional, with bond lengths significantly lower than the corresponding van der Waals radii of the atoms. These interactions account for a plethora of chemical behaviours, such as the higher boiling point of water over hydrogen sulphide (100.0 °C *vs* -60.7°C) and specific recognition/binding in biochemical systems.[138]

Despite its utility, the above classical description of the hydrogen bond is considered as a subset of what should be broadly be considered as hydrogen bonds; the proton donor group X-H needs to be *slightly* polar (e.g., C-H or P-H) and the counterpart acceptor A does not need to be a particularly electronegative atom or anion, but rather only has to supply an accessible concentration of negative charge or electron density.[135]

3.4.2 Hydrogen Bonding in Imidazolium Salts

It is generally believed that imidazolium ions usually bind through the C_2 position, however, unusual binding through $C_{4,5}$ (carbon at the back of the imidazole ring) has also been observed.[113] Thus, imidazolium salts have three potential acidic *C-H* sites available for hydrogen bonding. The shortest hydrogen bonds are typically observed at C_2 because of the higher positive charge on C_2-*H*.

The importance of hydrogen bonding to imidazolium ions has been recognised for many years and this is partly due to the importance of imidazolium-based salts as potential ionic liquids.[139, 140] In 1993, Seddon identified the importance of hydrogen bonding in ethylmethylimidazolium (EMIM) iodide, which is representative of the most extensively studied class of ionic liquid namely imidazolium-based ionic liquids.[140] In the crystalline state there is an unambiguous hydrogen bond between the hydrogen atom attached to the C_2 atom of the imidazolium ring and the iodide ion [2.93(3) Å in comparison to the van der Waals radii *ca.* 3.3 Å].[139] The ethylmethylimidazolium tetrachlorometalate complex, [EMIM][$CoCl_4$] also contains these types of interactions with the shortest hydrogen bond contact [H···Cl] at 2.261 (5) Å.[140]

Extensive hydrogen bonding is also evident in **[1-H][Cl]**. The hydrogen-bonding array was completed by a solvent molecule, methanol, that was incorporated into the crystal lattice as shown in Figure 3-8. Each hydroxyl hydrogen atom of the methanol engaged the anion chloride and the hydroxyl oxygen engaged the imidazolium ion through a [C-H···O] interaction with a bond length of 2.287 Å. [Cation···anion···cation] linear arrays are common in crystalline samples containing the imidazolium ion.[119]

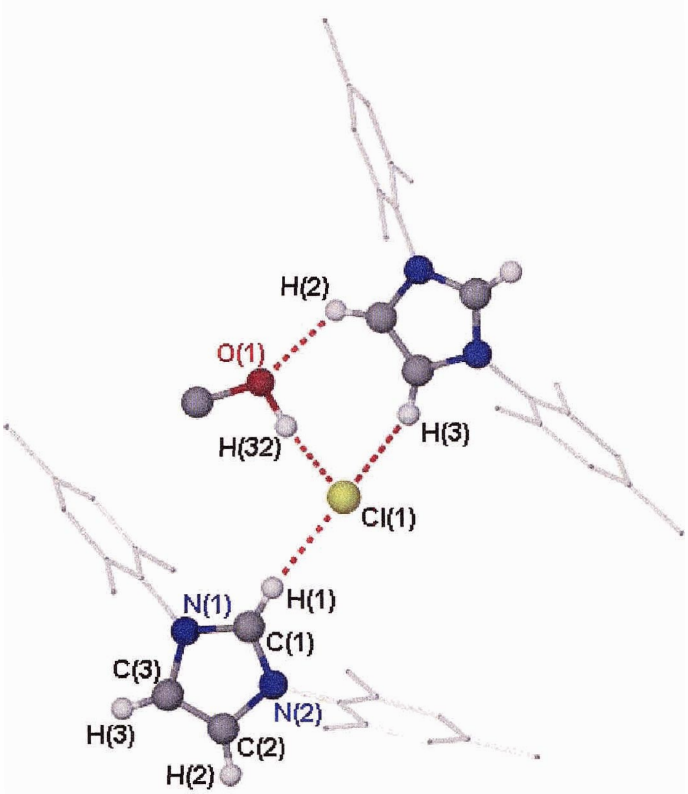
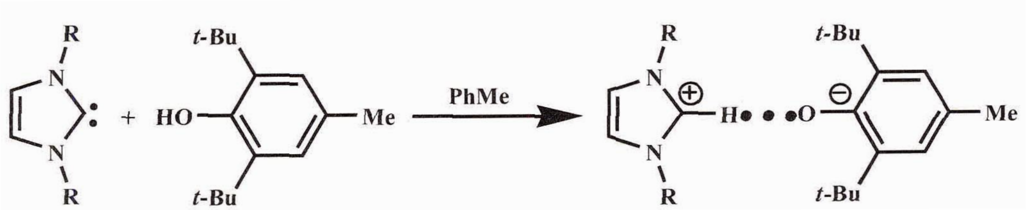


Figure 3-8: Hydrogen bonding in [1-H][Cl]·CH_3OH. Some hydrogen atoms are omitted for clarity.[119]

3.4.3 Imidazolium Ions as an Unusual Donor of Hydrogen Bonds

The [C-H···O] interaction has only recently been identified and reviewed as a significant hydrogen bonding interaction.[135] One recent example of such interactions is between a carbene and a bulky phenol (Scheme 3-6).



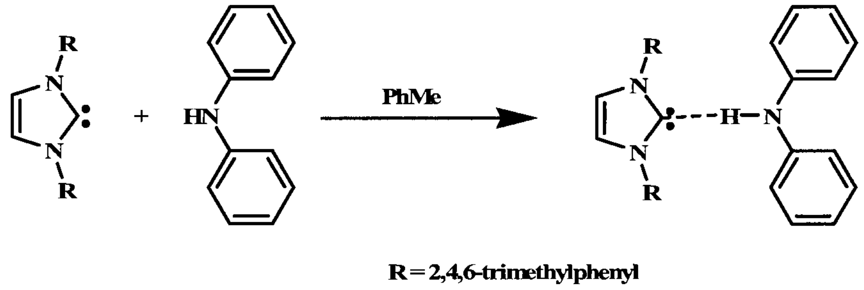
R= 2,4,6-trimethylphenyl

Scheme 3-6: Synthesis of an imidazolium phenolate salt.

The X-ray structure showed a close contact between the ion-ion pair with a [C-H···O] distance of 2.842 (4) Å, between C and O and a H···O distance of 1.759 (4) Å.

The H···O bond length was significantly shorter than any previously reported hydrogen bonds between C-H donors and oxygen acceptors, suggesting a stronger interaction.[141]

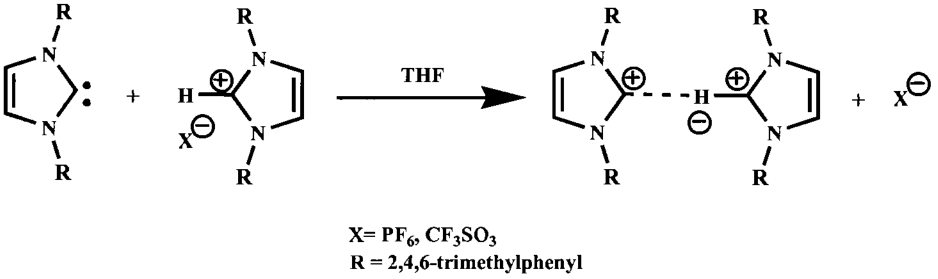
Another example of an unusual hydrogen bond is the product of the reaction between **NHC 1** and diphenylamine as shown in Scheme 3-7.[141] A neutral adduct with unprecedented [N-H···C] interaction was observed.



Scheme 3-7: Synthesis of a carbene-diphenylamine adduct.

3.4.4 Carbenes Accepting Acidic Hydrogen Sites [C-H···C]

As discussed before, carbenes are highly basic and can act as a proton acceptor. In 1993, Arduengo *et. al.* reported an unusual carbon-based donor and acceptor hydrogen bond pair, which was produced by the reaction of equimolar **NHC 1** and its protonated imidazolium trifluoromethanesulphonate salt in THF, as shown in Scheme 3-8.[119]



Scheme 3-8: Synthesis of an unsymmetrical NHC-imidazolium complex.

Distinct structural parameters were noted for the respective imidazolium rings, suggesting that one of the rings is predominantly carbene-like and the other imidazolium-like. The *bis*-carbene-proton complex as shown in Figure 3-9 also interacts with its counteranion to form an extended solid-state structure similar to that previously observed for *bis*-carbene silver (I) complexes in a [cation···anion···cation] alignment.[119]

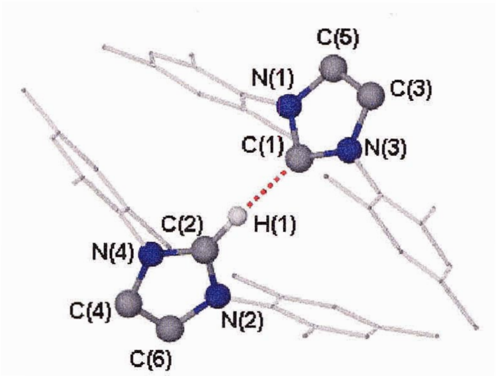
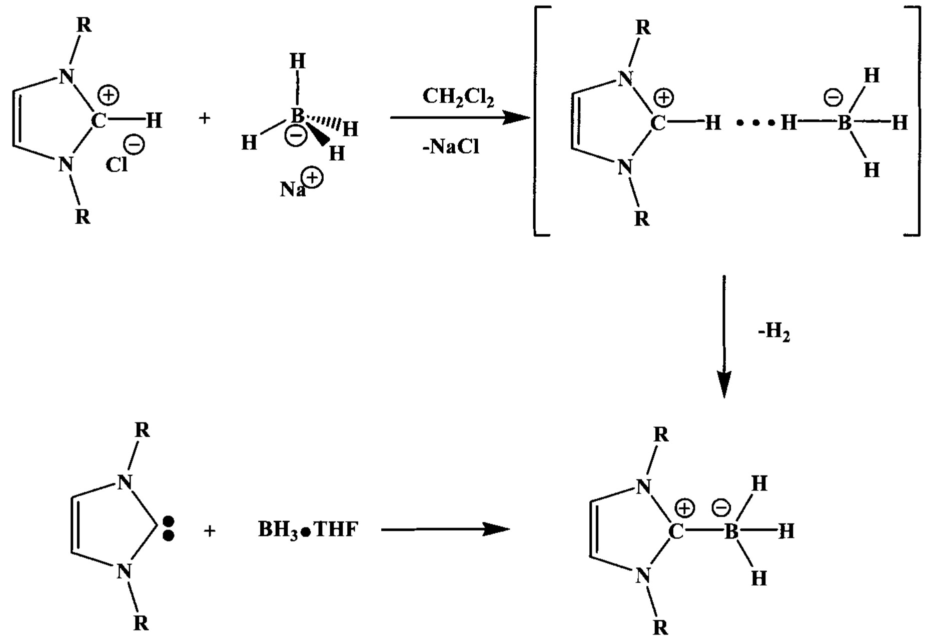


Figure 3-9: Molecular structure of an NHC-imidazolium complex. For clarity, lattice solvent molecules and hydrogen atoms, except those of the imidazolium cation are not shown.[119]

3.4.5 Attempts to Prepare Charge-Assisted [C-H···H-B] Hydrogen Bonds

Classical hydrogen bonding between proton donors and organic bases, which contain heteroatoms play a substantial role in chemical and biochemical processes. However, in recent years a new unusual type of hydrogen bond, known as dihydrogen bonding was determined. Dihydrogen bonding is an interaction analogous to hydrogen bonding between two oppositely charged hydrogen atoms and is generically represented as E-H(δ^-)···(δ^+)H-X, where E and X are atoms, which are more or less electronegative than hydrogen respectively. Dihydrogen bonding has also been shown to be an important structural element in the formation of solid-state borohydride materials and their subsequent reactivity[142] and in the formation of gallium nitride from gallazane precursors.[143]

Since **NHCs** and imidazolium salts show unusual hydrogen bonding, the synthesis of an **NHC**-based, charge assisted dihydrogen-bonded complex as shown in Scheme 3-9 was attempted. Two independent syntheses were performed and both gave the same product as shown in Scheme 3-9. The [H···H] bond in this system is thermodynamically unstable with respect to hydrogen gas evolution,[144] which resulted in the formal reductive coupling of the carbene with **BH_3**. The product was characterised by ^1H and ^{13}C NMR and IR spectroscopy, elemental analysis as well as X-ray crystallography studies. ^1H NMR spectroscopy showed a quartet at 0.4 ppm suggesting that BH_3 is present and B-H stretches were also observed in the IR spectrum.



R = 2,4,6-trimethylphenyl

Scheme 3-9: Preparation of an NHC-borane complex.

Curiously, the melting point of this crystalline material, **NHC 1·BH_3** was *ca.* 300 °C, significantly higher than that of **NHC 1** (150°C) or the related alane adduct, **NHC 1·AlH_3** complex (246-247°C),[145] suggesting strong intermolecular interactions for **NHC**

1·BH$_3$. In order to shed light on this, the structure of **NHC 1·BH$_3$** was determined by X-ray crystallography as shown in Figure 3-10.

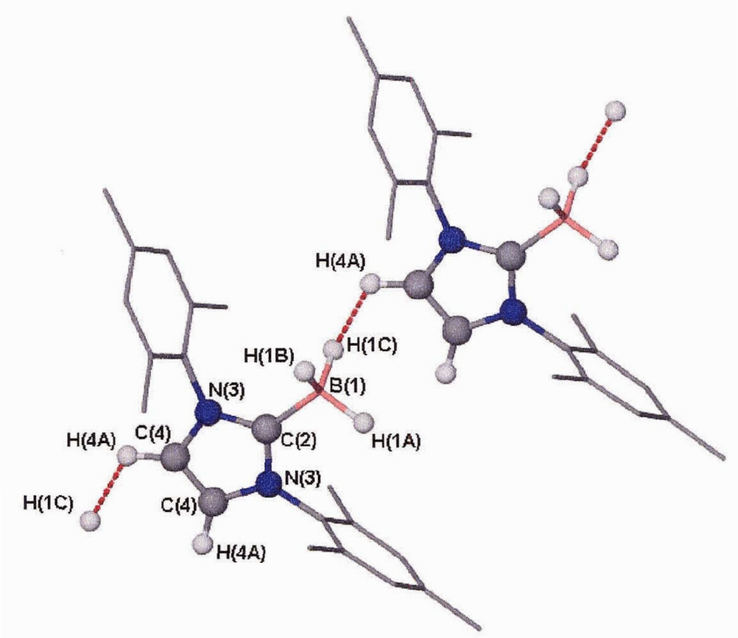


Figure 3-10: Molecular structure of the NHC 1·BH$_3$ adduct. For clarity, hydrogen atoms on the phenyl groups are not shown.

The structural parameters for **NHC 1·BH$_3$** obtained were consistent with previously reported carbene-trifluoroborane adducts such as **NHC 1·BF$_3$**.[146, 147] The closest intermolecular contact occurred through a novel [C-H···H-B] bond whose [H···H] distance (2.24 Å), as shown in Table 3-5, was well within the sum of van der Waals radii (2.65 Å). Further evidence that supported the formation of a dihydrogen bond was obtained by observing the strong similarities in the geometry and properties of the adduct with previously studied dihydrogen bonded systems.[148, 149, 150, 151] Borane-amine complexes are an important class of compounds that exhibit *inter*molecular dihydrogen bonding, which has a drastic effect on its physical properties. Due to its dihydrogen bonding, borane-amine has a much higher melting point (104°C) than its isostructural and isoelectronic molecule, ethane (-181°C).[152]

Bond Lengths (Å)			
B(1)-C(2)	1.596(4)	C(4)-C(4)	1.344(4)
C(2)-N(3)	1.354(2)	C(4)-H(4A)	1.05
N(3)-C(4)	1.385(2)	B(1)-H(1)	1.210
H(1A)···H(4)	2.238		
Bond Angles (°)			
N(3)-C(2)-N(3)	122.58(17)	C(4)-C(4)-N(3)	106.72(10)
N(3)-C(2)-B(1)	127.75(10)	B(1)-H(1A)-H(4A)	138.46
C(2)-N(3)-C(4)	111.03(16)		

Table 3-5: Important bond lengths (Å) and angles (°) for NHC·BH_3.

To support the observations of the presence of dihydrogen bonding in this molecule, calculations at the UB3LYP/6-311G level was carried out. This suggested a partial negative charge on the hydrogen atom attached at the boron, consistent with its hydridic nature, and a slight partial positive charge on H(4) as shown in Figure 3-11. While *individually* such interactions are weak and negligible, *collectively* they can significantly influence the macroscopic properties, as observed by the regular head-to-tail alignment of **NHC 1·BH_3** in the solid-state. Such dihydrogen interaction has also been noted in hydroboration reactions carried out in dichloromethane solvent where the partial charge on the hydrogen atoms in CH_2Cl_2 is +0.2. Hence it supports [C-H···H-B] interactions, which are likely formed in halocarbon solvents.[153]

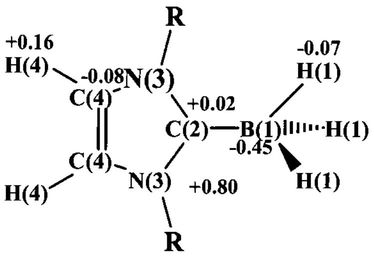


Figure 3-11: Estimated Mullikan partial charges on the NHC 1·BH_3 adduct calculated at UB3LYP/6-311G level.

One point to be noted is that there are similarities in structure between **NHC 1·BH_3** and the **NHC 1·BF_3** adducts previously reported, which exhibits a more conventional [F···H-C] hydrogen bond. Hence, this suggests that eventhough the [H···H] interaction is arguably weaker; they are important and comparably short as the so-called "normal" [C-H···X] interactions.

3.5 Conclusions

The reactivity of group 11 and 13 molecules with imidazolium salts were described. The synthesis and full characterisation of a monomeric imidazol-2-ylidene silver (I) complex was described and a dynamic equilibrium was identified between the **[1-AgCl]** and **[1-Ag-1][$AgCl_2$]** species in solution. The preparation of a **NHC 1·BH_3** complex, which exhibited unconventional intermolecular dihydrogen bonding interactions in the solid state, was also identified.

3.6 Experimental Section

3.6.1 General Procedure

[1-H][Cl] was prepared as previously described in the literature.[93] **[1-H][I]** was prepared by anion exchange with **[1-H][Cl]** using NaI as reported in literature.[93] All other chemicals were purchased from Aldrich and were used as received. Microanalysis was performed on an EA 1110 CHN, Carlo Erba Instrument by Mzi Keng Yang at Simon Fraser University. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Infra-red spectra were obtained using a Bomem MB spectrometer with the % transmittance values reported in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer in five-millimeter quartz tubes and are reported in parts per million (ppm) reference with residual solvent peak.

Dr. I. D. Gay recorded solid-state NMR spectra on a home-built instrument at Simon Fraser University operating at 3.5 T, which produces a resonance frequency of 37.55 MHz for ^{13}C and 6.95 MHz for ^{109}Ag. All spectra were obtained by cross-polarisation (CP), with a proton back flip. For ^{13}C, matched radio frequency fields of 55 kHz were used for cross-polarisation and the same field was used for proton decoupling; a contact time of 2 ms was used. For ^{109}Ag, cross-polarisation used matched fields of 25 kHz, with contact times of 30-50 ms and a decoupling field of 45 kHz was used during data acquisition. Spinning speeds of 2-3 kHz were used, electronically controlled to ± 1 Hz. ^{13}C spectra were referenced to tetramethylsilane (TMS), taking the high frequency peak of adamantane to be at 38.56 ppm. ^{109}Ag spectra were referenced to dilute aqueous Ag^{+} via the proton resonance of tetramethylsilane (TMS).[133]

3.6.2 Synthesis of [1-AgCl]

Excess Ag_2O (0.20 g, 0.86 mmol) was added to a solution of **[1-H][Cl]** (0.50 g, 1.47 mmol) in dichloromethane (30 mL). The solution was heated for 4 hours at 40°C and then filtered. After filtration the volume of the solution was reduced to 10 mL yielding colourless crystals. The crude product was recrystallised from tetrahydrofuran (THF). Yield (0.48 g, 73 %). M.p. 282-284 °C. ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) 7.12 (s, 2 H, C=C*H*), 6.97 (s, 4 H, Ar*H*), 2.37 (s, 6 H, *p*-CH_3), 2.05 (s, 12 H, *o*-CH_3). ^{13}C $\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2) δ (ppm) *Ag-C* signal was not observed, 141.9 (s, Ar-*C*-4), 137.6 (s, Ar-*C*-1), 136.9 (s, Ar-*C*-2,6), 131.5 (s, Ar-*C*-3,5), 125.0 (s, N*CC*), 23.0 (s, *p*-CH_3), 19.6 (s, *o*-CH_3). ^{109}Ag $\{^1H\}$ (18.61 MHz, CD_2Cl_2) δ (ppm) 630. IR (Nujol, cm^{-1}): 3158 (m), 2915 (s), 1607 (s), 1486 (m), 1236 (s), 1075 (m), 930 (s), 865 (m), 744 (m). Anal. Calcd for $C_{21}H_{24}$ $AgClN_2$: C, 56.33; H, 5.40; N, 6.26. Found: C, 56.14; H, 5.41; N, 6.31.

3.6.3 Synthesis of ^{13}C labelled [1-AgCl]

The synthesis was carried out according to the procedure described above (section 3.6.2). ^{13}C labelled imidazolium chloride (0.50 g, 1.47 mmol) synthesised as explained in section 2.6.3 and Ag_2O (0.20 g, 0.86 mmol) were heated to reflux for 4 hours in dichloromethane. The solution was filtered and the filtrate was concentrated on a rotary evaporator. The concentrated solution was allowed to crystalise slowly to give clear crystals. Yield (0.50 g, 76 %). M.p. 283-284 °C. ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) 7.13 (s, 2H, C=C*H*), 6.98 (s, 4 H, Ar-*H*), 2.36 (s, 6 H, *p*-CH_3), 2.04 (s, 12 H, *o*-CH_3). ^{13}C $\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2) δ (ppm) 186.09 (d, ^1J (^{13}C- ^{109}Ag) 270 Hz), 183.59 (d,

^1J (^{13}C-^{107}Ag) 234 Hz), 141.9 (s, Ar-*C*-4), 137.6 (s, Ar-*C*1), 136.9 (s, Ar-*C*-2,6), 131.5 (s, Ar-*C*-3,5), 125.0 (s, N*CC*), 23.0 (s, *p*-CH_3), 19.6 (s, *o*-CH_3). $^{109}Ag\{^1H\}$ (18.61 MHz, CD_2Cl_2) δ (ppm) 630. IR (Nujol, cm^{-1}): 3159 (m), 2916 (s), 1609 (s), 1484 (m), 1237 (s), 1074 (m), 932 (s), 864 (m), 746 (m). Anal. Calcd for $C_{21}H_{24}$ AgClN$_2$: C, 56.42; H, 5.35; N, 6.24. Found: C, 56.22; H, 5.38; N, 6.21.

3.6.4 Synthesis of [1-Ag-1]$^+$[AgCl$_2$]$^-$

[1-H][Cl] (0.34 g, 1.00 mmol) was dissolved in acetonitrile (10 mL) to which silver (I) oxide (0.12 g, 0.52 mmol) was added. The resulting solution was heated to reflux for 24 hours, and then filtered through Celite. The filtrate was reduced to 5 mL, and left to crystallise. A mixture of clear and pale yellow crystals were obtained. The pale yellow crystals were picked out and were analysed. Yield: (0.75 g, 85%). M.p. 290-292 °C. ^1H NMR (400 MHz, CD_3CN): δ (ppm) 7.23 (s, 2 H, NC*H*), 6.97 (s, 4 H, *m*-CH_3), 2.42 (s, 6 H, *p*-CH_3), 1.71 (s, 12 H, *o*-CH_3). ^{13}C $\{^1H\}$ NMR (100.61 MHz, CD_3CN): δ (ppm) 140.2 (s, Ar-*C*H), 135.9 (s, Ar-*C*H), 135.5 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 123.8 (s, *C*H-imidazole), 21.1 (s, *C*H_3), 17.3 (s, *C*H_3). IR (Nujol, cm^{-1}): 3151 (w), 3108 (w), 3080 (w), 2952 (s), 2922 (s), 1609 (m), 1488 (s), 1462 (s), 1281 (m), 1237 (m), 930 (m), 852 (s), 764 (s). Anal. Calcd for $C_{42}H_{48}N_4Ag_2Cl_2$: C, 56.33; H, 5.40; N, 6.26. Found: C, 55.88; H, 5.65; N, 6.49. MS (cation) (HRMS)[i] *m/z* 717.29304 amu (M^+), (Calcd. 717.3080 amu for M^+).

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[i] HRMS was performed by Dr. D. McGillvary at the University of Victoria.

3.6.5 Synthesis of $[\mathbf{1\text{-}Ag\text{-}1}]_2^+[\mathrm{Ag_4I_6}]^{2-}$

Silver (I) oxide (0.13 g, 0.58 mmol) and **[1-H][I]** (0.50 g, 1.16 mmol) were mixed in acetonitrile (50 mL) and heated to reflux for 24 hours. The resulting cloudy mixture was filtered through Celite and the solution was concentrated under vacuum to 10 mL and left to crystallise. Pale brown crystals were obtained. Yield (0.35 g, 34%). M.p. 210-211 °C. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.23 (s, 2 H, NC*H*), 6.97 (s, 4 H, *m-H*), 2.42 (s, 6 H, *p*-CH_3), 1.71 (s, 12 H, *o*-CH_3). ^{13}C {^{1}H} NMR (100.61 MHz, CD_3CN): δ (ppm) 140.1 (s, Ar-*C*H), 135.9 (s, Ar-*C*H), 135.5 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 124.0 (s, *C*H-imidazole), 21.2 (s, *o*-*C*H_3), 17.4 (s, *p*-*C*H_3). IR (Nujol, cm^{-1}): 3151 (w), 3122 (vw), 2953 (s), 2923 (s), 1580 (vw), 1487 (m), 1461 (s), 1377 (s), 1287 (m), 1235 (m), 931 (m), 855 (s), 749 (m). Anal. Calcd for $C_{84}H_{96}Ag_6I_6N_8$: C, 39.41; H, 3.68; N, 4.27. Found: C, 39.59; H, 3.98; N, 4.56. MS (HRMS of cation) *m/z* 717.2941 amu (M^+), (Calcd. 717.29304 amu for M^+).

3.6.6 Synthesis of NHC $\mathbf{1{\cdot}BH_3}$

[1-H][Cl] (0.50 g, 1.45 mmol) was dissolved in CH_2Cl_2 (20 mL) and to it one equivalent of $NaBH_4$ (0.06 g, 1.45 mmol) was added. Effervescence occurred upon addition of $NaBH_4$ and the reaction mixture was stirred for 4 hours. The solution was filtered through Celite, pumped to dryness and the crude residue was recrystallised in dichloromethane to give clear pale pink crystals. Yield: (0.39 g, 85%). M.p. 296-300 °C. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 6.96 (s, 4 H, Ar-*H*), 6.17 (s, 2 H, C=C*H*), 2.34 (s, 6 H, *p*-CH_3), 2.30 (s, 12 H, *o*-CH_3). 0.4 (q, 3 H, BH_3). ^{13}C NMR {^{1}H} (100.61 MHz, C_6D_6) δ (ppm) 139.6 (s, Ar-*C*H), 135.6 (s, Ar-*C*H), 129.4 (s, Ar-*C*H), 121.2 (s, $C_{4,5}$-H), 21.4 (s, *C*H_3), 17.9 (s, *C*H_3). IR (Nujol, cm^{-1}): 3170 (m), 2952 (s), 2922 (s), 2854 (s), 2332 (s), 2272 (s), 2213 (s), 1484 (s), 1413 (s), 1262 (s), 1233 (s), 1016 (s), 932 (w), 801 (s), 733 (s). Anal. Calcd for $C_{21}H_{27}N_2B_2$: C, 79.25; H, 8.55; N, 8.80. Found: C, 79.30; H, 8.40; N, 8.87. MS (cation) (EI) *m/z* 317.1 amu (M^+), (Calcd. 317.1 amu).

The reaction was repeated by treating **NHC 1** (0.50 g, 1.64 mmol) with 1 M **BH_3·THF** (1.64 mL, 1.64 mmol) in THF. Gas evolution occurred upon addition of **BH_3·THF** and the solution obtained was stirred for 4 hours after which THF was removed under vacuum. The pale pink powder obtained was recrystallised in CH_2Cl_2 to give **NHC 1·BH_3**. Yield: (0.45 g, 87%). M.p. 298-300 °C. ^1H NMR (400 MHz, C_6D_6): δ (ppm) 6.95 (s, 4 H, Ar-*H*), 6.16 (s, 2 H, C=C*H*), 2.32 (s, 6 H, *p*-C*H*$_3$), 2.30 (s, 12 H, *o*-C*H*$_3$). 0.39 (q, 3 H, B*H*$_3$). ^{13}C {^1H} NMR (100.61 MHz, C_6D_6): δ (ppm) 139.8 (s, Ar-*C*H), 135.7 (s, Ar-*C*H), 129.5 (s, Ar-*C*H), 121.0 (s, $C_{4,5}$-H), 21.3 (s, *C*H$_3$), 17.9 (s, *C*H$_3$). IR (Nujol, cm^{-1}): 3170 (m), 2952 (s), 2922 (s), 2854 (s), 2332 (s), 2272 (s), 2213 (s), 1484 (s), 1413(s), 1262 (s), 1233 (s), 1016 (s), 932 (w), 801 (s), 733 (s). Anal. Calcd for $C_{21}H_{27}N_2B_2$: C, 79.25; H, 8.55; N, 8.80. Found: C, 79.32; H, 8.48; N, 8.90. MS (cation) (EI) *m/z* 317.1 amu (M^+), (Calcd. 317.1 amu).

CHAPTER 4 : BASES IN PHOSPHONIUM-BASED IONIC LIQUIDS

Parts of this chapter were reproduced from the following journal articles:

1. Ramnial, T.; McCollum, B. M.; Taylor, S. A.; Gorodetsky, B.; Dickie, D. A.; Branda, N. R.; Walsby, C. J.; Clyburne, J. A. C. "Generation and Reactivity of Some Important Carbon Centred Bases and Boron Hydrides in Phosphonium-based Ionic Liquids." to be submitted.

2. Canal, J. P.; Ramnial, T.; Dickie, D. A.; Clyburne, J. A. C. "From the Reactivity of *N*-Heterocyclic Carbenes to New Chemistry of Ionic Liquids." *Chem. Commun.*, **2006**, 1809. (Reproduced by the permission of The Royal Society of Chemistry)

3. Gorodetsky, B.; Ramnial, T.; Branda, N. R.; Clyburne, J. A. C. "Electrochemical Reduction of an Imidazolium Cation: A Convenient Preparation of Imidazol-2-ylidenes and their Observation in an Ionic Liquid." *Chem. Commun.*, **2004**, *17*, 1972. (Reproduced by the permission of The Royal Society of Chemistry)

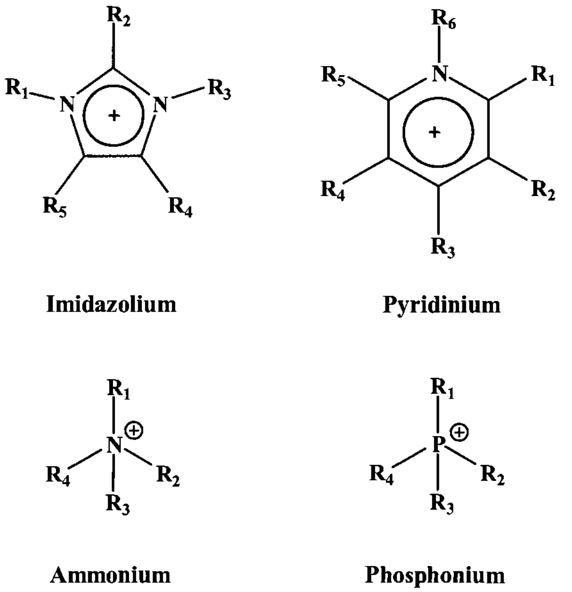
4.1 Introduction

To date, the majority of chemical reactions have been carried out in molecular solvents. Most of the understanding of chemistry has been based upon the behaviour of molecules in solution phase and mainly in *molecular* solvents and with water as the most common one. Nonetheless, certain type of solvents are high on the list of environmentally damaging chemicals for two simple reasons: (1) they are used in vast quantities and (2) they are usually toxic, volatile liquids and difficult to contain. This problem has led to a great focus on the design, manufacture and separation processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible.[154] Certain solvents especially the volatile organic compounds (**VOC**s) such as ethers need to be replaced since they are toxic, flammable.

The ideal solvent would be one that is biodegradable, non-toxic, that would dissolve the reactants and would support the chemistry. Some successful attempts have been made and new solvent systems such as supercritical water,[3, 4, 5] supercritical carbon dioxide,[6] fluorous solvents[155] and ionic liquids[156, 157, 158, 159] have been introduced. However, the use of some molecular solvent alternatives are limited since they are also reactive under certain conditions. For example supercritical carbon dioxide and fluorous solvents are sensitive to reactions with bases, and since certain organometallic reagents are water sensitive, they cannot be used in water. Nevertheless, some attempts at organometallic reactions in water, for example the Barbier-Grignard type reactions have been made and found to be feasible.[160] One point to be noted is that ionic liquids and supercritical carbon dioxide are not competing solvents for same applications. While **IL**s can be considered as alternatives for polar organic solvents, the use of supercritical CO_2 can cover those applications in which non-polar solvents are usually used.

Ionic liquids have advantageous chemical, physical, and “green” properties related to negligible vapour pressure, high chemical and thermal stability, high heat and electrical conductivities. They are stable over a wide range of electrochemical window (4.0 V) and they have the ability to dissolve a wide range of organic and inorganic compounds. Toxicology tests on **ILs** were not initially performed and thus **ILs** were believed to be non-toxic. The latest research does, however, indicate that this is not the case and some ionic liquids were found to be toxic to fish.[17] Ionic liquids have some toxicological issues (such as the hydrolysis of PF_6 or BF_4 anions to release HF), relative to conventional **VOCs**. They also have other properties as described above that attracted enormous attention as media for “Green” synthesis.[154, 158, 161] By definition, ionic liquids are two component mixtures *i.e.* the anion and the cation, which can be individually varied. Thus, the solvents can be designed with a particular end use in mind or to possess a particular set of physical and chemical properties. The most common classes of cations and anions are illustrated in Chart 4-1.

Common Cations **Common Anions**


Imidazolium Pyridinium
Ammonium Phosphonium

$Cl^-/[AlCl_3]$

Cl^-, Br^-, I^-

$[NO_3]^-, [SO_4]^-$

$[CF_3COO]^-, [CF_3$

$[BF_4]^-$

$[PF_6]^-$

$[(CF_3SO_2)_2N]^-$

$(CN)_3C^-$

Chart 4-1: Common class of cations and anions used in ionic liquids.

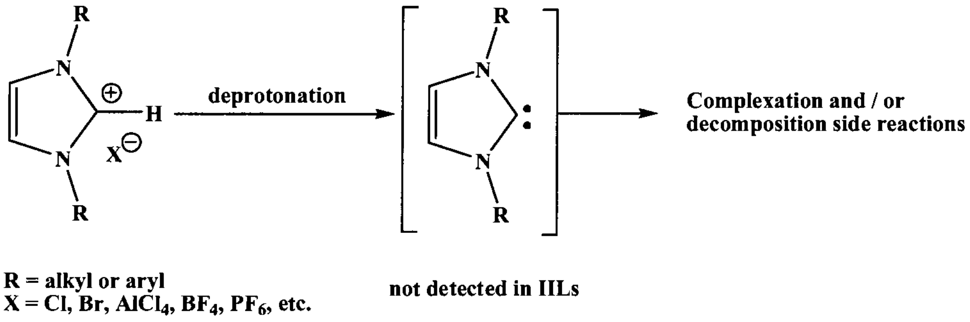
Ionic liquids can be further divided into two main categories. One group is the "simple" salts, which are made up of single anion and cation. These ions have electron precise octets and do not undergo any equilibrium. One example of such simple salt is tetra-*n*-butyl ammonium chloride. The other category is called the binary ionic liquids, which is actually made up of single cation, anion and an additive and there is an equilibrium between the additive and the anion. One example is the 1-butyl-3-methyl-imidazolium cation with $AlCl_3^-/Cl^-$, which is in equilibrium to give $AlCl_4^-$ and $Al_2Cl_7^-$ and Cl^-.

The belief that ionic liquids are not volatile can probably be traced to a report on the first-generation ionic liquids where 1-ethyl-3-methylimidazolium tetrachloroaluminate does not exhibit a measurable vapour pressure, even at the elevated temperature of 350°C.[6] Since then, the non-volatility of the ionic liquid has been assumed rather than tested until Earle *et.al.* recently showed that some ionic liquids can be vacuum distilled in a temperature range of 200-300°C.[13] Some of the ionic liquids that were vacuum distilled did, however, show traces of decomposition. Hence, the non-volatility is not a property that can be assumed for all thermally stable ionic liquids: vapour pressure is just another physical-chemical property that depends on the choice of anion and cation of the ionic liquid and needs to be experimentally determined.

4.1.1 Imidazolium-based Ionic Liquids

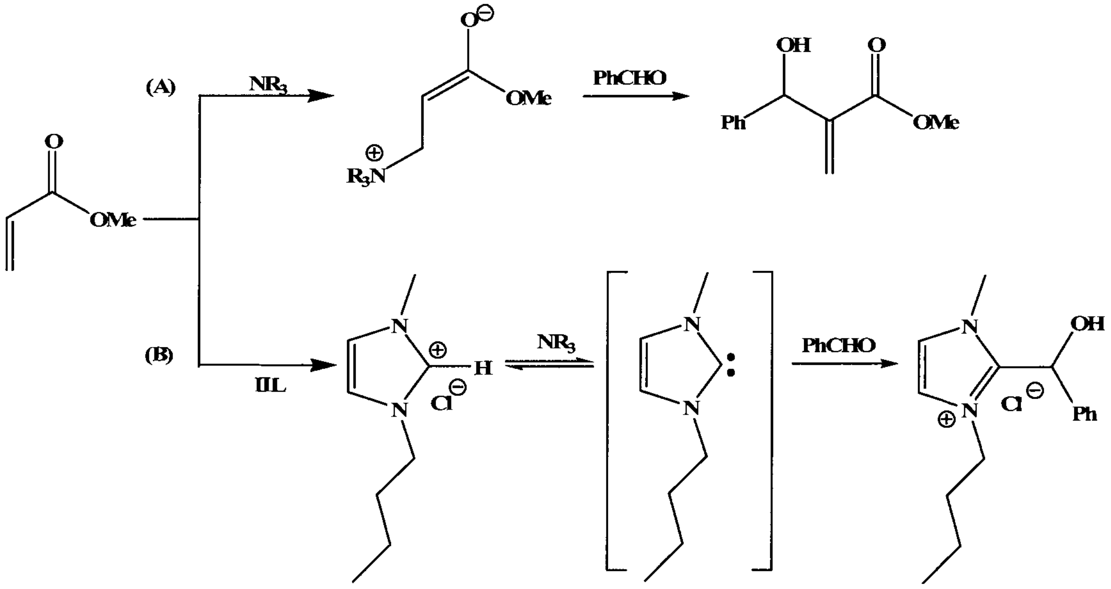
The most extensively studied class of ionic liquids (**ILs**) is based on imidazolium cations (**IILs**). These solvents exhibit high thermal stability and lower volatility compared to molecular solvents and some of them also form a homogeneous solution with a variety of common co-solvents such as benzene, toluene, hexanes and THF.[11] These ionic liquids have found applications in industry and other processes are still under commercialisation. One of the most exciting and impressive potential industrial application of ionic liquids is their use for the storage and delivery of gases that are highly toxic, flammable and reactive such as phosphines (PH_3), boron trifluoride (BF_3) and arsine (AsH_3).[162] Interestingly, the use of ionic liquids in industry is not limited to classic applications such as chemical synthesis, catalysis and electrochemistry, but also as performance chemicals, new materials and engineering fluids for machinery and equipment and for the use in automotive, textile, construction, oil and gas and energy industries.[163]

Ionic liquids are often assumed to be entirely innocent and that they do not take part in any chemical reaction. However, a recent review highlighted the rather unpredictable behaviour of this class of "green" solvent.[164, 165] Under certain conditions, both the cation and/or the anion can undergo "undesirable" transformations. For example, in some cases, the anion of the imidazolium ionic liquids can undergo hydrolysis. Some of the most studied **ILs** having BF_4 and PF_6 anions are hydrolysed to give HF, which is highly toxic and eats through glass thus turning this "green" system environmentally unfriendly. Imidazolium-based ionic liquids (**IILs**) have been known to support many reactions that proceed well in acidic reaction conditions.[166, 167, 168] However, the track record for **IILs** to support reactions involving strong bases is less than stellar.[165, 169, 170] The reactivity of imidazolium cations mainly stems from the relatively high acidity (pK_a = 22-24)[55, 56] of the C_2 hydrogen of the imidazolium ion. It is well known from the seminal work of Arduengo *et. al.* that deprotonation at the C_2 position (Scheme 4-1) of the imidazolium salts generates *N*-heterocyclic carbene ligands (as described in chapter 2).[171]



Scheme 4-1: Deprotonation of an imidazolium ion in an IIL to produce a transient NHC.

Scheme 4-1 shows deprotonation of the imidazolium ion in an **IILs** and suggests subsequent complexation of the putative carbene intermediate. This suggests that when imidazolium-based ionic liquids are used under basic conditions, there is a possibility for the formation of **NHCs**. In some cases deprotonation of the imidazolium salt to make **NHCs** or metal complexes of **NHCs** can be beneficial and one clear example is the palladium catalysed Heck reaction in **IILs**, where the palladium-carbene complex was formed *in situ*. Mechanistic studies showed that this reaction involves an induction period during which the palladium **NHC** complex is generated and this was shown to be the catalytic active species, which gave a higher yield of the product.[27(a), 172, 173] In other cases, deprotonation of the imidazolium ions can be detrimental, such as in the Baylis-Hillman reaction (Scheme 4-2(A)), the deprotonation of the **IIL** (Scheme 4-2(B)) results in a significant decrease in reaction yields.[169]



Scheme 4-2: (A) Baylis-Hillman reaction. (B) Baylis-Hillman in IIL, where IIL reacts with amine.

One way to overcome this deprotonation problem is to have a methyl group at the C_2 position. Kuhn *et. al.*[174], however, showed that deprotonation of the pentamethylimidazolium ion, which has a methyl group at the carbeneic centre, can still occur to give 1,3,4,5-tetramethyl-2-methylene-imidazoline, an olefin.

"Green" chemistry can be considered as a challenge since "Greener" solvents such as water and supercritical carbon dioxide have limited applications. They are convenient for reactions under acidic conditions, however they are not viable for reactions under basic conditions since they react with strong bases. It is interesting to note that more than 50% of reactions are based-catalysed, thus there is a need to find **ILs** that can be used for basic reactions and that can have relevance to "Green" chemistry. We resorted to phosphonium-based ionic liquids (**PILs**) since they are known to be more robust than ammonium, pyridinium and imidazolium-based ionic liquids.[41, 175]

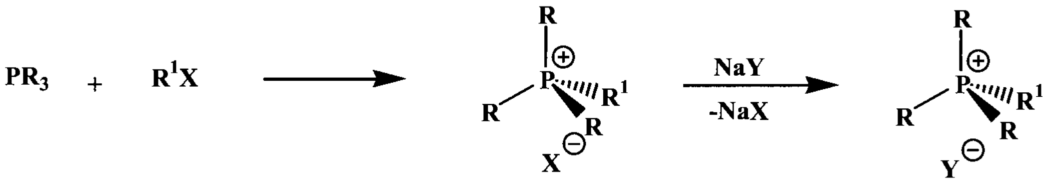
4.2 Phosphonium-based Ionic Liquids

Phosphonium-based ionic liquids (**PILs**) are unsymmetrical alkyl substituted phosphonium cations with a variety of potential anions to balance the charge. **PILs** have been available in a large scale for about ten years and their utility as a solvent medium has gained interest over the last couple of years, as evident by the number of review articles and industrial use.[168, 176] Numerous uses of **PILs** have been reported namely in catalysis: (1) tetraalkylphosphonium tosylates as solvents for hydroformylation;[177] (2) tetraalkylphosphonium halides as solvents for palladium-catalysed Heck reactions;[178] and (3) trihexyl(tetradecyl)phosphonium chloride as a solvent for palladium-catalysed Suzuki cross-coupling reactions[41] and as phase transfer catalysts.[179] These reactions cannot be performed in imidazolium or ammonium-based ionic liquids since deprotonation of the cations occurs. Interestingly, select **PILs**, being more robust do not undergo deprotonation or decomposition under these conditions.

The purification of certain **PILs** and their use as solvents to dissolve important carbon-centred ligands and bases are descrided in this chapter. The synthesis and reactivity of **NHCs** in **PILs** are also discussed.[180]

4.2.1 Purification of PILs

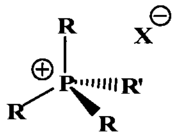
As explained is section 4.1, ionic liquids are inherently made up of two components, the anion and the cation. The formation of the quaternary cation, in this case the phosphonium cation, may be realised by the quaternisation of a phosphine. This reaction is most commonly achieved *via* treatment of the phosphine with a haloalkane.[6] The alkylation process possesses the following advantages (1) a wide range of cheap haloalkanes are available and (2) the substitution reactions generally occur smoothly at reasonable temperatures. Once the quaternary phosphonium halide salts are formed, other derivatives can be prepared *via* anion exchange as shown in Scheme 4-3.



Scheme 4-3: Synthesis of quarternary phosphonium halide and anion exchange to form other derivatives.

Ionic liquids are also known as "designer" solvents, which mean that the solvents can be customised with a particular end use in mind or to possess a particular set of properties. However, in the process of designing the ionic liquid for particular use, some of the starting materials or by-products can be retained as impurities. Therefore, they need to be purified prior to use. Though some ionic liquids were recently found to be distillable on small-scale,[13] most of them lack significant vapour pressure and this prevents the purification of some ionic liquids by distillation. The lack of measurable vapour pressure for most ionic liquids can be taken as an advantage and any volatile impurity can, in principle, be separated from an ionic liquid by distillation. Ionic liquids formed *via* anion metathesis can contain the halide anions as the most common impurity as well as unwanted cations that are inefficiently separated from the final product. The presence of such impurities can be extremely detrimental to the performance of the ionic liquids, particularly in reactions involving transition metal-based catalysts, which are often deactivated by halide ions. One point to be noted is that water is likely to be the major impurity in **PIL**s especially for water sensitive reactions.

In this study, three different phosphonium-based ionic liquids, which were donated by Cytec, Inc. (Niagara falls, Ontario), were examined. They were trihexyl(tetradecyl)phosphonium chloride (**PIL 1**), trihexyl(tetradecyl)phosphonium decanoate (**PIL 2**) and trihexyl(tetradecyl)-phosphonium diethylphosphinate (**PIL 3**) (Chart 4-2). **PILs 1**, **2** and **3** were purified using the method described below; however, most of the reactions discussed later were performed in **PIL 1** and **PIL 2** unless specified.



PIL 1: $X = Cl, R = C_6H_{13}, R' = C_{14}H_{29}$
PIL 2: $X = C_{10}H_{19}COO, R = C_6H_{13}, R' = C_{14}H_{29}$
PIL 3: $X = (EtO)_2PO_2, R = C_6H_{13}, R' = C_{14}H_{29}$

Chart 4-2: Structure of PILs used in this study.

Many trihexyl(tetradecyl)phosphonium-based ionic liquids can be produced *via* the process of anion exchange. For example, trihexyl(tetradecyl)phosphonium decanoate (**PIL 2**) is prepared *from* trihexyl(tetradecyl)phosphonium chloride and sodium decanoate. **PIL 2** was found to have favourable properties such as lower viscosity than **PIL 1**. Commercially produced **PIL**s, specifically **PIL 1**, were found to contain traces of residual starting material such as phosphines (observed through NMR spectroscopy studies, ^{31}P NMR: δ -50 ppm), acidic species (tested by making use of litmus paper) and water (^{1}H NMR: δ 1.5 ppm, increase in peak on the addition of water). **PIL 2**, on the other hand was tested for the traces of chloride ion contamination from its starting material, **PIL 1**. To a non-purified sample of **PIL 2** distilled water was added followed silver nitrate solution. The ionic liquid phase turned cloudy showing presence of chloride as a contaminant and since organometallic reagents are very sensitive to these species, we designed methods to purify the **PIL**s.

The acidic species in the **PIL**s were neutralised by washing with aqueous sodium hydrogen carbonate. *Care* should be taken since foaming may occur. The ionic liquid layer was washed vigorously with water and extracted using hexanes. The removal of hexanes or any other reaction volatile residuals was generally easily achieved by heating the ionic liquid at 70°C under vacuum. Water is usually one of the most problematic solvents to remove, and it is recommended that ionic liquids be heated to at least 70°C under vacuum with a small amount of toluene for azeotropic distillation for several days with stirring to remove water, which was tested by the absence of the ^{1}H NMR spectroscopic peak at 1.5 ppm. This step is very important since many reactions that we carried out in **PIL**s were water sensitive. Another method used to dry the ionic liquids is by the addition of potassium metal. Though we preferred the preceding method described, the addition of elemental potassium to **PIL**s during the cleaning process did relate well with basic chemistry of **PIL**s. **PIL**s did not react with potassium metal even though it is a source of the simplest base, the electron.[j]

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[j] The Lewis model for an acid and a base is that an acid is an acceptor of a lone pair of electrons and a base is a donor of a lone pair of electrons. However, in a broader aspect, a base can also be considered as a single electron donor and an acid as a single electron acceptor. A good example of one electron acid base complex is the intramolecular boron-boron one-electron σ bond reported by Gabbaï, F. P *et. al.* (*J. Am. Chem. Soc.* **2000**, *122*, 9054.)

4.3 Comparison of PILs and IILs

PILs are found to be thermally more stable than **IIL**s.[175] While the thermal decomposition point of neat ionic liquids varies depending on the anion, thermogravimetric analyses (TGA) indicated dynamic thermal stability in excess of 300°C for **PIL**s[175] and 250°C for most **IIL**s.[181] The TGA data reported are often not fully indicative since it shows only a dynamic property of the ionic liquid where the **IL** is heated for a short period of time, which is not representative of a real application since certain reactions need longer heating time. Hence, to find the thermal stability of the **PIL**s, they were analysed after heating at a temperature of 350°C for over a week. The **PIL**s were then analysed by GC-MS and they were found to be stable with no decomposition products such as hexene and tetradecyl(dihexyl)phosphine. On the other hand, heating the **IIL** 1-butyl-3-methylimidazolium chloride at 250 °C for 1 week resulted in its decomposition as determined by GC-MS analysis. Dealkylation of the imidazolium cation occurred to give 3-methylimidazole (*m/z* 82.1). This enhanced thermal stability of **PIL**s relative to quaternary nitrogen and imidazolium-based salts is an important factor when, for example, reaction products can be removed from an ionic liquid by high temperature distillation.

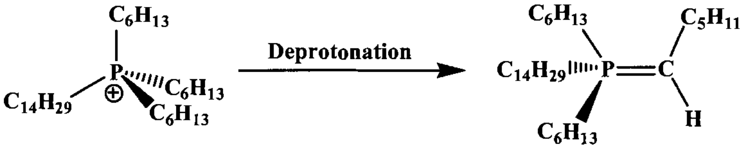
As observed during the purification step, the tested **PIL**s did not react with potassium, a source of the simplest electron, unlike imidazolium salts, which can be easily converted to **NHC**s by reacting with potassium metal as supported by cyclic voltammetry studies of **[1-H][Cl]** (Figure 2-2). This study led us to survey the reduction chemistry of **PIL**s by cyclic voltammetric studies, which were carried out *versus* a saturated calomel electrode (SCE) at 300 mV s^{-1} using ferrocene as the internal reference.

Standard concentrations (1.5 mM) of the imidazolium and phosphonium salts were used in anhydrous dimethyl sulfoxide (DMSO). **PIL**s were found to have a wider electrochemical window than the imidazolium salts. The reduction potential of the phosphonium salts was found to be dependent on the lengths of the alkyl chains attached to the phosphonium cation. A general increase in the reduction potential of the **PIL**s was observed with an increase in the lengths of the alkyl chains, for example trihexyl(tetradecyl)phosphonium chloride (Ep_{red} = -2.93 V) has a higher reduction potential compared to tetraethylphosphonium bromide (Ep_{red} = -2.06 V) as shown in Table 4-1. However, since the electrochemical window for DMSO is from -3.4 to +1.3 V,[182] the reduction potential of the phosphonium salts with very long alkyl chains such as tetra-*n*-octylphosphonium bromide could not be reliably obtained. The electrochemical reduction data of the ions shown below provide a better understanding of the reactivity of the **IL**s.

Salts	**Reduction Potential/V**
1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride	-2.23
1,3-*bis*(2,6-diisopropylphenyl)imidazolium chloride	-2.28
Tetraethylphosphonium bromide	-2.06
Trihexyl(tetradecyl)phosphonium decanoate (PIL 2)	-2.82
Trihexyl(tetradecyl)phosphonium chloride (PIL 1)	-2.93
Tetra-*n*-octylphosphonium bromide	Outside electrochemical window

Table 4-1: Reduction potential of Imidazolium salts and PILs.

This electrochemical study was important since it showed that the imidazolium salts are reduced before the **PIL**s. Imidazolium salts were found to deprotonate when reacted with potassium metal and bases such as potassium *tert*-butoxide or sodium hydride to give **NHC**s as detailed in Chapter 2. Similarly, deprotonation of the **PIL**s would result in a phosphorane as shown in the Scheme 4-4. However, when **PIL**s were reacted with potassium metal or potassium *tert*-butoxide, no evidence for deprotonation was observed as determined by ^{31}P NMR spectroscopy (anticipated peak is 26 ppm).[183]

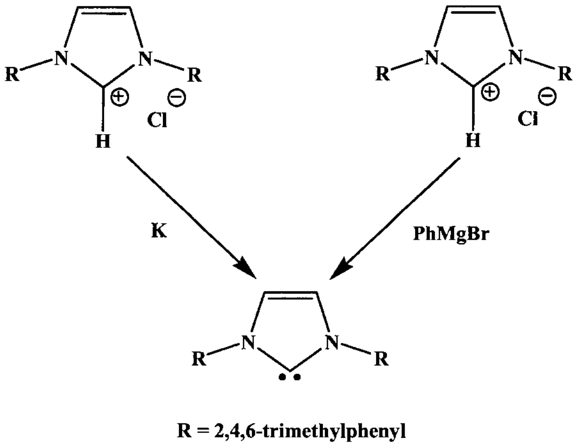


Scheme 4-4: Deprotonation of PILs cation.

4.4 Strong Bases in PILs

If electron transfer occurred from a strong base in **PIL**s, deprotonation or decomposition of the ionic liquid would occur to give a phosphorane or tetradecyl(dihexylphosphine) and hexene. These products could be identified by retention time and *m/z* values recorded by GC-MS spectroscopy, which was calibrated using a reference sample of tetradecyl(dihexylphosphine) and hexene. In order to test the tolerance of **PIL**s towards a strong base, a solution of **PIL** containing an **NHC** was prepared. **NHC**s are one of the most highly basic neutral ligands with pK_a values of the conjugate acid in the range of 22 to 24,[55, 56] slighly lower than **PIL**s. First, a solution of ^{13}C labelled **NHC** dissolved in **PIL**s was prepared. Since dissolution of the **NHC** in **PIL**s is slow several drops of a co-solvent such as benzene, toluene, or THF were added. The co-solvent was needed to facilitate dissolution of the **NHC** after which it was removed under vacuum with no decomposition of the remaining solution. The persistence of the solution was confirmed by ^{31}P and ^{13}C NMR spectroscopy and it was observed that the **NHC** in **PIL**s was stable for over a month under nitrogen. **NHC**s were unambiguously identified by the ^{13}C NMR resonance of a carbeneic carbon at ≈ 219 ppm as well as through reactivity studies (see below). The persistence of **PIL**s was analysed by ^{31}P NMR spectroscopy, which gave only one sharp resonance peak at 33 ppm corresponding to the **PIL**. Additional phosphorus peaks were not observed. Other neutral bases, such as triphenylphosphine and butyronitrile were also examined and were found to be persistent in **PIL**s as confirmed by spectroscopic studies such as IR and NMR spectroscopy and mass spectrometry.

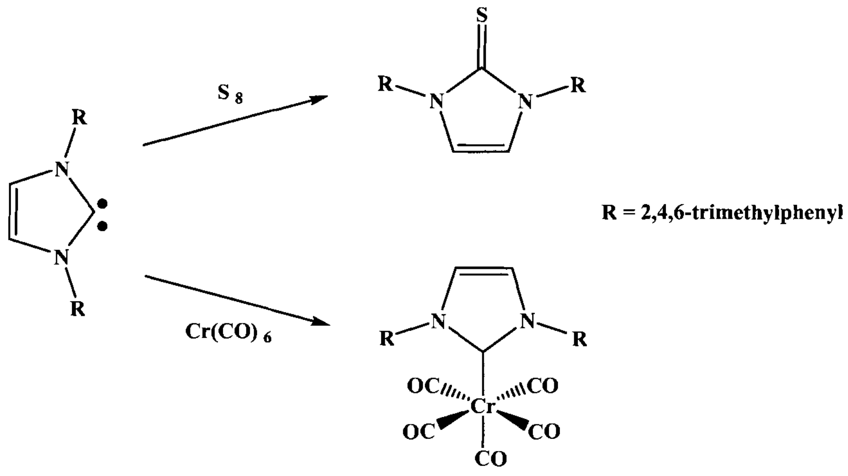
In section 2.2.1, we showed that imidazolium ions could be converted to nucleophilic carbenes by treatment with metallic potassium[66] and concurrently, we found that **PIL**s do not react with potassium. Hence, the imidazolium salts namely, 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride, **[1-H][Cl]** and 1,3-*bis*(2,6-diisopropylphenyl)imidazolium chloride, **[2-H][Cl]** in **PIL**s can be converted to their respective **NHC**s with potassium metal. After the reaction was complete, the excess potassium was filtered off and the solution obtained was analysed by ^{13}C and ^{31}P NMR spectroscopy. ^{13}C NMR spectroscopy data showed distinct carbeneic peak at 219 ppm and 221 ppm consistent with **NHC 1** and **NHC 2**, respectively. The stability of the **PIL**s was determined by two methods namely, ^{31}P NMR spectroscopy and GC-MS analysis. Only one resonance peak at 33 ppm was obtained from the ^{31}P NMR spectra, consistent with that of the **PIL** and GC-MS studies showed the absence of any deprotonation product (phosphorane) or the decomposition product, tetradecyl(dihexyl)phosphine and hexene.[57] Another method to synthesise **NHC 1** in **PIL 1** is by treating **[1-H][Cl]** with **PIL 1**/ PhMgBr in THF, a solution described in chapter 5 (Scheme 4-5). After the reaction was complete, the THF was pumped off under vacuum. The brown solution obtained was analysed by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and the data were consistent with **NHC 1** and **PIL 1**. Surprisingly, these basic solutions were stable in excess of one month at room temperature, under an inert atmosphere and were active for organic transformations as detailed in section 4.4.1.



Scheme 4-5: Methods to synthesise NHC 1 in PILs.

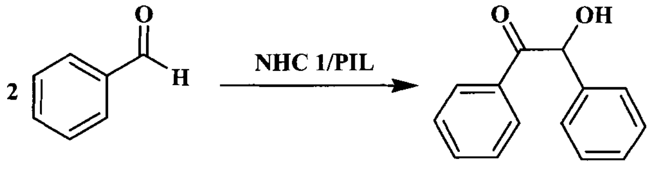
4.4.1 Reactions of NHCs in PILs

The stability of **NHC**s in **PIL**s was examined by well-established **NHC** chemistry (Scheme 4-6).[184] Spectroscopic techniques such as IR, NMR, MS and GC-MS were used to characterise the products obtained. A sample of **NHC 1** in **PIL 1** was treated with S_8 to produce 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-thione, **[1=S]** as indicated by ^{13}C NMR spectroscopy and mass spectrometry (m+1 = 336.3 amu).[185] Another typical carbene reaction is the coordination to transition metal sites. These complexes have attracted interest in catalysis.[105] The reactivity of **NHC 1** with $Cr(CO)_6$, a reaction previously reported in a molecular solvent was explored in **PIL 1**. This reaction resulted in the displacement of one carbonyl funtionality to afford [**1-Cr(CO)$_5$**], as identified by IR spectroscopy and mass spectrometry.



Scheme 4-6: Reactivity of NHC 1 in PIL 1.

As mentioned above, **NHCs** have received much attention in catalysis either as a ligand on a transition metal or as a base in organic transformations, one of which being the benzoin condensation.[186, 187] **NHCs** in **PILs** were found to perform a catalytic benzoin condensation reaction, which is a convenient and powerful method for the formation of C-C bonds from aldehydes. Typically aromatic aldehydes or glyoxals could be coupled using a cyanide anion as a catalyst.[186, 188] Interestingly, **NHC 1** (10 mol %) in **PIL 1** was found to catalyse the benzoin condensation of benzaldehyde in 40% yield as shown in Scheme 4-7. This yield was not optimised.



Scheme 4-7: Benzoin condensation of benzaldehyde in PIL 1.

4.5 Computational and Structural Studies

In theory, some strong bases should deprotonate or decompose the **PILs**, but this was not observed as illustrated in the reactivity studies above. In order to have an insight of what is causing such stability of the **PILs**, theoretical studies were performed. Since the imidazolium salts and **PILs** used are bulky with aryl and long alkyl chains, a simplified model namely the symmetrically substituted 1,3-diethylimidazolium ion and the phosphonium ion, $[P(C_2H_5)_4]^+$ (Chart 4-3) were used to estimate the Mullikan partial charges on C_2-proton and the alpha-protons in the respective ions as shown in Figure 4-1.[k] In this case, only the charges on the active sites were taken into consideration with the assumption that the bulkiness of the groups would not have a major impact on the charges.

Chart 4-3: Structures of the 1,3-*bis*(diethyl)imidazolium (left) and tetraethylphosphonium (right) ions used in computational studies.

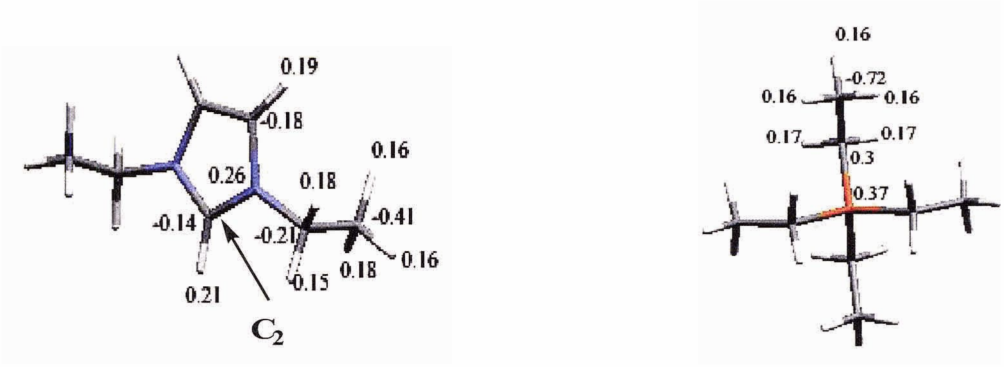


Figure 4-1: Estimated Mullikan partial charges on 1,3-*bis(*diethyl)imidazolium ion (left) and tetraethylphosphonium ions (right).

Calculations were performed with the Gaussian 98 package of programs and the geometry was optimised at the UB3LYP/6-31G level and partial atom charges were

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[k] All calculations were performed by our collaborator Brett M. McCollum and Dr. Paul W. Percival at Simon Fraser University.

calculated using the UB3LYP/6-311G*(2df,p) basis set.[f] The structural parameters calculated for both the imidazolium[189] and phosphonium ions[190] are comparable to those observed by X-ray crystallography. Of interest to this discussion are the estimated Mullikan partial charges on the reactive C_2-H of the imidazolium ion and the alpha-protons for the phosphonium ions, which are the potential points at which a strong base can interact with the cationic species. According to calculations, there is only a slight difference in the charges on C_2-H and alpha hydrogen on the phosphonium cation (Figure 4-1). Therefore the difference in deprotonation of the ions cannot be due to the positive charges on the hydrogen. There might be another factor that influenced the reactivity.

Steric considerations appeared to favour deprotonation of the **IIL**s *versus* **PIL**s. The imidazolium ring in **IIL**s is rigid whereas the alkyl chains on the phosphonium ions are floppy and flexible and thus provide more protection to the reactive proton. As shown in the space filling diagram of the relevant molecules; **[1-H]**$^+$ ion (Figure 4-2 left) and trihexyl(tetradecyl)phosphonium ion (Figure 4-2 right), it is very difficult to sterically shield the carbeneic site in the imidazolium ion, whereas in the trihexyl(tetradecyl)phosphonium ion there is considerable steric congestion and flexibility, hence diminishing the access to the reactive alpha-hydrogen site.

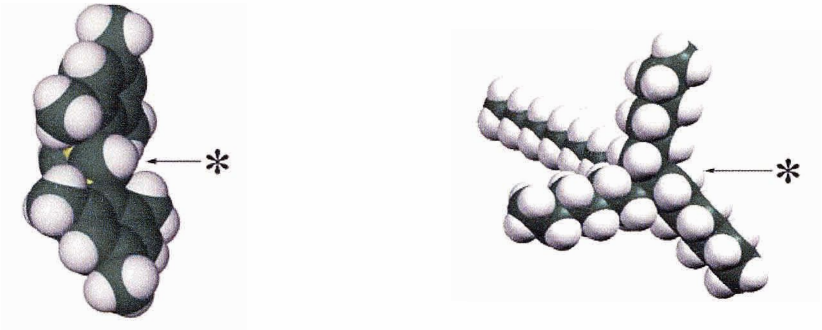

Figure 4-2: Space filling diagram for $[1\text{-H}]^+$ (left) and PIL ion (right). Highlighted (*) are the reactive C-H fragments of the ions.

The resistance of **PILs** towards reactions with bases therefore appeared to have primarily a steric or kinetic origin. Although it would be reasonable to expect that deprotonation of a phosphonium to phosphorane and a salt would be thermodynamically favoured, evidence of the reaction was not observed in our systems. Contrast this with the Wittig reagents, which are derived from materials analogous to **PILs**, but generally with significant shorter alkyl chains and with three phenyl rings. Since access to the reactive protic site on **PIL 1** is difficult, bases such as Grignard reagents fail to react with the phosphonium component of the **PIL**, in which they are dissolved. In support of our arguments, it is noted that a **PIL 2** solution containing either PhMgBr or a base such as potassium *tert*-butoxide is able to deprotonate $[Ph_3PCH_2CH_3]^+[Br]^-$ producing a phosphorane, which was identified by ^{31}P NMR spectroscopy (δ 15 ppm) and reactivity studies. This reactivity could be explained because the ionic species $[Ph_3PCH_2CH_3]^+[Br]^-$ has shorter alkyl chains than **PILs**, therefore it has an unprotected reaction site and they are slightly less basic than **PILs**.

4.6 Conclusions

Two different methods of purification of commercial samples of **PIL**s were described in this chapter. These purified **PIL**s were used to perform reactions under basic conditions and they were found to be stable in the presence of a **NHC**, a strong neutral base. The **NHC** can also be obtained by the deprotonation of the imidazolium salts. **PIL**s were used as solvent media for the synthesis of **NHC**s using potassium metal and to perform classical carbene reactivity studies.

4.7 Experimental Section

4.7.1 General Procedure

A MBraun UL-99-245 dry box and standard Schlenk techniques[191] on a double manifold vacuum line were used in the manipulation of air and moisture sensitive compounds. NMR spectra were recorded on a Varian AS 500 MHz spectrometer or a Bruker AMX 400 MHz spectrometer in five millimeter quartz tubes. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are reported in parts per million (ppm), referenced with residual solvent peak, $^{31}P\ \{^{1}H\}$ chemical shifts are reported with respect to 85% phosphoric acid (0 ppm). Infrared spectra were obtained using a Bomem MB spectrometer with the % transmittance values reported in cm^{-1}.

Gas Chromatography Mass Spectrometry (GC-MS) were carried out on the extracts using a Gas Chromatograph Electron Ionisation detector G 1800A GCD system. Volatile products were isolated from **PILs** *via* Kugelröhr distillation. Trihexyl(tetradecyl)phosphonium chloride **(PIL 1)**, trihexyl(tetradecyl)phosphonium decanoate **(PIL 2)** and trihexyl(tetradecyl)phosphonium diethylphosphinate **(PIL 3)** are commercially available as **IL 101**, **IL 103** and **IL 169** respectively from Cytec and were purified before use. Their purity was assessed by ^{1}H and ^{31}P NMR spectroscopy and GC-MS spectrometry. All other reagents and solvents were purchased from Aldrich and used without further purification. For electrochemistry, a PINE bipotentiostat AFCBP1 was used as power source.

4.7.2 Purification of PILs

To **PILs** (120 mL), a saturated aqueous sodium hydrogen carbonate solution (20 mL) was added and the mixture was stirred for 15 minutes. Vigourous foaming occurred after which the solution was washed thoroughly with water (3 × 150 mL). Hexanes (120 mL) were added to the washed ionic liquid layer followed by water (120 mL) in 3×40 mL aliquots. This resulted in a three-phase system with the organic layer at the top, ionic liquid in the middle and aqueous layer at the bottom. After extraction, the ionic liquid was dried by azeotropic distillation using toluene (20 mL), followed by exhaustive evacuation. **PIL 1**: ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 2.4-0.7 (various m). ^{31}P {^{1}H} NMR (161.98 MHz, C_6D_6) δ (ppm) 33. IR (neat, cm^{-1}) 2956 (s), 2923 (s), 2856 (s), 1466 (s), 1416 (m), 1378 (s), 1300 (m), 1263 (m), 1216 (m), 1112 (m), 989 (m), 814 (m), 721 (s). Anal. Calcd for $C_{32}H_{68}ClP$: C: 74.01; H: 13.20. Found: C: 74.30; H: 13.03. **PIL 2**: ^{1}H NMR (400 MHz, C_6H_6) δ 2.8-0.8 (various m). ^{31}P {^{1}H} NMR (161.98 MHz, C_6D_6) 33. IR (neat, cm^{-1}) 2956 (s), 2925 (s), 2856 (s), 1579 (s) (C=O stretch), 1465 (m), 1377 (m), 1265 (m), 1110 (m), 812 (m), 722 (m). Anal. Calcd for $C_{42}H_{87}O_2P$: C: 77.00; H: 13.39. Found: C: 77.15; H: 13.27.

4.7.3 Preparation of a solution of NHC 1 in PIL 1

A solution of **NHC 1** in **PIL 1** was prepared by dissolving **NHC 1** (0.20 g, 0.66 mmol) in **PIL 1** (10 mL) with the addition of toluene (1 mL) to solubilise the carbene. The toluene was then removed under vacuum and the spectroscopic data obtained were consistent with **NHC 1** synthesised in THF:[57] ^{1}H NMR (400 MHz, THF-d_8) δ 7.04 (s, 2 H, NC*H*), 6.94 (s, 4 H, Ar-*H*), 2.30 (s, 6 H, 4-C*H*$_3$), 2.02 (s, 12 H, 2,6-C*H*$_3$). ^{13}C {^{1}H} NMR (100.6 MHz, THF-d_8,) δ 219.7 (s, N*C*N), 139.7 (s, Ar-*C*-1), 137.6 (s, Ar-*C*-4), 135.7 (s, Ar-*C*-2,6), 129.7 (s, Ar-*C*-3,5), 121.3 (s, N*C*C), 21.0 (s, 4-*C*H$_3$), 18.0 (s, 2,6-*C*H$_3$).

4.7.4 Reduction of [1-H][Cl] with potassium in PIL 1 to give NHC 1

To a sample of **PIL 1** (10 mL), **[1-H][Cl]**[57] (2.00 g, 5.87 mmol) and an excess of potassium metal (0.35 g, 8.75 mmol), previously washed with anhydrous THF, were added. The reaction mixture was heated at 80°C under nitrogen for 24 hours. Hexanes (10 mL) were added to the resulting suspension and the solution was filtered through Celite. Hexanes were removed under vacuum which gave a residue that was characterised as a solution of **PIL 1** containing **NHC 1**. ^{1}H NMR (400 MHz, THF-d_8) δ 7.14 (s, 2 H, NC*H*), 6.96 (s, 4 H, Ar-*H*), 2.31 (s, 6 H, 4-C*H*$_3$) , 2.08 (s, 12 H, 2,6-C*H*$_3$). ^{13}C {^{1}H} NMR (100.6 MHz, THF-d_8) δ 215.8 (s, N*C*N), 139.9 (s, Ar-*C*-1), 138.2 (s, Ar-*C*-4), 136.2 (s, Ar-*C*-2,6), 129.8 (s, Ar-*C*-3,5), 122.1 (s, N*C*C), 21.6 (s, 4-*C*H$_3$), 18.6 (s, 2,6-*C*H$_3$). ^{31}P {^{1}H} NMR (161.98 MHz, C_6D_6) δ 33. These spectroscopic data were consistent with **NHC 1** dissolved in **PIL 1**.

4.7.5 Reaction of ^{13}C labelled [1-H][Cl] with PhMgBr in PIL 1

^{13}C labelled **[1-H][Cl]** (0.10 g, 0.29 mmol) was added to **PIL 1** (5 mL) to afford a creamy suspension to which 1.0 M PhMgBr in THF (0.35 ml, 0.29 mmol) was added drop-wise with stirring. The mixture turned clear yellow after stirring for 15 minutes. ^{1}H NMR (400 MHz, THF-d_8) δ 7.41 (s, 2 H, NC*H*), 7.15 (s, 4 H, Ar-*H*), 2.41 (s, 6 H, 4-C*H*$_3$), 2.18 (s, 12 H, 2,6-C*H*$_3$). ^{13}C {^{1}H} NMR (100.6 MHz, THF-d_8) δ 219.7 (s, N*C*N), 143.6 (s, Ar-*C*-1), 137.1 (s, Ar-*C*-4), 136.9 (s, Ar-*C*-2,6), 130.6 (s, Ar-*C*-3,5), 130.2 (s, N*C*C), 21.3 (s, 4-*C*H$_3$), 15.8 (s, 2,6-*C*H$_3$). ^{31}P {^{1}H} NMR (161.98 MHz, C_6D_6) δ 33. These spectroscopic data were consistent with **NHC 1** dissolved in **PIL 1** as explained in section 4.7.4.

4.7.6 Preparation of [1=S]

A solution of **NHC 1** was prepared by dissolving **NHC 1** (0.50 g, 1.64 mmol) in **PIL 1** (10 mL). Toluene (1 mL) was added to solubilise **NHC 1**. After dissolution the toluene was removed under vacuum, leaving behind a reddish brown solution. To this viscous solution, sulphur (0.05 g, 1.64 mmol) was added followed by a small amount of hexanes (2 mL) to decrease viscosity. The resulting mixture was then stirred for 4 hours at room temperature. Additional hexanes were then added (5 mL) and the mixture was filtered through Celite. The filtrate was evaporated to remove hexanes leaving a viscous yellow residue. ^{1}H NMR (400 MHz, C_6D_6) δ 6.78 (s, 4 H, Ar-$H_{3,5}$), 6.66 (s, 2 H, NC*H*), 2.32 (s, 12 H, 2,4-CH_3), 2.08 (s, 6 H, 4-CH_3). ^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6) δ 162.9 (s, NCN), 158.1 (s, Ar-C-4), 138.9 (s, Ar-C-2,6), 133.4 (s, Ar-C-1), 128.4 (s, Ar-C-3,5), 124.9 (s, N*C*C*N*), 22.4 (s, 4-*C*H$_3$), 20.9 (s, 2,6-*C*H$_3$). MS (CI) *m/z* 336.3 amu (Calcd *m/z* 336.3 amu). This ^{13}C NMR data was consistent with the previously reported data for **[1=S]**.[185]

4.7.7 Preparation of Pentacarbonyl [1-Cr(CO)$_5$] in PIL 1

A solution of **NHC 1** (0.20 g, 0.91 mmol) was prepared by dissolving it in **PIL 1** (10 mL). Toluene (2 mL) was added to solubilise the **NHC 1** in **PIL 1**. The toluene was then removed under vacuum. The **PIL 1** solution of **NHC 1** was treated with chromium hexacarbonyl (0.20 g, 0.91 mmol). A yellow precipitate (0.24 g, 77%) was obtained. The mixture was warmed at 60 °C for 2 hours, then the product was extracted using hexanes. IR (Nujol, cm^{-1}) ν(CO) 2056 (s), 1923 (vs), consistent with **[1-Cr(CO)$_5$]**.[192] MS (EI) *m/z* 497.5 amu, (Calcd *m/z* 497.5 amu).

CHAPTER 5 : GRIGNARD REAGENTS, NUCLEOPHILES AND CARBON-CARBON BOND FORMATION REACTIONS IN PILS

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1. Ramnial, T.; McCollum, B. M.; Taylor, S. A.; Gorodetsky, B.; Dickie, D. A.; Branda, N. R.; Walsby, C. J.; Clyburne, J. A. C. "Generation and Reactivity of Some Important Carbon Centred Bases and Boron Hydrides in Phosphonium-based Ionic Liquids." to be submitted.

2. Ramnial, T.; Taylor, S. A.; Clyburne, J. A. C.; Walsby, C. J. "Switch-hitting Behaviour for Grignard Reagents in Molecular and Ionic Solvents." *J. Amer. Chem. Soc.* submitted.

3. Canal, J. P.; Ramnial, T.; Dickie, D. A.; Clyburne, J. A. C. "From the Reactivity of *N*-heterocyclic Carbenes to New Chemistry of Ionic Liquids." *Chem. Commun.*, **2006**, 1809. (Reproduced by the permission of The Royal Society of Chemistry)

4. Ramnial, T.; Ino, D. D.; Clyburne, J. A. C. "Phosphonium Ionic Liquids as Reaction Media for Strong Bases." *Chem. Commun.* **2005**, 325. (Reproduced by the permission of The Royal Society of Chemistry)

5.1 Introduction

Conventional organic solvents are used in a range of industrial applications, including pharmaceutical production, microelectronic manufacturing, polymer processing and chemical synthesis.[193] However, volatile organic compounds (**VOCs**), which readily evaporate in the environment have been implicated as one of the sources of ozone depletion, global climate change and smog formation, thus having complex negative effects on biological systems.[194] Clearly, there is a need to find effective and economical ways to minimise pollution at the source and to develop environmentally friendly means to curtail these problems associated with **VOCs**.

Imidazolium-based ionic liquids, as explained in chapter 4, are found to be reactive towards active metals such as potassium and sodium, neutral bases such as **NHCs**, Grignard reagents and other nucleophiles. Basic reactions in ionic liquids are important since more than 50 % of chemical reactions are based catalysed, but have been found to be not viable in **ILs**.

As discussed in chapter 4, phosphonium-based ionic liquids (**PILs**) are thermally more robust than ammonium, pyridinium, and imidazolium-based ionic liquids and do not undergo deprotonation or decomposition in the presence of active metals or strong bases, such as **NHCs**. The use of **PILs** as solvents for strong bases such as Grignard reagents and other nucleophiles has, however, not been previously described. Phosphonium and ammonium based ionic liquids have been previously used for reactions under *slightly* basic conditions, for example in the alkylation of 2-naphthoxide [25, 26] (1) where the anion is not very basic (pKa ≈ 10),[195] therefore no deprotonation of the ionic liquid was observed.

Grignard reagents, which are organomagnesium halides having the general formula RMgX are very basic (pKa ≈ 45-50 depending on the R group)[196] and have been traditionally expected to potentially deprotonate the **PIL**s. However, the compatibility of **PIL**s with strong bases, reducing agents[180] and persistent radicals is illustrated in this chapter. The feasibility of replacing volatile and flammable solvents typically used for Grignard chemistry[197] and with more environmentally friendly and recyclable alternatives is also demonstrated. The synthesis of new **PIL**s solutions containing reducing agents such as BH_3 has also been identified, along with the generation and reactivity of phosphoranes (Wittig reagents) with organic reagents in **PIL**s[180] One point to remember is that the reactions mentioned below might not be totally "Green" in the **PIL**s due to the amount of solvent used for extraction, however they do show some new and unusual chemical reactivity when switching from the normal organic solvent to the **PIL**s.

5.2 Grignard Reagents

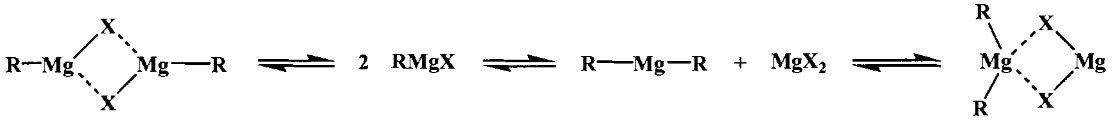
A Grignard reagent is an alkyl or aryl magnesium halide and is formed by the reaction of alkyl or aryl halides with magnesium metal as shown in Scheme 5-1, making the carbon nucleophilic. Since Grignard reagents react with water to give magnesium hydroxide and R-H, complete removal of water from the solvent medium is essential. Grignard reagents may also react with oxygen present in the atmosphere, inserting an oxygen atom between the carbon base and the magnesium halide group. Therefore, these reactions are generally carried out under an inert atmosphere such as nitrogen or argon. Most Grignard reactions occur in solvents such as anhydrous diethyl ether or tetrahydrofuran, because the oxygen of these solvents stabilises the Grignard reagent through an interaction with magnesium (Mg-O). NMR spectroscopy and X-ray crystallographic studies provided evidence for this interaction.[198]

$$\mathrm{RBr} + \mathrm{Mg} \longrightarrow \mathrm{RMgBr}$$

R = alkyl or aryl group

Scheme 5-1: Synthesis of a Grignard reagent.

It is believed that Grignard reagents undergo an equilibrium reaction known as the Schlenk equilibrium, which is a dynamic interconversion between RMgX (the Grignard reagent), R_2Mg and MgX_2 (Scheme 5-2) and the that Schlenk equilibrium is dependent on the polarity of the solvent.



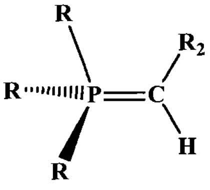
Scheme 5-2: The Schlenk equilibrium.

5.3 Stability of Grignard Reagents in PILs

Commercially available solutions of Grignard reagents in THF are perhaps among the most readily available strong carbon-based nucleophiles. The stability and reactivity of phenylmagnesium bromide, 2,4,6-trimethylphenylmagnesium bromide, ethylmagnesium bromide and ethynylmagnesium bromide were probed in **PIL**s, however most of the chemistry was carried out using phenylmagnesium bromide (PhMgBr). A clear solution with low viscosity was formed when **PIL 1** was mixed with commercially available 1 M Grignard reagents in THF.[197] These solutions are air and moisture sensitive, but can be stored under an inert atmosphere.

The stability of the **PIL 1**/PhMgBr THF mixture was analysed by ^{31}P NMR spectroscopy and GC-MS studies. ^{31}P NMR studies showed only one resonance peak at

33 ppm, consistent with **PIL 1**. No additional phosphorous peak corresponding to a phosphorane (Chart 5-1) was observed. The **PIL 1**/PhMgBr THF mixture was then quenched with water and extracted with dichloromethane and the extracts were analysed by GC-MS to check for the decomposition products of the **PIL 1**, namely hexene and tetradecyldihexylphosphine and the results showed no decomposition of the of the starting material, **PIL** solvent.



$R = C_6H_{13}$
$R_2 = C_{13}H_{27}$

Chart 5-1: A phosphorane, probable result of deprotonation of PIL.

The persistence of the Grignard solution in **PIL**s was confirmed by the addition of anhydrous bromine to a freshly made and an aged solution of the **PIL 1**/PhMgBr THF solution. After the reaction with bromine, the solution was quenched with distilled water and then extracted with hexanes. The extracts were analysed by GC-MS and the product yields were obtained by running GC-MS studies on a known concentration of the reference materials. Exclusive formation of PhBr (95%) was obtained when the freshly made **PIL 1**/PhMgBr THF solution was quenched with bromine and analysed by GC-MS. However, when the **PIL 1**/PhMgBr THF system, which was kept under an inert N_2 atmosphere for over a month, was quenched with bromine, 5% of biphenyl was detected along with PhBr (90%). Interestingly, for these aged solutions the presence of benzene, which would be obtained by the deprotonation of the **PIL 1** was not observed. Unfortunately, on complete removal of THF from the **PIL 1**/PhMgBr THF solution, the grignard reagent is no more stabilised and there is formation of biphenyl and a variety of products including dihexyl(tetradecyl)phosphine (*m/z* = 398.4) and hexene (*m/z* = 84.1) were formed due to the decomposition of the **PIL 1**. Hence, for best results a 1:3 ratio of THF:**PIL 1** was used.

To solve this problem of decomposition a different **PIL** was used. Trihexyl(tetradecyl) phosphonium decanoate, **PIL 2** was found to form stable *ether free* Grignard solutions without detectable decomposition of the **PIL**. To prepare these solutions 1 mL of THF were added to **PIL 2** in order to reduce the freezing point and the viscosity of the **PIL**. The solution was cooled to -78°C, followed by the addition of Grignard reagents dissolved in THF. The mixture was warmed to room temperature and stirred for 15 minutes and then THF was removed under vacuum. ^{1}H NMR spectroscopy was used to check for the complete removal of THF. The *ether free* Grignard solution was stable over a month under an inert N_2 atmosphere and this was confirmed by ^{31}P NMR spectroscopy and reactivity studies performed in the **PIL 2**/PhMgBr solution. The ^{31}P NMR spectrum contained a single resonance peak at 33 ppm, which was consistent with the chemical shift of **PIL 2**, therefore indicating no deprotonation or decomposition of the ionic liquid.

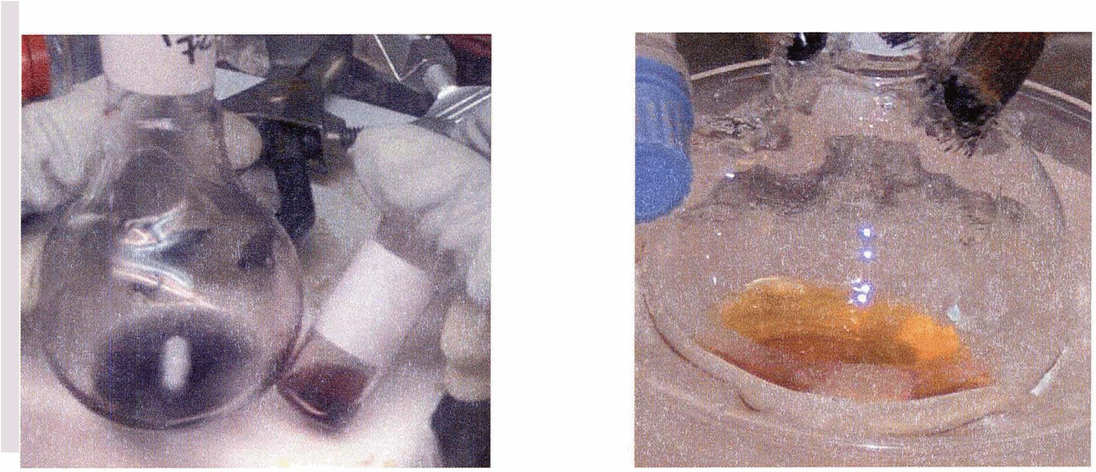


Figure 5-1: Colour change of PIL 2 on the addition of PhMgBr.

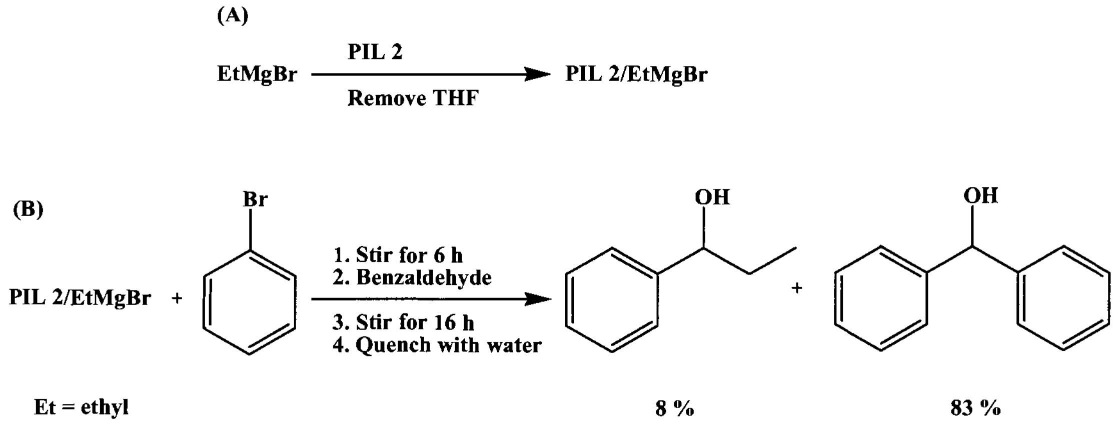
There was a colour change from pale yellow through a blue *via* burgandy (left) to orange red (right) when PhMgBr in THF was added drop wise to **PIL 2** (Figure 5-1) to make a 1 M solution. This unusual blue colour can be attributed to the interaction of a carbonyl group of **PIL 2** decanaote anion with the Grignard reagent to make a stable intermediate anion radical, which appeared blue.[199] We propose that coordination between the magnesium centre and the oxygen donor site from the decanoate anion has an important role to play in the stability of the new solutions (**PIL 2**/PhMgBr).[199] Interestingly, the coloured **PIL 2**/PhMgBr solutions were found to react normally with aldehydes and ketones, as will be detailed later. One point to be noted is that Grignard reagents are usually reactive towards carboxylate, however in this case the Grignard reagents did not react with the carboxylate anion of **PIL 2**. This stability is shown in the reactivity studies described later and the reason for the inertness of Grignard reagent towards the carboxylate anion will be discussed later in section 5.5.

After our report of Grignard reactions in **PIL**s, Wilhelm *et. al.* reported the use of a new imidazolium-based ionic liquid, 1,3-dimethyl-2-phenylimidazolium cation to overcome the deprotonation problem observed in **IIL**s. As reported, first THF was removed from commercially available solutions of a Grignard reagent, which was then added to the imidazolium-based ionic liquid to make the ionic liquid/Grignard reagent mixture. They claimed that this mixture did not contain any THF. However, when we repeated these reactions, we found out that even though the THF was removed under vacuum from the commercially available Grignard solutions, it still contained two molecules of THF bound to every magnesium centre. X-ray studies on crystalline Grignard reagent showing the presence of two THF molecules for stabilisation has also been previously reported.[200]

5.4 Attempted Preparation of Grignard Reagents and Transmetallation Reactions in PILs

Attempts to generate Grignard reagents in the **PIL**s by the reaction of phenylbromide and magnesium metal were not successful. This might be because the oxidative addition reaction of the magnesium metal into the carbon halide bond is slow and an additional co-solvent or a halide might be needed in order to facilitate this reaction. A recent publication has reported that a similar organometallic reagent, an alkylzinc complex was synthesised in a pyridinium based ionic liquid, but only in the presence of a bromide ion impurity.[201] It was also noted that the solution during this reaction was blue in colour and a viologen; which is toxic for the human health. Hence it is difficult to consider this reaction as "Green".

Despite the fact that we were not able to prepare the Grignard reagent in the **PIL**s, we were able to carry out transmetallation reactions in **PIL 2**. To cold **PIL 2**, ethylmagnesium bromide in THF was added and the molecular solvent (THF) was removed under vacuum as shown in Scheme 5-3 A. To this *ether free* solution, as tested by ^1H NMR spectroscopy and GC-MS, bromobenzene was added and stirred for 6 hours. To confirm if transmetallation reaction occured in this system, benzaldehyde was added and the mixture was stirred for an additional 16 hours followed by an aqueous quench and extraction with dichloromethane to give diphenyl-methanol in 83% yield. It was observed that the transmetallation reaction was not complete since a small amount of 1-phenyl-propan-1-ol (8%) was produced as shown Scheme 5-3 B.



Scheme 5-3: Transmetallation reaction between phenylmagnesium bromide and bromobenzene.

5.5 "Switch-Hitting" Behaviour of Grignard Reagents in Molecular Solvents and PILs

5.5.1 Introduction

The chemistry of Grignard reagents has primarily been studied in molecular solvents, mostly in THF and ethers.[196] As explained in section 5.3, we found that solutions of Grignard reagents dissolve and persist in **PIL**s. This discovery prompted us to compare the general reactions of Grignard reagents in molecular solvents and ionic liquids. The generation of persistent radicals and reactions of Grignard reagents with *p*-benzoquinone in molecular solvents and **PIL**s are described in this section. The identity of these radicals in molecular solvents and **PIL**s were shown by EPR studies as well as by using radical traps.

It was generally believed that the Grignard reaction proceeded *via* an ionic intermediate[202] until investigations using EPR spectroscopy revealed the formation of radical species in the reactions with benzophenone and its substituted derivatives.[203, 204] Grignard reagents are strong reducing agents and are easily oxidized, hence they are good candidates for electron transfer (**ET**) reactions. The oxidation potential of the Grignard reagent, namely PhMgBr, was measured in **PIL 1** and was found to be – 0.10 V *versus* saturated calomel electrode at a scan rate of 300 mVs^{-1} with ferrocene as an internal standard. This value was comparable to the estimated value of – 0.05 V for PhMgBr in THF.[205]

Grignard reagents are carbanion equivalents and are susceptible to both the electron transfer mechanism as well as the conventional polar mechanism.[206] As a result, in the presence of a good electron acceptor Grignard reagents cause a mechanistic dilemma of polar reactions *versus* electron transfer reactions and very often it is difficult to separate which pathway occurs. When there is electron transfer from electron-rich molecules to electron-deficient molecules, radical pairs can be produced. For Grignard reagents it is generally accepted that electron transfer leads to the formation of a radical ion pair and the collapse of this pair in the solvent cage (SC) provides a mechanism for the formation of new carbon-carbon bonds.[207]

This prompted us to study the reactivity of Grignard reagents with *p*-benzoquinone in molecular and ionic solvents, since quinones are known to be potential electron acceptors as well as electrophiles in polar solvents.[208] Previous reports indicated that the reaction between a Grignard reagent and a quinone is dependent on many factors namely the quinone substituents and the solvent.[209, 210]

5.5.2 A Novel "Reaction" between a PIL and O_2

Before carrying out any reactions, EPR studies[1] were performed on the **PIL**s to check for the presence of any paramagnetic species. Prior to spectroscopic analysis, the **PIL**s were purified as described in section 4.7.2. The first sample was prepared under inert atmosphere (nitrogen) and no signal was obtained in the EPR study of pure **PIL 2** as shown in Figure 5-2 A. However, when the **PIL 2** was exposed to air a broad, weak and featureless EPR signal at $g \approx 2$ was observed (Figure 5-2 B). Interestingly, the EPR signal decreases on pumping the headspace above the ionic liquid **(IL)** and after continuous pumping for a period of 24 hours almost no signal was observed (Figure 5-2 C). The recovery of the previous EPR signal was attained by the exposure of the diamagnetic **PIL** to dried oxygen gas. To help in the identification of the radical present, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a radical spin trap was added to **PIL 2**, which was previously exposed to air. Spin traps such as DMPO react with short-lived radicals to yield persistent paramagnetic products, which are detectable with EPR spectroscopy and exhibit distinctive ^{1}H and ^{14}N hyperfine couplings for particular substituents. This reaction produced a distorted four line spectrum as shown in Figure 5-3 with couplings of ~1.3 mT.

The distortion of the spectrum was assigned to viscosity effects. This data was consistent with the superoxide adduct of DMPO. The mechanism by which the superoxide adduct of DMPO was formed is not known, however we believe that there

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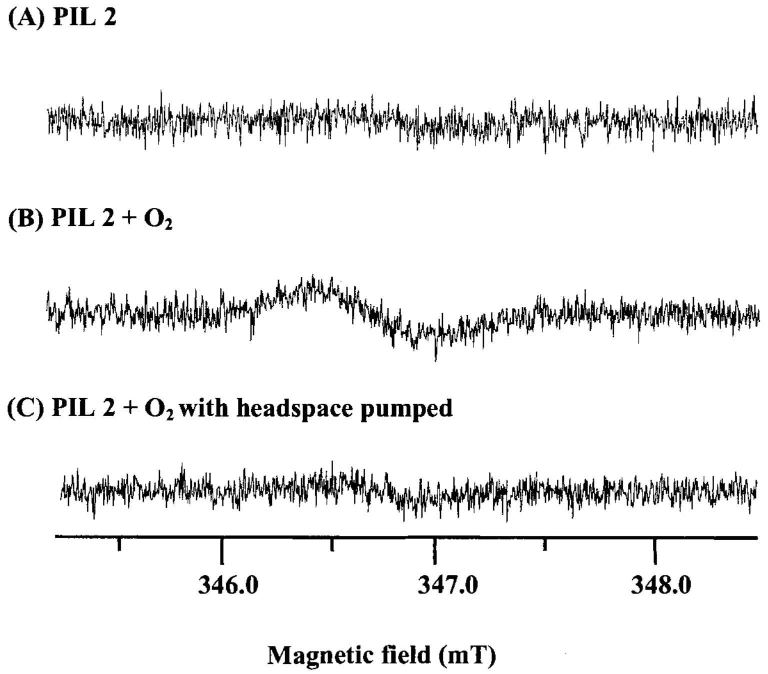
[1] The EPR spectrum was recorded by Stephanie Taylor and Dr Charles Walsby at Simon Fraser University.

might be a donation of an electron to dioxygen by an unknown species, possibly the anion of the **PIL**.


(A) PIL 2

(B) PIL 2 + O_2

(C) PIL 2 + O_2 with headspace pumped

Figure 5-2: EPR spectra of (A) PIL 2 (B) PIL 2 + O_2 (C) PIL 2 + O_2 with headspace pumped. Experimental conditions: modulation amplitude: 0.4 mT, MW freq. = 9.83 GHz, scan time = 41.94 s, time constant = 5.12 ms, microwave power = 0.64 mW.

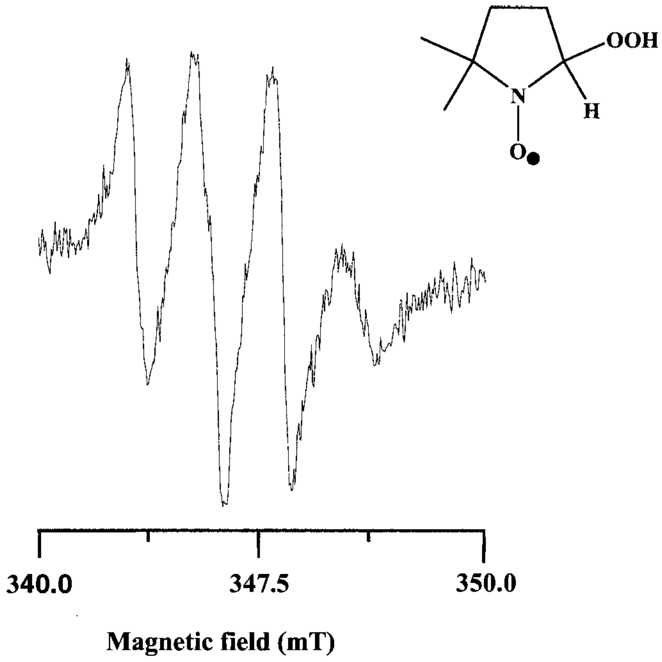


Figure 5-3: EPR spectrum of PIL 2 + O_2 + DMPO. Experimental conditions: 0.1 mT, MW freq. = 9.82GHz, scan time = 3156.29 s, time const. = 5.12 ms, microwave power = 0.64 mW.

5.5.3 Generation of Radicals in PILs

ILs are known to support persistent radicals.[6] To illustrate this, a radical, 2,2,6,6-tetramethylpiperidin-*N*-oxide (TEMPO), was added to **PILs** and it was found to be persistent. It exhibited a well-resolved three line spectrum at g ≈ 2, as shown in Figure 5-4 with some line broadening due to viscosity effects.[211]

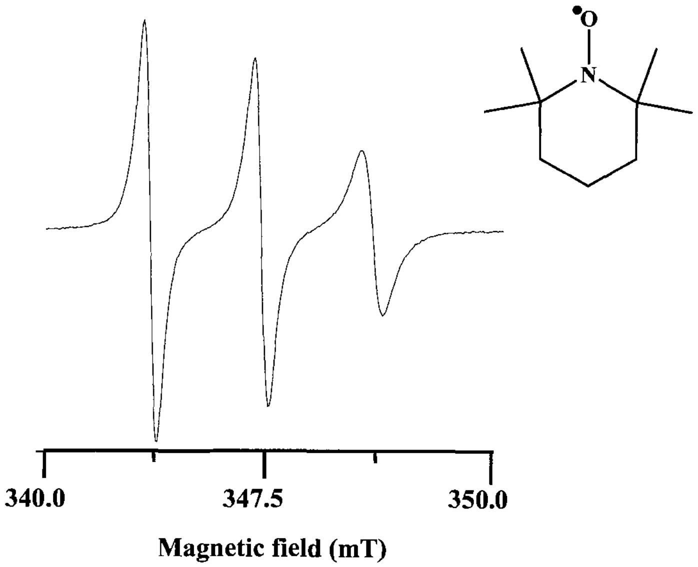
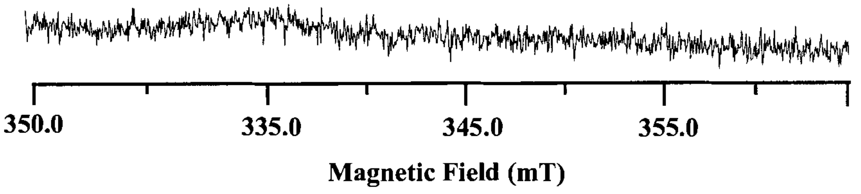


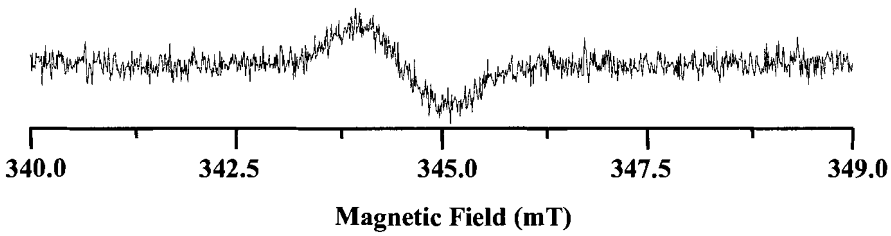
Figure 5-4: EPR spectrum of PIL 2 with TEMPO. Experimental conditions: modulations amplitude = 0.25 G, MW freq. = 9.82 GHz, scan time = 20 s, time const. = 10.24 ms, microwave power = 0.64 W.

As mentioned before, there was a colour change on the addition of Grignard reagents to **PILs** suggesting the presence of paramagnetic species. To identify what caused the colour change, careful examination of the starting materials and the **PILs** were performed by EPR studies. In all cases, Grignard reagents and **PILs** were individually proved to be diamagnetic with no EPR signal as shown in Figure 5-5. EPR studies were also performed on a sample of THF through which oxygen was bubbled and no EPR signal was observed.

(A) Phenyl Magnesium Bromide in THF



(C) Phenyl Magnesium Bromide in THF opened to air



(B) PIL 2

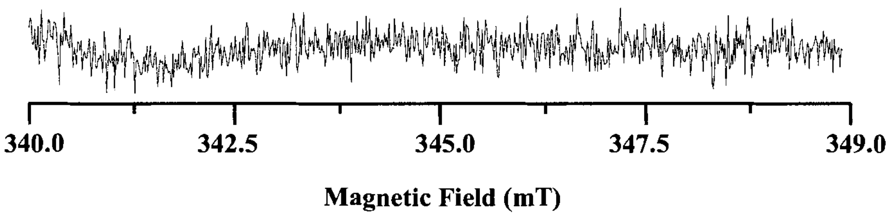


Figure 5-5: EPR spectra of (A) PhMgBr in THF using a flat cell, (B) PhMgBr in THF opened to air in flat cell, (C) PIL 2. Experimental Conditions: For A: modulation amplitude: 1.0 mT, MW freq. = 9.72 GHz, scan time = 41.94 s, time const. = 5.12 ms, microwave power = 0.64 mW. For B: modulation amplitude: 1.5 mT, MW freq. = 9.72 GHz, scan time = 41.94 s, time const. = 5.12 ms, microwave power = 0.64 mW. For C: modulation amplitude: 1.0 mT, MW freq. = 9.72 GHz, scan time = 41.94 s, time const. = 5.12 ms, microwave power = 0.64 mW.

The ESR studies of the blue solution gave a very weak signal, which overlaped with the signal obtained when the **PIL** was opened to air, suggesting the presence of a small amount of oxygen as impurity. However, when the nitrone spin trap, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was added to **PILs**/PhMgBr, a well-resolved 6-line spectrum was obtained during the EPR studies as shown in Figure 5-6. A few drops of toluene was later added to reduce the viscosity of the solution.

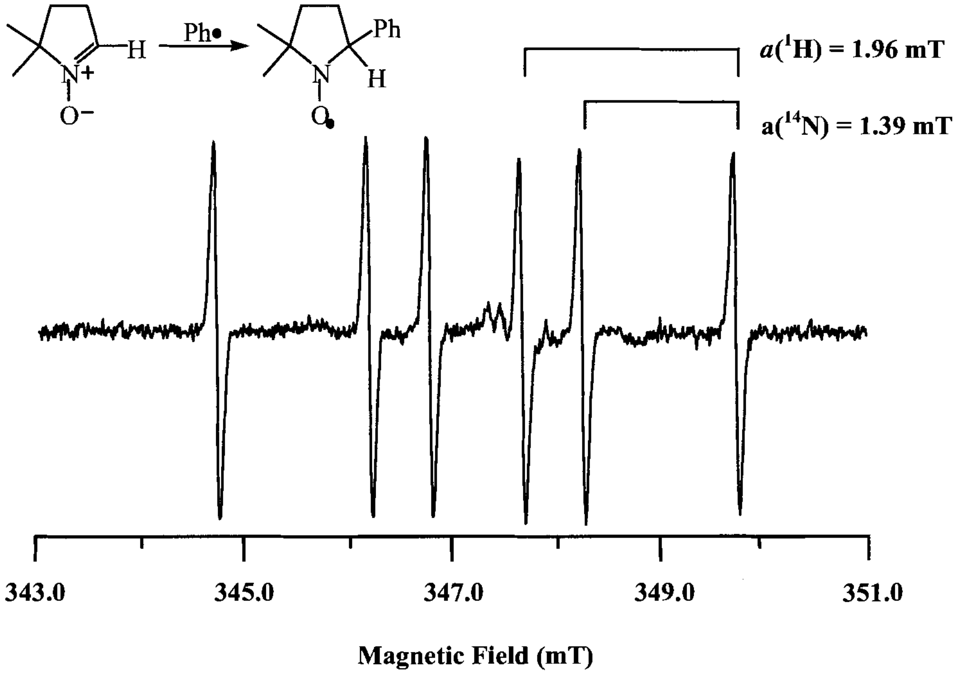


Figure 5-6: EPR spectrum of PIL 2/PhMgBr with DMPO diluted with toluene. Experimental conditions: modulation amplitude: 0.025 T, MW frequency = 9.82 GHz, scan time = 20.0 s, time constant = 5.12 s, microwave power = 0.64 W.

The ^{1}H and ^{14}N hyperfine couplings measured from the EPR spectrum were used for the spectral simulation. The simulated spectrum fitted the EPR spectrum obtained experimentally and these coupling values corresponded closely with those reported for the phenyl adduct of DMPO in toluene.[212] Similar experiments on a Grignard reagent dissolved in toluene gave an almost identical spectrum indicating that the ionic liquid, while fulfilling its role as a solvent, was not participating in the reaction.[212]

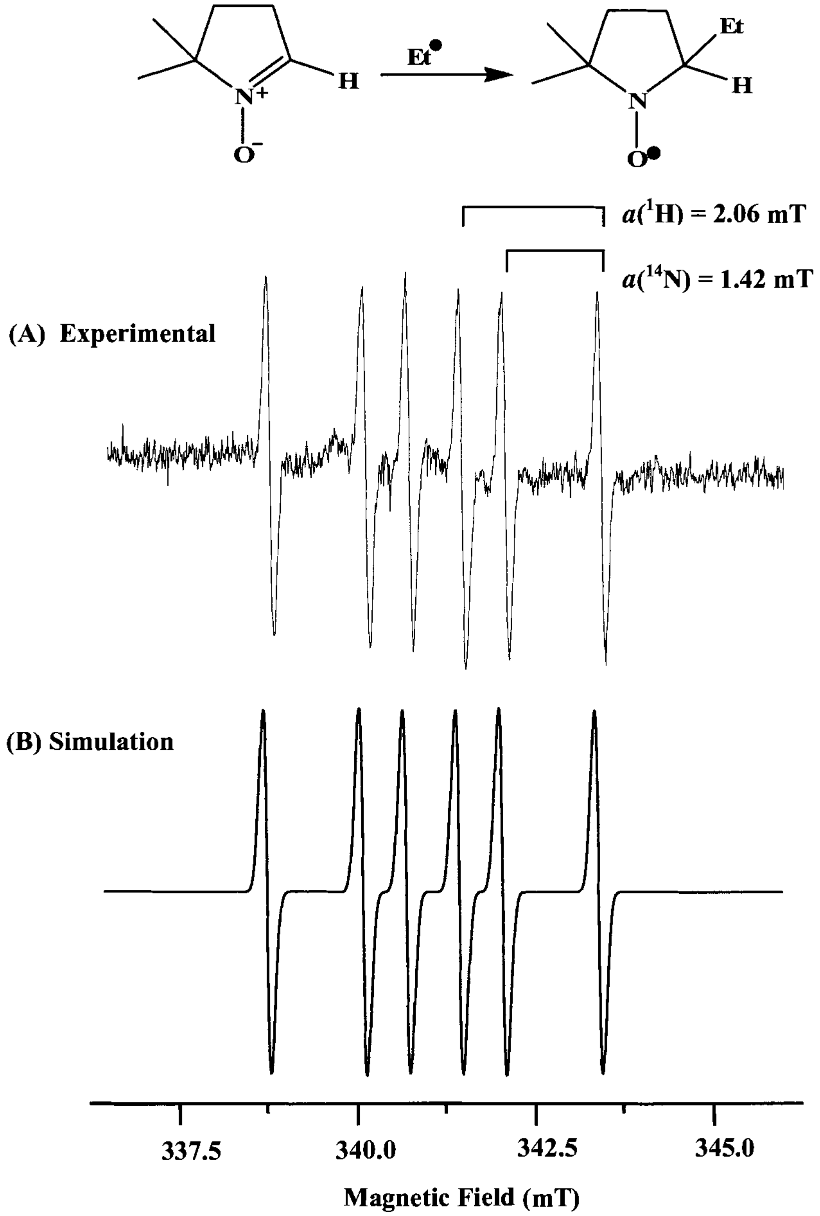


Figure 5-7: EPR spectra of (A) PIL 2/EtMgBr with DMPO diluted with toluene, and (B) simulation of (A). Experimental conditions: For A: modulation amplitude = 0.01 mT, MW frequency = 9.63 GHz, scan time = 671.089 s, time constant = 327.68 ms, microwave power = 0.64 W; For simulation (B): $a(^1H) = 2.06$ mT, $a(^{14}N) = 1.42$ mT, linewidth = 0.15 mT).

The EPR studies were repeated with another Grignard reagent, ethylmagnesium bromide. DMPO was added to a solution of **PIL 2**/EtMgBr followed by a few drops of toluene to reduce the viscosity of the solution. EPR studies showed a 6-line spectrum with distinctive ^{1}H and ^{14}N hyperfine couplings. These hyperfine couplings were used to simulate the spectrum, which was found to match the experimental data as shown in Figure 5-7. The coupling constants were in agreement with the literature report of the ethyl adduct of the DMPO.[213]

5.5.4 Reaction of *p*-Benzoquinone with Grignard Reagents in THF

Grignard reagents traditionally have been viewed as potential anions, capable of nucleophilic addition to carbonyl groups, for example *p*-benzoquinone (Chart 5-2). However, the mechanism of Grignard reaction still remains to be clarified since these reagents are also susceptible to a single electron transfer (SET) mechanism.[207] Electron transfer is a well-established chemical process that produces intermediate radical ion pairs due to electron transfer from electron rich donors to electron deficient acceptors. The subsequent coupling of such radical pairs provides an indirect mechanism for bond formation between a donor and an acceptor.[214] Hence, in the presence of good electron acceptors such as *p*-benzoquinone, Grignard reagents pose a mechanistic dilemma of nucleophilic addition *versus* a SET mechanism.

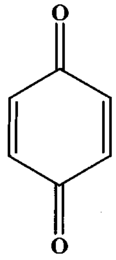
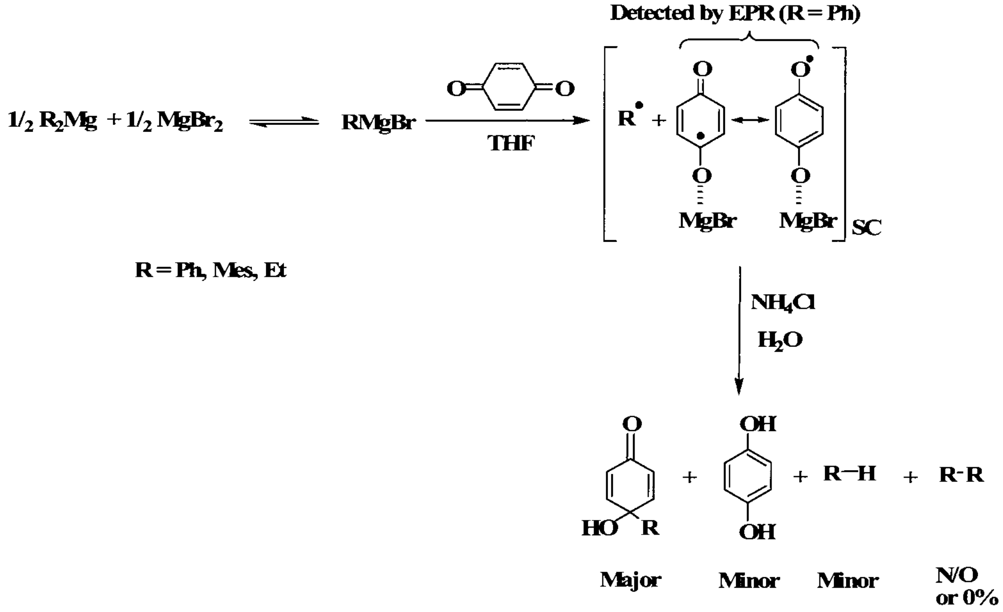


Chart 5-2: *p*-Benzoquinone.

To clarify the reaction pathway, Grignard reagents were reacted with *p*-benzoquinone in a molecular solvent (THF) and in **PIL**s. Three different Grignard reagents were used, namely phenylmagnesium bromide, ethylmagnesium bromide (EtMgBr) and 2,4,6-trimethylphenylmagnesium bromide (MesMgBr). Reported below are the detailed results of the reaction with PhMgBr. The products yields of the other Grignard reagents, which proceed *via* the same reaction mechanism are summarised in Table 5-1. Additon of PhMgBr to a yellow solution of *p*-benzoquinone in THF produced a blue solution over a blue precipitate. Product analysis by ^{1}H NMR spectroscopy and GC-MS showed the presence of 4-hydroxy-4-phenyl-2,5-cyclohexadienone (Scheme 5-4), a small amount of hydroquinone and benzene as shown in Table 5-1.



Scheme 5-4: Reaction of Grignard reagent with BQ in THF.

Solvent	RMgBr	BQ-R	Hydroquinone	R-H	R-R
THF	PhMgBr	94%	3%	3%	0%
	MesMgBr	97%	3%	4%	0%
	EtMgBr	80%	20%	N/O	N/O
PIL	PhMgBr	15%	85%	0%	80%
	MesMgBr	20%	80%	0%	78%
	EtMgBr	25%	75%	N/O	N/O

Table 5-1: Product analysis and yields of Grignard reagent with BQ in THF and PIL.

This reaction could be regarded as a nucleophilic addition of the Grignard reagent to the *p*-benzoquinone to give the adduct, however, when the blue solution, obtained after addition of PhMgBr to *p*-benzoquinone (**BQ**), was analysed by EPR spectroscopy, a signal was obtained showing the presence of a paramagnetic species. A 9-line spectrum with two pairs of distinct ^{1}H hyperfine couplings: $a(^1\mathrm{H} \times 2) = 0.25$ mT, $a(^1\mathrm{H} \times 2) = 0.22$ mT (Figure 5-8) was obtained. The coupling constants are not comparable to the value of 0.24 mT for the *p*-semiquinone radical,[215] suggesting that this species is an asymmetric *p*-semiquinone radical adduct. The *p*-semiquinone radical adduct can either have a metal bound to the oxygen or a phenyl group attached to the carbonyl carbon to be asymmetric. However, there was a lack of extra hyperfine coupling interactions, which would only occur if the phenyl group was attached to the carbonyl carbon. This indicated that the reduction in symmetry is due to an interacting atom with a low abundance of nuclear spin bearing isotopes, which in this case is likely magnesium. Magnesium has a 90% natural abundance of $I = 0$ isotope. The data recorded was consistent with an ionic type of interaction of a magnesium centred cation derived from the Grignard reagent with the anionic oxygen of the radical. This was also supported by reactivity studies where the solution was quenched with water and extracted with dichloromethane. The extracts were analysed by GC-MS and this showed the presence of hydroquinone and a very small amount of benzene, but the phenyl adduct was not observed.

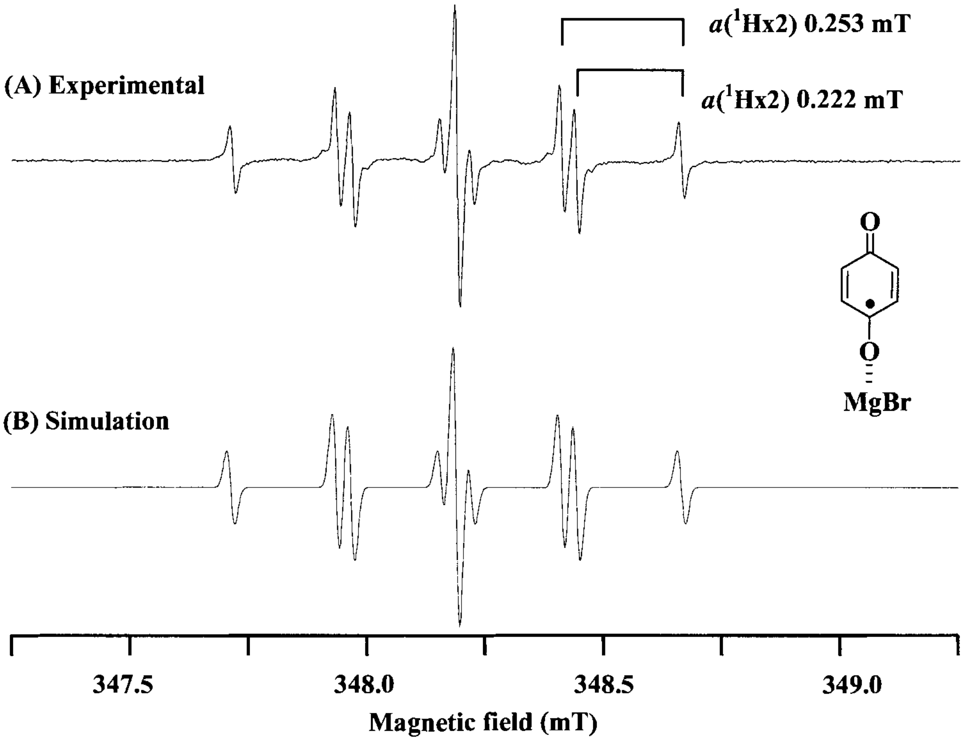


Figure 5-8: EPR spectra of the filtrate of PhMgBr with BQ in THF.

The blue solid obtained after filtration was dried and analysed by elemental analysis. It was found to be paramagnetic as well, however it gave a broad unresolved EPR spectrum. Interestingly, when the blue powder was washed repeatedly with THF a blue solution was obtained that gave the same 9-line EPR spectrum found previously, indicating the presence of coordianted unsymmetrical benzoquinone radical. Taken in total, the Mg•••*p*-semiquinone adduct is the sole paramagnetic product of this reaction.

Aqueous work-up of the mixture (blue solution and the blue precipitate obtained) produced 4-hydroxy-4-phenyl-2,5-cyclohexadienone,[216] hydroquinone[207] and a small amount of benzene as shown in Scheme 5-4 above. The blue solution in THF and blue precipitate were also analysed separately. When the blue solution was quenched with water, extracted with dichloromethane and then analysed by GC-MS, a small amount of benzene was observed.

We have probed the reaction system to account for benzene. In principle, benzene could have been: (1) present in the phenylmagnesium bromide Grignard reagent; (2) formed by quenching the phenylmagnesium bromide with water or; (3) formed by hydrogen atom abstraction from the solvent, THF in this case. To confirm the absence of benzene from the phenyl magnesium bromide, the Grignard reagent was quenched with D_2O. The result showed complete conversion of phenylmagnesium bromide to deuterated benzene (C_6H_5D), as determined by GC-MS, giving a *m/z* peak at 79.1. To verify the origin of the hydrogen atom obtained by the phenylmagnesium bromide, the filtrate from the reaction mixture of phenylmagnesium bromide with benzoquinone in THF was quenched with D_2O. No C_6H_5D was observed, instead the putative phenyl radical abstracts a hydrogen atom from THF to form non-deuterated benzene with a *m/z* peak at 78.1.

Although this reactivity appears as a *formal* nucleophilic attack, it is more likely that an electron transfer occurred to give a radical pair, which eventually collapsed to give the observed products (persistent radical effect).[217] The persistent radical effect (PRE) is a principle that explains the highly selective cross-coupling between a persistent and a transient radical when both species are formed at equal rates. In this case, after electron transfer *p*-benzoquinone radical anion, $\mathbf{BQ}^{\bullet-}$ and putative $\mathbf{Ph}^{\bullet}$ radicals are formed side by side, which later collapse to give **BQ-Ph** as shown in Scheme 5-5. A small amount of the $\mathbf{Ph}^{\bullet}$ can escape the cage and abstract a hydrogen atom from THF to form benzene as shown in Table 5-1. This showed that the lifetime of the putative $\mathbf{Ph}^{\bullet}$ radical is not long enough to combine with another $\mathbf{Ph}^{\bullet}$ radical to give **Ph-Ph** instead it abstracts a hydrogen atom to produce benzene.

5.5.5 Reaction of *p*-Benzoquinone with Grignard Reagents in PIL

When the same reaction (*p*-benzoquinone and Grignard reagents) was performed in **PIL**s, a completely different reaction occurred as indicated by product analysis (Table 5-1). When *p*-benzoquinone was added to a freshly prepared solution of **PIL 2**/PhMgBr or **PIL 1**/PhMgBr, the colour of the solution changed from orange to dark blue without the formation of a precipitate. After stirring for 3 hours, aqueous work-up was carried out on the dark blue solution (from **PIL 2**/PhMgBr) and analysis of the products obtained gave hydroquinone (85%) and 4-hydroxy-4-phenyl-2,5-cyclohexadienone (15%). The blue solution was also studied by EPR spectroscopy (only R = Ph) and the spectrum indicated the presence of two paramagnetic species (one major product and one minor product) as shown in Figure 5-9.

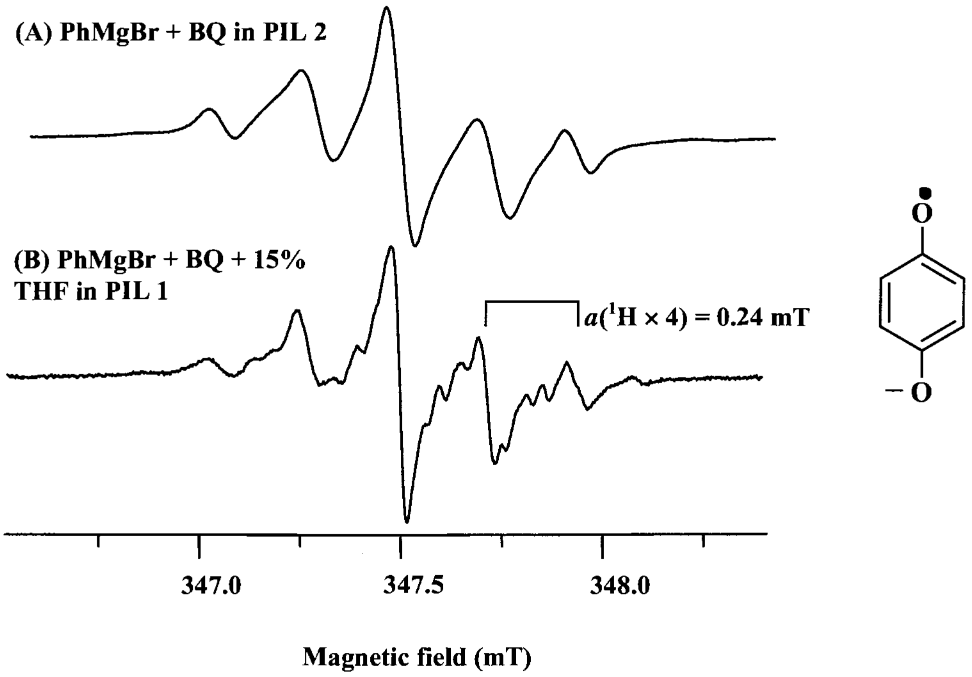


Figure 5-9: EPR spectra of $BQ^{\bullet-}$ radicals in PIL 1 and PIL 2.

The predominant species exhibit a five-line spectrum (≈ 80% identified by EPR studies) consistent with hyperfine couplings from four equivalent protons with $a(^{1}H)$ = 0.24 mT, which is in agreement with the literature value for the *p*-benzoquinone radical anion, $\mathbf{BQ^{\bullet-}}$.[215] This *p*-benzoquinone radical anion was obtained by electron transfer from PhMgBr to **BQ**. The broadening of the peaks can be attributed to the presence of a small amount of $\mathbf{[BQ\text{-}R]^{\bullet-}}$ present due to nucleophilic attack. In **PIL 1**, splitting of the five-line spectrum was observed as shown in Figure 5-10 and this indicated that the broad five-line spectrum was a mixture of the *p*-benzoquinone radical anion and the *p*-benzoquinone radical adduct. A simulation was carried out and showed that there was a mixture of the *p*-benzoquinone radical anion and the *p*-benzoquinone radical adduct in the ionic liquid (Figure 5-10). The overlap of the simulation and experimental EPR spectrum is also shown.

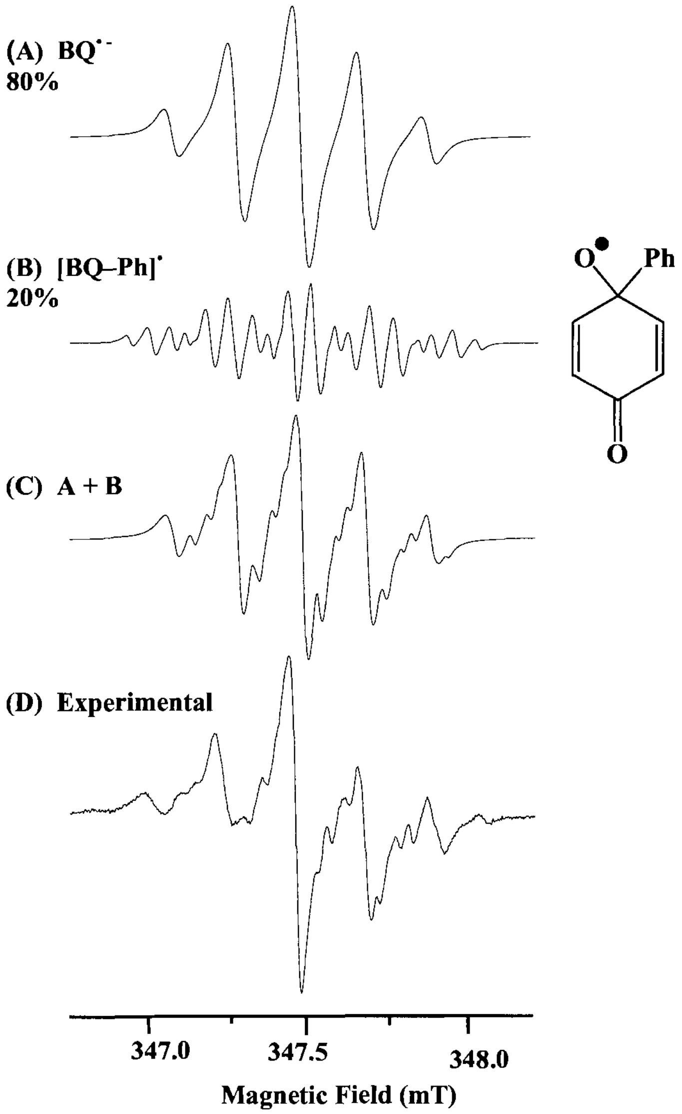
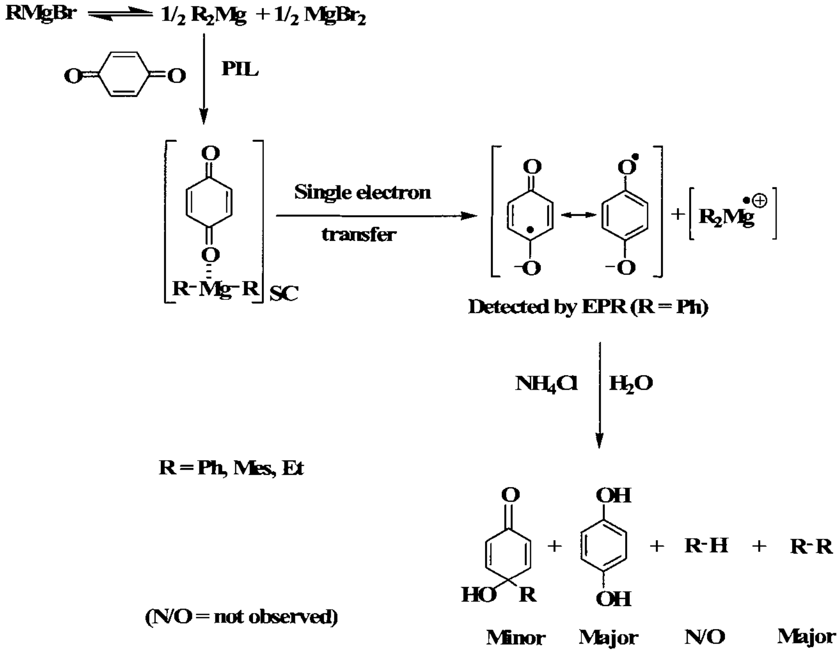


Figure 5-10: EPR spectra of (A) BQ$^{\bullet-}$ (B) [BQ–Ph]$^{\bullet}$ (C) A + B (D) PhMgBr + BQ in PIL 1. Simulation conditions: For A: *a*(^{1}Hx2) = 0.230 mT, *a*(^{1}Hx2) = 0.250 mT, line width 0.06 mT. For B: *a*(^{1}Hx2) = 0.242 mT, *a*(^{1}Hx2) = 0.165 mT, *a*(^{1}Hx2) = 0.066 mT, *a*(^{1}H) = 0.055 mT, linewidth 0.022 mT.

When the spectrum of PhMgBr and **BQ** in **PIL 1** with 15 % THF was compared to that performed in **PIL 2**, it was observed that both solutions contained the same radical species in very similar relative concentrations. A better resolution was obtained for **PIL 1**/THF solution, thus allowing us to determine that both contain a small amount of (≈ 20%) of the *p*-semiquinone radical adduct (**BQ-R$^{\bullet}$**) derived from the formal addition of a phenyl radical to **BQ**. The relative proportions of the radical species as determined by

EPR studies are in close agreement with the corresponding species from aqueous work-up.

For the reaction between PhMgBr and *p*-benzoquinone in **PIL 2**, the fate of the Grignard reagent was found to be biphenyl (≈ 80%). An explanation for this is **PIL 2** is more polar and its anion is a better donor than THF, hence a shift in the Schlenk equilibrium towards R_2Mg would occur. Single electron transfer occurs at this stage to form a *p*-benzoquinone radical anion, which on quenching gave a high yield of hydroquinone (Scheme 5-5). **Ph$^\bullet$** is linked to the magnesium metal ($PhMgPh^{\bullet+}$), which reductively eliminate to give **Ph-Ph**. This kind of reductive elimination has been previously observed in a diarylcadmium reagent.[218]

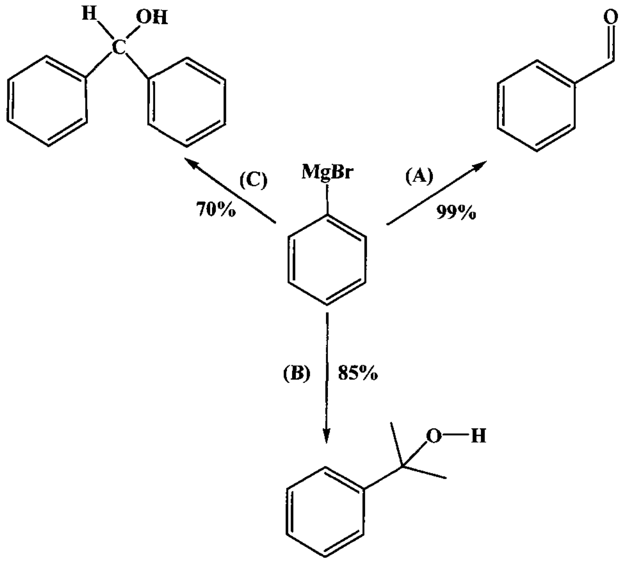


Scheme 5-5: Reaction of Grignard reagents with BQ in PILs.

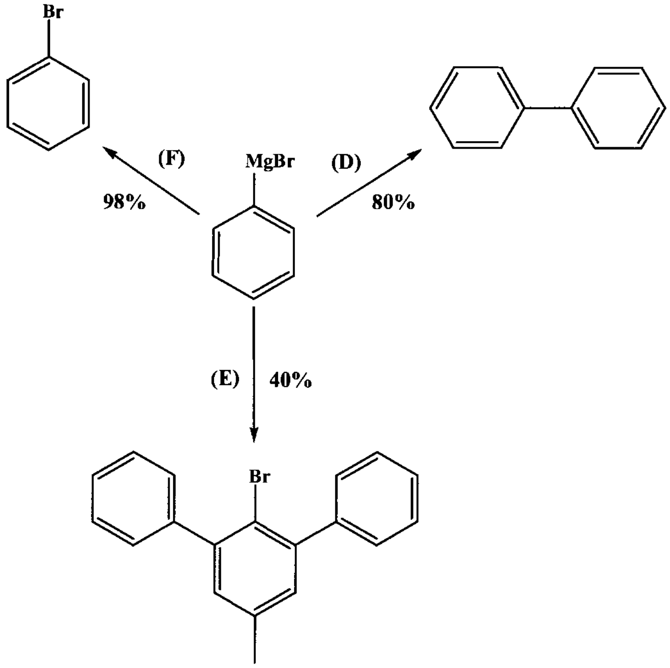
Analogous studies were performed with other Grignard reagents namely 2,4,6-trimethylphenylmagnesium bromide and ethylmagnesium bromide and the same kind of reactivity was observed in **PIL 2**. Finally, neither the formation of the $R_4P^{\bullet}$ was observed[219] nor the degradation of the **PILs** as would be suggested by the detection of tetradecyl(dihexyl)phosphine and hexene.

5.6 Carbon-Carbon Bond Formation Reactions using a Grignard Reagent in PILs

Grignard reagents are highly versatile tools for building the carbon skeleton of complex organic molecules. Hence, a survey of reactions including addition to carbonyl compounds (A, B, C) (Scheme 5-6), coupling reactions (D), benzyne reactions (E) and halogenation (F) (Scheme 5-7) were performed on Grignard reagents in **PILs** at room temperature in order to check for the stability (F) and reactivity (A-D) of Grignard reagents in **PILs**. The yields obtained in the **PILs** were in the comparable range obtained in molecular solvents.[196]



Scheme 5-6: Reaction of PhMgBr/ PIL 2 with carbonyl compounds. A few drops of either toluene or hexanes were added to reduce the viscosity of the IL. Reaction conditions: (A) DMF, stirred for 3 h; (B) Acetone, stirred for 3 h; (C) Benzaldehyde, stirred for 2 h.

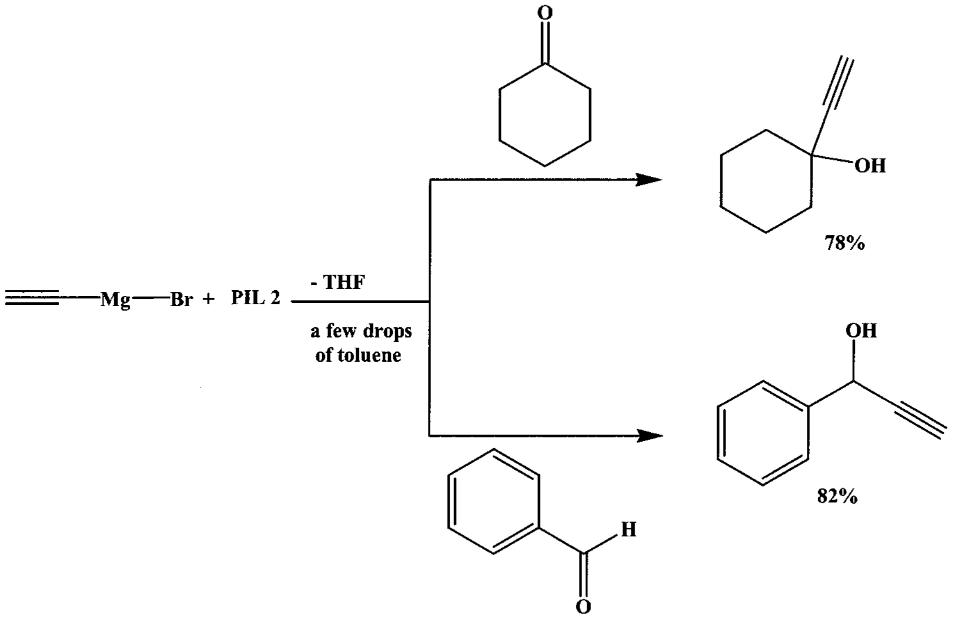


Scheme 5-7: Reactions performed in ether free PIL 2. A few drops of either toluene or hexanes were added to reduce the viscosity of the IL. (D) $CuCl_2$, stirred for 2 h; (E) 2,6-dibromo-4-methyl-iodobenzene, stirred for 3 h, quenched with Br_2; (F) Br_2, stirred for 1 h.

A stock solution of *ether free* 1 M **PIL 2**/PhMgBr was prepared and aliquots of the mixture were reacted with the electrophiles under conditions described in Scheme 5-6 and Scheme 5-7. After stirring for 16 hours, the reactions were quenched by the addition of distilled water under nitrogen and the products were extracted with hexanes. One point to be noted here is that the reaction conditions were not optimised. In the presence of hexanes and water, the mixture formed a three-phase system, with the organic layer on the top, ionic liquid in the middle and the aqueous layer at the bottom. The products, which were isolated from the organic layer, were analysed by GC-MS. In some cases, the low yields reported in Scheme 5-6 and Scheme 5-7 reflected the partitioning between the ionic liquid and the organic phase, however the yields can be improved by successive extractions using hexanes. Another method to remove the product from the **PILs** was by distillation and this could be achieved due to the high thermal stability of the **PILs** and the volatility of the products. Another Grignard reagent, 2,4,6-trimethylphenyl magnesium bromide with **PIL 2** was also studied and similar results were obtained as those reported for PhMgBr.

Among all the carbon-carbon bond formation reactions studied, reaction E (Scheme 5-7) is the most interesting one. It is a carbon-carbon bond formation reaction, which involves two benzyne intermediates.[220] This intermediate is very reactive and has a tendency to abstract a hydrogen atom or proton from a proton source. However, such a reaction is not observed in the **PIL**, suggesting that reactive molecules are relatively stable in the **PIL**s without hydrogen atom abstraction reactions occuring.

The reactivity and stability of another basic Grignard reagent, magnesium acetylides (ethynylmagnesium bromide) was also tested in **PIL**s. A known aliquot of 1 M ethynylmagnesium bromide in THF was added dropwise to **PIL 2** at -78 °C. The mixture was stirred until it warmed to room temperature and THF was pumped off in vacuo. A few drops of toluene were then added to reduce the viscosity of the solution. To aliquots of this solution, one equivalent of cyclohexanone and benzaldehyde was added and on quenching, 1-ethynyl-cyclohexanol (78%) and 1-phenylprop-2-yn-1-ol (82%) were obtained respectively without any observable degradation of the **PIL**s as shown in Scheme 5-8.



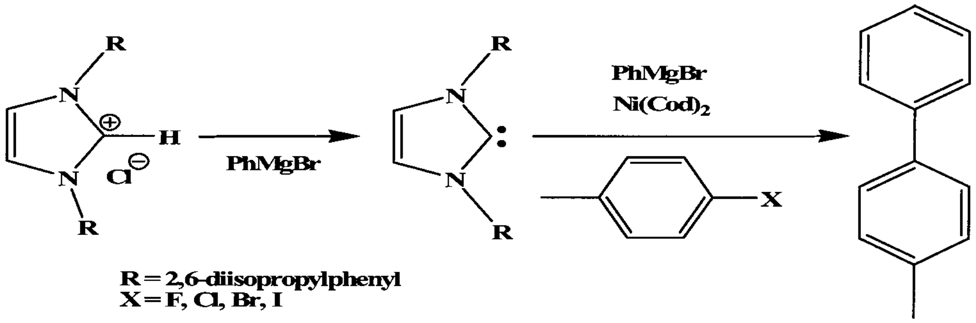
Scheme 5-8: Reaction of magnesium acetylides in PILs.

As shown in the reactivity studies above, **PIL 2** could be used as a good solvent medium for Grignard reactions. As explained before, most Grignard reactions are carried out in coordinating solvents, which are mostly ethers. These solvents are highly volatile and flammable and can be hazardous when used in large scale. Grignard reactions, being highly exothermic, need to be cooled at extremely low temperatures in ethereal solvent. However, **PIL**s have the benefit of having a high heat capacity; hence they do not require extreme cooling. **PIL 2** also demonstrates the potential to participate in "Green" processes since it can be washed with water and hexanes, dried, and re-used. Although the synthesis of Grignard reagents in **PIL**s was not successful as in ethers, transmetallation reaction of the Grignard reagent did occur as well as the previously discussed "new" chemistry.

5.7 Kumada-Corriu Reactions in PILs

Grignard reagents can undergo polar reactions as well as electron transfer reactions. Classical Grignard chemistry includes nucleophilic as well as catalytic reactions, however, the mechanism for the catalytic reactions are still debatable as they can occur through either polar or radical routes. We have shown that **PIL**s can support either radical or polar reaction pathways; hence they can be used as a reaction medium for catalytic reactions that involve either radicals or charge-separated intermediates. These are important synthetic tools for carbon-carbon bond formation reactions. However, some of these catalysts support reactions that involve species that are not compatible with most ionic liquids for numerous reasons such as (1) a low valent metal centre in the presence of (2) a strongly nucleophilic ligand in (3) a basic reaction media. To test the stability of the Grignard reagent in **PIL**s a Kumada-Corriu reaction was carried out. This involves the coupling of aryl Grignard reagents with aryl-halides in the presence of a Ni (0) complex of a nucleophilic carbene.

As explained before, **NHC**s and **NHC** complexes can be synthesised in **PIL**s. Taking advantage of this, an aliquot of the previously prepared solution of **PIL 2**/PhMgBr was also used as a host for a carbon-carbon bond formation reaction namely, the Kumada-Corriu reaction. This reaction involved coupling of the aryl-Grignard reagents with aryl halides in the presence of a Ni(0) complex of **NHC 2**, which was synthesised in a one-pot reaction as shown in Scheme 5-9.[221]



Scheme 5-9: Kumada-Corriu cross-coupling reactions in PIL 2.

There are other means for constructing new C-C bonds and one of the most powerful methods is by making use of transition metal catalysts. Among the growing number of palladium catalysed C-C coupling reaction the Suzuki-Miyaura reaction plays a leading role. In this reaction an aryl halide is coupled with an aryl or vinyl-boronic acid or boronic-ester to unsymmetric biaryls. The disadvantages of this reaction over the Kumada-Corriu cross coupling are (1) that the aryl or vinyl-boronic acid or ester are not commercially available and have to be synthesised (2) the palladium catalyst used is very expensive (250 mg for $357) compared to the nickel catalyst (2 g for $75).[m]

Hence, the Kumada-Corriu cross coupling reaction allows for a convenient and selective access to unsymmetrical biaryls. The formation of biaryls has been of great interest especially in catalytic cross-coupling reactions, which have successfully allowed the activation of aryl iodides, bromides and chlorides at room temperature; however, aryl fluorides remain quite inert. The activation of a C-F bond requires a highly electron rich centre such as Ni(0) and the use of a sterically hindered strongly basic, electron donating ligand such as **NHC 2**, which are both present in our system.[221] Also favouring the formation of biaryls from an aryl fluoride in the Kumada-Corriu system is the formation

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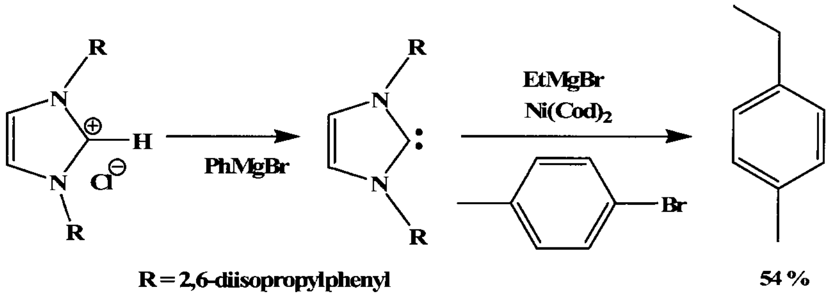
[m] Strem Catalogue 2005.

of strong Mg-F bonds (Scheme 5-9). The reaction was successfully repeated with 4-iodotoluene, 4-bromotoluene, and 4-chlorotoluene with the products yields reported in Table 5-2. In the reactions involving 4-bromotoluene and 4-iodotoluene there was a generation of *ca.* 25% of 4,4′-dimethylbiphenyl, a product due to a transmetallation reaction between PhMgBr and *p*-tolylhalide (transmetallation reaction in **PILs** was reported in section 5.4). It was observed that this reaction worked best for chlorotoluene and surprisingly can facilitate C-F bond activation.[222] These reactions have not been optimised.

Aryl halide	MePh-Ph	Me_2Ph_2
4-fluorotoluene	42%	0%
4-chlorotoluene	88%	0%
4-bromotoluene	73%	25%
4-iodotoluene	74%	22%

Table 5-2: Yields of Kumada-Corriu cross-coupling reaction in PILs.

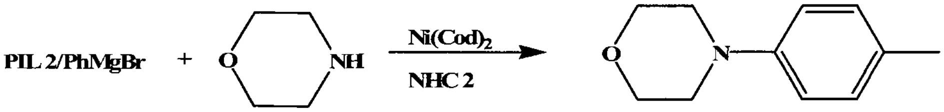
Kumada-Corriu type reactions involving alkyl Grignard reagents were also performed since these alkyl Grignard reagents are known to be more reactive than aryl Grignard reagents. The Grignard reagent used was ethylmagnesium bromide, which was reacted with 4-bromotoluene in **PIL 2** in the presence of Ni(0) catalyst of **NHC 2** to produce 4-ethyltoluene in a 54% yield (Scheme 5-10). This was interesting since ethylmagnesium bromide, being more reactive than phenylmagnesium bromide, is persistent in **PILs** and undergoes coupling reactions. Another reactive reagent, diethylzinc was also investigated with bromotoluene. This type of reaction has been rarely reported in literature and interestingly when reacted in **PILs** 68% yield of ethyltoluene was obtained, with no decomposition of the **PIL 2** in either case.



Scheme 5-10: Kumada-Corriu type reactions with alkyl Grignard reagent in PIL 2.

Carbon-carbon and carbon-nitrogen forming reactions are important for fundamental transformations in organic synthesis. Such reactions are generally useful and efficient when performed catalytically rather than stoichiometrically. Carbon-nitrogen bond formation reactions have been mediated by transition metal catalyst and we tried to carry out such reactions in **PIL**s.

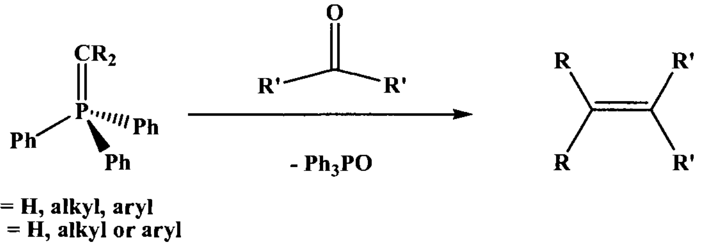
To test whether **PIL 2** supports amine formation, a coupling reaction was performed between **PIL 2**/PhMgBr and morpholine in the presence of a Ni(0) catalyst, which was prepared *in situ* by the reaction of *bis*(1,5-dicyclooctadiene)nickel (0) and **NHC 2**, as shown in Scheme 5-11. After quenching the reaction and analysis by GC-MS, 4-*p*-tolyl-morpholine was obtained in 58% yield. A small amount of biphenyl was also obtained as by-product due to homocoupling of the Grignard reagents.



Scheme 5-11: Amine synthesis in PIL 2.

5.8 Wittig Reactions in PILs

Phosphoranes such as Wittig reagents are some of the most valuable *carbon-based* nucleophiles. These reagents readily react with the aldehydes and ketones to produce C=C double bonds as shown in Scheme 5-12. Wittig reagents have been reported to be 'stabilised' ylides (pK_a of the conjugate acid *ca.* 8-11) in **IL**s. However, their generation in **IL**s has not been reported. Interestingly, we were able to generate not only a Wittig reagent but one that is highly basic, $Ph_3P{=}CH_2$ (pK_a of $[Ph_3P\text{-}CH_3]$ *ca.* 22.5 in DMSO) in **PIL**s and show its reactivity.



Scheme 5-12: Wittig reaction.

It was found to be possible to generate Wittig reagents in **PIL**s without any observable decomposition of the **PIL**s. For example a Wittig reagent was synthesised through the deprotonation of $[Ph_3PCH_2CH_3]^+[Br]^-$ in a solution of **PIL 2** containing either PhMgBr or other bases such as potassium *tert*-butoxide. The phosphorane produced was identified by a distinctive $^{31}P\{^1H\}$ resonance at 15 ppm,[223] consistent with the resonance observed for pure sample of $Ph_3P{=}CHCH_3$ *dissolved* in **PIL 2**. The resulting ylides (Table 5-3) were treated with aldehydes to generate an alkene and analysed by GC-MS after quenching with water and extracting with dichloromethane. It was noted that the E/Z isomers of the products could not be separated since their retention time were very similar. Hence, the reference used for the GC-MS studies was 1:1 ratio of E/Z isomers. A white residue was also obtained, which was characterised by mass spectrometry (278 amu) and found to be triphenylphosphine oxide, the by-product. The results of the C=C bond formation reactions in **PIL 2** are reported in the Table 5-3.

PIL and base	**Wittig Precursor**	**Wittig Reagent**	**RR'C=O**	**Alkene**	**Yield %**
PIL 2/PhMgBr	$[Ph_3PCH_2CH_3][Br]$	$[Ph_3P{=}CHCH_3]$	PhCH=O	$PhCH{=}CHCH_3$	96%
PIL 2 + $KOBu^t$	$[Ph_3PCH_2CH_3][Br]$	$[Ph_3P{=}CHCH_3]$	PhCH=O	$PhCH{=}CHCH_3$	88%
PIL 2/PhMgBr	$[Ph_3PCH_3][Br]$	$[Ph_3P{=}CH_2]$	PhCH=O	$PhCH{=}CH_2$	86%
PIL 2 + $KOBu^t$	$[Ph_3PCH_3][Br]$	$[Ph_3P{=}CH_2]$	PhCH=O	$PhCH{=}CH_2$	94%

Table 5-3: Yields of Wittig reactions in PIL 2.

5.9 Borane in PILs

5.9.1 Introduction

Borane (BH_3) is a six-electron compound with an empty p-orbital. In the gas phase or non-coordinating solvents, it exists as diborane, a hydride bridge dimer. Complexation of borane with Lewis basic solvents such as amines, sulfides, or ethers completes its octet and stabilises BH_3. The strength of the dative bond between borane and the Lewis base increases from ethers to amines. Boranes are extremely useful for the reduction of aldehydes, ketones, carboxylic acids, amides, lactams and nitriles. Although borane-tetrahydrofuran ($BH_3 \bullet THF$) is common, it is still volatile and highly flammable.

IILs can serve as useful materials for the transport of reactive gas such as BF_3 and PH_3.[162] PILs, especially those having a coordinating anion can form a stable coordination complex with borane, which makes the otherwise pyrophoric borane easy to handle and store. This work is an important contribution since it demonstrates a novel recyclable method for the delivery of a reactive and flammable gas to a reaction vessel using the new properties of the ionic liquid.

5.9.2 Synthesis and Stability of Borane Complexes of PILs

Borane (BH_3), being electron deficient, forms stable complexes with **PIL**s, having the empirical formula [R'_3RP][XBH_3], where X is the anion of the **PIL**. Two different methods were employed to synthesise these stable borane-phosphorous based ionic liquids: (1) passing gaseous B_2H_6 through the **PIL**s;[224, 225] (2) mixing one equivalent of a BH_3•THF solution with the **PIL**s followed by the complete removal of the THF by exhaustive evacuation. Both methods produced the same new **PIL** solutions, which were analysed by IR, ^1H and ^{11}B NMR spectroscopy and elemental analysis. The following species, $[BH_4]^-$, $[BH_3Cl]^-$, $[B_2H_7]^-$ and $[BH_2Cl_2]^-$ were observed for the new **PIL 1/BH$_3$** system as described by spectroscopic data below.

The IR spectra for these molecules were informative with B-H stretch in the 2000-2400 cm^{-1} regions. Specifically, the new **PIL 1/BH$_3$** system exhibited absorptions at 2212 (m), 2298 (s) and 2359 (s) cm^{-1} (Figure 5-11), which is consistent with the presence of $[BH_3Cl]^-$ as reported in the literature.[211, 226] **PIL 2/BH$_3$** exhibited peaks at 2139 (m), 2224 (m), and 2270 (s) cm^{-1} as shown in Figure 5-11. Relative to the C=O stretches of the decanoate anion of **PIL 2** (1579 cm^{-1}), a new peak for **PIL 2/BH$_3$** was observed at 1661 (s), consistent with coordination of the carboxylate anion. The **PIL 1/BH$_3$** ionic liquid is stable under an inert atmosphere but decomposes rapidly on exposure to air, apparent by the broad IR peak at 3330 cm^{-1}, which is due to a B-OH stretch.[226]

Unambiguous assignment of the ^1H NMR resonances of **PIL 1/BH$_3$** and **PIL 2/BH$_3$** was not possible because of the complexity of the spectra due to resonance overlap and high intensity of the proton peaks. For ^{11}B NMR spectroscopy, **PIL 1/BH$_3$** exhibited broad resonances including the sharp resonance peaks at –36 ppm corresponding to $[BH_4]^-$[227] and a broad peak corresponding to other boron anions such as $[BH_3Cl]^-$ anion to $[B_2H_7]^-$ and $[BH_2Cl_2]^-$ in a ratio of 1:100.[226] These boron hydride chlorides were obtained by ligand exchange, which have been previously reported.[226] A very broad signal *ca.* δ 50 to -25 ppm with sharp features at δ 18.6 ppm and -12.0 ppm and a sharp quintet at δ -35.3 ppm assigned to BH_4^- were observed. Elemental analyses of the new **PILs/BH_3** ionic liquids were in accord with the expected values.

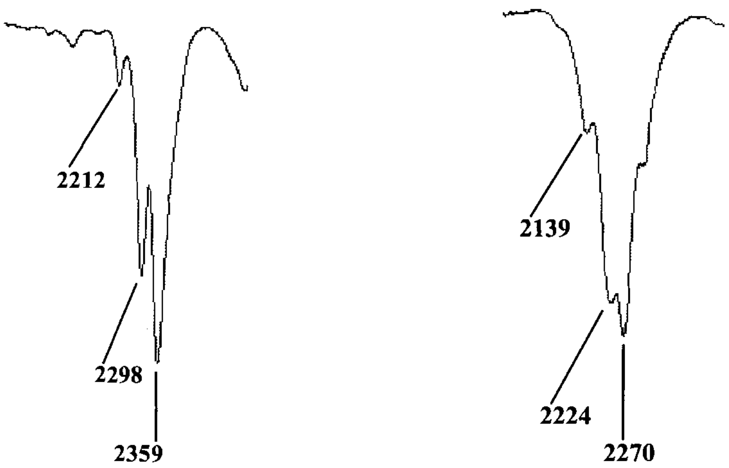


Figure 5-11: B-H stretches of PIL 1/BH_3 and PIL 2/BH_3.

To determine the number of hydrides available for reduction from the **PIL/BH_3** ionic liquids, a reactivity study using known amounts of **PIL 1•10%BH_3** and **PIL 2•10%BH_3** with a known excess of benzaldehyde was performed. This study revealed that there are *three hydrides available for reduction.*

5.9.3 Reductions using Borane in PILs

These new ionic liquids that contain borane, which were synthesised as explained in section 5.9.2, were used for classic reductions involving borane, namely reduction of the carbonyl groups. A series of reactions were performed by combining stoichiometric amounts (with respect to the number of hydrides available) of carbonyl compounds with the new **PIL/BH$_3$** compounds at room temperature. After the reaction was completed, the mixtures were quenched using saturated aqueous ammonium chloride solution and water followed by extraction using dichloromethane. Yields were determined by GC-MS of the extracts and the data presented in Table 5-4.

PIL/BH$_3$	Reactant	Product	Yield %
PIL 1/BH$_3$	Benzaldehyde	Benzyl alcohol	94
PIL 2/BH$_3$	Benzaldehyde	Benzyl alcohol	95
PIL 1/BH$_3$	Benzoyl Chloride	Benzyl alcohol	90
PIL 2/BH$_3$	Benzoyl Chloride	Benzyl alcohol	99
PIL 1/BH$_3$	Benzophenone	Benzhydrol	60
PIL 2/BH$_3$	Benzophenone	Benzhydrol	99
PIL 1/BH$_3$	Cinnamaldehyde	Cinnamyl alcohol	75
PIL 2/BH$_3$	Cinnamaldehyde	Cinnamyl alcohol	61
PIL 1/10%BH$_3$	Benzaldehyde	Benzyl alcohol	80
PIL 2/10%BH$_3$	Benzaldehyde	Benzyl alcohol	91

Table 5-4: Yields of reduction of carbonyl compounds with PILs/BH$_3$.

These anhydrous borohydride complexes were found to be recyclable and non-volatile, and hence they are a convenient source of hydride for standard chemical reductions.[228, 229] In our opinion these complexes can represent a new class of borane.[224] They may provide a new means of non-flammable *hydride transport* using a flowing medium, possibly allowing for a safer method of using boranes as an energy carrier.[162]

5.9.4 Other Hydrides as Reducing Agents in PILs

Reduction using other hydrides such as $NaBH_4$, $LiAlH_4$ and AlH_3 were also carried out in **PIL**s. $NaBH_4$ in **PIL 1** and **PIL 2** were found to reduce aldehydes and acid chlorides. A known amount of $NaBH_4$ was added to **PIL**s followed by a few of drops of toluene to reduce the viscosity of the mixture. To the white slurry, one equivalent of the carbonyl was added. After the reaction was stirred for 16 hours, it was quenched with saturated ammonium chloride and water and then extracted using dichloromethane. Analysis of the extracts by GC-MS gave the anticipated products as shown in Table 5-5. The yields were comparable to the reactions done in molecular solvent.

PILs/$NaBH_4$	Reactants	Products	Yield %
PIL 1/ $NaBH_4$	Benzaldehyde	Phenyl-methanol	99
PIL 2/ $NaBH_4$	Benzaldehyde	Phenyl-methanol	73
PIL 1/ $NaBH_4$	Benzoyl chloride	Phenyl-methanol	50
PIL 2/ $NaBH_4$	Benzoyl chloride	Phenyl-methanol	52

Table 5-5: Yields of reduction of carbonyl compounds in PILs/$NaBH_4$.

Among the reducing agents named above, $NaBH_4$ is the least reactive. The conventional solvents, which are often used to host these reactions, are ethanol and isopropanol. These solvents are relatively "Green" compared to other **VOC**s. On the other hand, $LiAlH_4$ and AlH_3, which are significantly more reactive than $NaBH_4$ are clearly incompatible with alcohols. Regrettably $LiAlH_4$ and AlH_3 also react with the cation portion of the **PIL**s to give tetradecyl(dihexyl)phosphine and hexene and the anion of **PIL 2** to give decanol, as determined by GC-MS, MS and NMR spectroscopy. When $LiAlH_4$ was added to **PIL 2** fizzing occurred and a certain degree of decomposition of the ionic liquid, **PIL 2** was observed. To identify the degree of decomposition **PIL 2** was treated with 10 mol % of AlH_3. After quenching with water, 10-15% decomposition of the ionic liquid was observed by the presence of hexene and phosphines in the solution,[230] consistent with a Hofmann-type elimination reaction.[231]

At the same time, there was also the generation of a new aluminum hydride species, which was capable of reducing aldehydes to alcohols and esters to aldehydes. The new **PIL 2** aluminium hydride solution was treated with water and extracted using hexanes. Analysis of the extracts showed the presence of decanol, obtained from the reduction of **PIL 2** anion, decanoate. Unambiguous assignment of the structure of the aluminum containing species has not been made, however reactivity studies showed the presence of two chemically reactive hydrides and the presence of the Al-H bond was confirmed by IR studies (ν(Al-H) 1767, 1717 cm^{-1}).

5.10 Interionic Interactions in PILs

As previously described in chapter 4, **PIL**s do not react with many strong bases, Grignard reagents, nucleophiles or certain hydrides. However, phosphonium salts have been found to interact with certain reagents and thus act as solvents and promoters (catalyst) for reactions such as nitroaldol reactions.[232] These phosphonium ions might function as mild Lewis acids and thus promote classical carbonyl addition processes.

As part of this study, we continued the investigation into the activation of carbonyl compounds by quaternary phosphonium cations as previously reported by McNulty *et. al.*[232] Although a plausible explanation for the interaction between the **PIL**s and carbonyl compounds has been suggested,[232] we realised that not one but two types of interactions between the solute (carbonyl compound) and the solvent (phosphonium centre) can occur. Coordination could occur through the interaction of the carbonyl oxygen with the quaternary cationic phosphonium site through a [P•••O] interaction (mode A) or through hydrogen bonding of the oxygen of the carbonyl to the hydrogen *alpha* to the phosphonium cation (mode B), as shown in Chart 5-3.

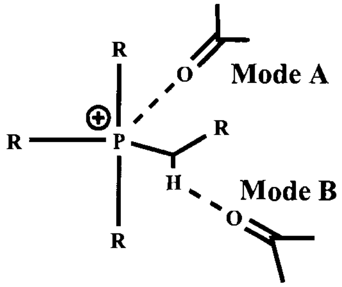


Chart 5-3: Possible interactions between a phosphonium ion and a carbonyl compound.

Since both modes are plausible, it is difficult to predict which type of interaction is preferred. The well known strength of the P-O bond supports mode A, however this interaction would require a reorganisation of the phosphorous coordination sphere resulting in a crowded and distorted trigonal bipyramidal geometry. This distortion is avoided in mode B, where the oxygen of the carbonyl is hydrogen bonded to the hydrogen *alpha* to the phosphonium cation. In order to probe the interaction between the phosphonium ion and the carbonyl, we performed two experiments namely vapour presure measurements and NMR spectroscopy titration experiments.

Vapour pressure measurements involved the use of Raoult's Law, which states that the relative decrease in the vapour pressure, p, of a solvent due to the addition of a solute is equal to the mole fraction of the solute in solution. For a two component solution, where p_1^o is the vapour pressure of pure component 1, p_1 is the vapour pressure of component 1 in solution and N_1 is the mole fraction of component 1, the relationship can systematically be represented by the equation shown below.

$$p_1 = p_1^o N_1$$

One point to be noted is that this relationship does not hold for non-ideal (i.e. real) solutions. Raoult's law assumes that there is no interaction between the solvent and the solute and this is rarely the case. Two possible deviations from the law exist:

1. *Negative,* where there are attractive forces between the two components and the resultant vapour pressure is reduced as there is a decreased tendency for components to leave the solution as vapour.
2. *Positive,* the attractive forces between the components are less than those within the components, which are more likely to go into the vapour phase.

The vapour pressure measurements were perfomed on pure samples of **PIL**s, ethanol, propionaldehyde and acetone and mixtures of these individual carbonyls with **PIL 1**. **PIL**s were found to have no measurable vapour pressure and the vapour pressure of the pure carbonyl molecules was measured first and then a known concentration of these organic compounds in **PIL 1** was made and the vapour pressure re-measured. The experiments were repeated three times for consistency with an error bar of 0.1 Torr. In general, a large negative deviation was observed for the vapour pressure measurement (*i.e.* a value less than predicted by Raoult's Law) as shown in Table 5-6, suggesting that there is an interaction between the carbonyl and the **PIL 1**. The deviation from Raoult's Law was in the order of ethanol > propionaldehyde > acetone. Though this study confirmed the presence of an interaction, no information was gained about the mode.

Solute	% of PIL 1	% of carbonyl added	P°(Torr) of pure solute	P°(Torr) of mixture expected	P°(Torr) of mixture observed
Ethanol	50	50	13.07	6.53	0.91
Ethanol	83	17	13.07	2.18	0.34
Propionaldehyde	50	50	6.40	3.03	3.93
Propionaldehyde	83	17	6.40	16.37	0.48
Acetone	50	50	69.9	34.95	12.66
Acetone	83	17	69.9	11.65	2.81

Table 5-6: Vapour pressure data of PIL 1 and solute measured at room temperature.

Hence to identify the mode of association between the ionic solvent and solute molecules NMR spectroscopy titration experiments were performed. Only minor changes (0.03 ppm) to the ^{31}P NMR spectrum of **PIL 1** were observed upon addition of the carbonyl compounds such as benzaldehyde or propionaldehyde. This result suggested that the local coordination sphere of the phosphorous site has not been affected. However, ^{1}H NMR studies were more indicative since a *downfield* shift of the proton *alpha* to the phosphorous was observed with increased concentration of the carbonyl compound (Table 5-7), suggestive that the mode of association between [solute•••solvent] involved a hydrogen bonding interaction.[233]

Experiment Number	Volume of PIL 1 (mL)	Volume of benzaldehyde (μL)	^{1}H NMR resonance for α-H
1	0.5	0	2.77
2	0.5	250	2.86
3	0.5	500	2.92
4	0.5	750	3.01
5	0.5	1000	3.11

Table 5-7: ^{1}H NMR data indicating downfield shift in alpha-H to phosphorous on addition of benzaldehyde.

To support that there is hydrogen-bond interaction present between the phosphonium cation and the carbonyl, a search of the Cambridge Crystallographic

Database was performed, which revealed a short [C-H•••O] hydrogen interaction (1.935(5) Å) between the cation and anion[234] in the simple phenoxide salt [Ph_3PCH_3][2,6-$Ph_2C_6H_3O$]. However, we considered the aforementioned salt as a poor model for our system (*i.e* arylphosphonium *v/s* alkylphosphonium). Therefore, the X-ray structure of another salt namely tetra-*n*-butylphosphonium acetate monoacetic acid as a model of the system, was investigated. The selected bond lengths and bond angles are shown in Table 5-8.

Bond Lengths (Å)			
O(1)-C(20)	1.229(2)	O(3)···H(3C)	1.2256(14)
O(2)-C(20)	1.286(3)	O(3)···O(3)	2.451(3)
O(3)-C(30)	1.287(2)	O(1)···H(5B)	2.388
O(4)-C(30)	1.235(2)	O(1)···C(5)	3.377
O(2)···H(2C)	1.2245(14)	O(4)···H(1A)	2.452
O(2)···O(2)	2.449(3)	O(4)···C(1)	3.437
Bond Angles (°)			
O(2)···H(2C)···O(2)	180.00(15)	C(5)-H(5B)···O(1)	178.25
O(3)···H(3C)···O(3)	180.00(15)	C(1)-H(1A)···O(4)	173.19

Table 5-8: Selected bond lengths (Å) and angles (°) for tetra-*n*-butylphosphonium acetate monoacetic acid.

The X-ray structure[n] revealed a tetrahedral phosphonium cation as expected, however the results of the anion contact are of more interest. The acetate and acetic acid fragment are indistinguishable, with a proton present equidistant between the anion and the cation forming a strong hydrogen bond[135] as shown in Figure 5-12. The carbonyl oxygens each form a weak [C-H···O] hydrogen bond to the hydrogen *alpha* to the phosphonium cation, consistent with a mode B interaction (Chart 5-3). Interestingly, when the extended structure was analysed it was observed that all four alkyl chains on the

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[n] The data for the X-ray structure was collected by Dr. Michael J. Jennings (University of Western Ontario) and solved by Diane A. Dickie (Simon Fraser University).

phosphonium cation are involved in this type of hydrogen bonding. Protons from C(1) and C(5) interact with the acetates within the asymmetric unit, while C(9) and C(13) are coordinated to symmetry-related fragments, which lead to the formation of an extensive three-dimensional hydrogen-bonded network, as shown in Figure 5-13.

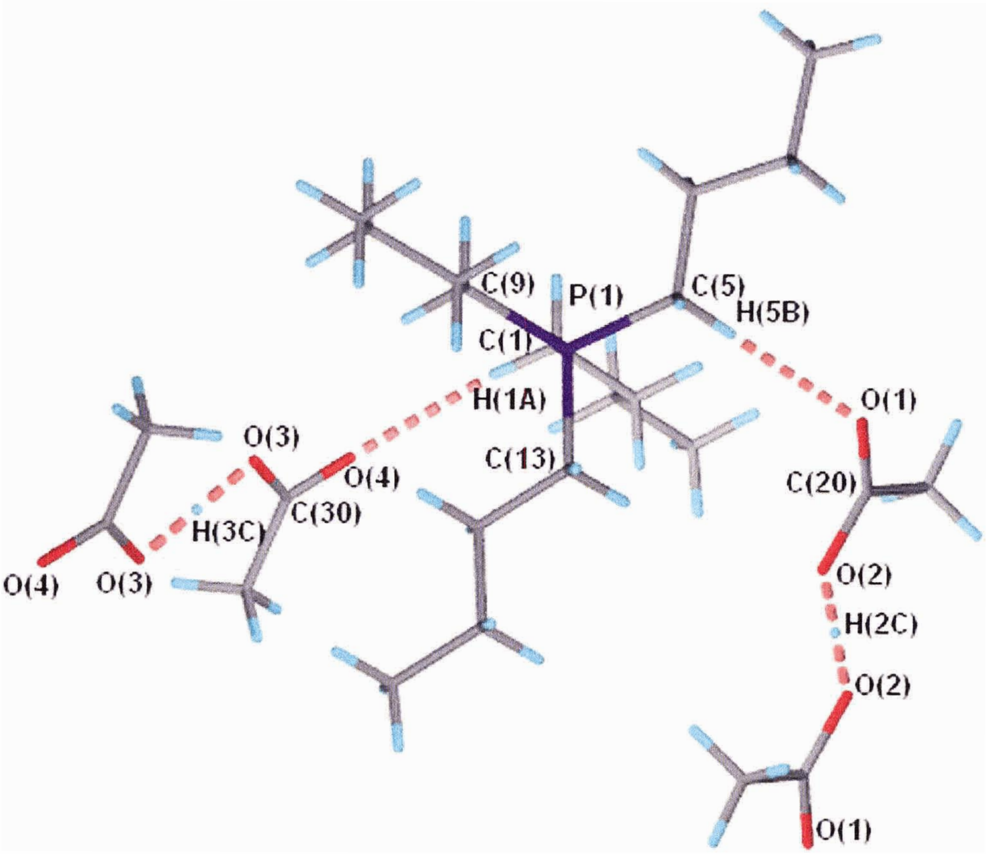

Figure 5-12: Molecular structure of tetra-*n*-butylphosphonium acetate monoacetic acid.

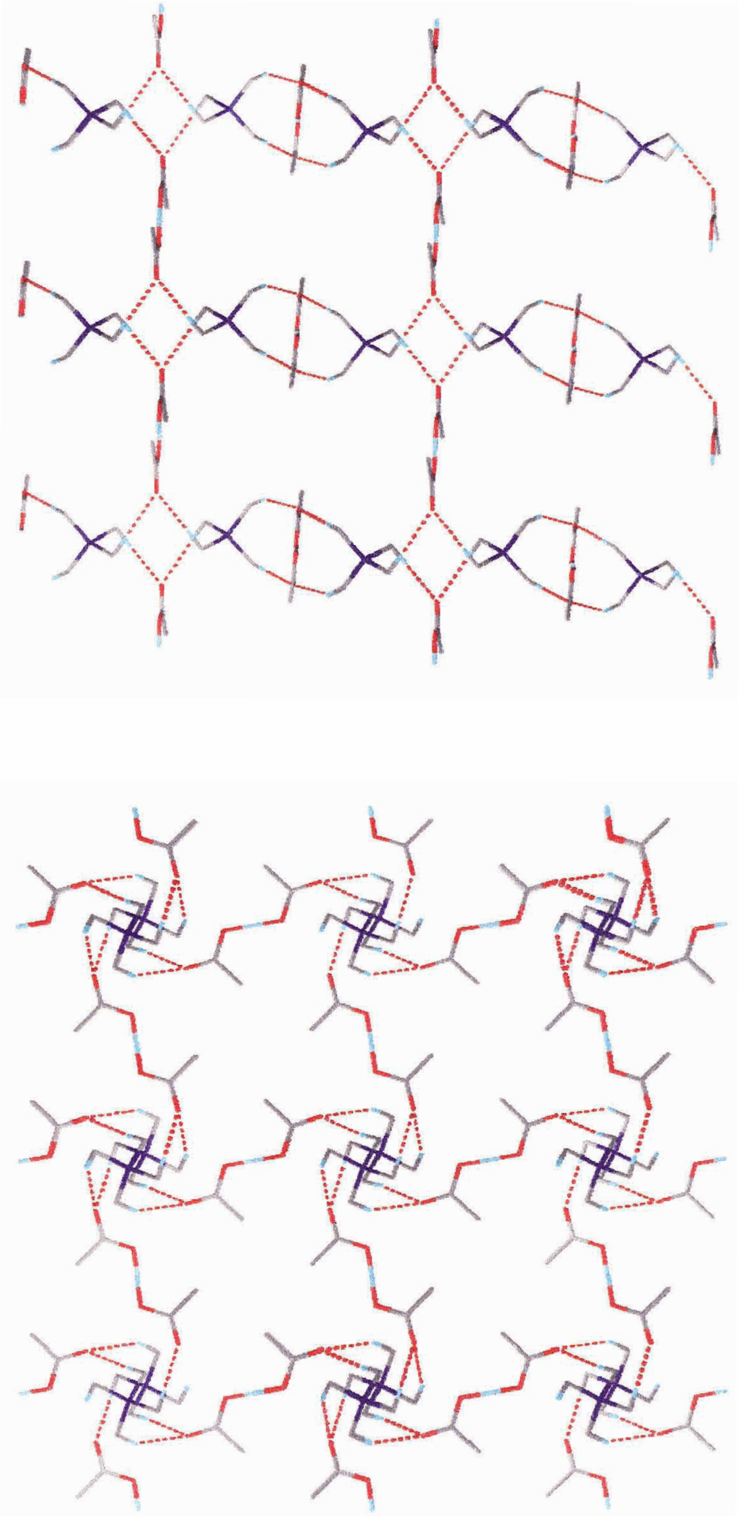

Figure 5-13: Three-dimensional network formed by [O-H···O] and [C-H···O] hydrogen bonds, viewed along the crystallographic *b* and *c* axes, respectively. For clarity, only the alpha carbon and hydrogens of each butyl are shown.

5.11 Conclusions

The preparation of ethereal and *ether free* Grignard reagents in **PIL**s was described in this chapter. The stability and reactivity studies of *ether free* Grignard reagents in **PIL 2** were also investigated. Other strong bases such as the Wittig reagents were synthesised and their reactions with carbonyls compounds to make alkenes were performed in **PIL**s. These observations open up the use of **PIL**s as a reliable reaction media for a wide variety of basic reagents. The problem associated with C-H activation in imidazolium ions are not observed for the **PIL**s. Spectrocopic and structural evidence suggest that the carbonyls are activated by hydrogen bonding interactions with the **PIL**s.

5.12 Experimental Section

The general experimental procedure was the same as mentioned in chapter 4, section 4.7.1. For X-ray crystallography, data was collected at low temperature (-100 °C) on a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B. V., 1998). The X-ray structure was solved by Diane A. Dickie at Simon Fraser University.

5.12.1 Preparation of PIL 1/PhMgBr ethereal Solution

1.0 M **PIL 1**/PhMgBr THF solution was prepared by the drop-wise addition of the commercially available 1 M of PhMgBr in THF (5 mL, 5.00 mmol) to **PIL 1** (5 mL), cooled to –78 °C under an inert N_2 atmosphere. ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33 ppm, consistent with **PIL 1**. GC-MS: *m/z*: 84.1 amu (Calcd 84.1 amu) (hexene), *m/z*: 482.5 amu (Calcd 482.5) (tetradecyl (dihexyl)phosphine). Reactivity studies on the **PIL 1**/PhMgBr ethereal solution were also performed (as explained below) showing no degradation of the ionic liquid.

THF was removed under vacuum from the **PIL 1**/PhMgBr THF solution and the solution tested by GC-MS. GC-MS: *m/z*: 84.1 amu (Calcd 84.1) (hexene), *m/z:* 72.1 amu (Calcd 72.1) (tetrahydrofuran), *m/z*: 482.5 amu (Calcd 482.5 amu) (tetradecyl(dihexyl)phosphine).

5.12.2 Stability Studies: Reaction of PIL 1/PhMgBr ethereal solution with Bromine

The reactivity of a freshly prepared sample of **PIL 1**/PhMgBr and a one-month-old **PIL 1**/PhMgBr ethereal solution were compared. To an aliquot (5 mL of 1.0 M **PIL 1**/PhMgBr ethereal solution) of both freshly prepared solution and a one-month-old **PIL 1**/PhMgBr THF solution, one equivalent of Br_2 was added and the mixtures were stirred for 1 hour. The reactions were then quenched with distilled water (20 mL) and extracted with hexanes (20 mL). The extracts were analysed by GC-MS. GC/MS: *m/z*: 156.0 amu (Calcd 156.0 amu) (bromobenzene, yield: 95%); *m/z*: 154.1 amu (Calcd 154.1) (biphenyl, yield 5%). Benzene (obtained by deprotonation of the **PIL**) was not detected by GC-MS indicating there is no degradation of the **PIL 1**/Grignard reagent ethereal solution.

5.12.3 Stability Studies: Reaction of PIL 1/PhMgBr ethereal solution with N,N′-dimethylformamide

To both a freshly prepared sample of 1.0 M **PIL 1**/PhMgBr and a one-month-old **PIL 1**/PhMgBr THF solution (5 mL), N,N′-dimethylformamide (0.37 g, 5.00 mmol) was added drop-wise and the solution stirred under N_2 for 3 hours. The reaction mixtures were then quenched with saturated ammonium chloride followed by water. A single extraction step was performed by adding hexanes and the benzaldehyde was extracted in the hexanes layer. The hexanes layer was then dried with anhydrous magnesium sulphate and filtered. The extracts were analysed by GC-MS with both the freshly and aged solution. GC-MS: *m/z*: 106.0 (Calcd 106.0 amu) (benzaldehyde, yield ≈55 %). There was no degradation of **PIL**. ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33 ppm, consistent with **PIL 1**.

5.12.4 Preparation of *ether free* PIL 2/Grignard solution

Commercially available 1.0 M PhMgBr (5 mL) in THF was added to **PIL 2** (5 mL) with a few drops of THF (up to 1 mL) at -78 °C. The mixture was stirred and warmed to room temperature. When PhMgBr in THF was added drop wise to **PIL 2**, the colour changed from pale yellow to orange red going *via* a blue colour.

Tetrahydrofuran (THF) was removed under vacuum. Absence of THF was confirmed by ^{1}H NMR spectroscopy. To the viscous orange red solution obtained, hexanes (2 mL) were added to reduce viscosity. This solution was then treated with one equivalent of either bromine or N,N'-dimethylformamide followed by quenching with saturated aqueous ammonium chloride and addition of water and extraction with dichloromethane. The dichloromethane layers were then analysed by GC-MS. GC-MS: *m/z*: 156.0 amu (Calcd 156.0 amu) (bromobenzene, yield 98%); *m/z*: 106.0 amu (Calcd 106 amu) (benzaldehyde, yield 99%) respectively.

5.12.5 Reaction of *p*-benzoquinone with Grignard reagent in THF

To a solution of *p*-benzoquinone (0.40 g, 3.70 mmol) dissolved in THF (10 mL), PhMgBr in THF (3.7 ml, 3.70 mmol) was added dropwise. An abrupt colour change of the solution was observed from pale yellow to dark blue with the formation of a dark blue precipitate. The blue solution and blue precipitate were analysed separately by EPR spectroscopy studies and both showed the presence of a *p*-benzoquinone radical adduct. After EPR spectroscopy studies the THF mixture was quenched with saturated ammonium chloride (5 mL) and water and then extracted with dichloromethane (20 mL) and dried with anhydrous magnesium sulphate. The dichloromethane solution was analysed by GC-MS. GC-MS: *m/z*: 186.2 amu (Calcd 186.2 amu) (4-hydroxy-4-phenyl-2,5-cyclohexadienone, yield 94%); *m/z*: 110.1 amu (Calcd 110.0 amu) (dihydroxyenzene, yiled 3%); *m/z*: 78.1 (Calcd 78.1 amu) (benzene, yield 3%). The reaction was repeated with different Grignard reagents namely, ethylmagnesium bromide and 2,4,6-trimethylphenylmagnesium bromide and the results are recorded in Scheme 5-4. All the yields were calculated by GC-MS.

5.12.6 Reaction of *p*-benzoquinone with Grignard reagent in PILs

A fresh solution of a Grignard reagent was made in **PIL 2** as explained before (section 5.12.4). An aliquot of the solution was reacted with one equivalent of *p*-benzoquinone dissolved in **PIL 2** with a few drops of toluene (≈ 1 mL) added to increase solubility. A colour change was observed from orange to dark blue. EPR studies were carried out on the sample showing the presence of a mixture of *p*-benzoquinone and the *p*-benzoquinone phenyl adduct. After EPR spectroscopic studies the ionic liquid mixture was quenched with saturated ammonium chloride (5 mL) and water and then extracted with dichloromethane (20 mL) and the extracts were analysed by GC-MS. GC-MS: *m/z*: 186.2 amu (Calcd 186.2 amu) (4-hydroxy-4-phenyl-cyclohexa-2,5-dienone, yield 15%); *m/z*: 110.1 amu (Calcd 110.1 amu) (hydroquinone, yield 85%); *m/z*: 154.1 amu (Calcd 154.1 amu) (biphenyl, yield 80%) and benzene. The spectroscopic data were consistent with reported values. For 4-hydroxy-4-phenyl-2,5-cyclohexadienone: M.p. 102-103°C. ^{1}H NMR (400 MHz, d$_6$-acetone) δ (ppm) 7.28-7.45 (5H, m), 6.83 (2H, d), 5.042 (1H, s), 6.05 (2 H, d). IR (CHCl$_3$, cm^{-1}) 3418 (s), 3371 (s), 3030 (m), 1656 (s), 1599 (s). For hydroquinone: ^{1}H NMR (400 MHz, d$_6$-acetone) δ (ppm) 7.66 (4 H), 6.657 (2 H).

The same procedure was carried out with different Grignard reagents namely 2,4,6-trimethylphenylmagnesium bromide and ethylmagnesium bromide. GC-MS: *m/z*: 186.1 amu (Calcd 186.1 amu) (4-hydroxy-4-2,4,6-trimethylphenyl-2,5-cyclohexadiene, yield 20%); *m/z*: 139.2 amu (Calcd 139.2) (4-hydroxy-4-ethyl-2,5-cyclohexadiene, yield 25%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.88 (2 H, s), 6.82 (2 H, s), 6.69 (2H, d), 6.61 (2H, d), 2.42 (6 H, s), 2.33 (3H, s). IR (CHCl$_3$, cm^{-1}) 3387 (s), 3030 (s), 1783 (s), 1658 (m), 1609 (m), 1505 (m).

5.12.7 Transmetallation reactions

1.0 M EtMgBr in THF was added drop wise to cold **PIL 1** (5 mL). The solution was allowed to stir for 30 minutes and then the THF was removed under vacuum. One equivalent of bromobenzene (0.78 g, 5.00 mmol) was then added to this solution and stirred for 6 hours. Then, one equivalent of benzaldehyde (0.53 g, 5.00 mmol) was added to the mixture and stirred for 16 hours, then quenched with water and extracted using dichloromethane (20 mL). The extract was analysed by GC-MS. GC-MS: *m/z*: 184.1 amu (Calcd 184.1 amu) (diphenyl-methanol, yield 83%); *m/z*: 136.2 amu (Calcd 136.2 amu) (1-phenyl-propan-1-ol, yield ≈ 8%).

5.12.8 Addition reaction of *ether free* PIL 2/PhMgBr

Aliquots (5 mL) of the freshly prepared 1.0 M **PIL 2**/PhMgBr *ether free* solution were treated with one equivalent of reactant (e.g., aldehyde, ketone, etc). The solutions were stirred under N_2 for 1-3 hours. The reaction mixtures were quenched with saturated aqueous ammonium chloride (2 mL) followed by the addition of water (25 mL). Hexanes (20 mL) were added to establish a three-phase system and the products were extracted into the hexanes layer. The extracts were analysed by GC-MS and data recorded as shown in Scheme 5-6 and Scheme 5-7.

5.12.9 Kumada-Corriu cross-coupling reaction with Ni catalyst in PIL 2

To cold **PIL 2** (5 mL) at -78 °C, 1.0 M PhMgBr in THF (5 mL, 5 mmol) was added. The reaction mixture was allowed to warm up to room temperature while stirring followed by the removal of THF under vacuum. A few drops of toluene (≈ 0.5 mL) were added to the reaction mixture to reduce viscosity, followed by the addition of one equivalent (*wrt* PhMgBr) of either 4-fluorotoluene, 4-chlorotoluene, 4-bromotoluene or 4-iodotoluene. To this solution, the complex *bis*[1,3-di(2′,6′-diisopropylphenyl)-imidazolin-2-ylidene]nickel (0) (0.05 mol %), prepared *in situ* by the reaction of nickel 1,5-dicyclooctadiene and an *N*-heterocyclic carbene in **PIL 2**, was added. On addition of nickel 1,5-dicyclooctadiene to **NHC 2**, a colour change from pale yellow to dark green was observed. The reaction mixture was stirred for 18 hours at room temperature under nitrogen, then quenched with a few drops of methanol and extracted with dichloromethane (20 mL) and water. The dichloromethane layer was then dried by using anhydrous magnesium sulphate and then analysed by GC-MS. Yields are tabulated in Table 5-2. In all cases a small amount (< 2 %) of biphenyl was observed.

5.12.10 Stability and reactivities of magnesium acetylides in PILs

To **PIL 2** (5 mL), commercially available 1.0 M ethynylmagnesium bromide (5 mL) in THF was added drop wise at -78 °C. The mixture was stirred and allowed to warm to room temperature. THF was removed under vacuum leaving a viscous brown solution to which a few drops of toluene (≈ 1 mL) were added to reduce viscosity. To this solution one equivalent of cyclohexanone (0.49 g, 5.0 mmol) was added and it was stirred for 16 hours under nitrogen. The reaction mixture was quenched with a few drops of saturated ammonium chloride (≈2 mL), washed with water and extracted with dichloromethane (20 mL). The dichloromethane layer was then dried using anhydrous magnesium sulphate, and then filtered off. The dichloromethane layer was analysed by GC-MS. GC-MS: *m/z*: 124.2 amu (Calcd 124.2 amu) (1-ethynyl-cyclohexanol, yield 78 %).

To an aliquot of 1.0 M of ethynylmagnesium bromide in **PIL 2**, one equivalent of benzaldehyde was added, which was allowed to stir for 16 hours under nitrogen. The reaction mixture was then quenched with a few drops of saturated ammonium chloride and water and then extracted with dichloromethane. The extract was analysed by GC-MS after drying with anhydrous magnesium sulphate. GC-MS: *m/z*: 132.2 amu (Calcd 132.2 amu) (1-phenylprop-2-yn-1-ol, yield 82 %).

5.12.11 Reactivity of amines in PILs

To **PIL 2** (5 mL), commercially available 1.0 M PhMgBr (5 mL, 5.0 mmol) in THF was added at -78 °C. The mixture was stirred, warmed to room temperature and then the THF was removed under vacuum leaving a viscous orange solution. A few drops of toluene (≈ 1 mL) were added to reduce viscosity of the solution. One equivalent of morpholine (0.44 g, 5.0 mmol) was added drop wise followed by 0.05 mol% of the *bis*[1,3-di(2′,6′-diisopropylphenyl)imidazolin-2-ylidene]nickel(0) complex. The nickel complex was prepared *in situ* by the reaction of nickel 1,5-dicyclooctadiene and the free **NHC 2** in **PIL 2**. On addition of the Ni catalyst, a subsequent colour change from orange to brown was observed. To this reaction mixture one equivalent (with respect to morpholine) of 4-chlorotoluene was added then stirred for 16 hours under nitrogen at 85°C. After cooling to room temperature, the reaction was quenched with a few drops of methanol (1 mL) and water and extracted using dichloromethane (20 mL). The dichloromethane layer was then dried using anhydrous magnesium sulphate, filtered off and analysed by GC-MS. GC-MS: *m/z*: 177.2 amu (Calcd 177.2 amu) (4-p-tolyl-morpholine, yield 58 %).

5.12.12 Wittig Reaction: Formation of Methylstyrene in PIL 2

To a cold (-78 °C) sample of **PIL 2** (5 mL), 1.0 M PhMgBr in THF (1.2 mL, 1.2 mmol) was added and allowed to slowly warm to room temperature. The THF was removed under vacuum and to the resulting solution a few drops of hexanes (≈ 2 mL) were added to reduce viscosity. Triphenylethylphosphonium bromide (0.40 g, 1.10 mmol) was then added to the solution. A subsequent colour change from white to reddish orange was observed and the mixture was stirred under nitrogen for 1 hour. ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 15ppm, for the phosphorane, which resulted from the deprotonation of triphenylethylphosphonium bromide. Benzaldehyde (0.11 g, 1.10 mmol) was then added to the mixture and an instant colour change from yellow to white was observed. The mixture was allowed to stir for 2 hours and then quenched with a few drops of saturated ammonium chloride (1 mL). The product was extracted with dichloromethane (20 mL) and water. The dichloromethane layer was then dried using anhydrous magnesium sulphate and analysed by GC-MS. GC-MS: *m/z*: 118.1 amu (Calcd 118.1 amu) (methylstyrene, yield 96%). The presence of triphenylphosphine oxide, Ph_3PO (0.27 g, 0.97 mmol) was confirmed by mass spectrometry. M.S (EI) *m/z* 278.1 amu (Calcd. = 278.1 amu).

5.12.13 Synthesis of New PILs/BH_3

New **PIL**s, $[R'_3RP][XBH_3]$ were made by using two different methods. Gaseous B_2H_6 gas, prepared as reported in literature,[224, 225] was passed through one equivalent of **PIL**s for 30 minutes to form $[R'_3RP][XBH_3]$ complexes. The same complexes were also obtained by mixing one equivalent of 1.0 M **BH₃•THF** solution (5 mL) in **PIL** (5 mL) followed by complete removal of the THF by exhaustive evacuation. ^{1}H NMR of **PIL 1**

(400 MHz, C_6D_6) δ (ppm) 2.4 - 0.7 (various m). ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33. IR (neat, cm^{-1}) 2956 (s), 2923 (s), 2856 (s), 1466 (s), 1416 (m), 1378 (s), 1300 (m), 1263 (m), 1216 (m), 1112 (m), 989 (m), 814 (m), 721 (s). Anal. Calcd for $C_{32}H_{68}ClP$: C: 74.01; H: 13.20. Found: C: 74.30; H : 13.03. ^{1}H NMR (400 MHz, C_6D_6) of complex **PIL 1/BH$_3$**: δ (ppm) 2.7- 0.8 (various m). ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33. ^{11}B NMR of **PIL 1/BH$_3$** (128.38 MHz,C_6D_6) showed a very broad signal *ca* δ 50 to -25 ppm with sharp features at δ 18.6 ppm and -12.0 ppm and a sharp quintet at δ -35.3 ppm assigned to BH_4^-. IR (neat, cm^{-1}): 2956 (s), 2924 (s), 2855 (s), 2298 (s), 2212 (m), 2037 (m), 1465 (s), 1416 (s), 1378 (m), 1337 (s), 1261 (m), 1215 (m), 1166 (m), 1115 (s), 1071 (m), 814 (s), 721 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{71}BClP$: C: 72.09; H: 13.42. Found: C: 72.39; H: 13.64. ^{1}H NMR of **PIL 2** (400 MHz, C_6H_6) δ 2.8-0.8 (various m). ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33. IR (neat, cm^{-1}) 2956 (s), 2925 (s), 2856 (s), 1579 (ν (C=O) stretch) (s), 1465 (m), 1377 (m), 1265 (m), 1110 (m), 812 (m), 722 (m). ^{1}H NMR (400 MHz, C_6D_6) of complex **PIL 2/BH$_3$**: an **upfield** shift of the ^{1}H NMR, δ (ppm) 2.6 - 0.8 (various m). ^{31}P NMR (161.68 MHz, C_6D_6) δ (ppm) 33. ^{11}B NMR of **PIL 2/BH$_3$** (128.38 MHz, C_6D_6) showed a very broad peak *ca* δ 50 to -25 ppm with sharp resonances at δ 18.1 ppm, δ 2.1 ppm and a very sharp quintet at δ -35.3 ppm assigned to BH_4^-. IR (neat, cm^{-1}): 2956 (s), 2925 (s), 2855 (s), 2224 (m), 2270 (s), 2139 (m), 1661(s) (C=O stretch of **PIL 2/BH$_3$** complex), 1579 (m) (νC=O stretch of uncomplexed **PIL 2**), 1466 (s), 1416 (s), 1378 (m), 1337 (s), 1297 (m), 1150 (m), 1111 (m), 1075 (m), 720 (m), 669 (s). Note: As explained in section 5.9.2, **PIL 1/BH$_3$** and **PIL 2/BH$_3$** undergo ligand exchange with **PIL**s, hence pure **PIL/BH$_3$** could not be isolated.

5.12.14 Reduction of carbonyls using PILs/BH_3

1.0 M **PILs/BH_3** complexes were synthesized as explained in section 5.12.13. Aliquots of the freshly prepared solution were treated with one equivalent of different carbonyls, namely benzaldehyde, benzoyl chloride, benzophenone and cinnamaldehyde. The reaction mixture was stirred for 16 hours under inert N_2 atmosphere and then quenched with saturated ammonium chloride and water. The products are extracted with dichloromethane (20 mL), dried using anhydrous sodium hydroxide, and analysed by GC-MS. The yields of the extracts are presented in Table 5-4.

5.12.15 Reduction of carbonyls using $NaBH_4$ in PILs

$NaBH_4$ (0.20 g, 5.3 mmol) was added to **PILs** (5 mL) to form a white slurry. A few drops of toluene (≈ 1 mL) were added to reduce the viscosity of the mixture, without any dissolution of the $NaBH_4$. To this mixture one equivalent of carbonyls namely, benzaldehyde and benzoyl chloride are added drop wise and stirred at room temperature under inert N_2 atmosphere for 18 hours. After completion of the reaction, it was quenched with saturated ammonium chloride and water then extracted with dichloromethane (20 mL). The dichloromethane layer was dried using anhydrous magnesium sulphate and analysed by GC-MS. The results are shown in Table 5-4.

CHAPTER 6: GENERAL CONCLUSIONS

Volatile organic compounds (**VOCs**) readily evaporate in the environment and they have been implicated as a source of ozone depletion, global climate change and smog formation thus having negative impact on the biological systems. Successful attempts to replace or limit the use of **VOCs** have been made. The replacement solvents that have been reported prior to our work, however, were all found to have limitations and reactive with bases. This thesis illustrates the reactivity of imidazolium-based ionic liquids towards bases, reducing agents and active metals by making use of imidazolium salts as a model for imidazolium-based ionic liquids.

Basic reactions in ionic liquids are important since more than 50 % of chemical reactions are based-catalysed. Phosphonium-based ionic liquids are thermally more robust than ammonium, pyridinium and imidazolium-based ionic liquids. Reactivity studies were performed in two different phosphonium-based ionic liquids in the presence of strong bases (Grignard reagents and **NHCs**), active metal (potassium) and reducing agents (borane, potassium *tert*-butoxide). The phosphonium-based ionic liquids are found to be an inert solvent media for those reactions and they allow electron transfer without any decomposition. This research will open up the use of phosphonium-based ionic liquids as a reliable reactions media for a wide variety of basic reagents and as a safe carrier of borane.

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