REACTIVITY AND STRUCTURE IN IONIC LIQUIDS

A Thesis presented by

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In partial fulfilment of the requirements
for the degrees of

Doctor of Philosophy
of the
University of London

and

Diploma of Imperial College

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Imperial College
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To my family, especially my parents and brother

for their constant love and support

and

To my two best friends

Alex Comely and Huma Jehan

'You do not really understand something unless you can explain it to your grandmother.'

- Albert Einstein

'The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' ('I found it!'), but rather 'hmm... that's funny'...'

- Isaac Asimov

'If we knew what it was we were doing, it would not be called research, would it?'

- Albert Einstein

ABSTRACT

A series of room temperature ionic liquids have been synthesized and characterized. These were all based on dialkylimidazolium cations, and used the non-coordinating anions BF_4^-, PF_6^-, ClO_4^-, NO_3^-, $CF_3SO_3^-$, $CH_3SO_3^-$, $(CF_3SO_2)_2N^-$, and $CH_3CH(OH)CO_2^-$. Acidic, neutral and basic forms of the ionic liquids based upon $AlCl_3$, $FeCl_3$ and $SnCl_2$ were also prepared.

A series of Diels-Alder reactions have been studied, initially in [emim][BF_4], with a view towards the choice of one as a probe reaction to study and compare the relative properties of a series of ionic liquids. Reactions that were optimised in the ionic liquid were those between trans-crotonaldehyde and cyclopentadiene, methacrolein and cyclopentadiene, cyclopentadiene and methyl methacrylate, cyclopentadiene and methyl acrylate, isoprene and maleic anhydride, isoprene and 1,4-benzoquinone, 2,3-dimethyl-1,3-butadiene and maleic anhydride.

The reaction between cyclopentadiene and methyl acrylate was chosen as the probe reaction and was initially optimised in [pmim][ClO_4],[emim][CF_3SO_3], [emim][NO_3] and [emim][PF_6]. Based on these results, a complete study, including extensive kinetic work, was carried out in the ionic liquids mentioned above. Unlike other recent solvent advances in this field that were based on the theory of solvophobicity, the results from this study displayed strong evidence that hydrogen bonding interactions between the solvent system and the dienophile contributed to significant accelerations in rate of reaction, and improved product selectivities. $Sc(OTf)_3$, a strong Lewis acid, was used in catalytic quantities, giving an endo/exo ratio of over 16 for the same reaction

Model nickel and nickel phosphine complexes, based on those used industrially in the Lewis acidic form of the ionic liquid [bmim]Cl-$AlCl_3$ to dimerise lower olefins, have been prepared and dissolved in both Lewis acidic and Lewis basic forms of this ionic

liquid. The structural configurations of each complex in each form of the ionic liquid have been studied, using a combination of electronic absorption spectroscopy, the EXAFS technique, proton NMR (where applicable) and mass spectrometry (where applicable). The EXAFS technique also included a study of the solid forms of each of the nickel complexes, in order to determine the precision of this procedure. An accurate picture of how each complex behaves upon dissolution in each liquid has been obtained.

ACKNOWLEDGEMENTS

Although it appears to be customary and almost expected to acknowledge one's supervisor first and foremost in a thesis, I would hope that this does not appear to be the reason why that pattern is being adhered to in my case. It is a conscious decision. I have spent five years under the supervision of Dr Tom Welton, and when thinking of how to approach my acknowledgements section, I must admit that my respect for and gratitude towards him is immense.

As a student, I am very proud to have had Tom as my supervisor, and it has been a pleasure for me to be in his research group. I am particularly grateful to have had a supervisor who has encouraged me to push myself. Without a doubt, it is Tom who has made me believe that the work I have undertaken is of relevance. I am impressed in the way that Tom manages and runs his group, his relaxed and friendly demeanour that is the core of the excellent yet productive atmosphere in the group, and of course that he is so down-to-earth and approachable so as to make anyone, from a project student to a professor, feel welcome and appreciated. Whatever I decide to do from this point onwards I would hope that I have learnt from and can use some of his qualities to benefit my life.

Much of the work in this thesis has been made possible through the advice or input of other people. I would like to mention the EPSRC which has funded my project, the staff at the Daresbury laboratory for advice on EXAFS assignment, Dr Brent Young and Prof David Goodgame for useful advice on NMR and IR spectroscopy respectively, my joint supervisor Dr Nick Long, and the entire technical staff of the department – in particular Simon Bastians. I would like to mention Judith Wolff, Thorsten Fischer and Stéphane Lagréne, who have all worked on projects under my supervision, and contributed to some of the work in this thesis.

I would like to thank my colleagues and friends from the Welton group, past and present for many good times together; both at work and at play. I feel I must acknowledge Nicola, Narmatha, Fiona, Paul Salter, Victoria, Phil and James, all of whom have been excellent colleagues and friends to work with. I would like to single out two individuals from the group. Firstly Paul Smith, who being something of an expert with computers, has had to put up with a barrage of questions from me, but who coped admirably under the pressure! Secondly and most of all I must thank our postdoc Llewellyn, who has given so much priceless input and advice to my project (as well as being a patient proof reader, especially at 4pm on a Friday afternoon, when I would invariably appear with a pile of papers!). As well as this, he has also illuminated the group with the joys of cricket and rugby, shared many a 'Mark & Lard' moment with me in the lab, and along with his wife Jess has started an annual institution called the Stevenage summer barbacue. Many thanks should also go out to the members of the Widdowson, Steinke and Armstrong groups, with whom we share lab space.

The last few years have blessed me with some wonderful friendships, and strengthened some older ones. I feel that this has been of great relevance to my research and general spirit. I would love to mention each of the following people separately, but I fear it would require a thesis in itself to accomplish this!

I have made some excellent friends from the department, some of whom have left Imperial College, but with whom I still maintain contact. I would particularly like to mention Matt, Charlie, Phil & Guillaine, Wazir, Dimitri, Matt 'stores' and Anna.

Having spent an Erasmus year in France, I would like to mention my 'non-UK' friends who I have visited (or meant to visit!) or who have visited me, in particular Céline & Pascal, Anne-Laure & Christophe, Nasser & Cécilia (Strasbourg); Volker & Sylvie (San Fransisco), Mike (Buffalo, New York State); Karolina and Nimeet (New York); Jan & Inge, Pieter, Arne, Eric 'Eros' (it's really his name!), Elena & Arne (Antwerp), Lucia, Srdjan (Lausanne); Steffen (Cologne); Andreas (Munich); Gerhard & Stéphanie (Frankfurt); Gernot & Alessandro (Offenburg); Agnés, Miriam, Sébastian (Paris);

Susanne, Tamara, Camilla, Linda, Sofi (Stockholm); Cicilie & Inge (Oslo); Sonata, Kari, Nina (Helsinki).

I would like to mention my friends in London with whom I have spent many memorable times, especially Kamal, Sylvia, Jenny, Michael & Carol, Elliott, Fasih, Noor & Issy, Ralph, Chai, Chrissy & Philip, Zina, Natasha and Dean.

To everyone who has lived in 5 Churston Mansions, thanks for putting up with me and in some cases becoming good friends – Caroline, Chiara, Mark, Ellie, Mithi, Tomoko.

I would also like to thank my closest friends who have been excellent companions and listeners for me, and have always inspired and touched me with their kindness – Alex and Huma (thankyou for always being there for me), Charlieinthailand (who is slowly getting better at pool with my coaching!), Julie (we have to meet up soon), Eric (les français ont **toujours** raison) & Amalia, Harsh (he who laughs last laughs loudest!) and Pete (it's grim up north).

Outside of chemistry, my big passion remains music. Throughout these PhD years I have been lucky enough to present The Electric Café, a radio show on national student radio. I would like to thank everyone at SBN and Channelfly for making that a possibility, and believing in my DJing skills. During the course of my musical experiences I have befriended some musicians/DJs who have kept me inspired. I would like to mention Rudolf Kremers, Russ Gabriel, James Hoggarth, Sami Birnbach (Morpheus), Alex Knight, Steve Zzonked, Dominic Glynn, Warren No Bones, Kaisa Compost, John Metcalfe, The Thievery Corporation, Charlie Hall, Ges-E and Larry Heard.

Finally, and most importantly, I would like to send my deepest thanks and love to all my family, especially my parents and my brother Rounik, who have been my biggest supporters and well-wishers.

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LIST OF ABREVIATIONS

α	alpha
Å	Ångstrom (1 x 10^{-10} m)
acac	acetylacetonate
β	beta
bmim	1-butyl-3-methylimidazolium
bmmim	1-butyl-2,3-dimethylimidazolium
BP	1-butylpyridinium chloride
°C	degree centigrade
^{13}C	carbon isotope
ca.	circa
cal	calorie
cm^{-1}	wavenumber
Co.	Company
Cp	cyclopentadiene
CP66	an azacyclophone
Δ	delta
d	doublet
d	referring to a chemical that is deuterated
DiCp	dicyclopentadiene
dm	decimetre
DMD	2,3-dimethylbutenes
dppe	diphenylphosphinoethane
EAN	ethylammonium nitrate
emim	1-ethyl-3-methylimidazolium
e.g.	for example
$E_T(30)$	Reichardt's scale of solvent polarity
E_T^N	Reichardt's normalised scale of solvent polarity
EI	electron ionization

etc	et cetera
EXAFS	Extended X-Ray Absorption Fine Structure Spectroscopy
FAB	fast atom bombardment
G	Gibb's free energy
GC	gas chromatography
GC Mass spectrometry	gas chromatography – mass spectrometry
Gn	Guanidinium
η	eta
H	enthalpy
^{1}H	proton
hmim	1-hexyl-3-methylimidazolium
HOMO	highest occupied molecular orbital
hr	hour
Hz	Hertz
Im	imidazole
IR	infrared
J	coupling constant
k	rate constant
k_2	second order rate constant
L	ligand
ln	natural logarithm
log	logarithm to base 10
LPDE	lithium perchlorate diethyl ether (generally a 5.0 M solution)
LUMO	lowest unoccupied molecular orbital
μ	micro (1×10^{-6})
m	medium
m	muliplet
m/z	mass over charge ratio
M	molar
M2P	2-methylpentenes
MA	methyl acrylate

MBI	1-butyl-3-methylimidazolium chloride
mol	(mole) Avagadro's constant (6.022×10^{23})
mol%	mole percent
nH	n-hexenes
nm	nanometre (1×10^{-9} m)
NMR	nuclear magnetic resonance
N/X	ratio of *endo*-product formation over *exo*-product formation
OTf (or triflate)	trifluoromethylsulfonate
π	pi bonding orbital
π^*	pi anti-bonding orbital
P_i	internal pressure
ppm	parts per million
prods/DiCp	ratio of product formation over dicyclopentadiene formation
q	quartet
R	Gas constant ($8.315\ JK^{-1}mol^{-1}$)
rel.	relative
rtp	room temperature and pressure
δ	sigma orbital
s	second
s	singlet
S	entropy
S	solubility
S_p	solvophobicity
SDS	sodium dodecylsulfate
st	strong
t	triplet
T	absolute temperature (measured in Kelvin)
TBP	tetrabutylphosphonium chloride
Tf_2N (or imide)	trifluoromethanesulfonimide
THF	tetrahydrofuran
UV-VIS	ultraviolet / visible
%vol	percentage by volume

vs.	*versus*
w	weak
wrt	with respect to
X	molar ratio
XANES	X-Ray Absorption Near Edge Spectroscopy

SECTION 1

ROOM TEMPERATURE IONIC LIQUIDS

1. GENERAL INTRODUCTION TO IONIC LIQUID CHEMISTRY

1.1. Background

The study of substrates in solution is a broad topic in chemistry, simply due to the fact that it brings together many wide-ranging fields that would otherwise be thought of as completely separate. This is because a vast range of laboratory reactions (from biological chemistry through organic and organometallic chemistry to physical chemistry) take place in the liquid phase, and the majority of these use a solvent that is not one of the reacting substrates. As mankind's chemical knowledge has been developed and refined over the centuries, so the importance of the solvent in any given reaction has been pushed further and further to the forefront of importance. This is because chemists have learnt that one solvent may appear to 'drive' a reaction more than another, and the means (both individually for a particular solvent, and generally for a group of solvents) by which they do affect the given reaction is of great interest.

Although the number of publications showcasing new reactions and synthetic methods seems to increase exponentially annually, it would appear that less work is done on the media and environments that surround and affect these reactions. In fact, relatively few liquids are in general use as solvents, although in theory, any liquid may be used as a solvent.

The beginning of the 1990's brought the realisation that cleaner technologies (or the so-called 'Green Revolution') would be needed to sustain the global ecosystem of this planet. Mainstream science and the media transmitted the concepts of global warming, chemical poisoning and mass pollution to the general public. As well as changing the way the general public thought about natural resources and waste disposal, it brought the wholesale realisation to the chemical industry that the issue of using dangerous solvents must be addressed. Many substrates used in chemical processes are more hazardous than solvents. However, priority lies with solvents since they are used in huge amounts, and they are very often volatile liquids that are difficult to contain.

It seems fitting therefore that the advent of the usage of room temperature ionic liquids as reaction solvents occurred during this period. Although still in its infancy as a field of chemistry, it appears more and more likely (as new studies and works are published in this domain) that synthetic chemists will in the near future, come to depend upon these solvent systems as a viable option for conducting reactions in. This is not only due to the fact that they provide a versatile and useful liquid phase for many important reactions, but also because they have properties that are attractive in view of the adverse attention the chemical industry has received due to solvents and processes that are harmful to the environment.

It should be noted that the terms molten salt and ionic liquid, although they appear to mean the same thing, are being used in different ways. They are similar in that an ionic liquid and a molten salt are both liquids that consist only of ions. Until recently, both were used to describe room temperature or low melting point salts. However, it has become common practice[1.1] to think of molten salts in terms of high-melting, highly viscous and very corrosive media. Ionic liquids are generally considered to be liquids at lower temperatures and have a relatively low viscosity. With this form of definition, a point where these so-called "molten salts" and "ionic liquids" meet or combine is inevitable. This has been arbitrarily set at 100 °C. So any salt that melts at less than 100 °C can be termed an ionic liquid. The phrase room temperature ionic liquid is also used quite often. Again, this is a more specific version of an ionic liquid. As the name suggests, it can be classed as a salt which is in liquid phase at room temperature under normal atmospheric conditions. Every ionic liquid used in this study was in the liquid phase at room temperature.

This chapter will attempt to give a general overview of room temperature ionic liquids and the general properties that set them apart from other solvents. A few examples of their synthetic use to date will be given, though more detailed accounts of their use as solvent systems for the Diels-Alder reaction (see chapter 4) and the dimerisation of simple olefins by an organometallic nickel catalyst system (see chapter 8) are described in detail elsewhere.

1.2. Historical Overview

Despite the great interest that has been shown in ionic liquids over the last 10 years, they are not a new class of compounds. The first literature reference to a room temperature ionic liquid appeared in 1914.[1.2] The ionic liquid was ethylammonium nitrate ($[EtNH_3][NO_3]$), which has a melting point of 12 °C. The first ionic liquids composed of chloroaluminate ions were developed in 1948 by Hurley and Wier.[1.3] The cationic part of the ionic liquid consisted of ethyl pyridinium bromide. They examined this salt in electroplating studies, using it as a bath solution to electroplate various metals with aluminium. Since these liquids are exclusively made up of ions and therefore conduct, the first studies on them concentrated solely on their electrochemical properties.

Many discoveries can be said to occur "before their time", when the chemical understanding of their importance has not yet reached its maturity. This is certainly the case with ionic liquids. Since their initial discovery, the literature shows some sparse mentions and brief periods of interest. Initially, it is known that any interest in these liquids was purely down to their electrical properties and potential use in electrochemical systems.

Ionic liquid chemistry was taken up again in the late 1970's, when the groups of Osteryoung[1.4] and Wilkes[1.5] succeeded in preparing room temperature chloroaluminate melts. Again, the focus of interest was on any application that could benefit from their electrochemical properties. These were citied as being electrolytes in batteries, photoelectrochemical cells and electroplating. However, the first mention of the possibility of their use as a reaction solvent was made by Wilkes.[1.5]

It was in the early 1980's that research began to concentrate on this aspect of the applications of ionic liquids. As positive results emerged, this slowly began to overshadow their previously intended use as electrolytes. This will be discussed in more detail later in this chapter. First, the types of compounds that can make up ionic liquids,

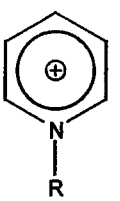
and second, the properties which make these solvents so attractive for synthetic use should be mentioned. Both these subjects will be discussed briefly in this section. However, reviews do exist which treat these subjects in more detail.[1.6]

1.3. Ionic Liquid Composition

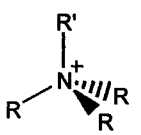
The different modes of preparation of ionic liquids are discussed elsewhere (chapter 2). However, as an introduction to these compounds, the different types of ionic liquids should be mentioned.



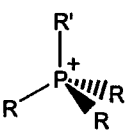
N,N'-dialkylimidazolium cation



N-alkylpyridinium cation



Alkylammonium cation



Alkylphosphonium cation

Figure 1.1: Important types of cation used in ionic liquids

The most important cations used in the formation of ionic liquids are shown above in figure 1.1. Even more chemical variation is permitted by changing the anion involved. Examples of anions include $[AlCl_4]^-$, $[BF_4]^-$, $[PF_6]^-$, $[NO_3]^-$ and $[ClO_4]^-$. A more comprehensive discussion of the anions and cations used in this study is provided in chapter 2.

1.4. Properties of Ionic Liquids

1.4.1. General Properties of Ionic Liquids

It should be noted that a wide range of ionic liquids now exist, with varying anions and cations. Only the physical and chemical properties of ionic liquids as a general family of compounds will be dealt with in this chapter.

1.4.1.1. Low Melting Points

This is the fundamental aspect that makes these liquids so useful in synthetic applications. Most common salts have extremely high melting points due to closely packed crystal structures and strong bonds formed between the composite ions. It would be possible to obtain a liquid of almost any salt, but the working temperature of this melt, in most common cases, would be in the order of several hundred degrees celsius. The use of these liquids as reaction solvents or media to study dissolved organometallic complexes requires that they do not decompose or destroy the reagents or substrates dissolved within. Clearly, in the case of more well-known salts (eg: NaCl, LiBr, etc) this

is not possible, since most organic reagents could not exist at such temperatures. Ionic liquids provide an ionic environment at temperatures that can accommodate laboratory reagents.

Certain ionic liquids have melting points that are actually lower than those of most organic solvents. For example, haloaluminates can be cooled to around –90 °C before fusing. This is useful when investigating or reacting theramally labile organometallic reactants or intermediates.

1.4.1.2. Good Solvating Abilities

This is, of course, what defines a solvent. If it cannot dissolve a substrate, an ionic liquid cannot be called a solvent with respect to that substrate. In the case of room temperature ionic liquids, they are able to solvate a wide range of organic and inorganic materials. This makes it possible to bring unusual combinations of reagents into the same phase.

1.4.1.3. Polarity

Despite being composed entirely of ions, the freedom which these ions have to move, even at low temperatures indicates that they are poorly coordinating. That is, it is energetically easier to disrupt the solid state of the salt and form a liquid. Yet because the liquid is composed of ions, the polarity of the system is high. Therefore, such liquids could theoretically be used as solvents to stabilise highly polar reaction pathways or intermediates. Both the high polarity (see Section 2) and low coordination (see Section 3) have been exploited in reactions.

1.4.1.4. Multi-Phase Possibilities

Ionic liquids are immiscible with a number of organic solvents and so provide a nonaqueous, polar alternative for two-phase systems. This characteristic has already been exploited in the indutrially accepted dimerisation of lower olefins, also called the Dimersol® process (see section 3).

All of the room temperature ionic liquids from this study can be classed as hydrophobic or hydrophilic, according to how they interact with water. Hydrophobic ionic liquids form two phase systems when mixed with water, and so can be used to form immiscible polar phases with water.

This general characteristic can prove to be very useful when carrying out catalytically driven reactions, since careful choice of the ionic liquid can allow easy separation of the reaction products from the system without disturbing or destroying the catalyst, which will remain in the ionic liquid phase. For a full discussion on this, see chapter 8.

1.4.1.5. Low Vapour Pressures

The full implications of this will be discussed in more detail later, but from a chemical viewpoint, a solvent that has little or no vapour pressure is nonvolatile. This means that the separation of ionic liquids from volatile organic compounds is possible through high-vacuum systems as the former do not evaporate.

1.4.2. Comparative Properties of Ionic Liquids

The selection of the components used to form the anionic and cationic parts of the ionic liquid can have a large influence on how the general properties described above will vary. This is an exciting feature of ionic liquids, since it gives rise to many possibilities to actually choose a solvent that fits the requirements of the reagents or system being studied. Although this form of 'solvent tailoring' is still in its infancy, it remains a very real possibility in the near future. Listed below are some of the properties of ionic liquids that change as the component anions and cations are varied.

1.4.2.1. Melting Point

The defining characteristic for an ionic liquid is its melting point. Since alkali metal halides have characteristically high melting points, whereas halides with suitable organic cations melt at temperatures under 150 °C, the link between the structure and chemical composition of an ionic liquid and its melting point should be highlighted. The combination of low symmetry,[1.1] weak intermolecular interactions,[1.7] and good charge distribution in the cation[1.9] have all been shown to be properties that help give salts low melting points.

The anion also plays a part in influencing the melting point. Table 1.1 below shows the melting points of different salts, all containing the 1-ethyl-3-methylimidazolium (emim) cation.[1.5] In most cases, increasing the size of the anion leads to a further decrease of the melting point.

Table 1.1: The influence of different anions on the melting point of imidazolium salts[1,5]

Imidazolium salt	Melting point / °C
[emim]Cl	87
[emim][NO_2]	55
[emim][NO_3]	38
[emim][$AlCl_4$]	7
[emim][BF_4]	6
[emim][CF_3SO_3]	-9
[emim][CF_3CO_2]	-14

Section 1.4.1.3 above (discussing the polarity of ionic liquids in general) mentioned that poorly coordinating anions and cations make up ionic liquids because even at low temperatures they are free to move. There are two main factors that contribute to an ion's ability to coordinate; its polarity and the delocalisation of charge. Table 1.1 shows a variety of different anions with the same cation. It can be seen that the relatively compact chloride anion would possess a much more localized charge than, say, the $[CF_3SO_3]^-$ anion. Not only is the size of the anion over which the single charge (in all cases a single charge is present) is spread of importance, but also the ability of the charge to be spread over a much of the surface of the anion as possible. It is clear from looking at the two examples given, that the latter ($[CF_3SO_3]^-$) would possess various resonance forms, especially around the SO_3 system, making the charge more delocalised, and the substrate more likely to form salts which melt at lower temperatures.

1.4.2.2. Thermal Stability

The thermal stability of ionic liquids is governed by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds (where applicable). Ionic liquids

synthesised by direct protonation of an amine or phosphine show low thermal stability. Many melts with trialkylammonium anions decompose at temperatures below 80 °C *in vacuo*. The maximum working temperature for quaternary ammonium chloride salts is about 150 °C, whereas [emim][BF_4] is stable up to about 300 °C.[1,8] Therefore, some ionic liquids have a liquid range of up to or even more than 400 °C (for example [emim][imide] – m.p. –3 °C; stable up to more than 400 °C). Conventional solvents such as water or most organic solvents cannot match these figures.

1.4.2.3. Density

In general terms, studies have shown that the density of imidazolium ionic liquids can be varied to within a certain range by the choice of the anion.[1,7] Fine adjustment is then possible by careful choice of the cation. As the bulk of the organic cation increases (for example, by adding longer alkyl chains to the imidazolium cation), the density of comparable ionic liquids will decrease.

1.4.2.4. Lewis Acidity and Coordination Ability

The nature of the anion of the ionic liquid will essentially decide these characteristics. Coordination ability was discussed above in section 1.4.2.1). Some ionic liquids use known Lewis acids to form the anionic part of their structure. In particular, the class of ionic liquids called chloroaluminate melts are of particular interest, since the Lewis acidity/basicity of the melt can be adjusted by altering the molar ratios of the components added to form the melt. The ionic liquid [bmim]Cl-$AlCl_3$ is made up of 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) and aluminium trichloride ($AlCl_3$). If added in eqi-

molar amounts, a neutral ionic liquid will be formed, consisting mainly of the species $[AlCl_4]^-$. However, if a molar excess of $AlCl_3$ is used in the preparation, then the resulting melt will be Lewis acidic in character, where the Lewis acidic $[Al_2Cl_7]^-$ and $[Al_3Cl_{10}]^-$ anions will exist. Conversely, if a molar excess of [bmim]Cl is used, then the resulting melt will be Lewis basic in character, where the Lewis basic chloride anion will exist. The Lewis acidic species are weakly coordinating, whereas the Lewis basic species are strongly coordinating. Other anions (which can only be used in an equimolar ratio to the cation) can also determine the Lewis acidity of the resulting ionic liquid.[1.10]

1.4.2.5. Polarity

Solvent polarity is the most commonly used form of solvent classification. It is widely thought that ionic liquids will be highly polar solvents; the simplest definition of a polar solvent being one that will dissolve and stabilise dipolar or charged substances. Solvent polarity is normally measured in an empirical fashion. A well-understood, easily measurable and strongly solvent-dependant process is analysed in a large number of different solvents. From these data a scale of relative polarity can be inferred. A widely used measure of solvent polarity is the spectral absorption of a solvatochromatic dye. The relative solvating ability of a particular liquid can be derived from a measured absorption maxima. Among the most widely used, especially in ionic liquids, is the Reichardt's dye.[1.11]

Figure 1.2 below, shows the solvochromatic dye Reichardt's dye (2,4,6-triphenylpyridinium *N*-4-(2,6-diphenylphenoxide) betaine). It exhibits one of the largest solvochromatic shifts known (375 nm between diphenyl ether and water). The dye will change colour according to the type of solvent it is used in, and its scale comprises the whole visible region of the spectrum. The $E_T(30)$ scale works by registering the $\pi \rightarrow \pi^*$ absorption band of intramolecular charge transfer. It has units, so a normalised version of

the scale (E_T^N) was introduced, which ranges from between the least polar solvent TMS (0.000) to the most polar solvent water (1.000). It can register effects arising from the solvent dipolarity, hydrogen bonding, and Lewis acidity, and is considered to be a good method of measuring these factors. However, the word polarity is often used in a confused manner, and often to describe the scale that Reichardt's dye can measure. Polarity in an isolated sense (i.e. excluding contributions from hydrogen bonding and Lewis acidity) is not easy to measure. The measurement here includes these factors and it should be stressed that they are not easily removed. It is not generally relevant to use Reichardt's dye as a good judge of the polarity of a substrate. In this study it has been to give comparative measures of the strength of potential hydrogen bond donor groups on species. This is discussed in detail elsewhere (see chapter 6).

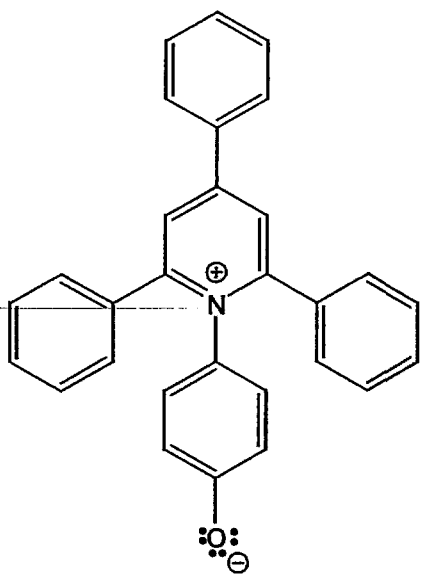


Figure 1.2: Reichardt's dye[1.11]

This scale and the results it can achieve will not be discussed any further here, suffice to say that despite the fact that polarity is not easy to isolate, the E_T^N scale is the most accepted form of measuring solvent polarity in ionic liquids that is in general use today.

1.4.3. Environmental Aspects

At the beginning of this chapter, some global environmental problems that face the chemical industry were highlighted. It was also mentioned that one of the future paths of the so-called 'green chemistry' movement could lie in the development of our knowledge and understanding of ionic liquid chemistry, leading to its increased usage in laboratory synthesis and large-scale manufacturing processes alike.

One of the biggest environmentally damaging factors concerning the chemical industry is its large-scale use of volatile solvents. These are difficult to contain, handle and store. Consequently, large amounts will escape into the atmosphere, causing pollution. On a global scale, this is a significant factor towards the erosion of the environment. However, as ionic liquids have no vapour pressure they are not in the least volatile. Thus, being easier to contain and handle (in this respect) makes them an attractive proposal as a new solvent system for many processes.

As will be discussed later, in chapter 8, many processes that use expensive catalysts must constantly replenish the catalytic material since it is more often than not lost when the product of the reaction is extracted. Due to their solvation properties and the fact that they can be altered to adjust their solvation properties, ionic liquids can be produced that dissolve catalytic materials but do not mix with the reaction products. These two-phase reactions permit easy separation of the reaction products from the catalyst, and also preserve the life of the catalyst, thus allowing recycling of the catalyst and avoiding wastage.

Ionic liquids can also be cleaned if necessary, and re-used after most applications. This would of course, reduce the initial cost of the solvent, and benefit the environment in that the yield of any product per volume of solvent would greatly increase. Waste disposal is a big problem for the chemical industry, and anything that can reduce this must surely be of benefit to the environment.

It appears that ionic liquids do deserve their tag as 'Green Solvents'. However, one criticism that is often made of things that are supposedly 'good for us' is that they do not taste, look, or perform as well as the conventional product that is 'not as good for us'. In the case of ionic liquids, work is still being carried out to investigate their performance in known reactions, relative to conventional solvent methods. The fact that ionic liquids they have many variations, and differing physical and chemical properties for each variation, means that they have the potential to be designer solvents. If they can be understood to a high degree, then in the future chemists could produce very specific solvent systems in the knowledge or with an informed prediction that they will suit a certain reaction. At the moment, work is still being carried out to collect this data and build a library of information on ionic liquids.

The work in this thesis will concentrate on three aspects of this data collection. The first is a comparative spectroscopic study of several ionic liquids. The properties of ionic liquids listed above are known, but need to be understood from first principals so that they can really be understood, and accurate predictions can be made according to what properties other ionic liquids will have. The second aspect involves the Diels-Alder reaction, which is a well-known organic reaction. Not only is it useful to know how different solvents will affect the reaction, but also to examine whether the reaction reveals any information on how ionic liquids behave and use their special properties when substrates are added to them. The third involves the study of structures of model complexes of nickel, based on active nickel complexes that are used in ionic liquids in industry to catalyse the dimerisation of lower olefins.

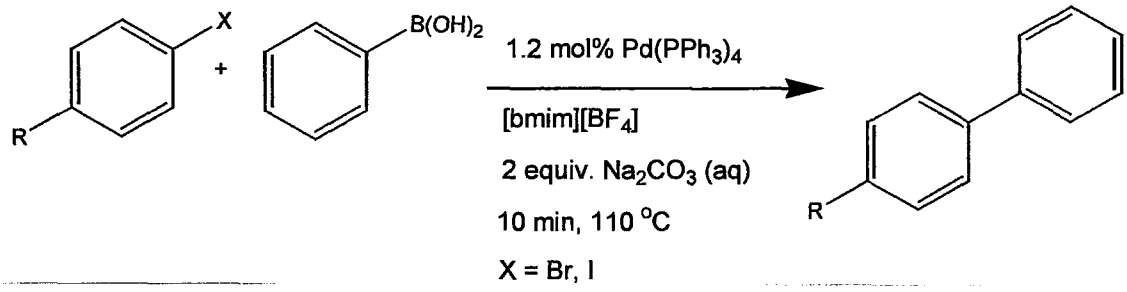
For the last two aspects listed, it would be interesting to know whether the ionic liquids involved use their physical properties (polarity, solvation abilities) to interact with the complexes or substrates, or whether they chemically alter the reactions or processes in some way. The answer might be only one, or both, or a combination of both, or even a separate reason for each study chosen. However, it is certain that much data will be provided by the outcome of the results gained.

1.5. Ionic Liquids as Reaction Solvents

A more thorough treatment of this subject can be found in several recent reviews.[1.6] In recent years, much interest has been focused on the use of ionic liquids as media for synthetic chemistry. This is not only due to the already discussed environmental benefits that they bring. In many cases, ionic liquids have proved to produce results for known reactions that are as good as, if not better than many traditional organic solvents. The reaction types that will be dealt with in detail in this thesis are Diels-Alder reactions (see section 2), and the nickel phosphine catalysed dimerisation of simple olefins (known as the Dimersol® process, see section 3). For this reason, they will not be discussed here. Other reactions that have benefited from the use of ionic liquids as the solvent media are hydrogenations[1.12] and Friedel-Crafts reactions.[1.13] A brief example of a catalytic and a stoichiometric reaction, respectively, follow.

1.5.1. Palladium Catalysed Suzuki Cross-Coupling Reactions in Ionic Liquids

The Suzuki cross-coupling reaction is an extremely versatile methodology for the generation of new carbon-carbon bonds.[1.14] As with many catalytically driven processes, a major problem remains the loss of catalyst by a number of means, including decomposition, loss into the product and poor reagent solubilities. To counter these problems, Welton, Matthews and co-worker[1.15] have recently attempted this reaction in the ionic liquid [bmim][BF_4]. Scheme 1.1 and table 1.2 below show the reactions attempted and results obtained.



Scheme 1.1: The Suzuki cross-coupled reaction in [bmim][BF_4]. Work by Welton, Matthews and co-worker[1.15]

The first attempt at this reaction (entry 6) showed some catalyst decomposition (by the precipitation of a black solid), and gave only a modest yield of 30 %. This entry, being the first attempt, was carried out using the original Suzuki conditions, which involved adding all substrates together and heating at 110 °C for 6 hours[1.16]). However, from this starting point, modification of the original conditions significantly boosted the yields of

the desired products. This also led to enhanced reaction rates and no catalyst decomposition.

The new conditions reported by Welton, Matthews and co-worker included heating the catalyst with the aryl halide in [bmim][BF_4] at 110 °C with vigourous stirring until complete dissolution was observed. At this point the catalytic solution was allowed to cool to ambient temperature and the reaction started by the addition of the arylboronic acid and an aqueous solution of Na_2CO_3.

Table 1.2: Results of the Suzuki cross-coupled reaction in [bmim][BF_4] with variation of the aryl halide. Results from Welton, Matthews and co-worker[1.15]

Entry	X	R	Yield (%)[a]	TON[d]	TON h^{-1}
1	I	H	86 (95)	72	430
2	Br	H	93 (95)	78	465
3	Cl	H	1 (1)	1	5
4	Br	Cl	17	14	85
5	Br	$COCH_3$	67 (97)	56	335
6	Br	CH_3	30[b]	25	150
7	Br	CH_3	69 (92)	58	345
8	Br	CH_3	72[c]	60	360
9	Br	CH_3	68	57	340
10.1	Br	OCH_3	81 (92)	67	401
10.2	Br	OCH_3	89	73	441
10.3	Br	OCH_3	77	64	381
10.4	Br	OCH_3	82	68	406

[a] Isolated yields after 3 hours in parentheses

[b] Suzuki reaction without prior activation of catalyst. Decomposition of catalyst observed

[c] Lower catalyst concentration, $Pd(PPh_3)_4$ (0.3 mol%). Reaction time 1 hr

[d] TON = Turnover number (no. mols product formed per mol catalyst)

Entry 8 in table 1.2 shows that the reaction can be carried out to high yield with significantly low catalyst concentration (0.3 mol% which is one tenth of the concentration generally required). Entry 9 was the only run conducted under air, and showed no signs of catalyst decomposition. This shows that once the catalyst solution has been generated, the reaction shows analogous results.

Further investigations involved varying the nature of the arylhalide. Electron-rich and electron-deficient variants were used in the reaction. Entry 2 shows a 93 % yield (455 TON h^{-1}) was achieved in ten minutes using bromobenzene and phenylboronic acid in [bmim][BF_4], whereas under the original Suzuki conditions a yield of 88 % was observed after six hours (5 TON h^{-1}).[1.16] Entry 10.1 illustrates the formation of 4-methoxybiphenyl. Under the original Suzuki conditions it was produced in a 40 % yield in six hours (2 TON h^{-1}).[1.16] In [bmim][BF_4] the same reaction, using the refined conditions took ten minutes to produce a yield of 81 % (401 TON h^{-1}). These two runs showed an approximate increase in reactivity in the order of 90 and 200 respectively, on changing from the original Suzuki conditions to the refined conditions with [bmim][BF_4] as the reaction solvent.

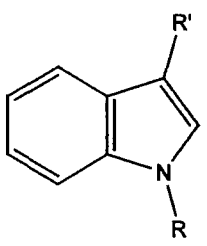
Isolation of the biaryl products from the ionic liquid reaction mixture was possible by extraction with diethyl ether, sublimation or precipitation by the addition of water. In all cases, no apparent leaching of the palladium species into the product was observed.

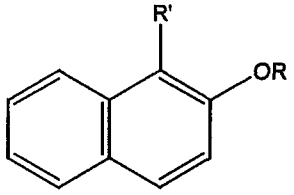
Another clear advantage of this reaction was the fact that the ionic liquid reaction system could be cleaned and re-used. Two by-products formed in the reaction are $NaHCO_3$ and $Na[XB(OH)_2]$. These appeared to modify the miscibility of [bmim][BF_4] with water, such that two phases were formed at ambient temperature (normally [bmim][BF_4] is termed a hydrophilic ionic liquid and will associate freely with water). When large excesses of water were added, the by-products were invariably soluble in the aqueous phase. This enabled the removal of by-products with water, leaving a clean ionic liquid/catalyst solution. Entries 10.2 – 10.4 in table 1.2 show the repeated runs of the same ionic liquid/catalyst solution (once cleaned in the manner described) for the reaction with 4-

bromoanisole and phenylboronic acid. No further modification was required on the catalytic solution for its re-use. The recycling procedure accommodated approximately three runs before a significant loss of catalytic activity was observed.

1.5.2. Regioselective Alkylation in Ionic Liquids

The ionic liquids [bmim][PF_6] and [bmim][BF_4] have been used as alternatives to commonly used dipolar aprotic solvents for the regioselective alkylations at the heteroatom of indole and 2-napthol by Seddon and co-workers.[1.17] In both cases, it is usually achieved by the pre-formation of ambident indolyl or 2-naptholate anions, and subsequent treatment with the appropriate alkyl halide. The reaction is solvent dependant, the typical choice being DMF, which meets the criteria of being dipolar and aprotic. Until ionic liquids were employed as the solvents for these reactions, problems with product isolation and solvent recovery were apparent.





1 R=R^1=H

2 R=Et, Bu, Me or $PhCH_2$; R^1=H

3 R=R^1=Et, Bu, Me, or $PhCH_2$

4 R=R^1=H

5 R=Et, Bu, Me or $PhCH_2$; R^1=H

6 R=R^1=Et, Bu, Me, or $PhCH_2$

Figure 1.3: Starting materials used and products obtained in the selective alkylations of indole, **1**, and 2-napthol, **4**, in the ionic liquid [bmim][PF_6]. Work by Seddon and co-workers[1.17]

The procedure of Heaney and Ley for the *N*-alkylation of indoles in organic solvents with solid KOH was followed, using [bmim][PF_6] as the solvent system.[1.18] The products were easily extracted with diethyl ether. The results are shown below in table 1.3.

Table 1.3: The reaction of indole, **1**, and 2-napthol, **4**, with a selection of alkyl halides in the ionic liquid [bmim][PF_6]. Work by Seddon and co-workers[1.17]

Substrate	Alkyl halide	Yield (%)	Products	Ratio
1	EtBr	92	**2+3**	(>99:1)
1	BuBr	93	**2+3**	(>99:1)
1	MeI	91	**2+3**	(93:7)
1	BnBr	94	**2+3**	(95:5)
4	EtBr	94	**5+6**	(>99:1)
4	BuBr	98	**5+6**	(>99:1)
4	MeI	97	**5+6**	(97:3)
4	BnBr	95	**5+6**	(95:5)

In the case of indole, almost exclusive *N*-alkylation to form products of the form **2** was seen in each case. The yields shown took 2-3 hours to achieve. Only the more strongly reactive alkyl halides $PhCH_2Br$ and MeI showed any traceable amount of the unwanted dialkylated product **3**. The same general trends applied to 2-napthol, with almost exclusive *O*-alkylation being observed, except with the same two reactants that were considered more strongly reactive.

Filtration was sufficient to remove residual insoluble KOH and precipitated potassium halide. Vacuum drying was observed to render the ionic liquid fit for re-use. No appreciable decrease in regioselectivity was observed after numerous re-uses and recyclisations of the ionic liquid.

2. PREPARATION AND PROPERTIES OF A RANGE OF ROOM TEMPERATURE IONIC LIQUIDS

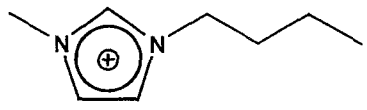
2.1. Preparation of Ionic Liquids

2.1.1. Air-Stable Ionic Liquids

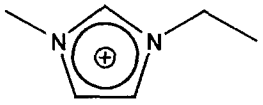
A large variety of air-stable ionic liquids were prepared during the course of this project. One of the ionic liquids used in this project was arbitrarily designated as the 'standard' air-stable ionic liquid. Therefore the others showed variations in both the cation and anion. The 'standard' ionic liquid used was [bmim][BF_4], because when the anion was varied, the $[bmim]^+$ cation was always used, and when the cation was varied, the $[BF_4]^-$ anion was always used. Although cation variation was applied, it should be noted that only imidazolium-based cations were used in this study.

2.1.1.1. Cation Variation

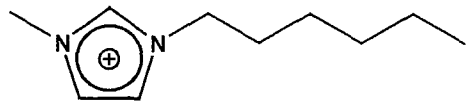
Figure 2.1 below shows the structures of the so-called 'standard' cation (that was described above) and the variants that were succesfully prepared. In the form that they are shown in figure 2.1, they could either be part of the ionic liquid, or a halide salt for future use in ionic liquid preparation. Each cation was prepared by a simple quaternisation/addition reaction between 1-methylimidazole (except in the case of the 1-butyl-2,3-dimethylimidazolium cation which used 1,2-dimethylimidazole as the starting substrate) and the appropriate alkyl halide. In all cases (except those specifically mentioned below) a near-quantitative yield was achieved. As is standard with air-stable ionic liquids, the preparation is *via* the metathesis of a halide salt with, for instance, a silver, group I metal or ammonium salt of the desired anion.



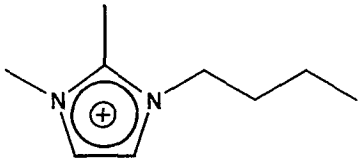
1-butyl-3-methylimidazolium cation



1-ethyl-3-methylimidazolium cation



1-hexyl-3-methylimidazolium cation



1-butyl-2,3-dimethylimidazolium cation

Figure 2.1: Imidazolium cations synthesised for this study. The 1-butyl-3-methyl imidazolium cation is the 'standard' cation. All ionic liquids generated from these cations contained the anion $[BF_4]^-$

It was found that as the length of the alkyl side-chain increased, so too did the amount of heat needed for reaction (indicating the facility of reaction in each case). The 1-ethyl-3-methylimidazolium cation complex had to be prepared at 0 °C with constant stirring and the dropwise introduction of the alkyl halide, since otherwise the reaction was so vigourous that local concentration effects would have caused extensive decomposition. The 1-butyl-3-methylimidazolium chloride salt was prepared in the same way, but letting the reaction mixture stabilise slowly at room temperature after mixing was necessary, followed by a 24 hour reflux at 80 °C. The same procedure was applied to the 1-butyl-2,3-dimethylimidazolium cation complex. In the case of the 1-hexyl-3-methylimidazolium cation complex, both reactants could be added simultaneously. Stronger heating (110 °C) was needed to drive the reaction.

This indicates that as the chain length increases, so too does the effort required to cause a reaction. This is due to the fact that alkyl halides of shorter chain lengths are more polar in character, leading to a greater degree of electrophilicity at the reactive carbon.

Recrystallisations were carried out to remove any traces of unreacted imidazole. The imidazole has a high boiling point and is non-volatile, so its removal at this point was considered more facile. The recrystallisations were performed using pre-dried acetonitrile/toluene mixtures, leaving white crystalline solids.

In the case of the 1-hexyl-3-methylimidazolium cation, a recrystallisation using this method resulted in a brown solid, which was unchanged from the initial product obtained. In order to remove the brown colouration, two washes were carried out using toluene. The resulting solid was white, and the ionic liquid synthesis could now be carried out.

The same situation was observed for the 1-butyl-2,3-dimethylimidazolium cation. However, instead of the formation of a coloured solid, the presence of impurities (in this case, the starting material 1,2-dimethylimidazole) was detected by ^{1}H NMR, following the recrystallisation step. Instead of washing the product to remove the impurity, the reaction was repeated. Toluene was added as a solvent. 1-butyl-2,3-dimethylimidazolium chloride (the form in which the cation was prepared) is insoluble in toluene, whereas the starting material 1,2-dimethylimidazole is soluble. Once dissolved, excess chlorobutane was added and the mixture heated under reflux. The quality of the product was such that no recrystallisation was required to purify it further.

The only species that could not be succesfully generated was the 1-(2',2',2'-trifluoroethyl)-3-methylimidazolium cation. Several attempts were undertaken to synthesise this compound. The starting materials used were 2-bromo-1,1,1-trifluoroethane and 1-methylimidazole. No reaction was observed under reflux at 110 °C. It was feared that the high volatility of the alkyl halide during transfer to the reaction vessel was responsible for this. In the second attempt, a sealed glass pressure vessel was used and the alkyl halide (cooled to –20 °C) transferred *via* cannula to the 1-methylimidazole (frozen at –80 °C), to eliminate this factor. The contents of the vessel were then frozen at –80 °C and left to warm up under a static vacuum. Heat was applied to the sealed vessel with extreme care. However, no reaction was observed. Thus, it

appears that the presence of the highly electronegative trifluorormethyl group prevents the Br-C bond from becoming polar enough to permit a reaction to occur.

2.1.1.2. Anion Variation

Figure 2.2 below shows the structures of the 'standard' anion (that was described above) and other anions which made up ionic liquids that were either prepared, or whose preparation was attempted. In the form they are in figure 2.2, it should be assumed that they form part of the ionic liquid, with the $[bmim]^+$ group forming the countercation. As is standard with air-stable ionic liquids, the preparation is *via* the metathesis of a halide salt with, for instance, a silver, group I metal or ammonium salt of the desired anion. In all cases, except where indicated, a group I metal salt of the anion was used with 1-butyl-3-methylimidazolium chloride.

$[BF_4]^-$	Tetrafluoroborate	$[CF_3SO_3]^-$	Triflate (or OTf)
$[PF_6]^-$	Hexafluorophosphine	$[CH_3SO_3]^-$	Methyl sulfonate
$[NO_3]^-$	Nitrate	$[(CF_3SO_2)_2N]^-$	*N*-Trifluoromethanesulfonate (or imide)
$[ClO_4]^-$	Perchlorate	$[(Me_3Si)_2N]^-$	Bis (trimethtylsilyl)amide
		$[(CH_3CH(OH)CO_2]^-$	Lactate

Figure 2.2: Anions used in this study. The tetrafluorborate anion is the 'standard' anion. All ionic liquids generated from these anions contained the cation $[bmim]^+$

The ionic liquids [bmim][ClO_4] and [bmim][$CH_3CH(OH)CO_3$] were prepared exclusively by the addition of [bmim]Cl to the appropriate sodium salt of the anion. The ionic liquid [bmim][imide] was prepared exclusively by the addition of [bmim]Cl to the lithium salt of the anion. In these cases, acetone was used as the solvent. The main problem, after metathesis, was the removal of dissolved sodium or lithium chloride. This would prove to be crucial for the ionic liquids used as Diels-Alder solvents since, as shall be seen in chapter 6, chloride anions can act as Lewis bases and hinder the reaction. Most of the unwanted salt could be removed by filtration following the reaction step, but three methods were used to achieve a totally chloride-free ionic liquid in the salt metathesis cases.

The first involved adding dry dichloromethane to the neat ionic liquid. A white precipitate was observed to form as the dissolved salt is not soluble in dichloromethane (which mixes freely with the ionic liquid). The ionic liquid/dichloromethane mixture was then filtered to remove the salt.

The second method was a simple gravity filtration of the neat ionic liquid through a short column of neutral alumina. However, this method was time consuming because the ionic liquid could not be forced down by gas pressure as this might force the dissolved salt down with it. In all cases, the filtration took a few days for approximately 50 cm^3 of ionic liquid. In all cases, activated charcoal was added to the neat ionic liquid before filtration, and the mixture stirred for 12 hours. This was designed to remove any colouration from the ionic liquid. The activated charcoal was removed during the flitration through neutral alumina. Although this was a time-consuming process, all ionic liquids made were purified by this method, as a precaution.

The third method involved adding dichloromethane to the ionic liquid. On precipitation of the salt, a small amount of water was added (normally a third of the volume of dichloromethane added). The water would normally associate with these ionic liquids, but in this case the dichloromethane forced water into a separate layer. Vigourous mixing of both layers, followed by separation of the water layer from the ionic

liquid/dichloromethane layer ensured that the water removed the dissolved salt. This was confirmed by the disappearance of the white precipitate. This is most likely due to the fact that the salt is more readily soluble in water than the ionic liquid. This was repeated three times. However, water would also remove some of the ionic liquid. The water washings were collected and the ionic liquid extracted from it with dry dichloromethane (three times). The dichloromethane washings were combined with the original ionic liquid/dichloromethane mixture. This was by far the most effective method of preparing chloride-free ionic liquids when group I metal salts of the anion were used. However, only ionic liquids whose alkyl side chain lengths were four carbon units or longer could be purified in this way.

The ionic liquid [bmim][BF_4] was also prepared by the addition of [bmim]Cl to the sodium salt of the anion. The third method of chloride removal, described above, was used. However, another method of preparing a chloride-free ionic liquid was also attempted. This time the anion was introduced in its acid form (HBF_4). The reaction was conducted in two layers to aid the immediate separation of HCl from the ionic liquid, upon their formation. [bmim]Cl was dissolved in the minimum amount of water, and dichloromethane added to form a second layer. The acid had to be added with extreme care to prevent an exothermic reaction from taking place. It was hoped that during the reaction the ionic liquid would go into the organic layer, and HCl into the aqueous layer. Upon completion of the reaction, the aqueous layer was separated from the organic layer. Upon removal of dichloromethane, an ionic liquid was left. Mass spectrometry confirmed the removal of all chloride anions.

The acid method was used exclusively to prepare the ionic liquids [bmim][PF_6], [bmim][CH_3SO_3] and to attempt the synthesis of [bmim][NO_3]. [bmim][PF_6] is known to be a hydrophobic ionic liquid, as opposed to [bmim][BF_4] which is hydrophilic. In the case of [bmim][PF_6], a dichloromethane layer was not deemed necessary, since the ionic liquid itself would not dissolve in the water layer by its very nature. Thus the acid HPF_6 was added to [bmim]Cl dissolved in the minimum amount of water. During the course of the reaction, a second layer was seen to form, as the hydrophobic ionic liquid was

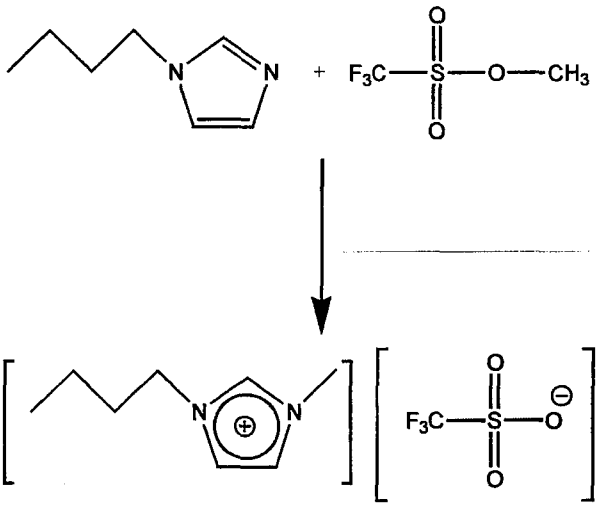
formed. The two layers were separated, and the neat ionic liquid washed with water to remove any chloride that may be present. As the ionic liquid is hydrophobic, the addition of a hydrophobic solvent (eg: dichloromethane) was not necessary since the water would not associate with it anyway.

In the case of [bmim][CH_3SO_3], the same method used to prepare [bmim][BF_4] by acid was used. However, after reaction it was found that the ionic liquid was not present in the organic layer, but instead the aqueous layer. This is most likely to be due to the fact that the [CH_3SO_3]$^-$ anion is a relatively good base (in comparison to the other anions in this study), making the salt more soluble in water.

The final ionic liquid to be prepared by the acid method was [bmim][NO_3]. The same procedure as with [bmim][BF_4] was followed. However, isolation of a yellow coloured liquid *in vacuo* believed to be the reaction product was short-lived. Overnight, the yellow product decomposed so that when it was dried *in vacuo* the following day, it too was removed. Ionic liquids have no vapour pressure, so it is clear that the material evaporated off was not an ionic liquid. It is believed that maybe some excess HNO_3 (starting material) in the ionic liquid caused decomposition. Alternatively, like the [CH_3SO_3]$^-$ anion, [NO_3]$^-$ is more strongly basic and therefore could be soluble in the water layer. Leaving the product like this overnight could have led to decomposition. This could not be investigated further, and the cause of the decomposition was not properly understood. Instead the formation of [bmim][NO_3] *via* the metathesis of [bmim]Cl with the sodium salt of the anion was attempted. Although a less sure method of preventing chloride impurities remaining in the ionic liquid, it was deemed the easiest and surest way to make the ionic liquid. The liquid was succesfully made in this way, and the chloride removed *via* washes with water followed by filtration through neutral alumina.

The ionic liquid [bmim][OTf] was prepared by the addition of [bmim]Cl to the lithium salt of the anion. The third method of chloride removal, described above, was used. However, another attempt was made to prevent chloride impurities remaining in the ionic liquids. This time, an alternative synthesis was carried out that would avoid the presence

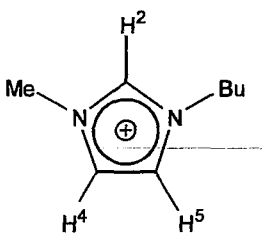
of any chloride in the starting materials themselves. Scheme 2.1 below shows the strategy. This method has been described in the literature[1.7] as a novel way of preparing ionic liquids. It works as a bypass to create the dialkylimidazolium salt, so necessary up until now in the synthesis of ionic liquids. This, of course, is a time-consuming step to omit, since the imidazolium salts need careful purification (by recrystallisation), handling and storage. Instead a starting mono-alkylated imidazole is combined with the anion joined to the remaining alkyl group (in this case, the methyl group) needed by the imidazole to form $[bmim]^+$. As has been seen, this is the exact method normally used to arrive at the imidazolium halide salt, the precursor to the ionic liquid cation. Instead, the formation of the imidazolium halide is avoided, and the ionic liquid reached in one step, with no halide involvement. The solvent used was dichloromethane, and an overnight reflux at low temperature (60 °C) sufficed to complete the reaction.



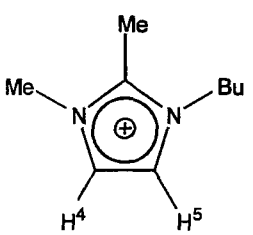
Scheme 2.1: The synthesis of [bmim][OTf] *via* the combination of 1-butylimidazole and trifluoromethylsulfonate[1.7]

This method is very easy to carry out, time saving, and prevents the formation of unwanted products that must be removed separately. Of course, applying it to some of the other ionic liquids that have been prepared could be a problem, since it relies on an alkylated version of the anion existing. If this form of the anion could easily be prepared separately, then it would be cleaner to prepare the ionic liquid through this route than *via* the imidazolium halide salt.

The only anion that did not give an ionic liquid was that of the bis(trimethylsilyl)amide species. It was attempted *via* its lithium salt reacting with [bmim]Cl. Unlike other ionic liquids prepared in this way, the reaction was exothermic and vigourous, giving an orange/brown solid in a liquid of the same colour. On removal of the reaction solvent (dichloromethane) *in vacuo*, a thick red/brown sludge was left. The $[N(SiMe_3)_2]^-$ complex is widely used in organic chemistry as a strong base. Figure 2.3a below shows the structure of the imidazolium ring for the $[bmim]^+$ complex.



(a) 1-butyl-3-methylimidazolium cation



(b) 1-butyl-2,3-dimethylimidazolium cation

Figure 2.3: Structures of the $[bmim]^+$ and $[bmmim]^+$ cations

It is known that the proton labelled H^2 is highly acidic, and is also a hard base. Although the anion used here shares the Lewis basic nitrogen group with the $[amide]^-$ ionic liquid, it is probable that the groups attatched to the amide nitrogen in each case vary its

hardness and also the strength of its Lewis basicity. The simple reason is that the [imide]$^-$ and closely-related [OTf]$^-$ anions can use their SO_2^- and SO_3^- groups respectively to form different resonance structures that will spread the negative charge over a wider area, thus creating a softer base. However, the $[N(SiMe_2)_2]^-$ complex is unable to form resonance forms, and thus disperse its negative charge over a wider area, so it remains relatively hard, with the negative charge concentrated on the amide nitrogen atom. What could have been observed during the course of the reaction was the attack of the H^2 proton by the anion to form a polymer, not the association of the anion with the cation to form an ionic liquid.

A second attempt was made to produce an imidazolium-based ionic liquid with $[N(SiMe_3)_2]^-$ as the anion, this time using the 1-butyl-2,3-dimethylimidazolium cation, which is illustrated in figure 2.3b. The reasoning behind this can be seen in the diagram. With a methyl group blocking the 2-position on the inmidazolium ring, it was hoped that the absence of the most acidic proton in the system would lead to an ionic liquid being formed. However, the same results were again observed, indicating the formation of a polymer. It could be assumed from these results that although the two position was not attacked by the anion, the H^4 and H^5 protons are still present and sufficiently acidic to allow attack from the anion to occur.

Despite this, it is surprising that the H^4 and H^5 protons were acidic enough to cause this reaction. Another, more likely theory as to why this liquid did not form (with either cation) is that the complex $SiMe_3Cl$ forms, due to the strength of the Si-Cl bond. Silicon is well known to abstract halides. This complex is known to be very stable and could well form in preference to the ionic liquid.

If time had permitted, it would have been interesting to try the same reaction with an imidazolium cation whose ring positions were fully alkylated. Maybe the anion cannot form an ionic liquid, but this step would have put the factor of polymer formation *via* the attack of the acidic ring protons to rest, and given the ionic liquid a chance to form.

2.1.2. Air-Sensitive Ionic Liquids

These ionic liquids were formed by adding the appropriate imidazolium halide to the appropriate anion halide salt. The complex corresponding to the cation used was always [bmim]Cl and three different complexes were used to produce the anions. They were $AlCl_3$, $FeCl_3$ and $SnCl_2$. When a 1:1 molar ratio of the two complexes was used, a neutral ionic liquid of [bmim]Cl-$AlCl_3$, [bmim]Cl-$FeCl_3$ and [bmim]Cl-$SnCl_2$ respectively was produced. As has been discussed earlier in chapter 1, increasing the molar ratio in the favour of the metal chloride gives a more Lewis acidic ionic liquid (this is because of the formation of $[M_2Cl_{x+1}]^-$ anions compared to the presence of only $[MCl_x]^-$ anions found in the neutral melt). Conversely, increasing the molar ratio in the favour of the imidazolium chloride gives a more Lewis basic ionic liquid (this is because of the formation of Cl^- anions compared to the presence of only $[MCl_x]^-$ anions found in the neutral melt). In both cases, the anions described ($[M_2Cl_{x+1}]^-$ in the Lewis acidic version, and Cl^- in the Lewis basic version) are not the only species present, but their presence, even in small quantities, serves to alter the character and properties of the ionic liquid under study.

The purification of these ionic liquids must be undertaken before the actual synthesis of the ionic liquid itself. This means that the liquids themselves cannot be easily purified, so all components must be pure before the formation of the ionic liquid. For example, aluminium chloride should be repeatedly sublimed at high vacuum up to eight or nine times, until it can form an ionic liquid that is pure enough for spectroscopy. No solvent is used in the production of the ionic liquids, since the solids simply fuse together and become a liquid in a matter of seconds. The main precaution that must be taken is to ensure an air-free environment since the metal chlorides used are all anhydrous and highly air-sensitive.

2.2. Spectroscopy of Ionic Liquids

All ionic liquids made were identified by FAB+ and FAB- mass spectrometry, ^{1}H NMR, ^{13}C NMR and IR techniques (see chapter 3). However, certain techniques, rather than providing simple identification, could serve to give more data on the nature and properties of the ionic liquids themselves.

Table 2.1 below shows the results for ^{1}H NMR and IR studies concerning the acidic strength of the ring proton H^2 on the imidazole function (see figure 2.3a, above). All NMR studies were carried out using neat samples of the ionic liquid with the deuterated solvent in a capillary tube to prevent association with the ionic liquid itself, and to act as an internal standard. It is important to note this, since the effect being studied here is within the ionic liquid itself, and so dilution with a solvent could alter any properties worth noting.

Table 2.1: ^{1}H NMR shifts and IR stretches of the protons on the imidazolium ring for ionic liquids made in this study

Ionic liquid	^{1}H NMR			IR
	H^2 shift / ppm	H^4 shift / ppm	H^5 shift / ppm	H^2 stretch / cm^{-1}
[emim][BF_4]	7.54	6.44	6.36	3165
[bmim][BF_4]	7.65	6.58	6.49	3162
[hmim][BF_4]	7.76	6.61	6.54	3159
[bmmim][BF_4]	-	6.33	6.28	-
[bmim][PF_6]	7.34	6.35	6.31	3171
[bmim][imide]	7.61	6.52	6.44	3158
[bmim][ClO_4]	7.84	6.70	6.66	3156
[bmim][OTf]	7.86	6.62	6.55	3148
[bmim][CH_3SO_3]	8.54	7.04	6.95	3148
[bmim][NO_3]	8.64	7.06	6.98	3147
[bmim][lactate]	9.23	7.42	7.29	3150

An increase in the chemical shift of the proton refers to a more electron deshielded species. The more deshielded a proton is, the better its ability to act as a Lewis acid (hydrogen bond acceptor). Similarly, a decrease in the wavenumber of the stretch of the H^2 proton refers to it being more electron deshielded, and thus more Lewis acidic.

The first four entries are interesting to note, since they refer to changes made directly to the cation itself. Consider entries 2-4. The main difference between these cationic species is that the imidazolium alkyl side chain increases from two carbons ($[emim]^+$) to six carbons ($[hmim]^+$).

It would normally be expected that the longer the alkyl side chain, the more ability it has to donate electron density into the main ring system, to quench the positive charge. This means that for longer alkyl side chains, less electron density would be expected to be drawn from the ring protons (especially H^2), making them less Lewis acidic.

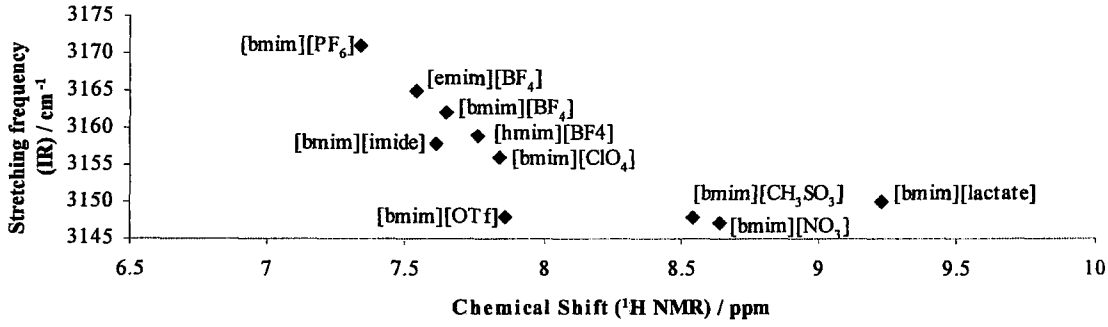
However, what is seen here is a decrease in the chemical shift as the alkyl chain gets shorter. All that can be said, on the basis of the results from table 2.1, is that as the alkyl side chain gets longer, the H^2's proton NMR signal gets higher, indicating a stronger Brønsted acid. This corresponds directly with the IR data, which shows the stretching frequency getting lower.

This can be assumed to be a constant factor because the ionic liquids $[emim][BF_4]$, $[bmim][BF_4]$ and $[hmim][BF_4]$ do form a trend in the correct order. The fact that the anion remains unchanged in each case is deliberate, designed to compare the properties of the cations.

The use of $[bmmim][BF_4]$ in this study does not give very much interest, but its usefulness, when performing synthesis in these liquids shall be seen in later chapters. Its structure has been illustrated in figure 2.3b. In this case, the 2-position on the imidazole ring is occupied by a methyl group, which means there is no H^2 proton present.

The graph for the ^1H NMR chemical shift *versus* the IR stretch for the H^2 proton for all liquids studied (except [bmmim][BF_4]) are shown below in figure 2.4.

Figure 2.4: Proton NMR vs. IR Stretch of the H^2 Imidazolium Proton for a selection of Ionic Liquids



It is difficult to comment on the rest of the results without first knowing how the ionic liquid cation interacts with the corresponding anion. When the hydrogen bond acceptor ability of the cations is talked about, it must be clear that this is influenced by the hydrogen bond donor ability of the corresponding anion. A recent study[1.19] has measured the hydrogen bond donator abilities of some of the anions used in this study (the application of the study being towards room temperature ionic liquids). The trend showed that the hydrogen bonding strength between water molecules and the anions increases in the order $[PF_6]^- < [BF_4]^- < [imide]^- < [ClO_4]^- < [CF_3SO_3]^- < [NO_3]^-$. The study measured and compared the ATR and transmission IR spectra of dissolved water in the ionic liquids of the anions mentioned. The agreement between the results from figure 6.4 and this study's results show is not conclusive. The cation used to make these ionic liquids was kept constant throughout in order to be able to compare the anions effect used. The results are not conclusive, but some evidence is seen that as the hydrogen bond accepting ability of

the anion increases, so the hydrogen bond donating strength of the H^2 proton on the cation undergoes a similar increase.

These results provide a preliminary look into the nature of how these solvents arrange themselves structurally. Not much has been said about how and why ionic liquids are being used as reaction solvents for a variety of processes with great success. Perhaps it is due to their ability to form very solvophobic environments that push reactions faster, or that their electronic properties interact with substrates creating more reactive intermediates, or even it is something to do with their potential hydrogen bonding abilities; within themselves or to other compounds being used in their environment. Maybe it is a combination of these factors, or the fact that separate factors play a part in different processes. The forthcoming work will attempt to find an answer to these questions.

3. EXPERIMENTAL FOR SECTION 1

3.1. Moisture-Stable Ionic Liquids

3.1.1. General

A number of moisture-stable room temperature ionic liquids were used in synthetic work during this study. In the case of the majority, their preparation is described below. However, [emim][NO_3], [pmim][ClO_4], [emim][PF_6] and [emim][OTf] were all purchased from Fluka Chemical Co. and used as received.

All manipulations (except for those that followed the acid method, below) were carried out using standard vacuum and Schlenk techniques under an atmosphere of dry nitrogen, or in a drybox under an atmosphere of dry nitrogen. The reactions which followed the acid method were conducted in air, until the aqueous layer was discarded. They were then conducted in an anaerobic atmosphere of nitrogen.

Solvents were distilled from the relevant drying agents prior to use, except for acetone. AnalaR grade acetone was used without pre-drying. Toluene was left standing over Na for 24 hours and the distilled (benzophenone was used as a moisture indicator). Ethyl acetate and dichloromethane were distilled from fresh CaH_2. Nitromethane was distilled from $CaCl_2$.

Reagents were distilled from the relevant drying agents prior to use, unless otherwise stated. 1-methylimidazole, 1-butylimidazole and 1,2-dimethylimidazole were distilled under vacuum from KOH. 1-chlorobutane, 1-bromoethane and 1-bromohexane were washed with conc. H_2SO_4 then distilled from P_2O_5. 2-Bromo-1,1,1-trifluoroethane was obtained with high purity in sealed ampules from the Aldrich Chemical Co., and was used as received.

Where an imidazolium salt is described as being recrystallised from an acetonitrile/toluene mixture, it was first dissolved in the minimum volume of acetonitrile. A quarter of this volume of toluene was then added, and the mixture left at –20 °C for 12 hours. The liquid was decanted from the crystalline solid.

Where an imidazolium salt is described as being recrystallised from a nitromethane/toluene mixture, it was first dissolved in the minimum volume of nitromethane. A quarter of this volume of toluene was then added, and the mixture left at –20 °C for 12 hours. The liquid was decanted from the solid, which was then dried *in vacuo*.

Once isolated and purified, all ionic liquids were stirred with activated charcoal for 12 hours. the ionic liquid/activated charcoal mixture was passed, by gravity, through a short column of neutral alumina (where the charcoal was left behind) and then heated to between 70-100 °C *in vacuo* for 12 hours in order to remove any residual water.

Chloride content of the ionic liquids was determined by a $AgNO_3$ test. AgCl has a solubility of 1.4 mgl^{-1} in water, hence all of the ionic liquids synthesised will have a chloride content below this value.

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded by the mass spectrometry laboratory of the Department of Chemistry of Imperial College, University of London. Infrared spectra were recorded on a Mattson Satellite FTIR machine.

3.1.2. Imidazolium Halide Salts

3.1.2.1. 1-Ethyl-3-methylimidazolium Bromide - [emim]Br

To a vigorously stirred solution of 1-methylimidazole (100 cm^3; 1.25 mol) in toluene (125 cm^3) at 0 °C was added 1-bromoethane (103 cm^3; 1.38 mol) dropwise. The solution was allowed to warm to room temperature and then left stirring for 24 hours, after which it was placed in a freezer at *ca.* –20 °C for 12 hours. The toluene was removed by decantation, and the remaining viscous oil/semi-solid was recrystallised from an acetonitrile/toluene mixture to yield a white crystalline solid, which was dried *in vacuo* to give [emim]Br in approximately 90 % yield.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 10.24 (1H, s, NC**H**N), 7.55 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 7.45 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 4.35 (2H, q, J=8.6 Hz, NC**H**$_2CH_3$), 4.05 (3H, s, NC**H**$_3$), 0.89 (3H, t, J=7.6 Hz, NCH_2C**H**$_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 136.74 (s, N**C**HN), 123.74 (s, CH_3N**C**HCHN), 122.12 (s, CH_3NCH**C**HN), 45.19 (s, N**C**H_2CH_3), 36.64 (s, N**C**H_3), 15.72 (s, NCH_2**C**H_3).

- Infrared spectrum (nujol mull) cm^{-1}: 3135 (m, aromatic C-H), 2724, (m, aliphatic C-H), 2672 (m, aliphatic C-H), 1788 (w, aromatic C-H), 1569 (m, Im ring), 1461 (st, Im ring), 1376 (st, Me C-H), 1337 (m, Im ring), 1167 (m, Im ring), 1091 (m, Im ring C-H), 1031 (m, Im ring C-H), 956 (m, Im ring C-H).

NB: For the imidazolium salts and ionic liquids to follow, the signals in the range 1788 cm^{-1} to 956 cm^{-1} (the fingerprint region for the imidazolium ring) were found to be almost identical in all cases. These have therefore been omitted from the spectral analyses to follow.

- Mass spectrum (FAB +ve) m/z: 111 $(M\text{-}Br)^+$, 95 $(M\text{-}Br\text{-}CH_3)^+$, 83 $(M\text{-}Br\text{-}2CH_3)^+$, 69 $(M\text{-}Br\text{-}CH_3\text{-}CH_2CH_3)^+$, 55 $(M\text{-}Br\text{-}CH_3\text{-}CH_2CH_3\text{-}N)^+$

3.1.2.2. 1-Butyl-3-methylimidazolium Chloride - [bmim]Cl

To a vigorously stirred solution of 1-methylimidazole (100 cm^3; 1.25 mol) in toluene (125 cm^3) at 0 °C was added 1-chlorobutane (144 cm^3; 1.38 mol) dropwise. The solution was allowed to warm to room temperature and then heated to reflux at *ca.* 80 °C for 24 hours, after which it was placed in a freezer at *ca.* –20 °C for 12 hours. The toluene was removed by decantation, and the remaining viscous oil/semi-solid was recrystallised once from an acetonitrile/toluene mixture and then once from ethyl acetate to yield a white crystalline solid, which was dried *in vacuo* to give [bmim]Cl in approximately 90 % yield.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 10.54 (1H, s, NC**H**N), 7.55 (1H, d, J=1.9 Hz,CH_3NC**H**CHN), 7.40 (1H, d, J=1.9 Hz, CH_3NCHC**H**N), 4.26 (2H, t, J=7.3 Hz, NC**H**$_2(CH_2)_2CH_3$), 4.11 (3H, s, NC**H**$_3$), 1.82 (2H, m, NCH_2C**H**$_2CH_2CH_3$), 1.30 (2H, m, $N(CH_2)_2C$**H**$_2CH_3$), 0.89 (3H, t, J=7.3 Hz, $N(CH_2)_3C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 137.87 (s, N**C**HN), 123.68 (s, CH_3N**C**HCHN), 121.70 (s, CH_3NCH**C**HN), 49.87 (s, N**C**$H_2(CH_2)_2CH_3$), 36.58 (s, N**C**H_3), 32.13 (s, NCH_2**C**$H_2CH_2CH_3$), 19.45 (s, $N(CH_2)_2$**C**H_2CH_3), 19.45 (s, $N(CH_2)_3$**C**H_3).

- Infrared spectrum (nujol mull) cm^{-1}: 3151 (m, aromatic C-H), 2742, (m, aliphatic C-H), 2689 (m, aliphatic C-H).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}Cl)^+$, 109 $(M\text{-}Cl\text{-}2CH_3)^+$, 96 $(M\text{-}Cl\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}Cl\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}Cl\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}Cl\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$.

3.1.2.3. 1-Hexyl-3-methylimidazolium Bromide - [hmim]Br

To a vigorously stirred solution of 1-methylimidazole (100 cm^3; 1.25 mol) in toluene (125 cm^3) at 0 °C was added 1-bromohexane (194 cm^3; 1.38 mol) dropwise. The solution was allowed to warm to room temperature and then heated to reflux at *ca.* 110 °C for 24 hours, after which it was placed in a freezer at *ca.* –20 °C for 12 hours. The toluene was removed by decantation, and the remaining viscous oil/semi-solid was recrystallised once from a nitromethane/toluene mixture (which yielded an oily brown coloured solid). It was washed twice with toluene to yield a white crystalline solid, which was dried *in vacuo* to give [hmim]Br in approximately 90 % yield.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 9.17 (1H, s, NC**H**N), 7.87 (1H, d, J=19.0 $CH_3NC\underline{H}CHN$), 7.73 (1H, d, J=18.7 $CH_3NCHC\underline{H}N$), 4.16 (2H, t, J=7.2 Hz, $NC\underline{H}_2(CH_2)_4CH_3$), 3.85 (3H, s, $NC\underline{H}_3$), 2.51 (2H, t, $NCH_2C\underline{H}_2(CH_2)_3CH_3$), 1.26 (6H, m, $N(CH_2)_2(C\underline{H}_2)_3CH_3$), 0.86 (3H, t, J=6.8 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 137.05 (s, N**C**HN), 124.10 (s, $CH_3N\underline{C}HCHN$), 122.75 (s, $CH_3NCH\underline{C}HN$), 49.29 (s, $N\underline{C}H_2(CH_2)_4CH_3$), 36.31 (s, $N\underline{C}H_3$), 31.12 (s, $NCH_2\underline{C}H_2(CH_2)_3CH_3$), 29.91 (s, $N(CH_2)_2\underline{C}H_2(CH_2)_2CH_3$), 25.71 (s, $N(CH_2)_3\underline{C}H_2CH_2CH_3$), 22.46 (s, $N(CH_2)_4\underline{C}H_2CH_3$), 14.43 (s, $N(CH_2)_5\underline{C}H_3$).

- Infrared spectrum (nujol mull) cm^{-1}: 3138 (m, aromatic C-H), 2728, (m, aliphatic C-H), 2668 (m, aliphatic C-H).

- Mass spectrum (FAB +ve) m/z: 413 $(M+hmim)^+$, 167 $(M-Br)^+$, 109 $(M-Br-CH_3-(CH_2)_2CH_3)^+$, 96 $(M-Br-CH_3-(CH_2)_3CH_3)^+$, 83 $(M-Br-CH_3-(CH_2)_4CH_3)^+$.

3.1.2.4. 1-Butyl-2,3-dimethylimidazolium Chloride - [bmmim]Cl

To a vigorously stirred solution of 1,2-dimethylimidazole (120 g; 1.25 mol) in toluene (125 cm^3) at 0 °C was added 1-chlorobutane (144 cm^3; 1.38 mol) dropwise. The solution was allowed to warm to room temperature and then heated to reflux at *ca.* 110 °C for 24 hours, after which it was placed in a freezer at *ca.* –20 °C for 12 hours. The toluene was removed by decantation, and the remaining viscous oil/semi-solid, recrystallised from an acetonitrile/toluene mixture to yield a white crystalline solid, which was dried *in vacuo* to give a mixture [bmmim]Cl and 1,2-dimethylimidazole. The mixture was dissolved in toluene and the reaction carried out again in exactly the same way using a smaller volume of 1-chlorobutane (60 cm^3; 0.575 mol). The toluene was removed by decantation, and the remaining white solid was recrystallised from an acetonitrile/toluene mixture to yield a white crystalline solid which was dried *in vacuo* to give [bmmim]Cl in approximately 80 % yield.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 7.68 (1H, d, J=1.97 Hz, $CH_3NC\underline{H}CHN$), 7.67 (1H, d, J=1.97 Hz, $CH_3NCHC\underline{H}N$), 4.12 (2H, t, J=7.18 Hz, $NC\underline{H}_2(CH_2)_2CH_3$), 3.75 (3H, s, $NC\underline{H}_3$), 2.95 (3H, s, $NC(C\underline{H}_3)N$), 2.08 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 1.27 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$), 0.90 (3H, t, J=7.18 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 144.77 (s, $N\underline{C}(CH_3)N$), 122.81 (s, $CH_3N\underline{C}HCHN$), 121.50 (s, $CH_3NCH\underline{C}HN$), 47.80 (s, $N\underline{C}H_2(CH_2)_2CH_3$), 35.24 (s, $N\underline{C}H_3$), 31.78 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 19.45 (s, $N(CH_2)_2\underline{C}H_2CH_3$), 13.00 (s, $NC(\underline{C}H_3)N$), 9.74 (s, $N(CH_2)_3\underline{C}H_3$).

- Infrared spectrum (nujol mull) cm^{-1}: 3178 (m, aromatic C-CH_3), 2740, (m, aliphatic C-H), 2685 (m, aliphatic C-H).

- Mass spectrum (FAB +ve) m/z: 153 $(M+bmmim)^+$, 393 $(M-Cl)^+$, 137=$(M-Cl-CH_3)^+$, 123 $(M-Cl-CH_3-CH_3)^+$, 110 $(M-Cl-CH_3-CH_2CH_3)^+$, 97 $(M-Cl-CH_3-(CH_2)_2CH_3)^+$, 81 $(M-Cl-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-Cl-CH_3-CH_3-(CH_2)_3CH_3)^+$

3.1.2.5. 1-(2',2',2'-Trifluoroethyl)-3-methylimidazolium Bromide (attempted)

To a vigorously stirred solution of 1-methylimidazole (24 cm^3; 0.307 mol) in toluene (20 cm^3) at 0 °C was added 2-bromo-1,1,1-bromoethane (28 cm^3; 0.307 mol) dropwise. The solution was stirred for 12 hours, whilst being allowed to warm to room temperature and then heated to reflux at *ca.* 110 °C for 2 hours, after which it was placed in a freezer at *ca.* –20 °C for 12 hours. A solution of the 1-methylimidazole in toluene was observed after this time.

In a specially reinforced glass pressure vessel, the same volume of 1-methylimidazole was frozen at –80 °C. 2-bromo-1,1,1-bromoethane was cooled to –20 °C and transferred dropwise *via* cannula to the pressure vessel. The contents of the pressure vessel were frozen ato –80 °C. When both reagents were completely solid, the atmosphere in the vessel was removed *in vacuo*, and the vessel allowed to gradually warm to room temperature, while the contents were stirred as they became liquid. Heat was applied (50 °C for 2 hours), but both starting materials were observed to remain unreacted in the vessel.

3.1.3. Ionic Liquids with a Common Anion ($[BF_4]^-$) and Various Cations

3.1.3.1. 1-Ethyl-3-methylimidazolium tetrafluoroborate – [emim][BF_4]

Sodium tetrafluoborate (32 g; 0.29 mol) was added to a solution of [emim]Br (55 g; 0.29 mol) in acetone (50 cm^3) and stirred for 24 hours. The suspension was filtered to remove the precipitated bromide salt and the reaction solvent removed *in vacuo*. The ionic liquid was washed with a small volume of dichloromethane (*ca.* 30 cm^3) to precipitate any dissolved bromide salt, which was removed by filtration. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.54 (1H, s, NC**H**N), 6.43 (1H, d, J=1.5 Hz, CH_3NC**H**CHN), 6.36 (1H, d, J=1.5 Hz, CH_3NCHC**H**N), 3.12 (2H, q, J=7.8 Hz, NC**H**$_2$(CH_2)$_2CH_3$), 2.77 (3H, s, NC**H**$_3$), 0.32 (3H, t, NCH_2C**H**$_3$), 1.15 (2H, t, J=7.6 Hz N(CH_2)$_2$C**H**$_2CH_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.36 (s, N**C**HN), 122.33 (s, CH_3N**C**HCHN), 122.66 (s, CH_3NCH**C**HN), 43.65 (s, N**C**H_2CH_3), 34.47 (s, N**C**H_3), 13.41 (s, NCH_2**C**H_3).

- Infrared spectrum (thin layer) cm^{-1}: 3166 (m, aromatic C-H), 3124 (m, aromatic C-H), 2989, (m, aliphatic C-H), 2672 (m, aliphatic C-H), 1057 (BF_4^-).

- Mass spectrum (FAB +ve) m/z: 309 $(M+emim)^+$ 111 $(M-Br)^+$, 95 $(M-Br-CH_3)^+$, 83 $(M-Br-2CH_3)^+$, 69 $(M-Br-CH_3-CH_2CH_3)^+$, 55 $(M-Br-CH_3-CH_2CH_3-N)^+$. (FAB –ve) m/z: 87 $(M-emim)^-$.

3.1.3.2. 1-Butyl-3-methylimidazolium tetrafluoroborate – [bmim][BF_4]

3.1.3.2.1. By the Salt Metathesis Method

Sodium tetrafluoborate (35 g; 0.32 mol) was added to a solution of [bmim]Cl (56 g; 0.32 mol) in acetone (50 cm^3) and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the reaction solvent removed *in vacuo*. The ionic liquid was washed with a small volume of dichloromethane (*ca.* 30 cm^3) to precipitate any dissolved chloride salt, which was removed by filtration. The mixture was then washed with small quantities of water (*ca.* 10 cm^3). The aqueous layer was removed and the water washes repeated twice. The water washings were collected and the ionic liquid extracted from it with a small quantity of dichloromethane (*ca.* 10 cm^3; three times). The dichloromethane washings were combined with the original ionic liquid/dichloromethane mixture. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

3.1.3.2.2. By the Acid Method

[bmim]Cl (40 g; 0.23 mol) was dissolved in the minimum amount of water (*ca.* 20 cm^3) and cooled to 0 °C. Dichloromethane (*ca.* 30 cm^3) was added to the solution. A 50 % aqueous solution of tetrafluoroboric acid was added dropwise in slight excess (45 g; 0.25 mol) to the stirred solution, which was then allowed to warm to room temperature, and left stirring for 24 hours. The aqueous layer was separated from the organic layer. Any residual ionic liquid left in it was extracted with a small quantity of dichloromethane (*ca.*

20 cm^3). This wash was repeated twice. The dichloromethane washings were combined with the ionic liquid/dichloromethane mixture. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.67 (1H, s, NC**H**N), 6.59 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.49 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 3.20 (2H, t, J=7.5 Hz, NC**H**$_2$$(CH_2)_2CH_3$), 2.90 (3H, s, NC**H**$_3$), 0.81 (2H, m, NCH_2C**H**$_2$$CH_2CH_3$), 0.27 (2H, m, $N(CH_2)_2C$**H**$_2$$CH_3$), -0.18 (3H, t, J=7.3 Hz, $N(CH_2)_3C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.66 (s, N**C**HN), 122.50 (s, CH_3N**C**HCHN), 121.19 (s, CH_3NCH**C**HN), 48.13 (s, N**C**$H_2(CH_2)_2CH_3$), 34.54 (s, N**C**H_3), 30.66 (s, NCH_2**C**$H_2CH_2CH_3$), 18.01 (s, $N(CH_2)_2$**C**H_2CH_3), 11.79 (s, $N(CH_2)_3$**C**H_3).

- Infrared spectrum (thin layer) cm^{-1}: 3161 (m, aromatic C-H), 3121 (m, aromatic C-H), 2965 (m, aliphatic C-H), 2939 (m, aliphatic C-H), 2877 (m, aliphatic C-H), 1059 (BF_4^-).

- Mass spectrum (FAB +ve) m/z: 365 $(M+bmim)^+$, 139 $(M-BF_4)^+$, 109 $(M-BF_4-2CH_3)^+$, 96 $(M-BF_4-CH_3-CH_2CH_3)^+$, 83 $(M-BF_4-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-BF_4-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-BF_4-CH_3-(CH_2)_3CH_3-N)^+$. (FAB –ve) m/z: 87 $(M-bmim)^-$.

3.1.3.3. 1-Hexyl-3-methylimidazolium tetrafluoroborate – [hmim][BF_4]

Sodium tetrafluoborate (27 g; 0.24 mol) was added to a solution of [hmim]Br (60 g; 0.24 mol) in acetone (50 cm^3) and stirred for 24 hours. The suspension was filtered to remove the precipitated bromide salt and the reaction solvent removed *in vacuo*. The ionic liquid was washed with a small volume of dichloromethane (*ca.* 30 cm^3) to precipitate any dissolved chloride salt, which was removed by filtration. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.76 (1H, s, NC**H**N), 6.60 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.54 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 3.20 (2H, t, J=7.5 Hz, NC**H**$_2$$(CH_2)_4CH_3$), 2.91 (3H, s, NC**H**$_3$), 0.83 (2H, m, NCH_2C**H**$_2$$(CH_2)_3CH_3$), 0.21 (6H, m, $N(CH_2)_2(C$**H**$_2$$)_3CH_3$), -0.23 (3H, t, J=7.3 Hz, $N(CH_2)_5C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.74 (s, N**C**HN), 122.56 (s, CH_3N**C**HCHN), 121.27 (s, CH_3NCH**C**HN), 48.45 (s, N**C**$H_2(CH_2)_4CH_3$), 34.63 (s, N**C**H_3), 30.01 (s, NCH_2**C**$H_2(CH_2)_3CH_3$), 28.84 (s, $N(CH_2)_2$**C**$H_2(CH_2)_2CH_3$), 24.56 (s, $N(CH_2)_3$**C**$H_2CH_2CH_3$), 21.27 (s, $N(CH_2)_4$**C**H_2CH_3), 12.56 (s, $N(CH_2)_5$**C**H_3).

- Infrared spectrum (thin layer) cm^{-1}: 3159 (m, aromatic C-H), 3121 (m, aromatic C-H), 2957 (m, aliphatic C-H), 2932 (m, aliphatic C-H), 2862 (m, aliphatic C-H), 1060 (BF_4^-).

- Mass spectrum (FAB +ve) m/z: 421 $(M+hmim)^+$, 167 $(M-BF_4)^+$, 109 $(M-BF_4-CH_3-(CH_2)_2CH_3)^+$, 96 $(M-BF_4-CH_3-(CH_2)_3CH_3)^+$, 83 $(M-BF_4-CH_3-(CH_2)_4CH_3)^+$. (FAB –ve) m/z: 87 $(M-hmim)^-$.

3.1.3.4. 1-Butyl-2,3-dimethylimidazolium tetrafluoroborate – [bmmim][BF_4]

Sodium tetrafluoborate (22 g; 0.20 mol) was added to a solution of [bmmim]Cl (37 g; 0.20 mol) in acetone (50 cm^3) and stirred for 24 hours. The suspension was filtered to remove the precipitated bromide salt and the reaction solvent removed *in vacuo*. The ionic liquid was washed with a small volume of dichloromethane (*ca.* 30 cm^3) to precipitate any dissolved chloride salt, which was removed by filtration. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 6.33 (1H, d, J=1.97 Hz, $CH_3NC\underline{H}CHN$), 6.28 (1H, d, J=1.97 Hz, $CH_3NCHC\underline{H}N$), 3.00 (2H, t, J=7.18 Hz, $NC\underline{H}_2(CH_2)_2CH_3$), 2.67 (3H, s, $NC\underline{H}_3$), 1.48 (3H, s, $NC(C\underline{H}_3)N$), 0.61 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 1.20 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$), -0.27 (3H, t, J=7.18 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 143.73 (s, $N\underline{C}(CH_3)N$), 121.04 (s, $CH_3N\underline{C}HCHN$), 119.70 (s, $CH_3NCH\underline{C}HN$), 46.70 (s, $N\underline{C}H_2(CH_2)_2CH_3$), 33.24 (s, $N\underline{C}H_3$), 30.39 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 17.99 (s, $N(CH_2)_2\underline{C}H_2CH_3$), 11.99 (s, $NC(\underline{C}H_3)N$), 7.40 (s, $N(CH_2)_3\underline{C}H_3$).

- Infrared spectrum (thin layer) cm^{-1}: 3184 (m, aromatic C-CH_3), 3151 (m, aromatic C-CH_3), 2964 (m, aliphatic C-H), 2939 (m, aliphatic C-H), 2877 (m, aliphatic C-H), 1058 (BF_4^-).

- Mass spectrum (FAB +ve) m/z: 393 $(M+bmmim)^+$, 153 $(M-Cl)^+$, 137 $(M-Cl-CH_3)^+$, 123 $(M-Cl-CH_3-CH_3)^+$, 110 $(M-Cl-CH_3-CH_2CH_3)^+$, 97 $(M-Cl-CH_3-(CH_2)_2CH_3)^+$, 81 $(M-Cl-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-Cl-CH_3-CH_3-(CH_2)_3CH_3)^+$. (FAB –ve) m/z: 87 (M-bmmim).

3.1.4. Ionic Liquids with a Common Cation ($[bmim]^+$) and Various Anions ($[A]^-$)

3.1.4.1. By the Salt Metathesis Method

$[A]^- = BF_4^-, ClO_4^-, NO_3^-, CF_3SO_3^-, (CF_3SO_2)_2N^-, CH_3CH(OH)CO_2^-, (Me_3N)_2Si^-$

The respective metal salt (0.32 mol) required to give the desired ionic liquid, was added to a solution of [bmim]Cl (56 g; 0.32 mol) in acetone (50 cm^3), except where specified, and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the reaction solvent removed *in vacuo*. The ionic liquid was washed with a small volume of dichloromethane (*ca.* 30 cm^3) to precipitate any dissolved chloride salt, which was removed by filtration. The mixture was then washed with small quantities of water (*ca.* 10 cm^3). The aqueous layer was removed and the water washes repeated twice. The water washings were collected and the ionic liquid extracted from it with a small quantity of dichloromethane (*ca.* 10 cm^3; three times). The dichloromethane washings were combined with the original ionic liquid/dichloromethane mixture. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent was removed *in vacuo*, and the resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

3.1.4.1.1. [bmim][BF_4]

Salt: $NaBF_4$ (35 g; 0.32 mol)

Yield generally quantitative.

See section 3.1.3.2.1 for full method and analysis.

3.1.4.1.2. [bmim][ClO_4]

Salt: $NaClO_4$ (39 g; 0.32 mol)

Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.84 (1H, s, NC**H**N), 6.70 (1H, d, J=1.7 Hz, $CH_3NC\mathbf{H}CHN$), 6.66 (1H, d, J=1.7 Hz, $CH_3NCHC\mathbf{H}N$), 3.33 (2H, t, J=7.5 Hz, $NC\mathbf{H}_2(CH_2)_2CH_3$), 3.07 (3H, s, $NC\mathbf{H}_3$), 0.95 (2H, m, $NCH_2C\mathbf{H}_2CH_2CH_3$), 0.38 (2H, m, $N(CH_2)_2C\mathbf{H}_2CH_3$), -0.05 (3H, t, J=7.3 Hz, $N(CH_2)_3C\mathbf{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.92 (s, N**C**HN), 122.78 (s, $CH_3N\mathbf{C}HCHN$), 121.49 (s, $CH_3NCH\mathbf{C}HN$), 48.53 (s, $N\mathbf{C}H_2(CH_2)_2CH_3$), 35.20 (s, $N\mathbf{C}H_3$), 30.86 (s, $NCH_2\mathbf{C}H_2CH_2CH_3$), 18.33 (s, $N(CH_2)_2\mathbf{C}H_2CH_3$), 12.27 (s, $N(CH_2)_3\mathbf{C}H_3$).

- Infrared spectrum (thin layer) cm^{-1}: 3156 (m, aromatic C-H), 3119 (m, aromatic C-H), 2963 (m, aliphatic C-H), 2938 (m, aliphatic C-H), 2876 (m, aliphatic C-H), 1090 (m, ClO_4^-), 621 (m, ClO_4^-).

- Mass spectrum (FAB +ve) m/z: 377 $(M+bmim)^+$, 139 $(M\text{-}ClO_4)^+$, 109 $(M\text{-}ClO_4\text{-}2CH_3)^+$, 96 $(M\text{-}ClO_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}ClO_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}ClO_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}ClO_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 99/101 $(M\text{-bmim})^-$.

3.1.4.1.3. [bmim][NO_3]

Salt: $NaNO_3$ (27.2 g; .32 mol)

Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 8.65 (1H, s, NC**H**N), 7.06 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.98 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 3.38 (2H, t, J=7.5 Hz, NC**H**$_2$(CH_2)$_2CH_3$), 3.12 (3H, s, NC**H**$_3$), 0.85 (2H, m, NCH_2C**H**$_2CH_2CH_3$), 0.26 (2H, m, $N(CH_2)_2C$**H**$_2CH_3$), -0.19 (3H, t, J=7.3 Hz, $N(CH_2)_3C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 136.86 (s, N**C**HN), 123.04 (s, CH_3N**C**HCHN), 121.81 (s, CH_3NCH**C**HN), 48.15 (s, N**C**H$_2$(CH_2)$_2CH_3$), 34.72 (s, N**C**H_3), 31.14 (s, NCH_2**C**$H_2CH_2CH_3$), 18.33 (s, $N(CH_2)_2$**C**H_2CH_3), 12.11 (s, $N(CH_2)_3$**C**H_3).

- Infrared spectrum (thin layer) cm^{-1}: 3147 (m, aromatic C-H), 3099 (m, aromatic C-H), 2962 (m, aliphatic C-H), 2937 (m, aliphatic C-H), 2875 (m, aliphatic C-H), 1347 (NO_3^-).

- Mass spectrum (FAB +ve) m/z: 340 (M+bmim)$^+$, 139 (M-NO_3)$^+$, 109 (M-NO_3-2CH_3)$^+$, 96 (M-NO_3-CH_3-CH_2CH_3)$^+$, 83 (M-NO_3-CH_3-(CH_2)$_2CH_3$)$^+$, 69 (M-NO_3-CH_3-(CH_2)$_3CH_3$)$^+$, 55 (M-NO_3-CH_3-(CH_2)$_3CH_3$-N)$^+$. (FAB –ve) m/z: 62 (M-bmim)$^-$.

3.1.4.1.4. [bmim][CF_3SO_3]

Salt: $NaCF_3SO_3$ (55 g; 0.32 mol)

Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.86 (1H, s, NC**H**N), 6.62 (1H, d, J=1.7 Hz, $CH_3NC\underline{H}CHN$), 6.55 (1H, d, J=1.7 Hz, $CH_3NCHC\underline{H}N$), 3.18 (2H, t, J=5.4 Hz, $NC\underline{H}_2(CH_2)_2CH_3$), 2.29 (3H, s, $NC\underline{H}_3$), 0.80 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 0.25 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$), -0.19 (3H, t, J=7.3 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.68 (s, N**C**HN), 122.59 (s, $CH_3N\underline{C}HCHN$), 121.35 (s, $CH_3NCH\underline{C}HN$), 117.42 (s, $\underline{C}H_3SO_3$), 48.25 (s, $N\underline{C}H_2(CH_2)_2CH_3$), 34.68 (s, $N\underline{C}H_3$), 30.70 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 18.00 (s, $N(CH_2)_2\underline{C}H_2CH_3$), 11.71 (s, $N(CH_2)_3\underline{C}H_3$).

- Infrared spectrum (thin layer) cm^{-1}: 3154 (m, aromatic C-H), 3115 (m, aromatic C-H), 2965 (m, aliphatic C-H), 2939 (m, aliphatic C-H), 2878 (m, aliphatic C-H), 1261 (st, $CF_3SO_3^-$), 1225 (m, $CF_3SO_3^-$), 1031 (st, $CF_3SO_3^-$), 638 (m, $CF_3SO_3^-$).

- Mass spectrum (FAB +ve) m/z: 427 $(M+bmim)^+$, 139 $(M-CF_3SO_3)^+$, 109 $(M-CF_3SO_3-2CH_3)^+$, 96 $(M-CF_3SO_3-CH_3-CH_2CH_3)^+$, 83 $(M-CF_3SO_3-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-CF_3SO_3-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-CF_3SO_3-CH_3-(CH_2)_3CH_3-N)^+$. (FAB –ve) m/z: 149 $(M-bmim)^-$.

3.1.4.1.5. [bmim][$(CF_3SO_2)_2N$]

Salt: $Li[(CF_3SO_2)_2N]$ (92 g; 0.32 mol)

Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.61 (1H, s, NC**H**N), 6.51 (1H, d, J=1.7 Hz, $CH_3NC\mathbf{H}CHN$), 6.44 (1H, d, J=1.7 Hz, $CH_3NCHC\mathbf{H}N$), 3.22 (2H, t, J=5.4 Hz, $NC\mathbf{H}_2(CH_2)_2CH_3$), 2.92 (3H, s, $NC\mathbf{H}_3$), 0.90 (2H, m, $NCH_2C\mathbf{H}_2CH_2CH_3$), 0.38 (2H, m, $N(CH_2)_2C\mathbf{H}_2CH_3$), -0.06 (3H, t, J=7.3 Hz, $N(CH_2)_3C\mathbf{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.10 (s, N**C**HN), 122.56 (s, $CH_3N\mathbf{C}HCHN$), 121.31 (s, $CH_3NCH\mathbf{C}HN$), 116.61 (s, $\mathbf{C}H_3SO_2$ (x2)), 48.52 (s, $N\mathbf{C}H_2(CH_2)_2CH_3$), 34.64 (s, $N\mathbf{C}H_3$), 30.68 (s, $NCH_2\mathbf{C}H_2CH_2CH_3$), 18.03 (s, $N(CH_2)_2\mathbf{C}H_2CH_3$), 11.54 (s, $N(CH_2)_3\mathbf{C}H_3$).

- Infrared spectrum (thin layer) cm^{-1}: 3158 (m, aromatic C-H), 3121 (m, aromatic C-H), 2967 (m, aliphatic C-H), 2941 (m, aliphatic C-H), 2880 (m, aliphatic C-H), 1138 (m, $(CF_3SO_2)_2N^-$), 1057 (m, $(CF_3SO_2)_2N^-$), 615 (m, $(CF_3SO_2)_2N^-$).

- Mass spectrum (FAB +ve) m/z: 558 $(M+bmim)^+$, 139 $(M-(CF_3SO_2)_2N)^+$, 109 $(M-(CF_3SO_2)_2N-2CH_3)^+$, 96 $(M-(CF_3SO_2)_2N-CH_3-CH_2CH_3)^+$, 83 $(M-(CF_3SO_2)_2N-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-(CF_3SO_2)_2N-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-(CF_3SO_2)_2N-CH_3-(CH_2)_3CH_3-N)^+$. (FAB –ve) m/z: 280 $(M-bmim)^-$.

3.1.4.1.6. [bmim][$CH_3CH(OH)CO_2$]

Salt: Na[$CH_3CH(OH)CO_2$] (36 g; 0.32 mol)

Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 9.23 (1H, s, NC**H**N), 7.42 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 7.29 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 6.58 (1H, s, $CH_3CH(O\mathbf{H})CO_2$), 3.70 (1H, m, $CH_3C\mathbf{H}(OH)CO_2$), 3.09 (2H, t, J=5.4 Hz, $NC\mathbf{H}_2(CH_2)_2CH_3$), 2.82 (3H, s, $NC\mathbf{H}_3$), 0.72 (2H, m, $NCH_2C\mathbf{H}_2CH_2CH_3$), 0.06 (2H, m, $N(CH_2)_2C\mathbf{H}_2CH_3$), -0.02 (3H, d, 5.8 Hz, $C\mathbf{H}_3CH(OH)CO_2$), -0.33 (3H, t, J=7.3 Hz, $N(CH_2)_3C\mathbf{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 178.00 (s, $CH_3CH(OH)\mathbf{C}O_2$), 136.80 (s, N**C**HN), 122.90 (s, $CH_3N\mathbf{C}HCHN$), 121.86 (s, $CH_3NCH\mathbf{C}HN$), 66.63 (s, $CH_3\mathbf{C}H(OH)CO_2$), 47.83 (s, $N\mathbf{C}H_2(CH_2)_2CH_3$), 35.07 (s, $N\mathbf{C}H_3$), 31.20 (s, $NCH_2\mathbf{C}H_2CH_2CH_3$), 20.52 (s, $\mathbf{C}H_3CH(OH)CO_2$), 18.19 (s, $N(CH_2)_2\mathbf{C}H_2CH_3$), 12.33 (s, $N(CH_2)_3\mathbf{C}H_3$).

- Infrared spectrum (nujol mull) cm^{-1}: 3150 (m, aromatic C-H), 3102 (m, aromatic C-H), 2963 (m, aliphatic C-H), 2936 (m, aliphatic C-H), 2875 (m, aliphatic C-H), 1585 (m, $CH_3CH(OH)CO_2^-$), 1125 (m, $CH_3CH(OH)CO_2^-$), 1036 (m, $CH_3CH(OH)CO_2^-$), 848 (m, $CH_3CH(OH)CO_2^-$).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}(CH_3CH(OH)CO_2)^+$, 109 $(M\text{-}CH_3CH(OH)CO_2\text{-}2CH_3)^+$, 96 $(M\text{-}CH_3CH(OH)CO_2\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}CH_3CH(OH)CO_2\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}CH_3CH(OH)CO_2\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}\ CH_3CH(OH)CO_2\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 89 $(M\text{-bmim})^-$.

3.1.4.1.7. [bmim][(Me$_3$N)$_2$Si]

Salt: Li[(Me$_3$N)$_2$Si] (53 g; 0.32 mol)

The reaction was conducted in dichloromethane (50 cm^3). On addition of the lithium salt of the anion, an exothermic and vigorous reaction took place, giving an orange/brown solid in a liquid of the same colour. On removal of dichloromethane *in vacuo*, a thick red/brown sludge was left. No reaction was possible.

The same lithium salt was reacted in the same manner with [bmmim]Cl, with similar results.

3.1.4.2. By the Acid Method

$[A]^- = BF_4^-, PF_6^-, CH_3SO_3^-, NO_3^-$

[bmim]Cl (40 g; 0.23 mol) was dissolved in the minimum amount of water (*ca.* 20 cm^3) and cooled to 0 °C. Dichloromethane (*ca.* 30 cm^3) was added to the solution, unless otherwise stated (see below for individual variations of method). An aqueous solution of the acid of the appropriate anion was added dropwise in slight excess (0.25 mol) to the stirred solution, which was then allowed to warm to room temperature, and left stirring for 24 hours. According to the ionic liquid, slight variations in the method took place after this (see the relevant sub-section below).

3.1.4.2.1. [bmim][BF_4]

Acid: 50 % aqueous solution of HBF_4 (45 g; 0.25 mol)

See section 3.1.3.2.2 for full method and analysis.

3.1.4.2.2. [bmim][PF_6]

Acid: 60 % aqueous solution of HPF_6 (61 g; 0.25 mol)

No dichloromethane was added to the aqueous solution of [bmim]Cl. After addition of the acid, two layers were observed to separate. After 24 hours, the two phases were separated. The organic layer that had formed throughout the reaction was washed three times with small quantities of water (*ca.* 20 cm^3). No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.34 (1H, s, NC**H**N), 6.35 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.31 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 3.08 (2H, t, J=7.5 Hz, NC**H**$_2$(CH_2)$_2CH_3$), 2.85 (3H, s, NC**H**$_3$), 0.75 (2H, m, NCH_2C**H**$_2CH_2CH_3$), 0.21 (2H, m, $N(CH_2)_2$C**H**$_2CH_3$), -0.24 (3H, t, J=7.3 Hz, $N(CH_2)_3$C**H**$_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 135.17 (s, N**C**HN), 122.34 (s, CH_3N**C**HCHN), 121.00 (s, CH_3NCH**C**HN), 48.27 (s, N**C**$H_2(CH_2)_2CH_3$), 34.47 (s, N**C**H_3), 30.41 (s, NCH_2**C**$H_2CH_2CH_3$), 17.91 (s, $N(CH_2)_2$**C**H_2CH_3), 11.62 (s, $N(CH_2)_3$**C**H_3).

- Infrared spectrum (thin layer) cm^{-1}: 3171 (m, aromatic C-H), 3125 (m, aromatic C-H), 2966 (m, aliphatic C-H), 2939 (m, aliphatic C-H), 2878 (m, aliphatic C-H), 837 (PF_6^-).

- Mass spectrum (FAB +ve) m/z: 423 $(M+bmim)^+$, 139 $(M-PF_6)^+$, 109 $(M-PF_6-2CH_3)^+$, 96 $(M-PF_6-CH_3-CH_2CH_3)^+$, 83 $(M-PF_6-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-PF_6-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-PF_6-CH_3-(CH_2)_3CH_3-N)^+$. (FAB –ve) m/z: 145 $(M-bmim)^-$.

3.1.4.2.3. [bmim][CH_3SO_3]

Acid: 70 % aqueous solution of CH_3SO_3H (34 g; 0.25 mol)

After reaction, the aqueous layer was separated from the organic layer. Any residual ionic liquid left in it was extracted with a small quantity of dichloromethane (*ca.* 20 cm^3). This wash was repeated twice. The dichloromethane washings were combined with the ionic liquid/dichloromethane mixture. The solvent was removed *in vacuo* leaving 1 cm^3 of a yellow oil. The aqueous layer was found to contain the ionic liquid, when the water was removed *in vacuo* at 100 °C. No precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 8.54 (1H, s, NC**H**N), 7.04 (1H, d, J=1.7 Hz, $CH_3NC\underline{H}CHN$), 6.95 (1H, d, J=1.7 Hz, $CH_3NCHC\underline{H}N$), 3.37 (2H, t, J=7.5 Hz, $NC\underline{H}_2(CH_2)_2CH_3$), 3.09 (3H, s, $C\underline{H}_3SO_3$), 2.83 (3H, s, $NC\underline{H}_3$), 0.86 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), 0.29 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$), -0.15 (3H, t, J=7.3 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Chloroform-*d*) δ/ppm: 136.44 (s, N<u>C</u>HN), 122.95 (s, $CH_3N\underline{C}HCHN$), 121.74 (s, $CH_3NCH\underline{C}HN$), 48.11 (s, $N\underline{C}H_2(CH_2)_2CH_3$), 38.84 (s, $\underline{C}H_3SO_3$), 35.21 (s, $N\underline{C}H_3$), 31.04 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 18.29 (s, $N(CH_2)_2\underline{C}H_2CH_3$), 12.42 (s, $N(CH_2)_3\underline{C}H_3$).

- Infrared spectrum (thin layer) cm^{-1}: 3148 (m, aromatic C-H), 3101 (m, aromatic C-H), 2962 (m, aliphatic C-H), 2938 (m, aliphatic C-H), 2874 (m, aliphatic C-H), 1334 (m, $CH_3SO_3^-$), 1190 (m, $CH_3SO_3^-$), 1041 (m, $CH_3SO_3^-$), 774 (m, $CH_3SO_3^-$).

- Mass spectrum (FAB +ve) m/z: 373 $(M+bmim)^+$, 139 $(M-CH_3SO_3)^+$, 109 $(M-CH_3SO_3-2CH_3)^+$, 96 $(M-CH_3SO_3-CH_3-CH_2CH_3)^+$, 83 $(M-CH_3SO_3-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-CH_3SO_3-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-CH_3SO_3-CH_3-(CH_2)_3CH_3-N)^+$. (FAB –ve) m/z: 95 $(M-bmim)^-$.

3.1.4.2.4. [bmim][NO$_3$]

Acid: 70 % aqueous solution of HNO_3 (23 g; 0.25 mol)

After reaction, the aqueous layer was separated from the organic layer. Any residual ionic liquid left in it was extracted with a small quantity of dichloromethane (*ca.* 20 cm^3). This wash was repeated twice. The dichloromethane washings were combined with the ionic liquid/dichloromethane mixture, which was yellow. The solvent was removed *in vacuo*, taking with it the yellow coloured volatile substance. The slightly yellow aqueous layer was treated in the same way (at an elevated temperature of 100 °C), giving the same result.

3.1.4.3. By the Direct Combination Method

$[A]^-=CF_3SO_3^-$

The method followed was the same as that described by Bonhôte and co-workers.[1,7] A solution of 1-butylimidazole (80 cm^3; 0.61 mol) in dichloromethane (300 cm^3) was stirred at 0 °C. Trifluoromethylsulfonate (100 g; 0.610 mol) was added dropwise to the solution. The reaction mixture was allowed to warm to room temperature, and then heated to reflux at *ca.* 60 °C for four hours. On cooling, the dichloromethane was removed *in vacuo*, leaving a pale pink solution. The resulting ionic liquid was purified and dried in the normal way. Yield generally quantitative.

See section 3.1.4.1.4. for analysis.

3.2. Moisture-Sensitive Ionic Liquids

3.2.1. General

All manipulations of moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of dry nitrogen, or in a drybox under an atmosphere of dry nitrogen. All starting materials were purified before use.

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded by the mass spectrometry laboratory of the Department of Chemistry of Imperial College, University of London. Infrared spectra were recorded on a Mattson Satellite FTIR machine.

3.2.2. Preparation of [bmim]Cl

The preparation followed and analyses used were identical to that described in section 3.1.2.2, except that the reaction product was recrystallised twice from an acetonitrile/toluene mixture.

3.2.3. Purification of Chlorometallates

3.2.3.1. Aluminium Trichloride

Aluminium trichloride (150 g), aluminium powder (1 g) and sodium chloride (2 g) were placed in a sublimation vessel. The vessel was sealed and evacuated. The top half of the vessel was fitted with a flexible brass coil, acting as a water condenser. The bottom half was immersed in a silicon oil bath. The contents of the vessel were heated steadily *in vacuo* until they reached molten state (*ca.* 220 °C). Aluminium trichloride was observed to sublime on the walls of the top half of the vessel, until roughly 10 % of the molten material (which was brown in colour) remained at the bottom. The vessel was allowed to cool to room temperature, and under an atmosphere of nitrogen, the sublimed material was removed. The sublimation process was repeated on the sublimed material as before. The procedure was repeated twice more in the same way. For subsequent sublimations, the addition of aluminium powder was omitted. Sublimations were repeated until the molten aluminium trichloride was colourless. This typically took between seven and ten repetitions in total.

3.2.3.2. Iron (III) Chloride

High purity anhydrous iron (III) chloride was purchased from Aldrich Chemical Co. and used from the bottle.

3.2.3.3. Tin (II) Chloride

High purity anhydrous tin (II) chloride was purchased from Aldrich Chemical Co. and used from the bottle.

3.2.4. Preparation of Chlorometallate Ionic Liquids

3.2.4.1. 1-Butyl-3-Methylimidazolium Chloride-Aluminium(III) Chloride Ionic Liquids

3.2.4.1.1. Strongly Lewis Acidic Ionic Liquid {X($AlCl_3$) = 0.65}

In an inert atmosphere glove box, [bmim]Cl (2.00 g; 11 mmol) was measured into a flask equipped with a magnetic stirrer bar. Sublimed aluminium (III) chloride (2.84 g; 21.0 mmol) was slowly added to the flask. The two solids began to melt and form a viscous colourless liquid. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.01 (1H, s, NC**H**N), 6.01 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 5.88 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 2.83 (2H, t, J=7.8 Hz, NC**H**$_2$(CH_2)$_2CH_3$), 2.58 (3H, s, NC**H**$_3$), 0.52 (2H, m, NCH_2C**H**$_2CH_2CH_3$), 0.00 (2H, m, $N(CH_2)_2C$**H**$_2CH_3$), -0.43 (3H, t, J=7.2 Hz, $N(CH_2)_3C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 133.56 (s, N**C**HN), 122.74 (s, CH_3N**C**HCHN), 121.45 (s, CH_3NCH**C**HN), 48.93 (s, N**C**H$_2$(CH_2)$_2CH_3$), 35.73 (s,

$N\underline{C}H_3$), 30.55 (s, $NCH_2\underline{C}H_2CH_2CH_3$), 18.17 (s, $N(CH_2)_2\underline{C}H_2CH_3$), 12.27 (s, $N(CH_2)_3\underline{C}H_3$).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}AlCl_4)^+$, 109 $(M\text{-}AlCl_4\text{-}2CH_3)^+$, 96 $(M\text{-}AlCl_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 302 $(M\text{-}bmim+AlCl_3)^-$, 169 $(M\text{-}bmim)^-$, 35/37 $(M\text{-}bmim\text{-}AlCl_3)^+$.

3.2.4.1.2. Slightly Lewis Acidic Ionic Liquid {X(AlCl$_3$) = 0.51}

The same procedure was followed, using [bmim]Cl (1.26 g; 6.9 mmol) and sublimed aluminium (III) chloride (1.00 g; 7.4 mmol). Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: as for section 3.2.4.1.1, except: 7.08 (1H, s, $NC\underline{H}N$), 6.08 (1H, d, J=1.7 Hz, $CH_3NC\underline{H}CHN$), 5.96 (1H, d, J=1.7 Hz, $CH_3NCHC\underline{H}N$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) as for section 3.2.4.1.1.

- Mass spectrometry as in section 3.2.4.1.1.

3.2.4.1.3. Neutral Buffered Ionic Liquid {X($AlCl_3$) = 0.50}

The same procedure as in section 3.2.4.1.2 was carried out, producing a slightly Lewis acidic ionic liquid. Dry sodium chloride (*ca.* 0.5 g) was dissolved in the liquid until no more would dissolve. Any excess sodium chloride was removed by filtration, producing a neutral ionic liquid. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.13 (1H, s, NC**H**N), 6.11 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.07 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 2.89 (2H, t, J=7.8 Hz, NC**H**$_2$(CH_2)$_2$$CH_3$), 2.58 (3H, s, NC**H**$_3$), 0.54 (2H, m, NCH_2C**H**$_2$$CH_2CH_3$), 0.02 (2H, m, N($CH_2$)$_2$C**H**$_2$$CH_3$), -0.45 (3H, t, J=7.2 Hz, N(CH_2)$_3$C**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 133.98 (s, N**C**HN), 122.65 (s, CH_3N**C**HCHN), 121.36 (s, CH_3NCH**C**HN), 48.84 (s, N**C**H$_2$(CH_2)$_2$$CH_3$), 35.76 (s, N**C**$H_3$), 30.58 (s, NCH_2**C**$H_2CH_2CH_3$), 18.17 (s, N(CH_2)$_2$**C**H_2CH_3), 12.29 (s, N(CH_2)$_3$**C**H_3).

- Mass spectrum (FAB +ve) m/z: 139 (M-$AlCl_4$)$^+$, 109 (M-$AlCl_4$-2CH_3)$^+$, 96 (M-$AlCl_4$-CH_3-CH_2CH_3)$^+$, 83 (M-$AlCl_4$-CH_3-(CH_2)$_2$$CH_3$)$^+$, 69 (M-$AlCl_4$-$CH_3$-($CH_2$)$_3$$CH_3$)$^+$, 55 (M-$AlCl_4$-$CH_3$-($CH_2$)$_3$$CH_3$-N)$^+$. (FAB –ve) m/z: 169 (M-bmim)$^-$, 35/37 (M-bmim-$AlCl_3$)$^+$.

3.2.4.1.4. Slightly Lewis Basic Ionic Liquid {X($AlCl_3$) = 0.48}

The same procedure as in section 3.2.4.1.1 was followed, using [bmim]Cl (1.42 g; 7.8 mmol) and sublimed aluminium (III) chloride (1.00 g; 7.4 mmol). Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: as for section 3.2.4.1.1, except: 7.58 (1H, s, NC**H**N), 6.26 (1H, d, J=1.7 Hz, $CH_3NC\underline{H}CHN$), 6.18 (IH, d, J=1.7 Hz, $CH_3NCHC\underline{H}N$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) as for section 3.2.4.1.5.

- Mass spectrometry as in section 3.2.4.1.5.

3.2.4.1.5. Strongly Lewis Basic Ionic Liquid {X($AlCl_3$) = 0.35}

The same procedure as in section 3.2.4.1.1 was followed, using [bmim]Cl (2.44 g; 18.3 mmol) and sublimed aluminium (III) chloride (1.00 g; 7.4 mmol). Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 8.79 (1H, s, NC**H**N), 6.79 (IH, d, J=1.7 Hz, $CH_3NC\underline{H}CHN$), 6.72 (1H, d, J=1.7 Hz, $CH_3NCHC\underline{H}N$), 3.08 (2H, t, J=7.8 Hz, $NC\underline{H}_2(CH_2)_2CH_3$), 2.79 (3H, s, $NC\underline{H}_3$), 0.59 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$), -0.02 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$), -0.45 (3H, t, J=7.2 Hz, $N(CH_2)_3C\underline{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.94 (s, N<u>C</u>HN), 122.62 (s, CH_3N<u>C</u>$HCHN$), 121.46 (s, CH_3NCH<u>C</u>HN), 48.16 (s, N<u>C</u>$H_2(CH_2)_2CH_3$), 35.29 (s, N<u>C</u>H_3), 30.77 (s, NCH_2<u>C</u>$H_2CH_2CH_3$), 18.12 (s, $N(CH_2)_2$<u>C</u>H_2CH_3), 12.29 (s, $N(CH_2)_3$<u>C</u>H_3).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}AlCl_4)^+$, 109 $(M\text{-}AlCl_4\text{-}2CH_3)^+$, 96 $(M\text{-}AlCl_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}AlCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 169 $(M\text{-bmim})^-$, 35/37 $(M\text{-bmim-}AlCl_3)^+$.

3.2.4.2. 1-Butyl-3-Methylimidazolium chloride-Iron(III) Chloride Ionic Liquids

3.2.4.2.1. Slightly Lewis Acidic Ionic Liquid {X($FeCl_3$) = 0.51}

In an inert atmosphere glove box, [bmim]Cl (1.03 g; 5.9 mmol) was measured into a flask equipped with a magnetic stirrer bar. Anhydrous iron (III) chloride (1.00 g; 6.2 mmol) was slowly added to the flask. The two solids began to melt and form a viscous dark green/black coloured liquid. Yield generally quantitative.

- ^{1}H/^{13}C NMR: these were not obtainable due to iron being paramagnetic.

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}FeCl_4)^+$, 109 $(M\text{-}FeCl_4\text{-}2CH_3)^+$, 96 $(M\text{-}FeCl_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 360 $(M\text{-bmim+}FeCl_3)^-$, 324 $(M\text{-bmim+}FeCl_2)^-$, 287 $(M\text{-bmim+}FeCl)^-$, 198 $(M\text{-bmim})^-$, 162 $(M\text{-bmim-}Cl)^-$ 35/37 $(M\text{-bmim-}FeCl_3)^-$.

3.2.4.2.2. Neutral Buffered Ionic Liquid {X($FeCl_3$) = 0.50}

The same procedure as in section 3.2.4.2.1 was carried out, producing a slightly Lewis acidic ionic liquid. Dry sodium chloride (*ca.* 0.5 g) was dissolved in the liquid until no more would dissolve. Any excess sodium chloride was removed by filtration, producing a neutral ionic liquid. Yield generally quantitative.

- $^{1}H/^{13}C$ NMR: these were not obtainable due to iron being paramagnetic.

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}FeCl_4)^+$, 109 $(M\text{-}FeCl_4\text{-}2CH_3)^+$, 96 $(M\text{-}FeCl_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 324 $(M\text{-bmim}+FeCl_2)^-$, 287 $(M\text{-bmim}+FeCl)^-$, 198 $(M\text{-bmim})^-$, 162 $(M\text{-bmim-Cl})^-$, 35/37 $(M\text{-bmim-}FeCl_3)^-$.

3.2.4.2.3. Slightly Lewis Basic Ionic Liquid {X($FeCl_3$) = 0.48}

The same procedure as in section 3.2.4.2.1 was followed, using [bmim]Cl (1.17 g; 6.7 mmol) and anhydrous iron (III) chloride (1.00 g; 6.2 mmol). Yield generally quantitative.

- $^{1}H/^{13}C$ NMR: these were not obtainable due to iron being paramagnetic.

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}FeCl_4)^+$, 109 $(M\text{-}FeCl_4\text{-}2CH_3)^+$, 96 $(M\text{-}FeCl_4\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}FeCl_4\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 324 $(M\text{-bmim}+FeCl_2)^-$, 287 $(M\text{-bmim}+FeCl)^-$, 198 $(M\text{-bmim})^-$, 162 $(M\text{-bmim-Cl})^-$ 35/37 $(M\text{-bmim-}FeCl_3)^-$.

3.2.4.3. 1-Butyl-3-Methylimidazolium chloride-Tin(II) Chloride Ionic Liquids

3.2.4.3.1. Slightly Lewis Acidic Ionic Liquid {X($SnCl_2$) = 0.51}

In an inert atmosphere glove box, [bmim]Cl (0.88 g; 5.0 mmol) was measured into a flask equipped with a magnetic stirrer bar. Anhydrous tin (II) chloride (1.00 g; 5.3 mmol) was slowly added to the flask. The two solids began to melt and form a viscous white coloured liquid. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.51 (1H, s, NC**H**N), 6.17 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.12 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 2.79 (2H, t, J=7.5 Hz, NC**H**$_2$$(CH_2)_2CH_3$), 2.52 (3H, s, NC**H**$_3$), 0.32 (2H, m, NCH_2C**H**$_2$$CH_2CH_3$), -0.23 (2H, m, $N(CH_2)_2C$**H**$_2$$CH_3$), -0.67 (3H, t, J=7.3 Hz, $N(CH_2)_3C$**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 134.69 (s, N**C**HN), 122.62 (s, CH_3N**C**HCHN), 121.34 (s, CH_3NCH**C**HN), 48.38 (s, N**C**$H_2(CH_2)_2CH_3$), 36.21 (s, N**C**H_3), 30.81 (s, NCH_2**C**$H_2CH_2CH_3$), 18.16 (s, $N(CH_2)_2$**C**H_2CH_3), 12.69 (s, $N(CH_2)_3$**C**H_3).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}SnCl_3)^+$, 109 $(M\text{-}SnCl_3\text{-}2CH_3)^+$, 96 $(M\text{-}SnCl_3\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 225 $(M\text{-bmim})^-$, 153 $(M\text{-bmim-}2Cl)^-$, 35/37 $(M\text{-bmim-}SnCl_3)^-$.

3.2.4.3.2. Neutral Buffered Ionic Liquid {X($SnCl_2$) = 0.50}

The same procedure as in section 3.2.4.3.1 was carried out, producing a slightly Lewis acidic ionic liquid. Dry sodium chloride (*ca.* 0.5 g) was dissolved in the liquid until no more would dissolve. Any excess sodium chloride was removed by filtration, producing a neutral ionic liquid. Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.52 (1H, s, NC**H**N), 6.18 (1H, d, J=1.7 Hz, CH_3NC**H**CHN), 6.13 (1H, d, J=1.7 Hz, CH_3NCHC**H**N), 2.80 (2H, t, J=7.5 Hz, NC**H**$_2$(CH_2)$_2$$CH_3$), 2.53 (3H, s, NC**H**$_3$), 0.35 (2H, m, NC$H_2$C**H**$_2$$CH_2CH_3$), -0.22 (2H, m, N($CH_2$)$_2$C**H**$_2$$CH_3$), -0.66 (3H, t, J=7.3 Hz, N(CH_2)$_3$C**H**$_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 134.70 (s, N**C**HN), 122.63 (s, CH_3N**C**HCHN), 121.34 (s, CH_3NCH**C**HN), 48.39 (s, N**C**H_2(CH_2)$_2$$CH_3$), 36.21 (s, N**C**$H_3$), 30.81 (s, NC$H_2$**C**$H_2CH_2CH_3$), 18.17 (s, N($CH_2$)$_2$**C**$H_2CH_3$), 12.69 (s, N($CH_2$)$_3$**C**$H_3$).

- Mass spectrum (FAB +ve) m/z: 139 (M-$SnCl_3$)$^+$, 109 (M-$SnCl_3$-2CH_3)$^+$, 96 (M-$SnCl_3$-CH_3-CH_2CH_3)$^+$, 83 (M-$SnCl_3$-CH_3-(CH_2)$_2$$CH_3$)$^+$, 69 (M-$SnCl_3$-$CH_3$-($CH_2$)$_3$$CH_3$)$^+$, 55 (M-$SnCl_3$-$CH_3$-($CH_2$)$_3$$CH_3$-N)$^+$. (FAB –ve) m/z: 225 (M-bmim)$^-$, 35/37 (M-bmim-$SnCl_2$)$^-$.

3.2.4.3.3. Slightly Lewis Basic Ionic Liquid {X($SnCl_2$) = 0.48}

The same procedure as in section 3.2.4.3.1 was followed, using [bmim]Cl (1.00 g; 5.7 mmol) and anhydrous tin (II) chloride (1.00 g; 5.3 mmol). Yield generally quantitative.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 7.76 (1H, s, NC**H**N), 6.28 (1H, d, J=1.7 Hz, $CH_3NC\mathbf{H}CHN$), 6.22 (1H, d, J=1.7 Hz, $CH_3NCHC\mathbf{H}N$), 2.86 (2H, t, J=7.5 Hz, $NC\mathbf{H}_2(CH_2)_2CH_3$), 2.58 (3H, s, $NC\mathbf{H}_3$), 0.66 (2H, m, $NCH_2C\mathbf{H}_2CH_2CH_3$), -0.19 (2H, m, $N(CH_2)_2C\mathbf{H}_2CH_3$), -0.64 (3H, t, J=7.3 Hz, $N(CH_2)_3C\mathbf{H}_3$).

- ^{13}C-NMR (270 MHz, Acetone-d_6) δ/ppm: 135.02 (s, N**C**HN), 122.62 (s, $CH_3N\mathbf{C}HCHN$), 121.36 (s, $CH_3NCH\mathbf{C}HN$), 48.31 (s, $N\mathbf{C}H_2(CH_2)_2CH_3$), 36.12 (s, $N\mathbf{C}H_3$), 30.89 (s, $NCH_2\mathbf{C}H_2CH_2CH_3$), 18.17 (s, $N(CH_2)_2\mathbf{C}H_2CH_3$), 12.66 (s, $N(CH_2)_3\mathbf{C}H_3$).

- Mass spectrum (FAB +ve) m/z: 139 $(M\text{-}SnCl_3)^+$, 109 $(M\text{-}SnCl_3\text{-}2CH_3)^+$, 96 $(M\text{-}SnCl_3\text{-}CH_3\text{-}CH_2CH_3)^+$, 83 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_2CH_3)^+$, 69 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_3CH_3)^+$, 55 $(M\text{-}SnCl_3\text{-}CH_3\text{-}(CH_2)_3CH_3\text{-}N)^+$. (FAB –ve) m/z: 225 $(M\text{-bmim})^-$, 35/37 $(M\text{-bmim-}SnCl_3)^-$.

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SECTION 2

REACTIVITY IN IONIC LIQUIDS

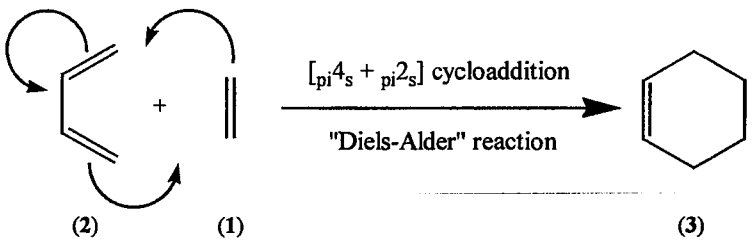
4. ROOM TEMPERATURE IONIC LIQUIDS AS SOLVENTS FOR DIELS-ALDER CYCLOADDITIONS

4.1. Background

In broad terms, cycloadditions are one of a series of organic process that occupy the category pericyclic reactions (other common examples include sigmatropic shifts and cheletropic reactions). Pericyclic reactions are described as "reactions in which all first-order changes in bonding relationships take place in concert on a closed curve".[2.1]

Cycloadditions are reactions involving the addition of two or more unsaturated molecules to each other to form a new ring. Again, the term cycloaddition is a broad term used to describe a variety of more narrowly defined reactions. The Diels-Alder reaction is one of these reactions. It is a powerful synthetic tool, used for the synthesis of six-membered rings, and provides excellent stereochemical control.

The Woodward-Hoffmann system of nomenclature of cycloadditions[2.1] classifies reactions by counting the number of π-electrons involved in bonding changes in the reacting molecules. Thus, a Diels-Alder reaction (Scheme 4.1) is a [4+2]-cycloaddition (in the chosen example, ethene (**1**) is formally known as the dienophile, and 1,3-butadiene (**2**) the diene). Although other nomenclatures have been used, the Woodward-Hoffmann system will suffice for this work.



Scheme 4.1: The Diels-Alder reaction between ethene (**1**) and 1,3-butadiene (**2**)

The first [4+2]-cycloaddition was reported by Diels and Alder[2.2] in 1928, and is considered a milestone in organic chemistry. The [4+2]-cycloadditions, named after their discoverers, were later joined by [2+1]-, [2+2]-, [3+2]-cycloadditions (also known as 1,3-dipolar cycloadditions), and those leading to more extended ring systems.

Since Diels' and Alder's pioneering work, many studies have been carried out to incorporate new substrates into this process (thus enlarging its possibilities as a general synthetic tool), and to refine or redefine the conditions of existing reactions (thus improving its efficiency and control over product selection). From a single piece of work, the Diels-Alder reaction has mushroomed into a field of synthetic organic chemistry in its own right. Consequently, a multitude of papers is published in the literature each year, leading to reviews that attempt to collate work into manageable and digestible sub-categories.

For sake of clarity, only the main reviews and primary literature that are directly relevant to the background of the work contained herein have been considered.[2.3]

4.2. Solvent Effects on Diels-Alder Reactions

The work that has been carried in this project out deals with the effects that room temperature ionic liquids have on the rate of reaction, *k*, and the *endo/exo* stereoselectivities (also called N/X) of certain Diels-Alder reactions. In some cases, solvents include salt solutions in various ionic liquids. To reach this stage in the development of the Diels-Alder reaction it was first necessary to understand in what way different types of conditions and environments can alter the parameters above.

This has led to such a degree of understanding that accurate predictions can now be made as to whether certain substrates will perform their reaction well in a given media. The

direction that research to date has pointed is towards tailoring the solvent towards the needs of specific substrates. This is now a distinct reality.

As previous work in the field of Diels-Alder chemistry was studied, it became increasingly apparent that, in terms of solvent effects, there are two broad topics to consider – traditional solvents and novel solvents. Traditional solvents include all common laboratory organic solvents, and were largely the media in which reactions were performed and then refined after the discovery by Diels and Alder.

Novel solvents were primarily defined as solvents that were not widely accepted or used at the time they were first considered to play an important part in the Diels-Alder reaction. As their use and ability to dramatically improve the rates and stereoselectivites of Diels-Alder reactions became more apparent, so it is possible to categorise them into four sub-categories:

(i) water and aqueous mixtures of conventional organic mixtures

(ii) aqueous salt solutions

(iii) nonaqueous solvents and their salt solutions (also known as 'water-like systems, for reasons that will be discussed later)

(iv) room temperature ionic liquids

Work from all four types of 'unusual solvent' has been important in our understanding of the nature of the Diels-Alder reaction.

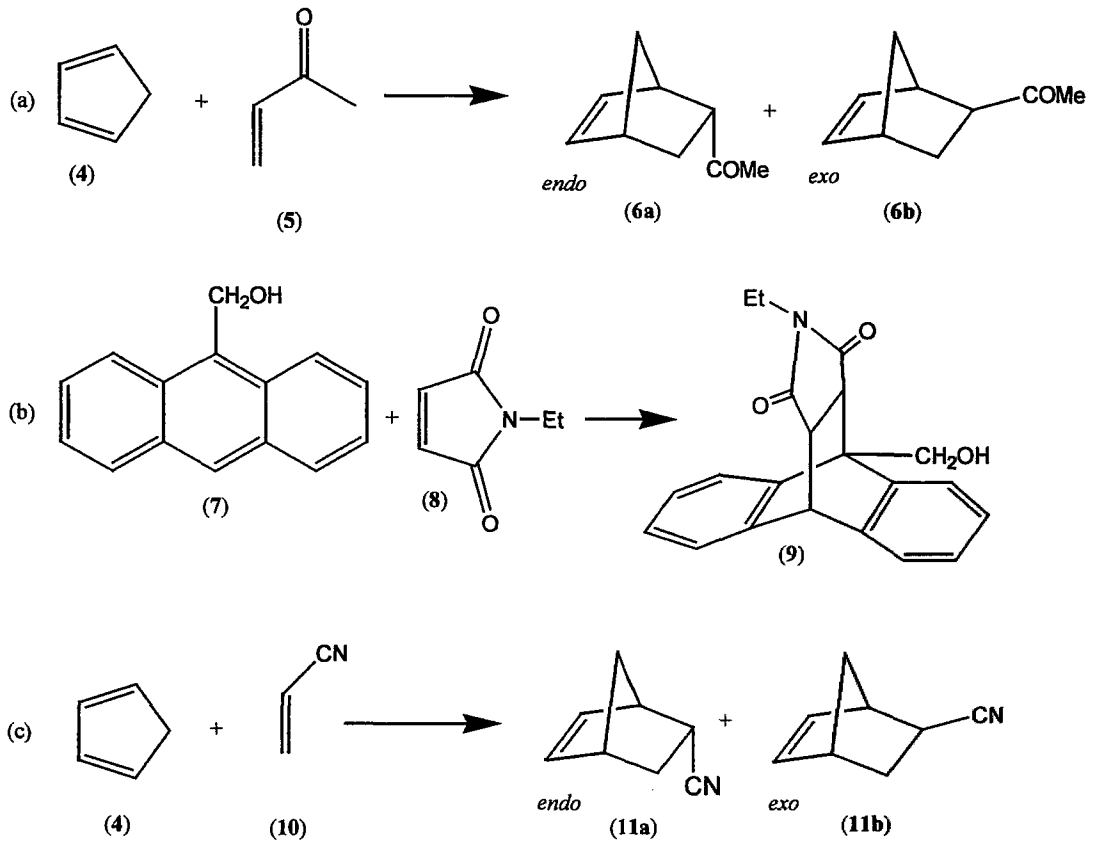
4.2.1. Water

For a wide range of traditional solvent systems, the effects of varying the solvent were small. It was Breslow and co-workers[2.4] who made the breakthrough when they first used water as the solvent for Diels-Alder reactions. Although water had previously been considered as a solvent from very early on in the lifetime of these reactions[2.5], Breslow first realized and explained the special effect it has on the Diels-Alder reaction.

Water is such a simple and readily available solvent that at first sight it may seem strange that it was not tried with more success earlier on in the study of Diels-Alder reactions. However, water is a poor solvent for dienes, and this would have almost certainly discouraged chemists at that stage. Another problem would have been that until quite recently, the available technology (in terms of gas chromatography analysis) was not sufficient to allow the use of these solvents.

Breslow first reported that the reaction between cyclopentadiene (**4**) and methyl vinyl ketone (**5**) proceeded over 700 times faster in water than in 2,2,4-trimethylpentane (Scheme 4.2a).[2.4a] Other reactions tried were anthracene-9-carbinol (**7**) with *N*-ethylmaleimide (**8**) (nearly 30 times faster in water than in 2,2,4-trimethylpentane – Scheme 4.2b),[2.4a] and that of (**4**) with acrylonitrile (**10**) (again, nearly 30 times faster in water than in 2,2,4-trimethylpentane – Scheme 4.2c).[2.4a] These results are shown in table 4.3. These examples illustrated, for the first time, that Diels-Alder reactions could undergo enormous rate enhancements, by the use of water as the solvent medium.

Breslow observed that the use of water enhanced the rate of reaction of these Diels-Alder reactions, with respect to organic solvents. The general opinion in the literature before Breslow was that the relatively high polarity of water would be the main factor for the improved performance of these reactions in water.[2.7] Breslow did have an alternative idea based on another property of water, that sets it apart from most organic solvents.



Scheme 4.2: Various Diels-Alder reactions attempted with water as a solvent, by Breslow and co-workers[2.4a]

The notion of solvophobicity was of course well known at that time. When applied specifically to water this becomes known as hydrophobicity. In simple terms, the hydrophobic effect is the tendency of nonpolar molecules and molecular segments to avoid contact with water. This can be achieved if such molecules either escape to a separate phase or organize themselves together into clusters in order to decrease the hydrocarbon-water interfacial area. In other words, the diene and dienophile will tend to aggregate in an aqueous system, thus minimizing the surface contact with water.

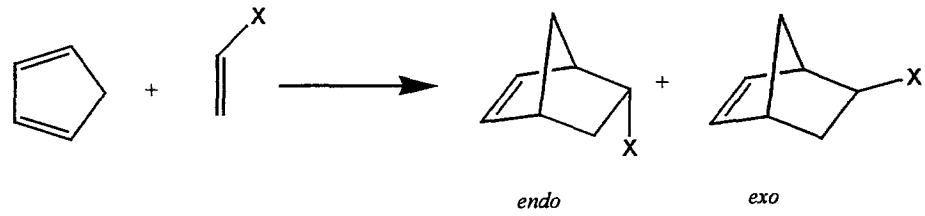
This process of aggregation of both components is called hydrophobic packing. If achieved it is quite clear that an acceleration of the Diels-Alder process could be achieved, as the reduced proximity and increased local concentration of the reactants would lead to more favourable reaction conditions. Breslow proposed that since the Diels-Alder reaction brings together two non-polar groups, it could be expected that water could improve the overall rate in this way.[2.4a]

Breslow was able to support this theory as the main factor accelerating the rate of reaction in water. He attempted all his three initial Diels-Alder reactions, not only in 2,2,4-trimethylpentane and water (to illustrate the effect water had), but also in methanol. The latter was used as a control solvent, because its polarity is in the same range as water.

The rate of reaction between (**4**) and (**5**) was increased only by about 12 times on changing the solvent from 2,2,4-trimethylpentane to methanol, but by 700 times on changing the solvent from 2,2,4-trimethylpentane to water. Similarly, the reaction between (**7**) and (**8**) proceeded 30 times faster in water than in 2,2,4-trimethylpentane, but was actually slower in methanol by a factor of about 0.8. The reaction between (**4**) and (**10**) proceeded, again 30 times faster in water than in 2,2,4-trimethylpentane, but only about twice as fast in methanol than 2,2,4-trimethylpentane. These results are shown in table 4.3.

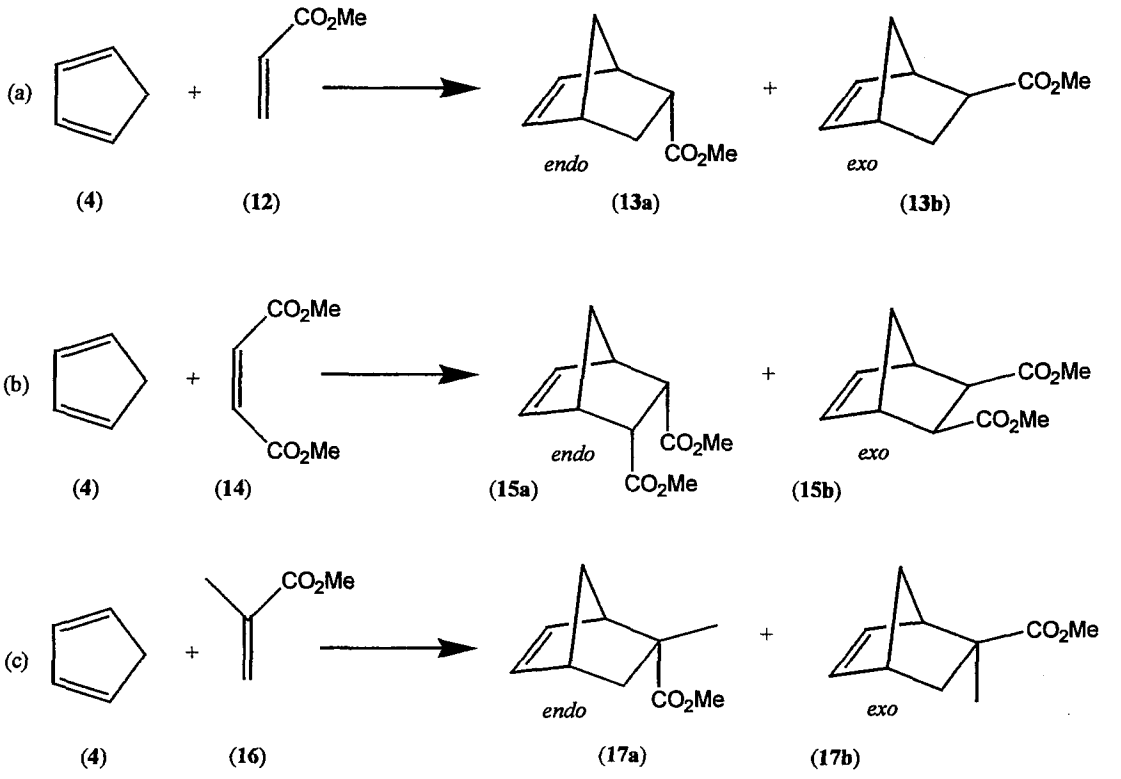
It should be stressed that Breslow did not fully discount the effect of the polarity of the reaction medium on the rates that he studied. Instead, he claimed that although polarity could and had been proved to play a part in the reactions before water's use as a solvent, it was not the major contribution in terms of a rate acceleration in water. Polarity effects could not be employed to explain conclusively why water has the effect it does on the reaction, because of the large discontinuous increase of rate in water is well above any expected polarity contribution. In fact, work on the Diels-Alder reaction up until Breslow had merely concluded that solvent effects on the kinetics were very small.[2.6,2.7]

Many Diels-Alder reactions can proceed to give a mixture of products. A common example is any reaction where cyclopentadiene (**4**) is the dienophile (see scheme 4.3), although the reaction between (**7**) and (**8**) yields a single product only. Chemists have, over the years, sought to enhance not only reaction rates, but also product selectivity. In the example given in scheme 4.3, two products are possible when cyclopentadiene reacts with the general dienophile shown. When the group X points upwards, a species called the *exo*-product is produced, and when X points downwards, the *endo*-product is produced. The ratio of the two species in the final product mixture is called the *endo/exo* ratio (or N/X). Being able to control and choose the product that results from any reaction has always been of significant importance to the synthetic chemist.



Scheme 4.3: The notion of the *endo*-product and the *exo*-product for Diels-Alder reactions, when using cyclopentadiene (**4**) as the diene

Breslow found that water can help to minimize the amount of *exo*-product formed, in the case of reactions using cyclopentadiene (**4**) as the dienophile, thus increasing the numerical value of N/X. The reactions between (**4**) and methyl acrylate (**12**), dimethyl maleate (**14**) and methyl methacrylate (**16**)[2.4b] (see scheme 4.4) all showed significant increases in N/X by using water as the solvent instead of excess cyclopentadiene (**4**). Again, as with his earlier rate studies, a solvent with a similar polarity to water (ethanol) was used as a control in these experiments. For this new characteristic of the reaction (N/X) that was being studied, as with rate, ethanol showed an increase in N/X, but not to the same extent as water. Full results are shown in table 4.1.

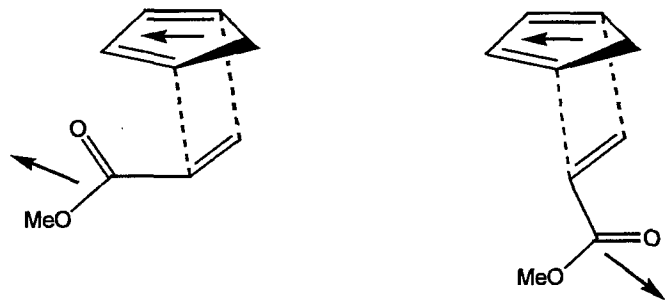


Scheme 4.4: Various Diels-Alder reactions carried out in water and other solvents by Breslow and co-workers[2.4b]

Table 4.1. Diels-Alder reactions carried out by Breslow[2.4b] in various solvents, using cyclopentadiene (**4**) and various dienophiles, and showing *endo*/*exo* ratios N/X

Medium	Formal concentration of diene and dienophile	Dienophile			
		Methyl Vinyl Ketone (**5**)	Methyl Acrylate (**12**)	Dimethyl Maleate (**14**)	Methyl Methacrylate (**16**)
Cyclopentadiene	Excess diene	3.85	2.9	2.8	0.43
Ethanol	0.15	8.5	5.2	4.5	0.6
Water	0.15	21.4	9.3	13.7	1.4
Water	0.30	18.6	5.9	-	-
Water	0.45	17.2	-	-	-

These results again point to the fact that polarity is not the only contributing factor here and somehow that the hydrophobicity of both reactants, and their resultant hydrophobic packing plays a greater role. It was Berson[2.7] who originally put forward a theory in 1962 as to how and why the polarity of a solvent could affect the outcome of N/X in a Diels-Alder reaction. His theory took the relative position of diene and dienophile at the moment they were positioned to react and form a transition state. Figure 4.1 shows that the *endo*-position, with the dipole moments of both the diene and the dienophile more-or-less aligned and pointing in the same direction, leading to a more polar transition state. Thus, using a more polar solvent would further increase this state, making it a more favourable reaction pathway.



endo-configuration *exo*-configuration

Figure 4.1: Berson's theory of solvent polarity influencing *endo*-/*exo*-product formation

Berson was, of course writing without the benefit of Breslow's breakthrough and subsequent results in the field. It should be said that for the small changes in N/X seen before the use of water as a solvent, Berson's theory holds true. However, when Breslow started to use ethanol and other solvents with a similar polarity to water, a new explanation was needed. This new explanation was not necessarily to replace any existing

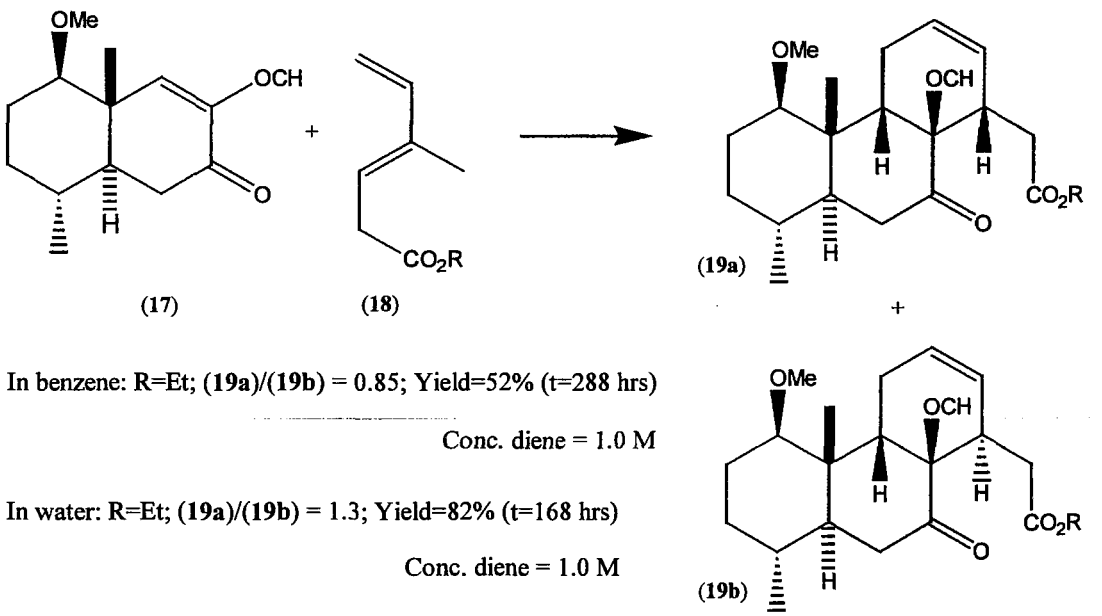
ideas about the properties that conventional solvents conveyed to the Diels-Alder reaction, but to allow for new and greater effects being observed.

The suggestion put forward by Breslow[2.4d] was simple yet elegant. The whole concept of hydrophobicity is based on the fact that the diene and dienophile are packed together into clusters within the solvent system. Although not considered to be in a separate phase as such, the molecules of the diene and dienophile work to try to avoid contact with water to the greatest possible extent. Being surrounded by a highly structured water environment means that a pressure is applied on these clusters. This is known as the internal pressure (P_i) of the system. The fact that this pressure is exerted by the surrounding aqueous environment leads to constraints over spatial availability for the hydrophobic molecules inside a typical cluster.

Breslow pointed out that the *endo*-transition state is spatially more compact than the *exo*-transition state. When this added factor of spatial constraint is considered, it seems inevitable that the *endo*-pathway should be favoured. As well as showing the dipole moments of the *endo*- and *exo*-transition states, figure 4.1 also shows qualitatively, the relative volume of each one. Breslow's reasoning can be understood from this diagram. Other work that Breslow carried out involving the use of dissolved salts that could change the size of cavities in the water system and also affect water's ability to repel or attract hydrophobic reagents resoundingly back up this theory. These will be discussed in more detail later.

Another pioneer of the use of water as the Diels-Alder solvent was Grieco and co-workers,[2.8] who in the literature talks less than Breslow of the reasons behind water's ability to catalyze the Diels-Alder reaction, but tried many new reactions by this method and found that both the rate of reaction and N/X were significantly influenced by water. Grieco's most memorable work concentrated on the synthesis of a group of compounds called quassinoids.

The reaction of dienophile (**17**) with the ester of 4-methyl (*E*)-3,5-hexadionoic acid (**18**) in benzene took 288 hrs and gave a major product that had undesirable stereochemistry (**19b**)[2.8a,2.8b] with a total yield of 52%. Trying the same reaction in water reduced the reaction time (168 hrs), improved the total yield (82%) and most importantly, gave a major product with the desired stereochemistry (**19a**) (see scheme 4.5 and table 4.2). However, Grieco found the most dramatic results on using (**17**) with the sodium salt of the diene acid. The reaction time was just 8 hrs, and by varying the diene concentration in the reaction mixture the desired product (**19a**) was formed a ratio of three to one over the other stereochemistry (**19b**) with a total yield of 100%.



In benzene: R=Et; (**19a**)/(**19b**) = 0.85; Yield=52% (t=288 hrs)

Conc. diene = 1.0 M

In water: R=Et; (**19a**)/(**19b**) = 1.3; Yield=82% (t=168 hrs)

Conc. diene = 1.0 M

In water: R=Na; (**19a**)/(**19b**) = 2.0; Yield=83% (t=8 hrs)

Conc. diene = 1.0 M

In water: R=Na; (**19a**)/(**19b**) = 3.0; Yield=100% (t=5 hrs)

Conc. diene = 2.0 M

Scheme 4.5: The Diels-Alder reaction carried out by Grieco and co-workers[2.8a,2.8b] in benzene and water

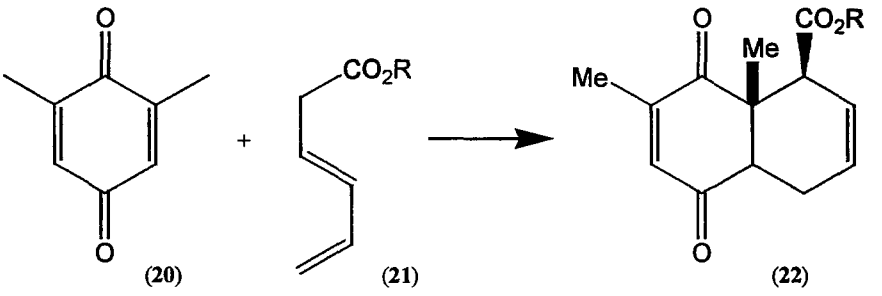
Grieco attributes his results to the aggregation of reactants. Although Grieco did not stress the factors that could be causing the reactions to accelerate, he mentioned the fact that the reaction is undergoing some sort of micellar catalysis, resulting in the mutual binding of the reactants. As can be seen from table 4.3, the variation of concentration of diene affected the rate, total yield and ratio of products markedly. Grieco argues that in water, and at higher concentrations of diene, the entropy requirements for the reaction in a micelle are lowered, due to the relative orientation of reactants in a micelle. This would lead to a rate increase. Furthermore, he speculates that if the transition state volume of (**19a**) were of a smaller volume than that of (**19b**), then unfavourable hydrophobic interactions would be minimized through more efficient micellar packing.

Table 4.2. Reaction of dienophile (**17**) with diene (**18**), as carried out by Grieco and co-workers[2.8b]

R (on diene)	solvent	concentration of diene	time	yield	product ratio (**19a**/**19b**)
Et	benzene	1.0 M	288 h	52%	0.85
Et	neat	-	144 h	69%	1.3
Et	water	1.0 M	168 h	82%	1.3
H	toluene	1.0 M	168 h	46%	0.7
H	neat	-	30 h	80%	1.4
H	water	1.0 M	17 h	85%	1.5
H	water-dioxane (1:1)	1.0 M	104 h	100%	0.8
H	water-MeOH (1:1)	1.0 M	97 h	99%	2.0
Na	water	0.1 M	120 h	46%	0.9
Na	water	1.0 M	8 h	83%	2.0
Na	water	2.0 M	5 h	100%	3.0

Another reaction that Grieco was able to improve on using water was that between 2,6-dimethylbenzoquinone (**20**) and sodium (*E*)-3,5-hexadienoate (**21a**). Previously, the reaction had been carried out in toluene using methyl (*E*)-3,5-hexadienoate (**21b**), giving only a trace of the product (**22**) after a week. However, in water (**20**) and (**21a**) react in 1

hour to give a 77 % yield (scheme 4.6). Again, micellar catalysis and molecular aggregation in water are cited as reasons for this rate acceleration.



	R	Reaction conditions	Yield
(21a)	Me	Toluene; rtp; 1 week	Trace
(21b)	Na	Water; rtp; 1 hour	77%

Scheme 4.6: The Diels-Alder reaction between 2,6-dimethylbenzoquinone (**20**) and (*E*)-3,5-hexadienoate variants (**21a/b**), carried out by Grieco and co-workers[2.8b]

It is significant that one of Breslow's papers[2.4c] appears to refute Grieco's claims that the effects of water on the Diels-Alder reaction are due to micellar packing. Breslow continued his study on the reaction of cyclopentadiene (**4**) and methyl vinyl ketone (**5**) for this work. Noting that the solubility of cyclopentadiene in water is only about 10 mM, he ran reactions with a fixed 10 mM amount of the dienophile and varied the diene concentration, starting at 1 mM and working up to 10 mM, whilst measuring the endo/exo ratio. At 1 mM and 2 mM it is 25 ± 0.5, at 4 mM and 8 mM it is 24.5 ± 0.4, and at 10 mM it is 24.0 ± 0.3. Although a very small change it suggests that the selectivity is in fact less at higher concentrations (i.e. when the maximum solubility point of cyclopentadiene is reached), at which point multi-molecular aggregation, or full-scale micellar formation is expected to occur. He concluded that the benefits of water on that

reaction were seen due to hydrophobicity, but more likely not at the stage of micellar or pre-micellar formation.

Further study of the aqueous system was made by Schneider and co-workers.[2.9] The reaction between cyclopentadiene (4) and diethyl fumarate (23) was studied. Although hydrophobicity was keenly discussed, it was pointed out that no quantitative study correlating it to Diels-Alder reactions yet existed. In fact the only such study of any solvent property that had been completed was on polarity,[2.7] and the use of water was not fully explained by the findings. Schneider[2.9a] completed his chosen reaction in a selection of solvents and different water-solvent mixtures. The log of the rate of reaction was plotted against a very recently formulated parameter,[2.10] *Sp*, which was used to measure solvophobicity. For the first time, a quantitative description of chemical rates as a function of solvophobicity existed (figure 4.2).

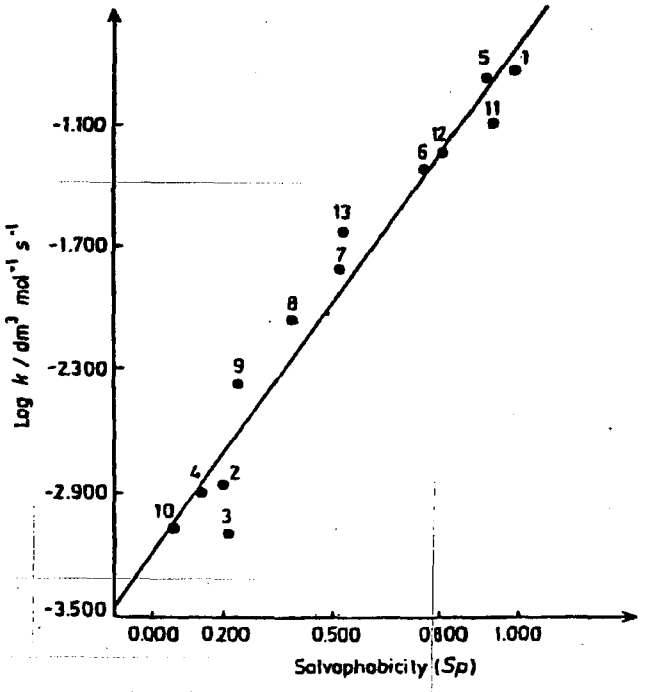


Figure 4.2: Log k_2 of the reaction between cyclopentadiene (4) and diethyl fumarate (23) *vs.* solvophobicity parameter *Sp*[2.10]. Graph by Schneider.[2.9a] **1:** H_2O; **2:** MeOH; **3:** MeCN; **4:** DMF; **5-10:** 10, 30, 50, 60, 70, 90% dioxane-H_2O; **11-13:** 10, 30, 60% MeOh-H_2O (aq mixtures in % vol. + vol.).

Although the work is not so relevant to this study, another pioneer of this field of chemistry is Lubineau and co-workers[2.11] (who used water to synthesize *trans*-butadienyl ethers using free glucose as the hydrophilic part).

4.2.2. Aqueous salt solutions

As discussed above, water has special properties that can dramatically enhance the Diels-Alder reaction. In turn, its effects on the process can be greatly altered by the introduction of soluble salts into the solvent system. Some salts aid the process, and others hinder it. Breslow and co-workers[2.4] initially brought this to attention, alongside their pioneering work using water as a Diels-Alder solvent. Two contrasting examples were used by him on the reaction between cyclopentadiene (**4**) and methyl vinyl ketone (**5**) (scheme 4.2a).[2.4a]

Lithium chloride (LiCl) is a salt that is known to increase the hydrophobic effect when introduced into an aqueous system (i.e. it "salts out" nonpolar material dissolved in water). Any substance that has this effect is called a "salting out" or antichaotropic agent. Guanidinium chloride (GnCl) has the opposite effect when introduced into an aqueous system. It actually changes the water structure so it decreases hydrophobic interactions (i.e. it "salts in" nonpolar material). Any substance with this property is called a "salting in" or chaotropic agent.

Breslow carried out the reaction in the presence of these salts, and observed that the hydrophobic effect – the main factor explaining the acceleration of the Diels-Alder reaction in water – was strengthened by the so-called "salting out" agents and weakened by "salting in" agents. LiCl in water (4.86 M) caused an increase in the rate, whereas GnCl in water (4.86 M) actually led to a decrease. Numerical results are shown in table 4.3. With these results, Breslow had shown further improvements to the rate of the Diels-

Alder reaction, and he was rapidly providing substantial evidence that the hydrophobic effect was the only tangible way of fully explaining water's special ability as a Diels-Alder solvent.

With the aid of molecular modeling, Breslow went on to predict that the transition state for the reaction between cyclopentadine (**4**) and methyl vinyl ketone (**5**) should be able to fit into the hydrophobic cavity of β-cyclodextrin (cycloheptaamylose). However, the smaller cavity of α-cyclodextrin (cyclohexaamylose) would only be expected to bind the cyclopentadiene, leaving no room for the dienophile.

Experimental results confirmed this. The rates of reaction of (**4**) with dienophiles (**5**) and acrylonitrile (**10**) (schemes 4.2a and 4.2c) are both accelerated in β-cyclodextrin, and retarded in α-cyclodextrin (see table 4.3). In fact β-cyclodextrin has a very large effect when compared to the "salting out" agent tested (lithium chloride), because of the relatively small quantity that is needed to produce effectively the same rate increase. The reaction between (**7**) and (**8**) (scheme 4.2b) was not accelerated by β-cyclodextrin, presumably because the transition state of this reaction is larger and so the "salting out" agent was unable to bind both the diene and dienophile (thus turning the salt into an inhibitor for this specific reaction).

As well as affecting the rate of reaction, dissolved salts also change the product selectivity, as Breslow[2.4c] later discovered. As discussed above, runs of the reaction were carried out between cyclopentadiene (**4**) and methyl vinyl ketone (**5**) at low concentration in order to show that micellar or pre-micellar aggregation did not bring any benefit to the reaction. In attempting to refute the micellar theory that Grieco[2.8] had put forward, Breslow had to also look for evidence of hydrophobicity to substantiate his explanation.

He performed runs of the reaction using 1 mM of the diene and 10 mM of the dienophile in 4.86 M aqueous LiCl and 4.86 M aqueous GnCl. As with rate of reaction the former did have a positive influence on N/X (increasing from 25.0 ± 0.5 in water alone to 28.0 ± 0.4 in 4.86 M aqueous LiCl), and the latter a negative influence (decreasing from 25.0 ±

0.5 in water alone to 22.0 ± 0.8 in 4.86 M aqueous GnCl). Breslow repeated that this did not rule out any contribution from any polar effects, but concluded that hydrophobic packing of diene and dienophile in a one-to-one transition state largely leads to high product selectivity in these media.

Table 4.3. Rate constants for Diels-Alder reactions attempted by Breslow[2.4a]

solvent	additional component	k_2 x 10^5, M^{-1} s^{-1}[a]
Cyclopentadiene (**4**) + Methyl Vinyl ketone (**5**), 20 C (see Scheme 4.2a)		
2,2,4-trimethylpentane		5.94[b]
MeOH		75.5
H_2O		4400
H_2O	LiCl (4.86 M)	10800
H_2O	$C(NH_2)_3^+Cl^-$ (or GnCl) (4.89 M)	4300
H_2O	cycloheptaamylose (10mM)	10900
H_2O	cyclohexaamylose (10mM)	2610
Anthracene-9-carbinol (**7**) + *N*-Ethylmaleimide (**8**), 30 C (see Scheme 4.2b)		
2,2,4-trimethylpentane		796
1-butanol		666
MeOH		344
CH_3CN		107
H_2O		22600
H_2O	cycloheptaamylose (10mM)	13800
Cyclopentadiene (**4**) + Acrylonitrile (**10**), 45 C (see scheme 4.2c)		
2,2,4-trimethylpentane		1.9
MeOH		4.0
H_2O		59.3
H_2O	cycloheptaamylose (10mM)	537
H_2O	cyclohexaamylose (10mM)	47.9

[a] second-order rate constants

[b] All data are the result of at least three runs at the same set of concentrations error limits are not shown as this is just a brief comparative study

It is useful to know which salts act as 'salting-in' and 'salting-out agents', but so far no one had suggested in what way these salts altered the water structure to allow Diels-Alder reactions to be improved, whether in terms of rate or selectivity. Breslow[2.4d] put forward some suggestions. As well as LiCl, NaCl can also act as a 'salting-out' agent. It is thought that these salts, when dissolved in water cause a volume contraction, as water collapses around the ions to solvate them. Therefore, less space exists for hydrocarbon solutes, and the energy cost to create space for them is greater. This is what makes the solvent system more hydrophobic in character.

The 'salting-in' effect is not clear to explain. As well as GnCl, another example of such a species is urea. According to the theory for 'salting-out', it has been suggested that large ions break up the organized structure of water and make cavitation easier, thus producing a less hydrophobic system. Although this seemingly provides a satisfactory explanation, the matter was not fully resolved. It will be discussed in more detail later.

As well as Breslow, others were keen to understand the reasoning behind the effects that different salts had on the Diels-Alder reaction. Schneider,[2.9] following up his work that has already been discussed above, used an *aza*-cyclophane called CP66[2.9a] and β-cyclodextrin to provide hydrophilic cavities. CP66 was used because as well as promoting hydrophobicity, it could provide positive charges. Once inside the cavity, dienophiles such as fumerate esters could be bound by electrostatic charges. This would also lead to a decrease of electron density at the olefinic bond, making the dienophile more reactive and hopefully accelerating the reaction. The reaction chosen was between cyclopentadiene (**4**) and diethyl fumarate (**23**).

In fact, in dioxane-water mixtures, the rate increase was modest only (in the order of between 1.5 and 3 times depending on the mixture ratio). β-cyclodextrin produced more striking results (figure 4.3).

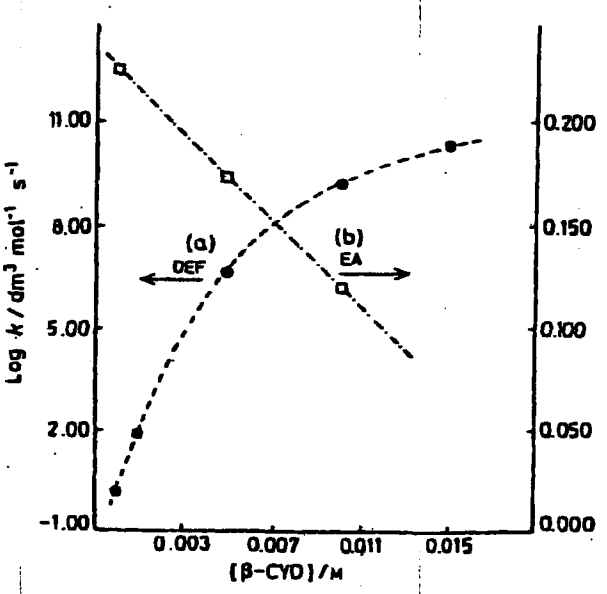


Figure 4.3: Rate constants k_2 of the reaction (a) diethyl fumarate (23) + cyclopentadiene (4), (b) ethyl acrylate (24) + cyclopentadiene (4) (all at 20.0 °C, in water, 0.1 vol% dioxane) *vs.* [β-cyclodextrin] in mol^{-1} dm^{-3}. Graph by Schneider.[2.9a]

β-cyclodextrin was also able to improve the stereoselectivites of Diels-Alder reactions that could not be bettered by water alone. Schneider and co-workers[2.9b] used the reaction between cyclopentadiene and derivatives of maleic and fumaric acid derivatives, finding a marked improvement of N/X in 0.015 M β-cyclodextrin in water over water alone. This study was later expanded to include 19 different dienophiles with cyclopentadiene (4).[2.9c]

Rizzo[2.12] looked beyond the Diels-Alder reaction and examined the work of other scientists explaining how salts and hydrophilic packing effected other areas of solution chemistry, namely the structure and stability of biopolymers. He found that the melting temperature (Tm) of proteins and nucleic acids changed according to the salt present. Some salts tend to stabilize the native structures of proteins and nucleic acids, making them more resistant to thermal denaturing (raising Tm), whilst others have the opposite effect (lowering Tm). A trend was observed in the effects that various salts have on proteins, named the Hofmeister series (after Franz Hofmeister who discovered it when

studying the solubility of proteins[2.13]). In general the Hofmeister series correlates to the size of the anion.

Rizzo tested this by performing the Diels-Alder reaction between anthracene-9-carbinol (**7**) and *N*-ethylmaleimide (**8**) (see scheme 4.2b) in water alone and then in aqueous solutions of various sodium salts, and comparing the kinetics. His results can be seen below in table 4.4.

Table 4.4. Effects of sodium salts on the second order rate constants of the reaction between anthracene-9-carbinol (**7**) and *N*-ethylmaleimide (**8**). Work by Rizzo[2.12]

sodium salt (2 M)	k_2 x 10^3 M^{-1} s^{-1}	k_{rel}	ionic radii (A)
water	230	1.00	-
Cl^-	308	1.34	1.67
Br^-	298	1.30	1.82
BF_4^-	224	0.98	2.44
ClO_4^-	205	0.89	2.64
PF_6^-	190	0.83	2.81
AsF_6^-	179	0.78	2.89

When the rate of reaction was plotted against the ionic radius, a very clear linear relationship is observed (figure 4.4). As the ionic radius of the dissolved salt's anion increases, the rate of reaction decreases, in some cases becoming slower than water alone. Rizzo also studied the effects of guanidinium salts on the reaction in the same way (table 4.5). This time the results clearly show that the bigger the anion, the greater the extent of deceleration of the reaction.

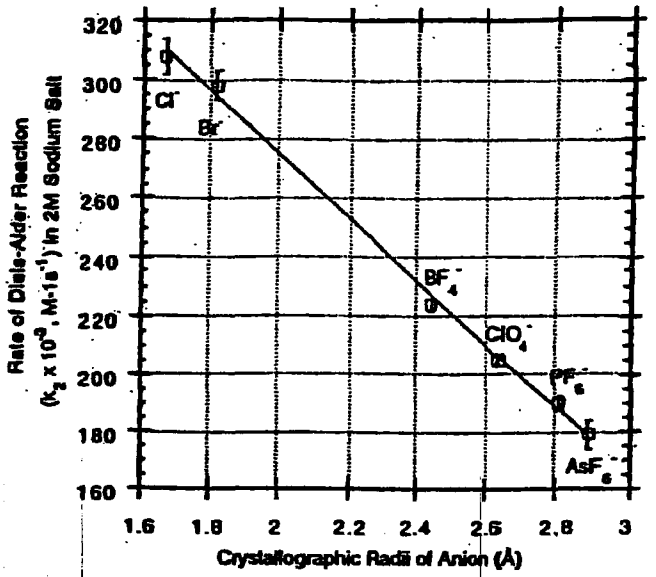


Figure 4.4: Rate of the Diels-Alder reaction between anthracene-9-carbinol (7) and *N*-ethylmaleimide (8) in 2 M sodium salt solution *vs* the crystallographic radii of the anions (correlation coefficient r=0.9988). Graph by Rizzo.[2.12]

Table 4.5. Effects of guanidinium salts on the second order rate constant of the reaction between anthracene-9-carbinol (7) and *N*-ethylmaleimide (8)

guanidinium salt (2 M)	k_2 x 10^3 M^{-1} s^{-1}	k_{rel}
water	230	-
Cl^-	129	0.56
Br^-	116	0.50
BF_4^-	92	0.40
SCN^-	87	0.38
ClO_4^-	86	0.37

Again, these results compared favourably with past work dealing with the effect such salts had on the solubility and stability of proteins. A study with guanidinium had shown that the minimum concentration for complete denaturation always decreased in the order $Cl^- > Br^- > I^- > SCN^-$, while the solubility increased through the same series. The Diels-Alder reaction follows the Hofmeister series. At this stage it was hypothesized that some surface contact between the salt and organic solute might be responsible for the hydrophobic effects and thus change of reaction rates according to the salt added.

Following on directly from this work, Kumar and co-workers[2.14] investigated these salts in water solution, initially concentrating on how their addition might affect the quantity described above as internal pressure (P_i).[2.14a] The internal pressure of a salt solution can be estimated from equation 4.1, where β is the thermal compressibility of the system and α is the thermal expansion of the system at absolute temperature T.

$$P_i = \alpha T/\beta \qquad \text{(equation 4.1)}$$

Choosing aqueous solutions of the same salts Rizzo had employed as solvent systems, Kumar used literature data[2.14a] of α and β to estimate P_i values (table 4.6). By plotting the corresponding rate of reaction against P_i for each salt, a linear relationship was found that matched Rizzo's results (figure 4.5). Rizzo had reported that for aqueous sodium salts, larger anions slowed the reaction. Kumar could indicate that larger anions led to a decrease in P_i, thus slowing the reaction according to the theory of hydrophobicity. And with guanidinium salts, Kumar's results showed that increasing the size of the anion again, decreased P_i and slowed the reaction further. So internal pressure (and thus hydrophobicity) can be directly related to anion size. This makes sense, since these Diels-Alder reactions are characterised by a negative activation volume it is appropriate that internal pressure should relate directly to the reaction rate.

Table 4.6. Values of internal pressure P_i, caused by 2 M salt solutions[2.14a]

sodium salts		guanidinium salts	
salt	P_i/bar	salt	P_i/bar
Cl^-	3805	Cl^-	1445
Br^-	3740	Br^-	1420
BF_4^-	2260	BF_4^-	1246
ClO_4^-	1550	ClO_4^-	1161
PF_6^-	1460		
AsF_6^-	1391		

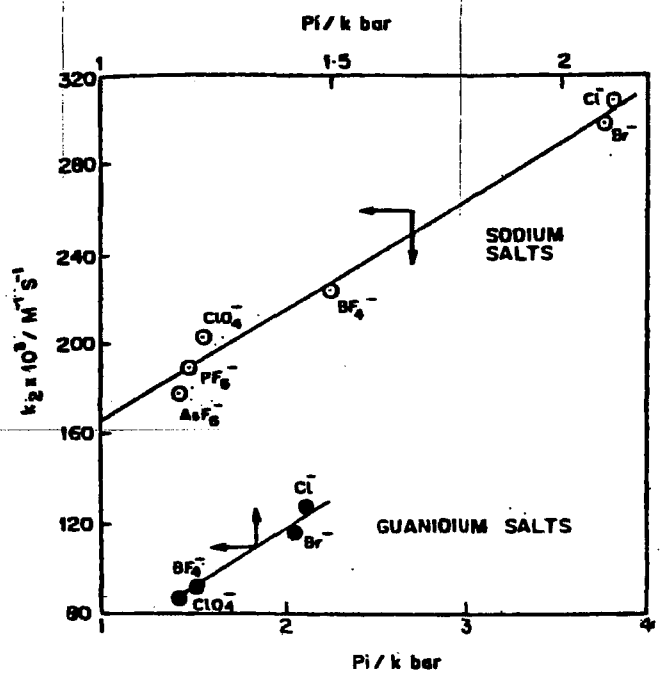


Figure 4.5: Rate constant, k_2, *vs.* pressure, P_i, caused by 2 M salt solutions. Graph by Kumar[2.14a]

More recent work published by Kumar and co-workers[2.14b] investigates the effects on N/X for the reaction between cyclopentadiene (**4**) and methyl acrylate (**12**). As in earlier publications the type of salt was investigated (LiCl, NaCl, NaBr, $CaCl_2$, GnCl, $LiClO_4$),

but unlike previous work the effect that each salt had on the reaction at varying concentrations (up to 6 M) was also measured.

The results obtained were plotted in the form of log(N/X) as a function of the salt concentration (figure 4.6). The data shows that one group of salts enhances N/X (LiCl, NaCl, NaBr and $CaCl_2$), and the others decrease the ratio (GnCl, $LiClO_4$). As the concentration of each salt gets higher, its effects on N/X begin to level off.

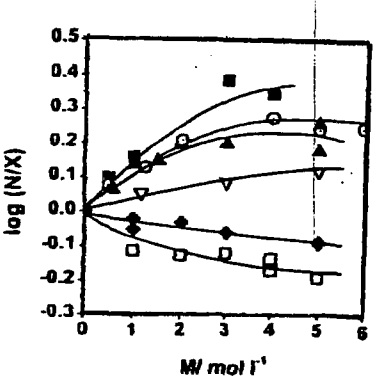


Figure 4.6: Log(N/X) *vs.* salt concentrations, *M*, of aqueous LiCl (■), NaCl (O), NaBr (▲), $CaCl_2$ (▽), GnCl (◆) and $LiClO_4$ (□) for the cyclopentadiene (4) + methyl acrylate (12) reaction. Graph by Kumar[2.14b]

In order to test that the relevance of this data did actually refer to each salt's ability to increase or decrease the hydrophobicity of the medium, the relative solubilities of methyl acrylate (**12**) in each solvent system were calculated. The results are shown below. Note that *S* denotes solubility. S^0_{MA} denotes the solubility of methyl acrylate in water alone, and S_{MA} denotes the solubility of methyl acrylate in the corresponding salt solution. The results are shown below (figure 4.7). As can be seen, the agreement is very close. Not only does the presence of salts that decrease N/X also decrease the solubility and vice versa, but the relative order of magnitude of solubility of each salt is unchanged when

compared with their relative abilities to change N/X. As well as log(N/X), the solubility of methyl acrylate does taper at salt concentrations.

As we already know from Kumar's work[2.14a] the rate of reaction can be directly linked to hydrophobicity via P_i. As many of the same salt systems are used in this work, we can also assume that N/X is dependent on the hydrophobicity of the solvent medium.

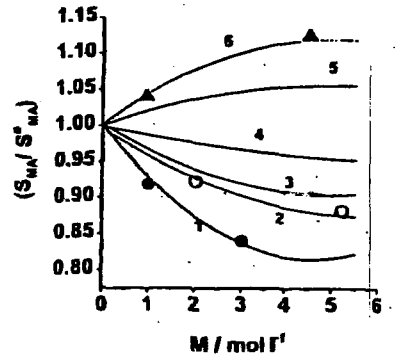


Figure 4.7: Computed relative solubilities of methyl acrylate, (S_{MA}/S^0_{MA}) *vs.* concentration of salt, *M*, for various aqueous salt solutions for the cyclopentadiene (4) + methyl acrylate (12) reaction: **1:** LiCl, **2:** NaCl, **3:** NaBr, **4:** $CaCl_2$, **5:** GnCl, **6:** $LiClO_4$. Graph by Kumar[2.14b]

4.2.3. Nonaqueous solvents and their salt solutions

The fact that nonaqueous polar solvents are referred to as 'water-like' in the literature not only highlights the profound effect aqueous systems had in this area of chemistry, but also implies that physical properties similar to water (to reproduce the same sort of rate and N/X improvements) are being sought after in new solvent systems. Based on previous work by others using water as a solvent for the Diels-Alder reaction, Lattes and co-workers[2.15] published a comprehensive study using a probe reaction in nonaqueous

solvents. The reaction was of cyclopentadiene (**4**) and methyl acrylate (**12**). The primary aim was to show that the highly structured solvent formamide could replace water and be used to prepare nonaqueous microemulsions that would allow the reaction to be driven quicker by solvophobicity. The reaction was performed in various formamide microemulsions to utilise the relationship between polarity and N/X. Some results for various solvents are shown below (table 4.7).

The results show that, apart from *N*-methyl acetamide, increasing solvent polarity does improve the selectivity of the reaction. However, the fact that *N*-methyl acetamide is the most polar solvent in the selection, and yet it gives an N/X value less than that of 1-butanol suggests that polarity is too simplified an explanation for the increase in N/X. Rather like Breslow[2.4] had compared two solvents of similar polarity (water and methanol) to explain hydrophobicity, Lattes uses his example to introduce the notion of solvophobicity into the formamide system, bettering even the results of water. Total product yield is also improved from 40 % (water) to 85 % (formamide).

Lattes tried the reaction in different compositions of formamide-solvent mixtures, and produced a conductivity diagram (conductivity against volume fraction of formamide) showing two distinct zones of optimum N/X selectivity zones.

Table 4.7. Effect of microemulsion components on the probe reaction between cyclopentadiene (**4**) and methyl acrylate (**12**)[2.15]

solvent	Dielectric constant (20 - 25 °C)	concentration of diene and dienophile	N/X
Isooctane	2.0	0.15	2.3
1-butanol	17.1	0.15	5.0
Water	78.5	0.15	7.4
Water	78.5	0.30	5.3
Formamide	109.0	0.07	6.9
Formamide	109.0	0.15	6.7
Formamide	109.0	0.30	6.7
N-Methyl acetamide	183.0	0.15	4.7

The next solvent to be tried was ethylene glycol, by Liotta and co-workers.[2.16] Their results for the reaction between 2,6-dimethylbenzaquinone (**20**) and methyl (*E*)-3,5-hexadienoate (**21b**) (scheme 4.6) are shown below (table 4.8). The solvents used in this study are all deuterated. This is because Liotta and co-workers followed their reactions (in terms of kinetics) via ^{1}H NMR *in situ*.

Table 4.8. Effect of solvent on the reaction between 2,6-dimethylbenzaquinone (**20**) and methyl (*E*)-3,5-hexadienoate (**21b**)[2.16]

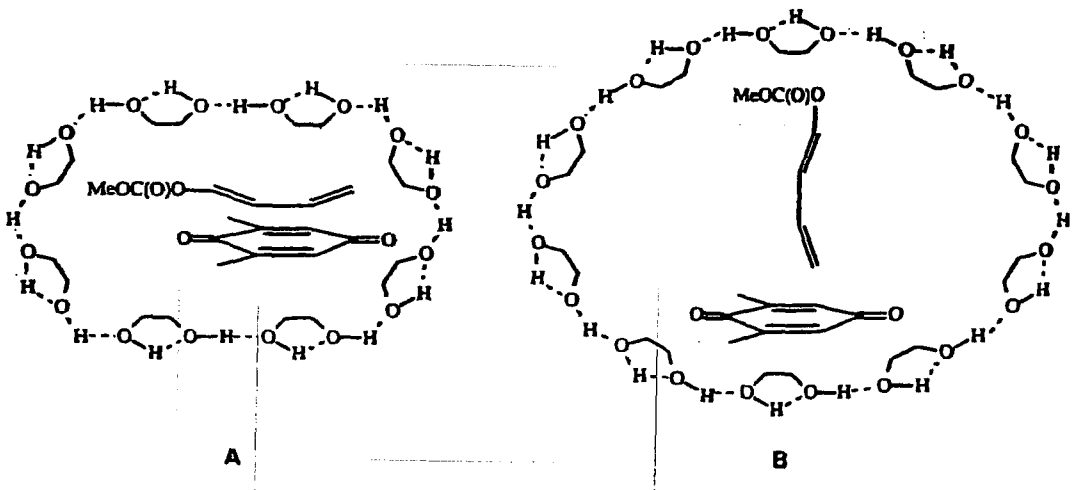
solvent	dielectric constant	relative rate
benzene-d_6	2.3	1.0
acetonitrile-d_3	36.2	1.8
dimethylsulfoxide-d_6	46.6	3.1
methanol-d_4	32.6	4.1
D_2O	78.0	no reaction
ethylene glycol	37.7	26.1

The group claim that when they tried the reaction (as Breslow had) in water it did not proceed at all. They explain that this is due to a total insolubility of their products in water, and that a degree of solubility is necessary. Herein lies a problem with the water system. If water cannot solubilise and therefore acts as a reaction solvent for various Diels-Alder substrates, then clearly a water-like solvent that can be chosen or tailored to meet this requirement is a more attractive proposition. Although salts can be introduced into the aqueous system to solubilise non-polar organic substrates with greater ease, it has been shown that these chaotropic agents actually slow down the reaction, making water a less attractive solvent.

Again, the results show that for solvent systems of comparative polarity to ethylene glycol, the rate is not even in the same order of magnitude but much less. This suggests

that solvophobic forces are also at work here. Again, some sort of molecular aggregation is proposed.

Ethylene glycol is capable of solubilising hydrophobic dienes and dienophiles to a greater extent than water. In view of this, many different molecular aggregates of varying composition, structure and with the reactants in relative conformations that would not lead to a reaction occurring theoretically become possible. It was suggested by Liotta that the stabilization energy associated with the favourable solvophobic-solvophobic interactions forming between reactants and solvent will be offset by a destabilization factor, related to the hydrogen bonding network of the solvent and its disruption when introduced to the reacting species. Figure 4.8 below shows two possible arrangements of the reacting species in ethylene glycol. Only A (π-stacking arrangement) is capable of leading to a reaction. However, B (end-on arrangement) is unlikely to occur as it occupies a larger volume and will disrupt the hydrogen-bonding network of the solvent system to a greater extent than A. As each hydrogen bond in the body of the solvent system contributes 3-5 kcal/mole in stabilization energy,[2.16] when aggregates form, their volume will be kept to a minimum.



A. π-stacked arrangement; B. end-on arrangement.

Figure 4.8: Representation of two possible arrangements of the reacting species (20) and (21b) in ethylene glycol. Diagram by Liotta[2.16]

Sauer and Braun[2.17] first investigated nonaqueous systems consisting of solutions of lithium perchlorate in diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane for use in the Diels-Alder reaction of cyclopentadiene (**4**) with methyl acrylate (**12**) (scheme 4.4a). As this was the first study of its kind, they primarily needed to optimize the solvent system itself. The results are shown below (table 4.9).

It should be noted that after this study, the system primarily used in the literature was that of diethyl ether with $LiClO_4$ (which will be referred to as LPDE). At similar concentrations of lithium perchlorate the N/X results of the probe reaction compare well. Presumably the LPDE system was employed for two reasons. The table shows that diethyl ether can hold larger concentrations of $LiClO_4$ which further improves N/X. Lithium perchlorate is not so soluble in the other solvents, and so these results cannot be achieved. The second reason is that the temperature of reaction is lower (room temperature) for the reaction in diethyl ether, but requires some heat in the two other solvents.

Sauer and Braun chose to attribute these results, not on solvophobicity, but polarity (as the right hand column in table 4.9 testifies). The scale they used to measure the polarity of varying concentrations of LPDE was that of E_T, devised by Reichardt and co-workers and discussed earlier in chapter 1. They showed that at higher concentrations of lithium perchlorate in diethyl ether, E_T showed a correlating rise (Note that in table 9 values for E_T are only shown where obtainable). This increase in polarity corresponds with the improved N/X data seen in table 4.9. However, as Breslow had so often said, this probably did not give a full explanation as to what was happening in the solvent.

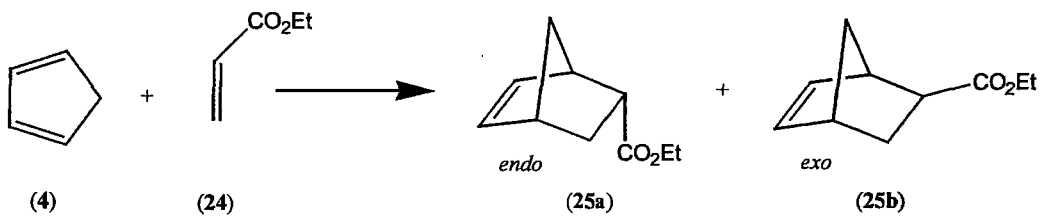
Table 4.9. Reaction of cyclopentadiene (**4**) and methyl acrylate (**12**) in varying concentrations of solutions of $LiClO_4$ with diethyl ether (20 °C), THF (40 °C) and 1,2-dimethoxyethane (40 °C)[2.17]

concentration (mmol/L)		$LiClO_4$ (% by mass)	N/X	solvent polarity	E_T
1	2				
Diethyl ether					
21.7	131	0.0	2.92	0.466	-
56.8	309	0.40	3.56	0.552	37.9
27.9	173	0.93	4.95	0.695	46.0
53.2	270	1.50	5.41	0.733	48.5
33.0	229	2.90	5.41	0.733	48.5
21.6	173	4.70	5.89	0.77	50.9
21.6	173	11.1	6.41	0.807	52.8
21.7	182	14.9	6.46	0.810	53.4
21.6	174	19.5	6.57	0.818	53.6
21.7	182	24.0	6.87	0.837	54.4
21.7	131	28.6	7.00	0.845	54.9
21.7	174	36.4	7.54	0.878	56.8
21.7	182	38.1	7.33	0.865	56.6
Tetrahydrofuran					
44.0	551	0.0	2.82	0.449	-
44.0	551	3.80	3.41	0.531	-
44.0	551	6.20	3.67	0.565	-
44.0	551	9.0	3.88	0.589	-
44.0	551	11.7	4.29	0.632	-
44.0	551	17.1	4.46	0.650	-
1,2-Dimethyl-oxyethane					
44.0	540	0.0	3.06	0.486	-
44.0	540	2.20	3.17	0.501	-
44.0	540	7.60	3.85	0.586	-
44.0	540	12.1	4.08	0.610	-
44.0	540	14.3	4.41	0.644	-

Grieco and co-workers[2.18] published a breakthrough paper in 1990, claiming that any solvent that could exploit the Diels-Alder reaction's hunger for high internal pressure (P_i) to drive it faster would improve the rate and selectivity further. That solvent was a 5.0 M

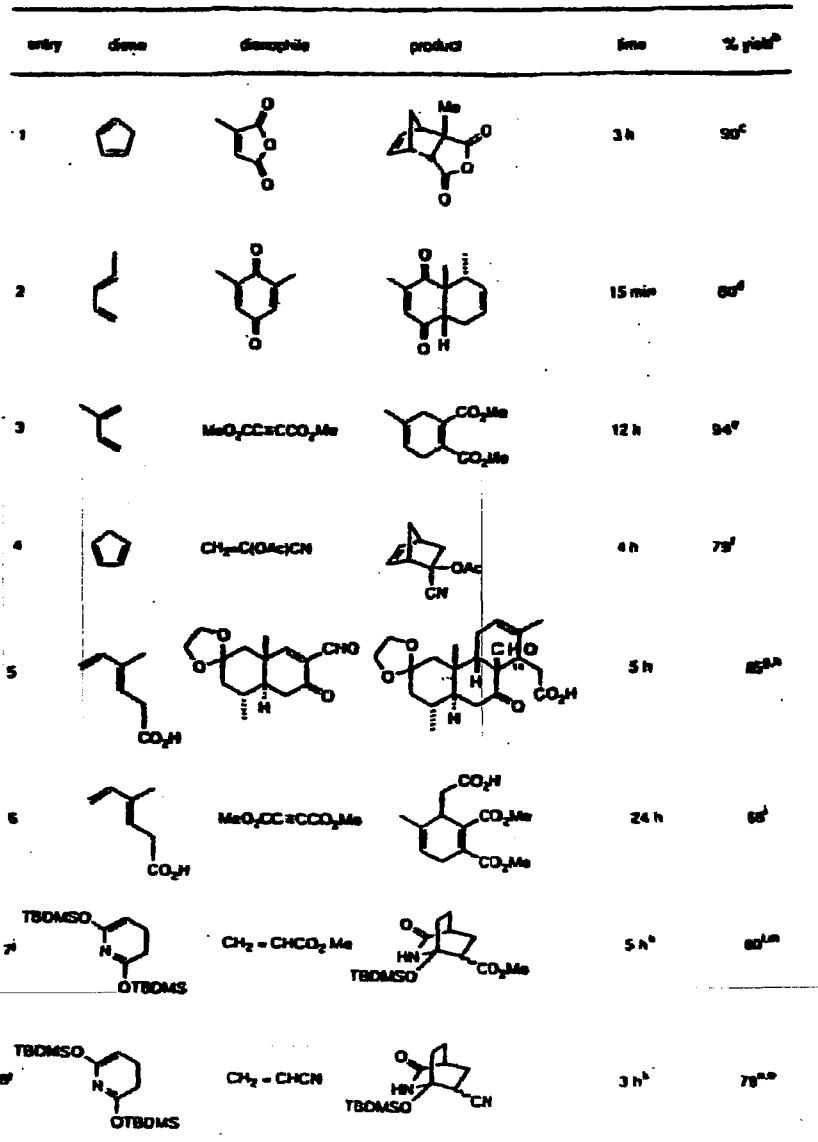
solution of lithium perchlorate in diethyl-ether (LPDE). Not only did they claim extraordinary improvements in the rate of reaction, but they also stated that Diels-Alder adducts that had previously been unreactable via conventional means could now be realized via this solvent system.

The first reaction chosen was between cyclopentadiene (**4**) and ethyl acrylate (**24**) (scheme 4.7). as a comparison for the new system they chose water. In 5 M LPDE after 5 hours at ambient temperature and pressure with a 1:1 molar equivalent of reactants, the reaction produced an isolated yield of 93% of cycloadducts. The N/X ratio was 8:1. The same reaction performed in exactly the same way in water, giving a 73% yield, with an N/X ratio of 4:1.



Scheme 4.7: Diels-Alder reaction of cyclopentadiene (**4**) and ethyl acrylate (**24**) carried out by Grieco and co-workers in 5.0 M LPDE[2.18]

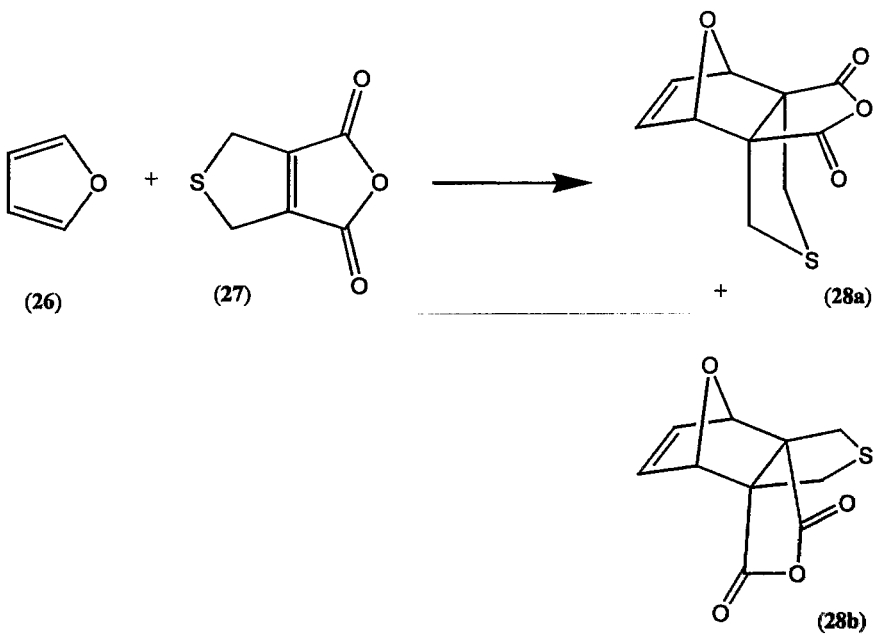
As aqueous solvent systems preclude the use of water-sensitive products, and many organic compounds are totally insoluble in water, this was a major breakthrough. More reactions were tried with a variety of substrates (table 4.10), all giving high yields in a short space of time. The reaction in all cases was homogenous. As marked on the table, several of the reactions are air-sensitive and could not be performed in an aqueous system.



[a] All reactions were performed 1.0 M in diene and 0.2 M in dienophile unless stated otherwise. [b] Isolated yields. [c] Yield of 94% after 24 h at 60 °C (neat).[14] [d] Yield of <20% after 24 h in water. [e] Yield of 50% after 12 h in water. [f] Yield of 27% after 24 h in water. [g] C(14)-βH:C(14)-αH ratio equal 2.3:1. [h] Yield of 90% after 4.5 in water, employing the diene carboxylate. Use of the dienoic acid in water was slow. [i] Yield of 60% after 24 h in water. [j] 3.0 equivalents of diene were employed. [k] The reaction is worked up with methanol to cleave the imino ether. [l] Yield of 74% (endo:exo ratio 1:11.5) after 72 h in benzene at 60 °C.[9] [m] An endo:exo ratio of 2.9:1 was observed in 5.0 M $LiClO_4$–Et_2O. [n] An endo:exo ratio of 1:3.7 was observed in 5.0 M $LiClO_4$–Et_2O. [o] Yield of 73% (endo:exo ratio of 1:9) after 48 h in benzene at 60 °C.[9]

Table 4.10: A selection of Diels-Alder reactions attempted by Grieco and co-workers in the solvent LPDE[2.18]

drive its reactions, which is not advisable since at high temperatures such reactions involving can undergo cyclorevision. The reaction between furan (**26**) and dienophile (**27**) (scheme 4.8) in dichloromethane required 6 hours and 15 kbar of pressure to yield an 85:15 mixture of cycloadducts (**28a**) and (**28b**). However in LPDE, at ambient temperature and pressure, a 70% yield of products with the same product ratio was observed after 9.5 hours. A direct correlation between the concentration of the LPDE solution and the rate of reaction was observed (table 4.11). All the reactions included in table 4.11 were attempted for 9.5 hours in the specified solvent system keeping the concentration of reactants constant each time. It is the yield at the end of this specified time period that tells us how far the reaction has progressed, and thus indicates a relative rate of reaction.



(26) (27) + (28a)

(28b)

Scheme 4.8: Diels-Alder reaction between furan (**26**) and dienophile (**27**) carried out by Grieco and co-workers in 5.0 M LPDE[2.18]

Table 4.11. Reaction of (**26**) and (**27**) in varying concentrations of LPDE[2.18]

molarity	% yield	ratio (**28a**):(**28b**)
1	15	85/15
2	22	87/13
3	36	86/14
4	62	83/17
5	70	85/15

Grieco and co-workers explained this rate acceleration in terms of solvophobicity caused by a large internal pressure in these solvent systems. A later work by Forman and Dailey[2.19] directly contrasted this, when they examined a wider range of Diels-Alder reactions. If the only effect playing a role was actually solvophobicity, then all Diels-Alder reactions should be accelerated in LPDE, since all Diels-Alder reactions have a negative activation volume (the one characteristic that is affected favourably by solvent systems with a high internal pressure) they claimed. However, when they tried certain reactions, the rate was unchanged, meaning solvophobicity was not a satisfactory explanation. They proposed that the lithium ion was acting as a Lewis acid catalyst for some cases, but not others (such as the reactions that were unaffected in LDPE). An example of a reaction that was accelarated in LPDE was between acrylonitrile (**10**) and 9,10-dimethylanthracene (**29**). Table 4.12 shows the results for identical reactions in various concentrations of LPDE. Figure 4.9 shows the relationship between the rate of reaction and concentration of lithium perchlorate in LPDE to be of linear dependence. If the lithium ion were actually acting as a Lewis acid catalyst, then the rate would be expected to depend on the concentration of the lithium ion. This is indeed the case.

Table 4.12. Second order rate constants (rtp) for the reaction between acrylonitrile (10) and 9,10-dimethyl-anthracene (29) in different concentrations of LPDE[2.19]

$k_2 \times 10^6$, $M^{-1} s^{-1}$	[$LiClO_4$], M
1.28	0
4.34	1.2
5.37	1.82
8.11	2.99
9.85	3.88
11.40	4.55

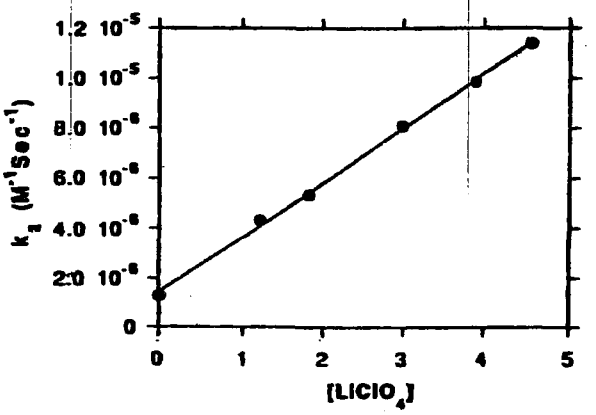


Figure 4.9: Second-order rate constants for the Diels-Alder reaction between acrylonitrile (10) and 9,10-dimethylanthracene (29) at 28 °C in ether *vs.* lithium perchlorate concentration[2.19]

More will be said later about Lewis acids and how they interact with Diels-Alder reactions. However, Forman and Dailey proposed that the lithium ion acts as a Lewis acid by complexing with the cyano group of acrylonitrile (10). Although Lewis acidity definitely does play a large part in the improved rate and selectivity of the reaction chosen, it is logical to assume that it does so in tandem with other factors, including polarity and, of course solvophobicity. It seems unlikely, especially in light of the work that has been discussed so far, that one solvent characteristic would entirely dictate the course of the Diels-Alder reaction.

4.2.4. Room Temperature Ionic Liquids

Although they have been in existence for much longer, it has only been in the last twenty years or so that ionic melts which are liquid at room temperature have started to be taken seriously as reaction media and thus tools for synthetic chemistry. The Diels-Alder work that exists to date in these solvents is still in its infancy, but nevertheless other reaction types have seen such improvements in efficiency and control, that they are being referred to as a new class of solvent media.

In terms of the Diels-Alder reaction, the first ionic liquid to be used as a solvent was ethylammonium nitrate ($[EtNH_3][NO_3]$) or EAN, as it will be referred to here. It was Jaeger and Tucker[2.20] who first used it as a solvent for the reactions between cyclopentadiene (**4**) and the dienophiles methyl vinyl ketone (**5**) and methyl acrylate (**12**) (see schemes 4.2a and 4.4a). The authors claimed that EAN shared many characteristics with water (caused by its high cohesive energy), so could also display the solvophobic effect in Diels-Alder reactions. The results for their study are shown in table 4.13. The most dramatic results were seen for the reaction between (**4**) and (**12**), so only this data has been included.

Table 4.13. Diels-Alder reactions of cyclopentadiene (4) and methyl acrylate (12) in EAN[2.19] and a variety of solvents

Solvent + added salt (where appropriate)	T, °C	(4) conc, M	(12) conc, M	N/X	Rate, $M^{-1}sec^{-1}$
EAN	25	0.20	0.20	6.7	-
EAN	20	0.010	0.20	6.7	1.7
EAN + LiCl	20	0.010	0.20	7.2	1.6
EAN + LiI	20	0.010	0.20	7.4	5.4
water	21	0.00040	0.012	-	30
water	25	0.15	0.15	9.3	-
water	20	0.15	0.15	7.4	-
1-chlorobutane	35	-	-	-	0.53
benzene	35	1.25	1.25	2.8	-
ethanol	30	-	-	5.2	-
methanol	26	-	-	7.0	-
formamide	20	0.15	0.15	6.7	-

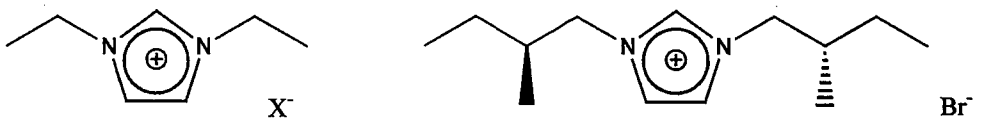
In the study, it can be seen that water still performs better than EAN, in terms of both rate and N/X. What is interesting is that the ionic liquid displays an enhancement in both parameters over organic solvents. Also of note is that for the first entry in table 4.13, a product yield of 98% was observed. The vast majority of work to date had attributed the improved rates and endo selectivity of this reaction in water on the hydrophobic association of reactants, based largely on salt effects, and not solvent polarity. In view of this, Jaeger and Tucker used EAN solutions of LiCl and LiI. The results are in table 4.13.

In water LiI is chaotropic ("salting in" agent) and LiCl is antichaotropic ("salting out" agent). They would be expected to decrease and increase respectively, both the rate and N/X. However in EAN, LiI acts contrary to its behaviour in water, as an antichaotropic agent. LiCl appears to affect the reaction in an antichaotropic manner (as it does in water), but to a smaller degree than LiI. In fact, Breslow and Guo[2.4d] had made the same observation with the non-aqueous solvents ethylene glycol and formamide. On addition

of salts that were chaotropic or antichaotropic in water, only an increase in rate was observed. This led them to conclude that both classes of salt had a special interaction with water only, which is why they claimed water to be unique. At the time of publication, Jaeger and Tucker did not explain why these salts acted as they did in EAN. It is possible that the effect may be due to the lithium cation acting as a Lewis acid catalyst.

Although the use of ionic liquids as Diels-Alder solvents was still in its infancy at this stage, it already held some advantages over water as a reaction medium. Firstly, EAN dissolves neutral organic compounds more easily than water. As has been seen, solvophobicity in general is not necessarily about solubility, but the interaction of the substrate with its solvent. So for a compound to be more soluble in a more solvophobic environment is not a paradox. Indeed, to be of any use on a synthetic scale, good solubility of the products in the solvent is needed. A second advantage that ionic liquids in general could have over water is that reactions that involve air- or moisture-sensitive Diels-Alder reagents can be attempted with the same chance of a possible solvophobic advantage over conventional organic solvents.

Howarth and co-workers[2.21] have also approached carrying out Diels-Alder reactions using novel salts. The salts they used were different in composition to EAN, namely moisture stable dialkylimidazolium salts ($R_2Im^+ X^-$). In this study the anion is either a bromide or trifluoroacetate species. Howarth claimed that the dialkylimidazolium salts were acting as Lewis acids.



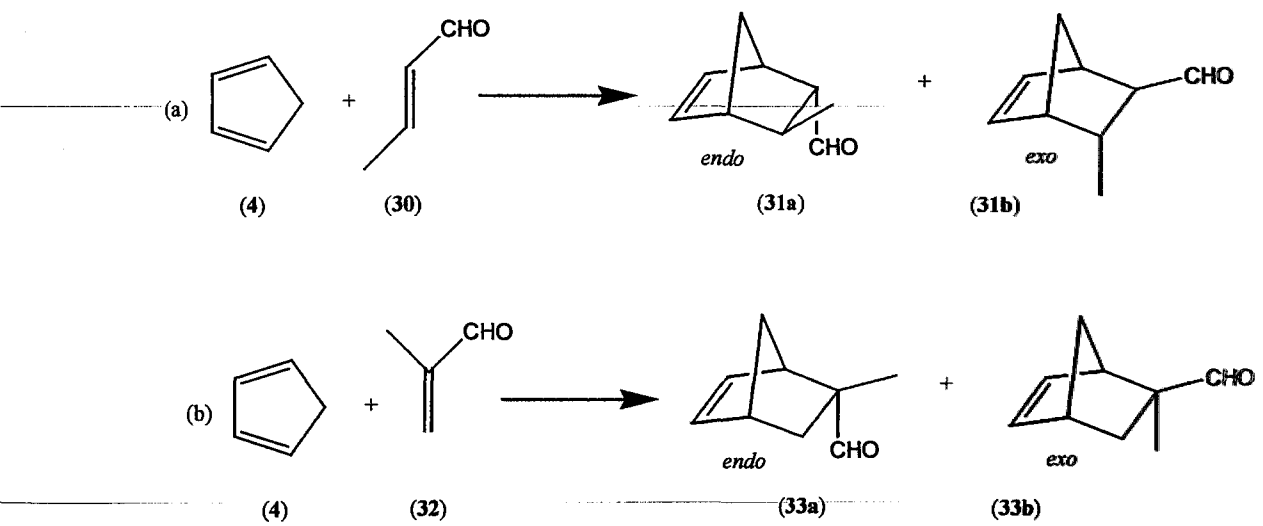
A: X=Br

B: X=CF_3CO_2

C

Figure 4.10: Dialkylimidazolium salts used by Howarth and co-workers[2.21]

Three different dialkylimidazolium salts were used (see figure 4.10) in dichloromethane solutions and the reactions followed were between either crotonaldehyde (**30**) or methacrolein (**32**) and cyclopentadiene (**4**) (see scheme 4.9). The results are shown in table 4.14 below.



Scheme 4.9: Various Diels-Alder reactions carried out by Howarth and co-workers[2.21]

Table 4.14. Results for the reaction between cyclopentadiene (**4**) and crotonaldehyde (**30**) or methacrolein (**32**) in the presence of dialkimidazolium salts A, B or C. By Howarth and co-workers[2.21]

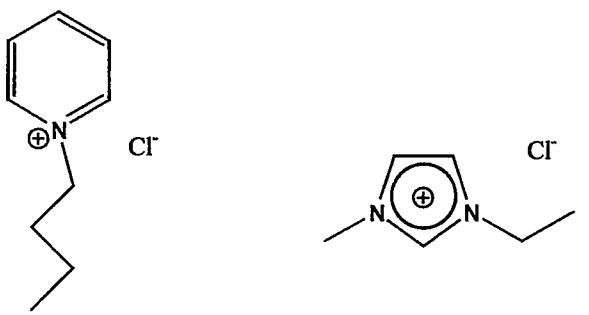
Dialkylimidazolium salt (see figure 4.11)	Dienophile			
	Crotonaldehyde (**30**)		Methacrolein (**32**)	
	Yield	N/X	Yield	N/X
A	35%	19.0	40%	5.7
B	37%	19.0	40%	6.7
C	36%	13.3	36%	9.0

It may not appear pertinent to display Howarth's work in this study. The three ionic species were not in anyway used alone as true solvent systems (they were mixed with dichloromethane). However, as will be seen later in the work for this study, the three species are all based on many of the ionic liquid systems that are in use today for synthesis.

Any evidence to back up the Lewis acidity theory is poorly dealt with by Howarth (the fact that the reaction was carried out under relatively low temperature is enough, in his opinion). However, it is known that imidazolium salts can and do act as Lewis acids. In this case it would have been interesting to somehow distinguish the effect of the solvent from the common solvophobicity approach. What is noteworthy is that by now steps were being taken in the direction of compounds that were very similar to the types of ionic liquids to be used, not only in this study, but nowadays as Diels-Alder reaction solvents.

There are cases of ionic liquids being used as the solvent system in Diels-Alder reactions. Lee[2.22] has recently investigated Diels-Alder reactions in water-sensitive chloroaluminate ionic liquids ($AlCl_3$:MCl, where MCl is either *N*-1-butylpyridinium chloride or 1-ethyl-3-methyl-imidazolium chloride – see figure 4.11). The reactions studied were between cyclopentadiene (**4**) and methyl acrylate (**12**) or dimethyl maleate (**14**) (see schemes 4.4a and 4.4b). Lee's reasoning for the use of these ionic liquids in particular was that they

exhibited properties that theoretically made them ideal for Diels-Alder chemistry. As well as being polar, exhibiting a degree of solvophobicity and solvating a wide variety of organic and inorganic solutes, Lee chose the possibility of Lewis acidity as their most valuable feature.



N-1-butylpyridinium chloride 1-ethyl-3-methylimidazolium chloride

Figure 4.11: Imidazolium salts used by Lee[2.22] to make chloroaluminate ionic liquids

In terms of the Diels-Alder reaction, Lewis acidity can play an important role in influencing selectivity and reactivity. This is thought to occur via coordination of the Lewis acid to an electron withdrawing group of the dienophile, in this case a carbonyl group on methyl acrylate or dimethyl maleate. In turn this lowers the energy of the LUMO of the dienophile, enhancing the possibility of overlap with the HOMO of the diene. The expected Lewis acid in these systems would be the chloroaluminate (III) species ($[Al_2Cl_7]^-$).

Chloroaluminate melts are unique amongst ionic liquids because their composition can easily be changed from Lewis acidic ($AlCl_3$ in excess) to Lewis basic (Cl^- in excess). The molar excess species [$AlCl_3$] in the acidic version of the liquid can combine with the

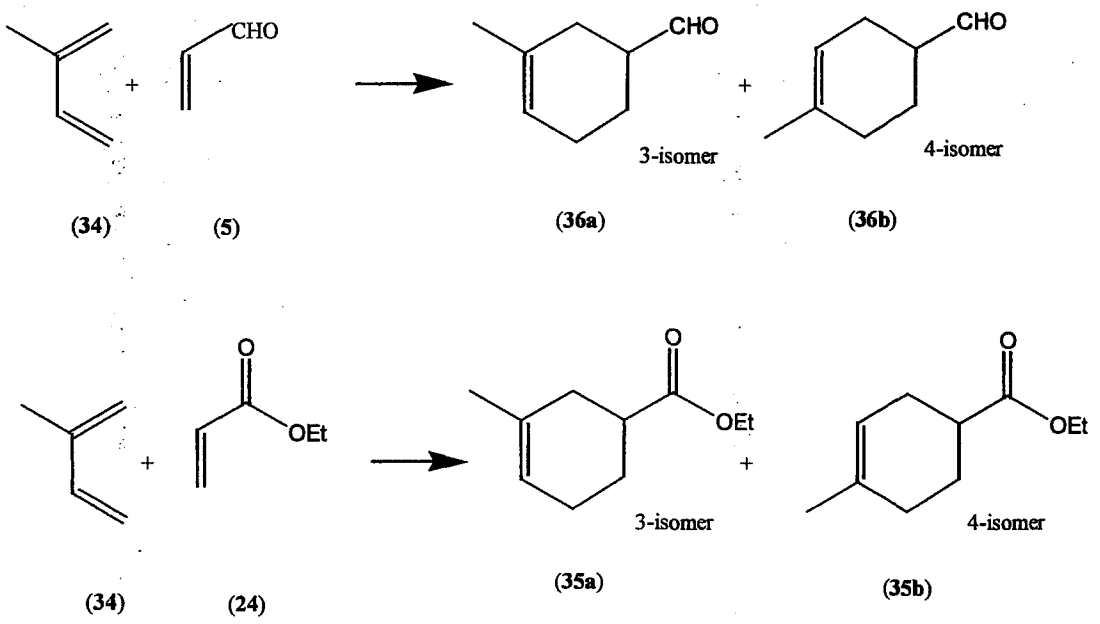
ionic liquid anion $[AlCl_4]^-$ to form the $[Al_2Cl_7]^-$ species. This is why this species is unique to the acidic version only.

The results for the reaction between cyclopentadiene (**4**) and methyl acrylate (**12**) are shown below in table 4.15.

Table 4.15. Diels-Alder reaction of cyclopentadiene (**4**) amd methyl acrylate (**12**) in room temperature chloroaluminate ionic liquids[2.22]

Melt composition (% $AlCl_3$)	Reaction time (Hrs.)	N/X	% Yield	$10^4\ k_2$ (M^{-1} sec^{-1})
48	22	4.88	32.3	-
48	72	5.25	95	12.5
51	22	19	53	-
51	72	19	79.4	297

Lee compared his results with those in table 4.13 (reaction rate for water is 30 $M^{-1}sec^{-1}$; reaction rate for EAN is 1.7 $M^{-1}sec^{-1}$), and found that although the basic melt gives a rate somewhere in between that of water and EAN, the acidic version provides a reaction that is far faster than both the other systems. Polarity has already been shown to account for only small changes in reaction rate, when other solvent systems are compared.[2.7] It would be hard to imagine that solvophobicity could provide such a dramatic change, when it already plays a key role in explaining the rate enhancements of water and EAN over traditional organic solvents. The fact that both the rate and N/X rise considerably from the basic to the acidic versions of the ionic melt indicates that Lewis acidity is in fact a key factor in this system.



Scheme 4.10: Various Diels-Alder reactions carried out by Seddon and co-workers[2.23]

Seddon and co-workers[2.23] have also tried similar reactions in room temperature ionic liquids. Whereas Lee's attempts used chloroaluminate liquids that are water-sensitive, Seddon used air- and water-stable liquids. The cationic part of the ionic liquids are all based on an imidazolium cation (1-butyl-3-methylimidazolium or $[bmim]^+$), and the anionic parts vary (trifluoromethanesulfonate or $[OTf]^-$, $[PF_6]^-$, $[BF_4]^-$ and $[lactate]^-$ were used). The dienophiles and dienes also varied (see schemes 4.2a, 4.2c, 4.4a, 4.7 and 4.10). A selection of the results they obtained is shown below (table 4.16).

Table 4.16. The reaction of dienophiles and dienes in various solvents[a]
Work by Seddon and co-workers[2.23]

No	Solvent	Dienophile	Diene	Temp, °C	Time, hr	Yield, %	Product labelling	N/X
1	[bmim][OTf]	dimethyl maleate (**14**)	Cp (**4**)	20	18	98	(**15a**) : (**15b**)	4.2
2	[bmim][OTf]	ethyl acrylate (**24**)	Cp (**4**)	20	18	96	(**25a**) : (**25b**)	6.0
3	[bmim][OTf]	acrylonitrile (**10**)	Cp (**4**)	20	2	80	(**11a**) : (**11b**)	1.7
4	[bmim][OTf]	acrylonitrile (**10**)	Cp (**4**)	20	24	98	(**11a**) : (**11b**)	1.6
5	[bmim][OTf]	acrylonitrile (**10**)	Cp (**4**)	-15	3	5	(**11a**) : (**11b**)	3.0
6	[bmim][OTf]	acrylonitrile (**10**)	Cp (**4**)	-15	24	96	(**11a**) : (**11b**)	2.4
7	[bmim][OTf]	acrylonitrile (**10**)	Cp (**4**)	-15	72	99	(**11a**) : (**11b**)	2.4
8	[bmim][lactate]	ethyl acrylate (**24**)	Cp (**4**)	20	2	87	(**25a**) : (**25b**)	4.4
9	[bmim][OTf]	ethyl acrylate (**24**)	Cp (**4**)	20	2	67	(**25a**) : (**25b**)	-
10	[bmim][lactate]	ethyl acrylate (**24**)	Cp (**4**)	20	24	99	(**25a**) : (**25b**)	3.7
11	[bmim][BF_4]	ethyl acrylate (**24**)	Cp (**4**)	-15	24	99	(**25a**) : (**25b**)	5.0
12	water	ethyl acrylate (**24**)	Cp (**4**)	20	1	30	(**25a**) : (**25b**)	3.5
13	5 M LPDE	ethyl acrylate (**24**)	Cp (**4**)	20	1	61	(**25a**) : (**25b**)	8.0
14	[bmim][PF_6]	ethyl acrylate (**24**)	Cp (**4**)	20	1	36	(**25a**) : (**25b**)	8.0
15	[bmim][OTf]	ethyl acrylate (**24**)	isoprene (**34**)	70	24	97	(**35a**) : (**35b**)	2.5[b]
16	[bmim][PF_6]	but-2-en-3-one (**5**)	isoprene (**34**)	20	18	11	(**36a**) : (**36b**)	4.0[b]
17	[bmim][PF_6][c]	but-2-en-3-one (**5**)	isoprene (**34**)	20	6	98	(**36a**) : (**36b**)	20[b]
18	[bmim][BF_4][d]	ethyl acrylate (**24**)	isoprene (**34**)	20	2	90	(**35a**) : (**35b**)	40[b]

[a] All reactions used a 1.5 : 1.0 : 1.0 molar ratio of diene : dienophile : solvent

[b] This ratio represents a 4- to 3-isomer ratio, not an N/X ratio

[c] 5 mol% ZnI_2 added

[d] 10 mol% $BF_3.OEt_2$ added

In comparing how the temperature affects the reaction, it is clear that higher temperatures give a lower N/X (see entries 4 and 6), where the solvent system is kept constant. The ionic liquid itself is also a factor in the reaction. For example, entries 8 and 9 were carried out under the same conditions, changing only the ionic liquid from [bmim][lactate] (entry 8) to [bmim][OTf] (entry 9). The yield at the end of 2 hours was 87% for the former and 67% for the latter. Although no formal reaction rate has been measured in this study, the results indicate that the rate in [bmim][lactate] is faster.

The comparison between an ionic liquid, water, and 5 M LPDE was also studied (entries 12, 13 and 14). Each solvent system was studied using the same reaction under identical conditions. After 1 hour, the faster reaction appears to be that in LPDE, but the ionic liquid [bmim][PF_6] has proceeded further than water. Again, this gives an indication of the relative rates. The N/X ratio for all three does however compare favourably for the ionic liquid, with exactly the same value for the corresponding reaction in LPDE. It would perhaps have been interesting to also use [bmim][lactate] as the ionic liquid comparison in the rate case, since after 20 hours at the same conditions it gives a near quantitative yield for the same reaction.

Entries 15-18 are interesting as they further strengthen the case for the use of Lewis acids in Diels-Alder reactions. The reaction between but-2-en-3-one (**5**) and isoprene (**34**) is slow when uncatalysed at ambient temperature (entry 16). The addition of a catalytic amount of 5 mol% zinc(II)iodide (a Lewis acid) dramatically increases, not only the rate but also the selectivity of the reaction (entry 17). The reaction between ethyl acrylate (**24**) and isoprene (**34**) is said by the authors to be slow at room temperature, but proceeds well with a temperature of 70 °C (entry 15). Although the addition of 10 mol% $BF_3.OEt_2$ (entry 18) gives a slightly lower rate than the uncatalysed version (entry 15), the reaction can now be carried out at ambient temperature. The ionic liquids used are different in the two entries, however the author claims that the uncatalysed reaction behaves similarly to [bmim][OTf] when [bmim][BF_4] is used. It is not mentioned, but presumably the Lewis acid catalyst is insoluble in the former solvent system.

It has been mentioned previously that ionic liquids can allow for Diels-Alder reactions that employ moisture-sensitive reagents to be studied. This is, of course not possible in water. Although pre-dried organic solvents could be used instead, the point is to try and utilise the benefits of a solvophobic or Lewis acidic solvent system with novel solvents, thus benefitting from a water-free system which behaves like water. Of course this could also be achieved with water-like solvents such as LPDE, but ionic liquids display another advantage over these reaction media.

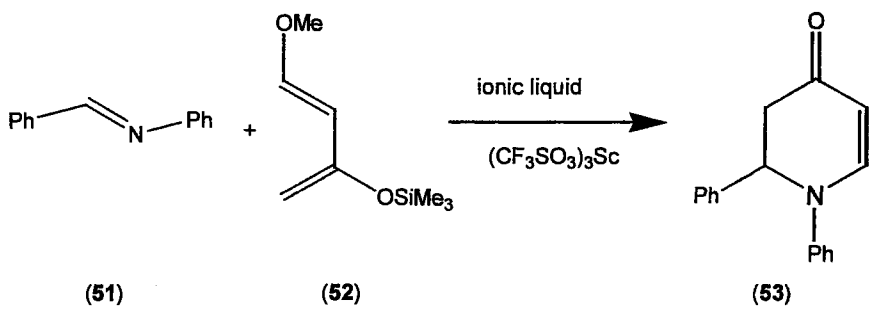
The fact that Seddon's work[2.23] was published in a journal named Green Chemistry is quite appropriate. With the emphasis nowadays on finding clean and environmentally-friendly processes to replace many existing methods, ionic liquids could well be the way forward. As they have no vapour pressure, they are relatively easy to contain and cannot contaminate the atmosphere as traditional organic solvents, and even water-like solvents can. From the work surveyed in this chapter, it is not even clear whether water (the most environmentally-friendly solvent of all) can be recycled, or easily purified for general usage. Seddon's study actually deals with the recycling and re-use of the ionic liquids, and finds that comparable yields and selectivities are possible.

It has always seemed likely that although greener processes are vital in this day and age, they would always be less attractive to industry in terms of performance. Here, we have a system that is not only comparable to the best solvents to date in terms of the Diels-Alder process, but is also clean and re-usable. It seems that the ionic liquids Seddon has used favour those employed by Lee[2.22] (chloroaluminates) simply because they are not moisture sensitive, thus making them easier to handle. They also hold a big advantage over the EAN system employed by Jaegar and Tucker[2.20] because EAN can be a potentially explosive compound. Again this would require strict handling requirements, which are not necessary for the types of liquids Seddon has employed.

A similar study employing similar ionic liquid solvents to those used by Seddon has been carried out by Welton and co-workers,[2.24] but this will not be discussed here since it forms the basis of the discussion section of this work in chapter 5.

Very recently, Kitazume and Zulfiqar[2.25] have performed a known aza-Diels-Alder reaction in an ionic liquid environment. The ionic liquid used was 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium trifluoromethanesulfonate. The reaction chosen was that between *N*-phenyl phenyl imine (**51**) with 1-methoxy-3-(trimethylsilyl)oxubuta-1,3-diene (**52**), illustrated in scheme 4.11 below. Aza-Diels-Alder reactions are normally carried out in organic solvents with the addition of a Lewis acid (eg: $ZnCl_2$, BF_3, $TiCl_4$, etc). It was found that the uncatalysed reaction in the ionic liquid did not proceed, so a

Lewis acid was added (microencapsulated scandium trifluoromethanesulfonate). This had the effect of producing a yield of 75 %. Both reactions were carried out at room temperature. It was also found that using certain imines allowed the ionic liquid system to be very easily recycled and re-used. After 20 hours, yields of upto 95 % were observed. Not only could the ionic liquid be recycled, but along with it the microencapsulated Lewis acid. This is very useful, since in existing industrial processes these substances are known to be damaging to the environment and expensive. The ionic liquid/Lewis acid system was recovered in about 99 % yield, and was re-used to repeat the same reaction giving the same performance, in terms of yield.



(51) **(52)** **(53)**

Scheme 4.11: The aza-Diels-Alder reaction between *N*-phenyl phenyl imine (**51**) and 1-methoxy-3-(trimethylsilyl)oxubuta-1,3-diene (**52**), carried out in 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium trifluoromethanesulfonate ionic liquid with encapsulated scandium triflurormethylsulfonate, by Kitazume and Zulfiqar[2.25]

5. DETERMINATION OF A DIELS-ALDER PROBE REACTION TO BE USED IN ROOM TEMPERATURE IONIC LIQUIDS

5.1. Research aims

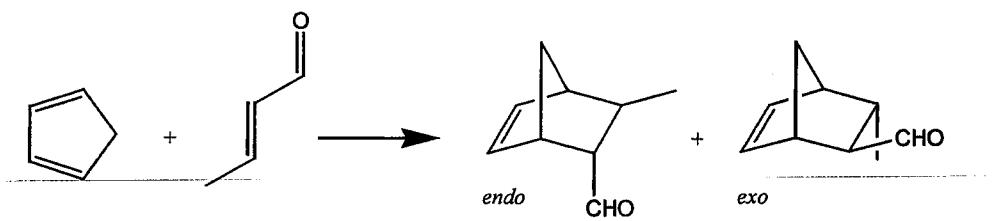
On commencing this section of research, the aims were flexible in that the scope of this study depended largely on the versatility of the novel solvent system to be able to somehow assist the Diels-Alder reaction. The objective was to attempt a series of well-known Diels-Alder reactions in a single ionic liquid, and observe whether they could be improved in terms of yield, length of reaction or product selectivity (where applicable) from when carried out in more traditional solvent systems. If this was not possible, then a single reaction that worked well in the chosen solvent system would be chosen for further study in a variety of room temperature ionic liquids. This reaction would provide a continuation of the work completed on improving the Diels-Alder reaction by means of solvent properties, and would allow us to compare directly ionic liquids to solvents previously used in this process (see chapter 4). However, the next objective would be to employ it as a generic probe reaction that could theoretically allow us to study the properties of a number of ionic liquid solvents, and how they vary in relation to each other.

5.2. Diels-Alder reactions performed in [emim][BF_4]

The reactions that follow have been classified according to the diene used. All reactions were carried out under an atmosphere of dry nitrogen. All reaction product mixtures were analysed by gas chromatography, unless otherwise stated.

5.2.1. Reactions involving the diene cyclopentadiene (4)

5.2.1.1. Reaction with the dienophile *trans*-crotonaldehyde (30)



(4) **(30)** **(31a)** **(31b)**

Scheme 5.1: Reaction between *trans*-crotonaldehyde **(30)** and cyclopentadiene **(4)**

Table 5.1: Results of the reaction between *trans*-crotonaldehyde (**30**) and cyclopentadiene (**4**)

Entry	Conc diene / M	Conc dieneophile / M	Time / hrs	Yield	N/X
1	5.690	1.385	48	13.9%	2.38
2	1.308	1.200	72	34.6%	3.61

The reaction between *trans*-crotonaldehyde and cyclopentadiene was performed twice. Under the variations of substrate concentration and reaction length shown in table 5.1, the yield and N/X were found to be low. Increased reaction time gave a higher yield. This is compared to the reaction in dichloromethane, where a 21 % yield after 45 hours was achieved,[2.26] or in dichloromethane solutions of 1,3-dialkylimidazolium salts, where the yield was 37 % after 48 hours.[2.21] One possible reason for the low yields observed in this reaction could be the lack of a particularly strong electron-withdrawing group on the dienophile. Although the aldehyde group has electron-withdrawing capabilities, they are not as strong as, for example, an ester or carboxylic acid group. A more electron-withdrawing group on the dienophile would reduce the electron-density around the reacting double bond, thus facilitating attack by the diene. As shall be seen below, the electron withdrawing group can greatly affect or reduce the reaction rate and yield. The improved yields in ionic liquids over organic solvents is almost certainly a product of the solvophobicity and the internal pressure created by the medium.

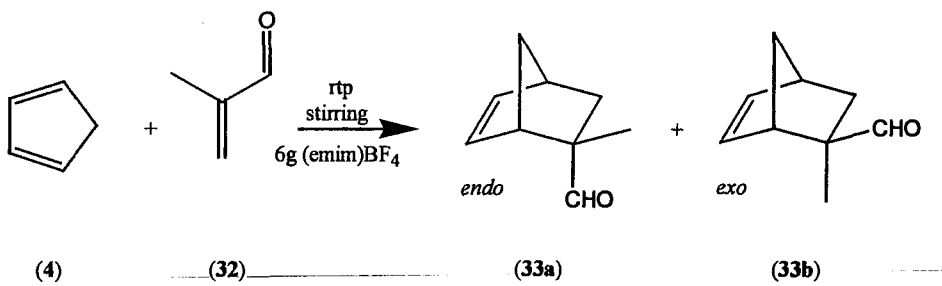
Again, N/X is believed to follow the same rules in this case. In the literature, an N/X value of about 19 for this reaction in other ionic liquids has been reported.[2.21] It is not clear as to why the ionic liquids we used cannot reproduce this selectivity.

It should be noted that in run 2, the amount of di-cyclopentadiene formed at the end of the reaction was noted. The amount of di-cyclopentadiene formed indicates the degree of the competition reaction in the process. Cyclopentadiene (**4**) may either take part in a

Diels-Alder reaction with a dienophile (such as crotonaldehyde in this case), or react with another cyclopentadiene molecule to form di-cyclopentadiene, also constituting a Diels-Alder reaction. We are used to seeing the vast majority of cyclopentadiene forming a reaction with the desired dienophile (typically, the ratio of the relative amount of combined products to the amount of di-cyclopentadiene is in the region of 9 or above. See below). However, in run 2 of this reaction the value of the ratio (to be referred to as prods/DiCp from now on) was 4.0. This suggests that the reaction is so slow, and the dienophile unreactive to such an extent, that the competition process is significant. The amount of cyclopentadiene used in the reaction was in slight excess to the amount of dienophile (see table 5.1) to allow for formation of dicyclopentadiene.

It should also be noted that in run 2, where the yield and N/X were both noticeably larger than the other run, the changes in the way the reaction was carried out was an increase in the time (from 48 to 72 hours). It is likely that the increased yield was brought about by the increased time of reaction.

5.2.1.2. Reaction with the dienophile methacrolein (32)



(4) (32) (33a) (33b)

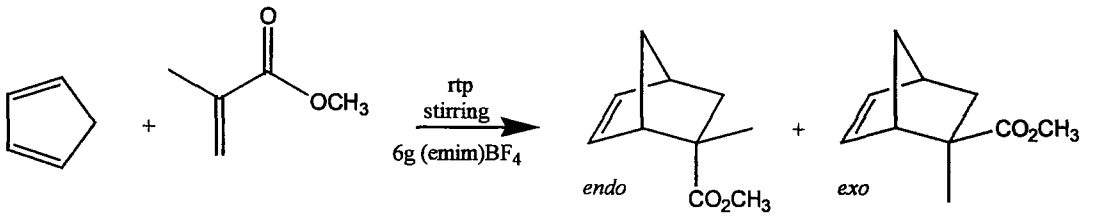
Scheme 5.2: Reaction between methacrolein (32) and cyclopentadiene (4)

The reaction between methacrolein and cyclopentadiene was attempted twice. The starting concentrations of cyclopentadiene and methacrolein were 1.308 M and 1.200 M respectively. After 72 hours stirring at room temperature, the yield was negligible. The reaction was repeated in the same way and left on for a longer amount of time (110hrs), after which a yield of 41.2% was observed. This is an improvement over the literature for this reaction, where, after 2 hours a 16 % yield was recorded when performed in dichloromethane,[2.26] and comparable to runs performed in dichloromethane solutions of 1,3-dialkylimidazolium salts, where a 40 % yield was obtained after 48 hours.[2.21] An N/X value of 0.15 was observed. Literature values of N/X for this reaction in organic solvents could not be found, but in dichloromethane solutions of 1,3-dialkylimidazolium salts they ranged from 0.11 to 0.18.[2.21] As with the yields obtained, our N/X values were similar.

The fact that the aldehyde group on the dienophile is not as electron-withdrawing as other possible functionalities points to the fact that methacrolein may not be a very reactive substrate for the Diels-Alder reaction. The low yields obtained here and in the literature point to this fact.

As for the reaction in section 5.2.1.1, the ratio prods/DiCp was low, its value being 4.18. This would normally be expected. This suggests, as with the previous reaction, that the competition reaction plays a significant part in removing unreacted cyclopentadiene from the system, and thus prevents the desired products being formed. Again, this is probably because the reaction is slow, and the dienophile not reactive enough to eliminate the competition. The amount of cyclopentadiene used in the reaction was in slight excess to the amount of dienophile to allow for formation of dicyclopentadiene.

5.2.1.3. Reaction with the dienophile methyl methacrylate (16)



(4) (16) (17a) (17b)

Scheme 5.3: Reaction between methyl methacrylate **(16)** and cyclopentadiene **(4)**

Table 5.2: Results of the reaction between methyl methacrylate **(16)** and cyclopentadiene **(4)**

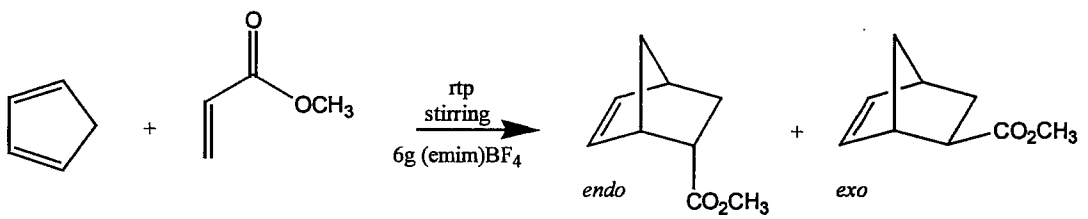
Entry	Conc diene / M	Conc dieneophile / M	Length of reaction / hrs	Yield	N/X	Prods/DiCp
1	3.738	2.880	110	11.4%	2.17	2.51
2	3.738	2.880	72	9.5%	1.31	2.66
3	0.141	0.109	110	6.0%	1.75	2.64

In the reaction between methyl methacrylate and cyclopentadiene, the use of a dienophile with an ester group next to the reacting double-bond was expected to increase not only the yield, but also N/X. It is well known that the presence of a stronger electron-withdrawing group than the aldehyde would make the carbon-carbon double bond on the dienophile less electron-rich and therefore more reactive in the presence of the diene. The results do not confirm this. Perhaps due to the presence of the electron-donating methyl group (adjacent to the carbonyl function) the electron-withdrawing effect is not as strong as it could be.

Although the yields were low, the N/X values achieved were 2.17. This compares to the use of water as a solvent, where Berson and co-workers[2.7] observed a value of 1.4.

As has been seen previously, with a low yield (reflecting a slower rate of reaction) the side reaction involving the dimerisation of cyclopentadiene becomes more significant. The prods/DiCp ratios in table 5.2 confirm that a slower main reaction leads to a greater association of cyclopentadiene with itself. The amount of cyclopentadiene used in the reaction was in slight excess to the amount of dienophile (see table 5.2) to allow for the formation of di-cyclopentadiene.

5.2.1.4. Reaction with the dienophile methyl acrylate (12)



(4) (12) (13a) (13b)

Scheme 5.4: Reaction between methyl acrylate (**12**) and cyclopentadiene (**4**)

Table 5.3: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**)

Run no.	Conc diene / M	Conc dieneophile / M	Temp / °C	Length of reaction / hrs	Yield	N/X	Prods/DiCp
1	1.050	0.963	25	2	77.0%	4.49	33.48
2	1.050	0.963	25	19.5	81.0%	4.18	36.04
3	1.050	0.963	60	116	71.0%	3.41	32.33
4	1.050	0.963	60	2	76.0%	3.55	57.82
5	1.050	0.963	60	19.5	77.0%	4.46	429.0
6	1.130	1.033	25	16	67.0%	5.17	57.82
7	1.500	1.369	25	72	90.9%	4.24	29.30
8	0.141	0.129	25	72	81.4%	5.17	51.63
9	0.141	0.129	25	2	41.0%	5.85	7.00

There are several ways of looking at the reaction between methyl acrylate and cyclopentadiene. The first thing to notice is that the majority of runs gave good yields, and N/X ratios that are comparable with the literature when conventional solvents were used for this reaction (when used as a solvent, ethanol gave an N/X value of 5.2).[2.7] However the literature shows that the same reaction carried out in water resulted in an N/X value of 9.2.[2.4b]

In terms of temperature, it can be seen from table 5.3 that increasing the temperature from 25 °C to 60 °C gave no yield or N/X advantage. Although run 5 compared showed similar results to run 1 (carried out at room temperature), heating the reaction gave no benefit, and so this was quickly discounted from the study. The length of time that was needed for complete reaction was decided to be around 72 hrs. Although the run that was kept on for 2 hours (run 9) gave a good N/X ratio, the yield was lower as the reaction had obviously not gone to completion. The best balance of maintaining the yield, yet achieving a good N/X was decided to be run 7.

Both the yield and also N/X are both significantly increased from the other experiments discussed earlier. The dienophile methyl acrylate is made more reactive for the Diels-Alder reaction by the presence of a strongly electron-withdrawing group adjacent to the double bond. Unlike methyl methacrylate, there is no adjacent methyl group to disrupt this effect by pushing electron density back onto the double bond.

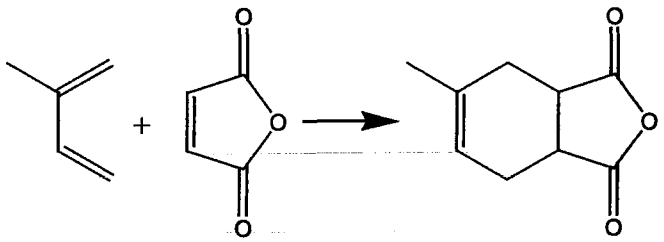
After reaction, the ionic liquid was washed repeatedly with small amounts of diethyl ether, and then dried *in vacuo* at 50 °C for six hours. This process was sufficient to remove all organic substrates associated with the Diels-Alder reaction from the ionic liquid. Proton NMR showed that the liquid exhibited a high level of purity. In terms of recycling the ionic liquid for use in the same reaction, it may have been enough to remove all reaction substrates as much as possible, leaving something behind. However, this result is encouraging for the use of the same solvent system with other Diels-Alder reactions or with a completely different class of reaction. The term recycling can often be used to mean the repeated use of a substrate in the same process. However, the results

from this study suggest that the ionic liquid is universally recyclable, when used in this process.

The outcome of this reaction was promising. It was clean and simple to perform, the solvent could be cleaned and re-used with ease, the conditions for optimised yields and N/X ratios were mild, and most importantly the ionic liquid seemed able to affect the reaction process (unlike the reactions already discussed). The reason that this is important is that it will be increasingly interesting to employ a reaction as a probe to run in different ionic liquids. To observe the relative differences between ionic liquids, it will be crucial to use a probe reaction that is sensitive to changes in its environment. The fact that [emim][BF_4] followed the theory that was predicted for ionic liquids to be a useful medium for improving and refining the Diels-Alder reaction, and that the reaction was sensitive to media changes such as temperature and initial substrate concentrations are both promising results for the prolonged use of this reaction in further ionic liquid studies.

5.2.2. Reactions involving the diene isoprene (34)

5.2.2.1. Reaction with the dienophile maleic anhydride (37)



(34) (37) (38)

Scheme 5.5: Reaction between isoprene (34) and maleic anhydride (37)

The reaction between maleic anhydride and isoprene gave, after 72 hours reacting at room temperature, a white solid with a yield of 77 %. A molar excess of 5:1 of diene (6.92 M concentration) to dienophile (1.38 M concentration) was used in the reaction. GC mass spectrometry was performed on the compound, which showed one dominant GC peak, confirmed to be that of the desired product (**38**). Although the yield was relatively high compared to some that have been observed so far in this section of work, it was thought that it could be higher. This was not due to doubts over the difficulty of reaction between the two reagents or possible side-reactions, but mainly because isoprene is extremely volatile. The initial run of this reaction was performed under a flow of dry nitrogen and the addition of excess isoprene was to allow for any isoprene that may have evaporated with the gas flow.

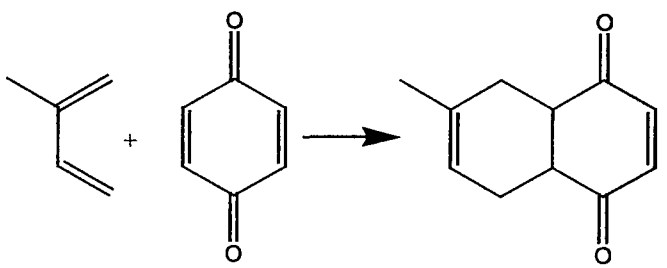
A second run of the same reaction was performed to try and minimise any isoprene loss due to evaporation. The reaction vessel was once again under an atmosphere of dry nitrogen, but no longer under a constant stream of the gas. All purging took place before the introduction of isoprene. When the reaction components were introduced, the vessel was sealed and thus became a closed system. The same conditions were used, resulting in an 86% yield, again analysed by GC mass spectrometry.

The difference in yield, although significant, was not large enough to justify evaporation of isoprene as being the dominant factor controlling the reaction yield, as this had been eliminated from the procedure. However, the same reaction, performed in the same way, but with a 1:1 molar ratio of diene to dienophile was carried out as a control. No product was obtained in this case.

The reaction itself is clean and simple to carry out under mild conditions giving good yields. However the fact that it needs such excesses of diene to proceed raise some doubts over whether it could be sensitive to the ionic liquid environment. Also the fact that there is no N/X ratio, or some sort of mixture of products gives one less parameter to measure the effects that the ionic liquid environment would have on the reaction. The extraction process (extraction with diethyl ether, followed by a recrystalisation from methanol) was

also slightly more cumbersome than, for example the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) (extraction with diethyl ether and removal of diethyl ether by rotary evaporation). Considering that the reaction chosen as a probe would need to be studied many times in different solvent media, this would count as a disadvantage. The cleaner the process, from reaction to work-up, the more advantageous it is for use as a probe reaction.

5.2.2.2. Reaction with the dienophile 1,4-benzoquinone (39)



(34) (39) (40)

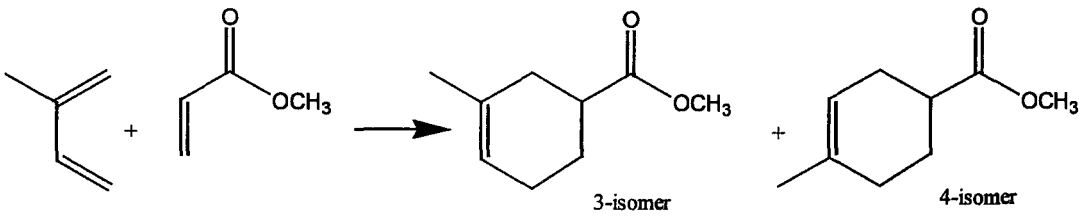
Scheme 5.6: Reaction between isoprene (**34**) and 1,4-benzoquinone (**39**)

The only way the reaction between 1,4-benzoquinone and isoprene could proceed was by heating to 70 °C, as 1,4-benzoquinone (a solid) could not otherwise dissolve into the ionic liquid. Isoprene, which is extremely volatile, was kept in the system by reflux. As with the reaction described earlier (section 5.2.2.1), a 5:1 molar ratio of diene (2.769 M concentration) to dienophile (0.554 M concentration) was used. After 15 hours a white solid was obtained with a yield of 20%. However GC mass spectrometry confirmed that the product was very impure, and none of the other peaks seen in the GC could be identified through mass spectrometry.

By lowering the temperature slightly, a vast improvement was made. Again, benzoquinone was dissolved in the ionic liquid at 70 °C. But then the reaction flask was cooled to 55 °C before isoprene was added, and kept under reflux conditions (again to hold the isoprene in the reaction) for 48 hours. A final yield of 77.0% was observed. GC mass spectrometry gave one dominant peak with two smaller peaks indicating that the product was not totally pure. The major GC peak was that of the desired product (**40**).

Although a good yield was obtained, the conditions used were not favourable for further study. In terms of temperature, and the excess of diene needed the reaction was not deemed to be as facile to undertake as some of the others that have been discussed earlier. Whereas the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) is relatively easy to isolate and purify, the product for this reaction (**40**) was extracted with diethyl ether but then had to be recrystalised three times from methanol. Again, this would count against it being used as a probe reaction.

5.2.2.3. Reaction with the dienophile methyl acrylate (12)



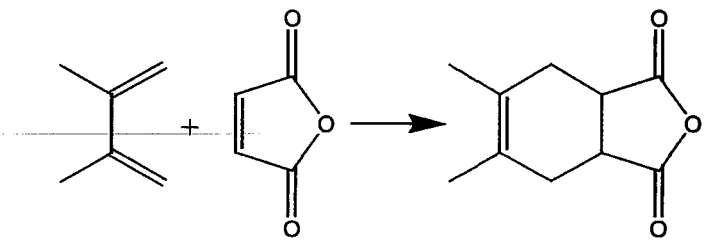
(34) (12) (36a) (36b)

Scheme 5.7: Reaction between isoprene (**34**) and methyl acrylate (**12**)

The reaction between methyl acrylate was attempted 4 times for different lengths of time. In each case a slight excess of the diene was used, to counter any loss through evaporation. The system was closed under an atmosphere of dry nitrogen. The times of reaction were 4.5 hours, 48 hours, 72 hours and 120 hours. All four runs resulted with no yield being observed. No starting materials were observed in the final analysis. This could have been due to the evaporation of isoprene, but it seems unlikely, since other reactions using isoprene had given a yield once the system was closed. The most likely reason appears to be a low reactivity between these substrate.

5.2.3. Reactions involving the diene 2,3-dimethyl-1,3-butadiene (42)

5.2.3.1. Reaction with the dienophile maleic anhydride (37)



(42) (37) (43)

Scheme 5.8: Reaction between 2,3-dimethyl-1,3-butadiene (**42**) and maleic anhydride (**37**)

In the reaction between maleic anhydride and 2,3-dimethyl-1,3-butadiene, the diene is slightly more reactive than isoprene because of the two electron-donating methyl groups on positions 2 and 3, that push electron density towards the double bonds, allowing them to attack a dienophile more readily. This should render it more willing to react with

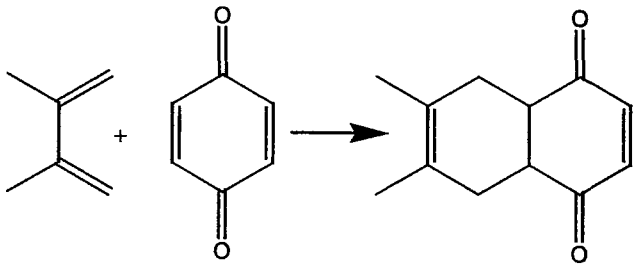
maleic anhydride, since it has two strongly electron-withdrawing carbonyl groups that activate the reactive double bond.

The reaction was attempted for 72 hours at room temperature, with starting concentrations of 1.385 M dienophile and 6.923 M diene (a 5:1 molar ratio of diene to dienophile). A white crystaline solid with a yield of 66.0% was observed. On analysis by GC mass spectrometry, the desired product had been formed.

A second run was carried out using a 1:1 molar ratio of starting materials (1.800 M concentration of each reactant), and stirred for 20 hours at room temperature. A yield of 71% was observed, again confirmed to be the desired product by GC mass spectrometry. It appears that the presence of the second methyl group on the diene does make a difference to its reactivity. This reaction was possible with isoprene as the diene, but not with such a molar ratio of starting materials, and not on this timescale. As well as being more reactive, 2,3-dimethyl-1,3-butadiene is less volatile than isoprene, hence a molar ratio of 1:1 of the starting materials sufficed to produce a good yield, and a closed system was not necessary to maintain the diene's presence in the reaction vessel.

As with the trend seen in the reactions between maleic anhydride and isoprene, and then maleic anhydride and 2,3-dimethyl-1,3-butadiene, we would expect the latter reaction to display greater reactivity, because of the diene involved. Due to the presence of an added electron-donating methyl group (compared to isoprene) on 2,3-dimethyl-1,3-butadiene, the reacting double bonds should be more electron-rich and therefore more reactive.

5.2.3.2. Reaction with the dienophile 1,4-benzoquinone (39)



(42) (39) (44)

Scheme 5.9: Reaction between 2,3-dimethyl-1,3-butadiene (**42**) and 1,4-benzoquinone (**39**)

In the reaction between 1,4-benzoquinone and 2,3-dimethyl-1,3-butadiene, the dienophile was dissolved in the ionic liquid at 70 °C (using a 0.55 M concentration). A 5:1 molar ratio of diene to dienophile was used (2.77 M 2,3-dimethyl-1,3-butadiene). After 70 hours of stirring at this temperature, a product was obtained. GC mass spectrometry showed that the desired product (**44**) was formed in very low yield (trace only). The major GC peak was confirmed to be the compound shown in figure 5.1 (**45**). Clearly, the double bond on each side of the molecule has been attacked by the diene.

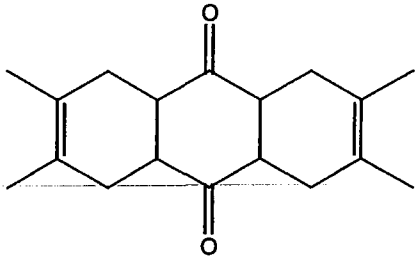


Figure 5.1: Compound (**45**), formed from the double Diels-Alder reaction of 1,4-benzoquinone with 2,3-dimethyl-1,3-butadiene

2,3-dimethyl-1,3-butadiene is more reactive than isoprene – even too reactive in this case. Due to a combination of its fivefold excess in this reaction and its relatively high reactivity, a double reaction is seen.

The reaction was attempted in a variety of ways. The ratio of diene to dienophile was kept constant each time. The temperature was varied from 25 °C to 80 °C, and the time of reaction from 15 to 120 hours. The results from GC mass spectroscopy showed an array of peaks in the GC each time (implying a very impure sample), consisting of either starting materials or unwanted by-products.

5.2.4. Conclusions of probe reaction selection study

The reactions showed mixed results after reaction. Table 5.4, below, shows the full of results of this section of work. Although only two reactions failed to work completely in the chosen ionic liquid (those between 2,3-dimethyl-1,3-butadiene (**42**) and benzoquinone (**39**), and isoprene (**34**) and methyl acrylate (**12**)), some showed no significant improvement on or were even less succesful than examples from the literature. To reach the yields of some reactions required relatively high temperatures, or large excesses of the diene. Choosing a reaction to act as a probe in several ionic liquid systems was not merely about the greatest advances on yields or product selectivity from the literature. The conditions of the reaction, ease of separation and work-up of the products were also points to be considered.

The reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) was chosen. Not only did it show high yields and very favourable product selectivity, but it could be carried out at room temperature, higher concentrations (meaning less ionic liquid used per unit volume of product to be synthesised) and the products were easily extracted. Also of great interest was the fact that it was possible to remove all organic substances from the

ionic liquid without damaging it in anyway, for repeated use. This showed that the recycled ionic liquid was not merely suitable for repeated use as a solvent for the same Diels-Alder reaction, but also as a solvent system for Diels-Alder reactions using other substrates, and even completely different reactions.

Table 5.4: Overview of all Diels-Alder reactions attempted in this chapter, with selected results and literature examples (where applicable)

Entry	Diene	Dienophile	Conditions	Yield	Selectivity (where appropriate)	Literature conditions	Results from literature (ref)
1	Cyclopentadiene	*Trans*-Crotonaldehyde	1.306 M diene / 1.200 M dienophile / 72 hrs / rtp	34.6%	N/X = 3.61	1,3-diethylimidazolium trifluoromethylcarbonate - DCM solution / 55 °C / 2 hrs	Yield = 37% N/X = 20 (2.21)
2	Cyclopentadiene	Methacrolein	1.308 M diene / 1.200 M dienophile / 110 hrs / rtp	41.2%	N/X = 0.15	1,3-diethylimidazolium trifluoromethylcarbonate - DCM solution / 55 °C / 2 hrs	Yield = 40% N/X = 0.15 (2.21)
3	Cyclopentadiene	Methyl methacrylate	3.738 M diene / 2.880 M dienophile / 110 hrs / rtp	11.4%	N/X = 2.17	water / time not specified / temp not specified	Yield unspecified N/X = 1.4 (2.7)
4	Cyclopentadiene	Methyl acrylate	1.500 M diene / 1.369 M dienophile / 72 hrs / rtp	90.9%	N/X = 4.24	water / time not specified / temp not specified	Yield unspecified N/X = 9.2 (2.4b)
5	Isoprene	Maleic anhydride	6.920 M diene / 1.380 M dienophile / 72 hrs / rtp	86%	-	-	-
6	Isoprene	1,4-benzoquinone	2.769 M diene / 0.554 M dienophile / 48 hrs / 55 °C	77%	-	-	-
7	Isoprene	Methyl acrylate	Various	None	None	-	-
8	2,3-dimethyl-1,3-butadiene	Maleic anhydride	1.800 M diene / 1.800 dienophile / 20 hrs / rtp	71%	-	-	-
9	2,3-dimethyl-1,3-butadiene	1,4-benzoquinone	various	None	-	-	-

5.3. Preliminary studies into the variation of the ionic liquid system, using the chosen Diels-Alder probe reaction

5.3.1. Variation of the ionic liquid used as a solvent

Table 5.5: The effects on the chosen probe reaction (cyclopentadiene (**4**) + methyl acrylate (**12**)), caused by variation of the ionic liquid system

Run no.	Ionic liquid	Conc diene / M	Conc dienophile / M	Temp / °C	Yield	N/X	Prods/DiCp
1	[emim][BF_4][a]	1.500[d]	1.369[d]	25	90.9%	4.24	29.30
2	[pmim][ClO_6][b]	-	-	25	74.5%	5.37	33.48
3	[emim][OTf][c]	-	-	25	55.7%	4.81	12.51
4	[emim][NO_3]	-	-	45	57.1%	3.29	8.35
5	[emim][PF_6]	-	-	70	34.5%	3.25	7.77
-	[$EtNH_3$][NO_3][20]	-	-	25	98.0%	6.69	-

[a] This is the reaction run labelled entry 7 in table 5.3

[b] $[pmim]^+$ is the 1-propyl-3-methylimidazolium cation

[c] $[OTf]^-$ is the triflate anion $[CF_3SO_3]^-$

[d] Densities of ionic liquids in runs 2-5 are unknown, though similar to [emim][BF_4] - as densities were required to calculate the concentrations of diene and dienophile used, they are not available for reactions 2-5, but can be considered to be close to those for run 1.

NB: All reactions were run for 72 hours

Having chosen a suitable Diels-Alder reaction to perform in the ionic liquid [emim][BF_4], some additional runs were carried out in other ionic liquids. This was considered a preliminary study in order to deduce whether or not the reaction between cyclopentadiene (**4**) and methyl acrylate (**12**) could work in a selection of ionic liquids. Those chosen all

had a cation based on the imidazolium ring structure with variation only of the alkyl side-chains. The anion varied more dramatically. The ionic liquids chosen and results for each run are shown in table 5.5. The last row of entries in table 5.5 is to compare our results with a study carried out in the literature of the same reaction in ethylammonium nitrate ionic liquid by Jaeger and Tucker.[2.20] Apart from the last row of entries, these results have all been published by this group in the literature.[2.24]

Out of the ionic liquids we tried, [emim][BF_4] (run 1) still shows the best yield after 72 hours (indicating a comparatively faster rate of reaction). The ionic liquid [pmim][ClO_6] (run 2) shows the best N/X ratio. The lower N/X selectivities in [emim][NO_3] (run 4) and [emim][PF_6] (run 5) are probably due to the higher temperatures that were needed for these reactions. Both systems in question displayed a lower prods/DiCp ratio than the other runs, indicating that the elevated temperatures in both cases led to the accelarated formation of di-cyclopentadiene. Higher temperature also could have favoured the increased formation of the *exo*-product, which is the thermodynamic product.

When compared to the reaction in ethylammonium nitrate, our results show a lower N/X ratio. In terms of internal pressure this could be explained by the local structure in both solvents. The ethylammonium salt is held together by N-H hydrogen bonds, rather than the weaker C-H hydrogen bonds that dominate in our imidazolium salts. It is possible that this causes a more highly ordered structure in ethylammonim nitrate, a factor that would certainly aid the strength of internal pressure and solvophobicity within the solvent system, and thus increase the N/X ratio and also the rate (i.e. the yield after a set time).

5.3.2. Addition of a Lewis acid to the [emim][BF_4] solvent system

Work carried out by Forman and Dailey[2.19] that has been discussed earlier (see chapter 4) claimed that the significant rates and N/X ratios obtainable in LPDE (lithium perchlorate in diethyl ether) were due to the Lewis acidity of the lithium cation. It had earlier been claimed that these solvents accelarated the Diels-Alder reaction through solvophobicity alone. It was decided to use solutions of lithium tetrafluoroborate in [emim][BF_4] as a solvent system. When lithium tetrafluoroborate in solution is compared the solvent alone, the only species that is new to the system is the lithium cation itself. By keeping the solvent system constant and introducing a known Lewis acid, it was hoped that some sort of improvement would be observed. The results are shown below in table 5.6.

Table 5.6: The effects on the chosen probe reaction (cyclopentadiene (**4**) + methyl acrylate (**12**)), caused by the addition of lithium tetrafluoroborate to the ionic liquid system [emim][BF_4]

Run no.	Conc lithium tetrafluoroborate/ M	Conc diene / M	Conc dienophile / M	Temp / °C	Yield	N/X	Prods/DiCp
1	0[a]	1.500	1.369	25	90.9%	4.24	29.30
2	0.25	0.970	0.800	25	63.4%	5.45	39.00
3	0.5	0.970	0.800	25	53.2%	5.80	61.50
4	1.0	0.970	0.800	25	60.4%	5.13	11.82
5	2.0	0.970	0.800	25	66.2%	5.67	15.95

[a] This is the reaction run labelled entry 7 in table 5.3
NB: All reactions were run for 72 hours

Although the rates and N/X ratios for all runs form no clear trend or pattern, it can be seen that all the systems that saw the introduction of lithium tetrafluoroborate showed

higher N/X values than the ionic liquid alone. The yields are all appreciably lower. This could be due to the lower concentrations of starting materials that were used. Another reason could be related to the rate and solvophibicity. The yield after a set amount of time gives us an indication of the relative rate of reaction. As we would expect the Lewis acidity of the lithium to accelerate the reaction by association with the carbonyl oxygen, so we might also expect the highly ordered structure of the ionic liquid to be disrupted by the introduction of another salt into the system. If this were the case, we would see both these factors acting against each other. Table 5.6 shows that at higher concentrations of lithium tetrafluoroborate the yields rise. The lowest yield is seen on run 3, where a 0.5 M solution of the lithium salt is present. If the above factors hold, then at the lowest concentration (run 2), we would be seeing enough lithium cation to increase the N/X ratio, but not enough to appreciably disrupt the solvent structure. Run 3 is approximately where we would expect the balance to lie. In this instance, there is more structural disruption than run 2, but not yet enough lithium cation to outweigh the loss of solvophobicity. In runs 4 and 5, we would expect the benefits of the introduction of more lithium cation into the system to outweigh the loss of disruption to the solvent structure.

6. A COMPARATIVE STUDY OF THE PROPERTIES AND CHARACTERS OF A RANGE OF ROOM TEMPERATURE IONIC LIQUIDS USING A DIELS-ALDER PROBE REACTION

6.1. Research aims

In the last chapter, a suitable Diels-Alder probe reaction for use in a range of ionic liquids was chosen. The intended utilisation of the probe reaction was to study the comparative performances of a range of Diels-Alder reactions. Some comparative work involving that reaction in several different ionic liquid systems was also studied in chapter 5. The work that comprises this chapter is a continuation of that study.

For this work, it was decided to try the same reaction in selected ionic liquids, primarily to study the ionic liquids themselves, but also to optimise the reaction. We have already seen how the rate of reaction and product selectivity of Diels-Alder reactions in imidazolium-based ionic liquids, although relatively good, are not yet up to the levels in the ionic liquid ethylammonium nitrate, or the non-aqueous solvent system lithium perchlorate in diethyl ether. Although the chosen probe reaction was attempted in a series of ionic liquids in chapter 5, no major steps have yet been taken to gain a better understanding of how each separate ionic liquid environment varies, and how each one affects the reaction. We can postulate a number of general theories:

(i) That as a class of solvents, ionic liquids hold common universal properties that influence the probe reaction in general ways.

(ii) That each ionic liquid is unique and influences the probe reaction in its own manner.

(iii) That the answer lies somewhere between (i) and (ii). Maybe the ionic liquids as a general group of solvents have common properties that improve the probe reaction to a certain standard. After this it is perhaps the individual solvent's characteristics that either improve or degrade the performance of the reaction from this standard.

The aim of this work is to understand the properties and relative characteristics of all the ionic liquids used in this study to try and eliminate any hypotheses that do not fit until the correct answer remains. If hypothesis (ii) or (iii) is correct, then it is hoped that this comparative knowledge within ionic liquids will eventually lead to solvent tailoring to directly suit the substrates and reaction conditions employed. With a deeper understanding of ionic liquids and how their properties apply practically to the world of synthesis and solvent chemistry, it is hoped that we can eventually apply our knowledge to other Diels-Alder reactions, and also other classes of reactions.

All chemical reactions depend to some extent on the solvent employed. It is hoped that we can eventually use the term solvent tailoring with respect to ionic liquids (or even the choice of not using ionic liquids for certain reactions) to mean a correct solvent choice before the reaction is performed. This would be based on our knowledge of the characteristics of the substrates involved in the reaction, the mechanism of the reaction, the types of products synthesised and if a product mixture exists, the product or products that are needed from the reaction. If these factors can be synchronised with the choice of a solvent, based on its properties and how it can influence the reaction in question in the most positive way possible, then solvent tailoring will be a reality. It would clearly be too ambitious to imagine that this is possible at the present, or that it is close to being possible. The long-term aim of this work is to take steps towards this becoming a reality.

6.2. The reaction between cyclopentadiene (4) and methyl acrylate (12) in a variety of ionic liquids

The reaction chosen in chapter 5 as our probe reaction for further studies in ionic liquids was exclusively employed in this chapter of work. It was hoped that the reactions that were attempted and discarded in chapter 5 could be re-tried and improved upon, based on the knowledge obtained of ionic liquid systems. However, the time scale of this project did not allow for this.

This, the first section of this work will concentrate on the data of the probe reaction attempted in a number of ionic liquids. The work has been organised into sections, or groups of liquids, loosely based on the anion used (since the cations are all based on 1,3-dialkyl imidazolium salts). The catagories that will be studied are as follows.

(i) Moisture-stable ionic liquids (both those composed of the terafluorborate anion with cationic variations, and those composed of the 1-butyl-3-methylimidazolium cation with anionic variations will be dealt with separately within this section).

(ii) Moisture-sensitive ionic liquids composed of anions with flexible Lewis acidity/basicity.

Studies that have been carried out, where known Lewis acids and bases are added to the ionic liquid system have been included, as appropriate, in these sections.

6.2.1. Moisture-stable ionic liquids

6.2.1.1. Moisture-stable ionic liquids composed of the terafluorborate anion with cationic variations

Table 6.1: Results of the reaction between methyl acrylate **(12)** and cyclopentadiene **(4)** in $[BF_4]^-$ ionic liquids

Ionic Liquid	Conc diene / M	Conc dieneophile / M	Yield	N/X	Prods/DiCp
[emim][BF_4]	1.270	1.110	90.7%	4.46	16.86
[bmim][BF_4]	1.270	1.110	84.6%	4.56	22.26
[hmim][BF_4]	1.270	1.110	86.0%	4.26	18.23
[bmmim][BF_4][a]	1.270	1.110	83.6%	3.26	10.24

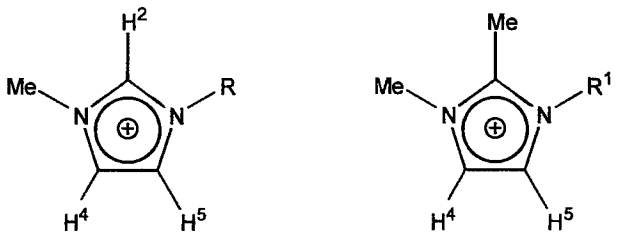
[a] $[bmmim]^+$ is the 1-butyl-2,3-dimethylimidazolium cation

NB: All reactions were carried out at 25 °C for 72 hours

In terms of yield, the reaction that worked best was that carried out in the ionic liquid [emim][BF_4]. The other reactions have very similar yields. In this case we are not merely comparing the same reaction under different conditions such as concentration or temperature, but the same reaction in different solvent systems. Potentially, they could profoundly alter the reaction conditions and environment.

The N/X ratios are all remarkably similar for the first 3 systems. But when [bmmim][BF_4] is used as the solvent system, N/X is dramatically lower. It is also notable that the prods/DiCp ratio is also lower for this reaction. If we use the solvophobicity model to examine this reaction, then we must examine the structures of the imidazolium

cations that make up the ionic liquids, since the anions are all constant. Figure 5.1 (below) shows the structures of the cations used in each of the four reactions.



(a) R = ethyl ; 1-ethyl-3-methylimidazolium cation

(b) R = butyl ; 1-butyl-3-methylimidazolium cation

(d) R = hexyl ; 1-hexyl-3-methylimidazolium cation

(d) R^1 = butyl ; 1-butyl-2,3-dimethylimidazolium cation

Figure 6.1. Structures of imidazolium cations used in the ionic liquids made for this study

The factor that would cause solvophobicity is a highly ordered local solvent structure. In ionic liquids this is caused by hydrogen bonding. We would expect C-H hydrogen bonding to occur between the imidazolium cations of the liquids we have used. In figure 6.1 (a-c) the proton on ring position 2 (H^2) is the most acidic.

In chapter 2, the ^{1}H-NMR and IR spectroscopy of these ionic liquids was discussed. In the ^{1}H-NMR spectra of the ionic liquids used in this study (see table 2.1), the proton on ring position 2 (apart from [bmmim][BF_4] which has no such proton) was expected to exhibit a smaller chemical shift as the alkyl side chain becomes shorter. This is because the alkyl side chain would be expected to donate less electron density into the ring as it gets shorter, causing the H^2 hydrogen's bonding electrons to become more localised in the ring. This means that it would hold less electron density and would be more likely to form hydrogen bonds. The same pattern was expected for the IR results of these liquids.

As the alkyl side-chain becomes longer, so the wavenumber of the C-H stretch would be expected to be lower, indicating a greater degree of hydrogen bonding.

In fact, the results seen in chapter 2 showed the exact opposite of these predictions. As the alkyl chain gets longer, the hydrogen bond acceptor ability and strength was shown to get stronger. So according to the solvophobicity theory, we would expect those liquids that have longer alkyl side chains to exhibit a higher N/X ratio for the Diels-Alder reaction in that liquid. The first three entries in table 6.1 show that there is no appreciable trend to make any assumptions on. Although the N/X values are quite similar for these three ionic liquids, no trend exists between them. If the factor of experimental error is applied to these results, then the order they arrange themselves into could very easily be different. Also, only three ionic liquids with imidazolium side chain length variations were used. This was because these results were one small part of a more global aim. It could be useful for a future project to use a greater number of ionic liquids with small variations of the imidazolium alkyl side chains.

What is interesting is the ^{1}H-NMR spectrum for [bmmim][BF_4]. As there is no proton on ring position 2 we might expect the protons H^4 and H^5 to lose more electron density to the imidazolium ring and partake more in hydrogen bonding. This is not the case, according to the spectroscopic measurements. In fact the chemical shifts for these 2 protons are both less than for the equivalent shifts in the spectra of the other ionic liquids used in this section of work. The IR spectrum is no different, and confirms this trend. Thus even the ring protons that exist on the $[bmmim]^+$ cation are not relatively strong hydrogen bond donors. This confirms the results we have from the Diels-Alder reaction.

As this hydrogen bonding ability decreases, so would the solvent structure, meaning a smaller contribution from solvophobicity. As has been discussed earlier, the amount of *endo*-product formed is linked to the solvophobicity, since it is this product that has the smaller transition state volume. Therefore the higher the degree of solvophobicity, the greater the value of N/X. This is not observed in the results for the first 3 liquids used in table 6.1. This could be due to the fact that an optimum cavity formation is needed to

accomodate the *endo*-transition state as it forms. The imidazolium cation with an ethyl side chain (species (a) in figure 6.1) might be allowed a closer proximity with the $[BF_4]^-$ anions as it forms hydrogen bonds, as its ethyl side chain is so short. It could well be that the imidazolium cation with a butyl side chain (species (b) in figure 6.1) is of an optimum length to allow sufficient hydrogen bonding and the correct proximity of the cations (due to the length of the butyl side chain) to form cavities of a better size for *endo* product formation.

The most dramatic results belong to those of the $[bmmim]^+$ cation. The N/X value is significantly lower than for the other 3 systems. Figure 6.1(d) shows the $[bmmim]^+$ cation has a methyl group on ring position 2. The methyl group blocks any hydrogen bonding from this position. Although hydrogen bonding can still occur from the protons H^4 and H^5, it would be expected to be weaker. Thus with less and weaker hydrogen bonding we would expect a less structured solvent system, leading to a lower degree of formation of *endo* product, and a smaller N/X ratio.

The lower prods/DiCp value for the reaction, when performed in the $[bmmim][BF_4]$ system is also worth noting. As the solvent system is less solvophobic, we would expect the reaction to go slower (water, which induces large amounts of hydrophobicity increases the rate of Diels-Alder reactions many times[2.4]). However, the competition reaction (the dimerisation of cyclopentadiene) is also a Diels-Alder reaction, with a negative change in volume as the reactants form a transition state. So this process too would be expected to be influenced by solvophibicity. How solvophobic systems work has been discussed previously (see chapter 4). It is known that they improve the selectivity by favouring the transition state with the lowest volume in the case of the probe reaction for this study. It is also known that they increase the rate of reaction in general by the generation of internal pressure within themselves that provides more impetus on the reactants to combine.

It may appear that solvophobicity is merely a qualitative concept. However there are quantitative results which show that the volume is smaller than the volume of the

substrates alone for Diels-Alder reactions.[2.27] Although the specific reaction studied here is not used, the reaction of methyl acrylate with isoprene (in the solvent butyl bromide) was measured as having a change in volume during activation of –30.8 cm^3/mol. The change in volume from the starting materials to the product was measured at –36.9 cm^3/mol. Similarly, the reaction between cyclopentadiene and dimethyl acetylenedicarboxylate (in ethyl acetate) was measured as having a change in volume during activation of –30.2 cm^3/mol, and a change in volume from the starting materials to the products of –33.9 cm^3/mol. Although the solvent would influence these figures, this tells us that in conventional organic solvents, at least, solvophobicity would be a factor that could encourage these reactions to go faster. This is because in a constrained environment, the transition state, and ultimately the product would be better suited to exist than both the starting materials together.

However, if we were expecting only solvophobic effects to be at work in these solvent systems then the data would prove to show another pattern. In a truly solvophobic system, the formation of dicyclopentadiene (prods/DiCp) would be expected to increase as solvophobic effects increase. A discussion of the factors that are believed to cause increased solvophobicity in these ionic liquids is presented above. From this we can presume that solvophobicity would be expected to increase in the order [bmmim][BF_4]< [hmim][BF_4]< [bmim][BF_4]< [emim][BF_4] (due to the relative size and ease of approach of the cations, except in the case of [bmmim][BF_4] which is constrained by a lack of hydrogen bond acceptor sites), and as the solvophobicity gets higher, so too would the ratio prods/DiCp. Table 6.1 shows this to a point, but not conclusively. Not only is the value for the prods/DiCp ratio in [emim][BF_4] unexpectedly low, but also the ionic liquids that exhibit a rise in solvophobicity in line with the prods/DiCp ratio do not do so in proportion to each other. Solvophobicity is a general solvent characteristic that should affect all such reactions fairly evenly. These results suggest that the effect taking place have a greater effect on the cyclopentadiene-methyl acrylate reaction than on the cyclopentadiene dimerisation reaction.

6.2.1.2. Moisture-stable ionic liquids composed of the 1-butyl-3-methylimidazolium cation with anionic variations

Table 6.2: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) in moisture-stable ionic liquids composed of the $[bmim]^+$ cation

Ionic Liquid	Conc diene / M	Conc dieneophile / M	Yield	N/X	Prods/DiCp
[bmim][BF_4]	1.270	1.110	84.6%	4.56	22.26
[bmim][OTf][a]	1.270	1.110	87.4%	4.49	13.71
[bmim][CH_3SO_3]	1.270	1.110	88.5%	3.88	12.16
[bmim][Tf_2N][b]	1.270	1.110	89.9%	4.32	12.16
[bmim][NO_3]	1.270	1.110	81.2%	3.27	8.26
[bmim][ClO_4]	1.270	1.110	74.4%	4.75	9.99
[bmim][PF_6]	1.270	1.110	92.9%	4.78	11.20

[a] $[OTf]^-$ is the triflate $[CF_3SO_3]^-$ anion

[b] $[Tf_2N]^-$ the imide $[N(CF_3SO_2)_2]^-$ anion

NB: All reactions were carried out at 25 °C for 72 hours

Having studied the effects on the probe reaction of changing the cationic part of the ionic liquid, it was decided to study the effects of changing the anionic part. The ionic liquids used in this study all share the same cation ($[bmim]^+$). Table 6.2 can be used as a comparative study of the ionic liquids chosen. Close inspection reveals some trends.

Consider the ionic liquids whose anions are similar to the triflate anion (rows 2-4 in table 6.4). It can be seen that the N/X ratio goes up in series for the these ionic liquids, as follows: [bmim][CH_3SO_3]< [bmim][Tf_2N]< [bmim][OTf]. We have carried out analyses of these three ionic liquids with Reichardt's dye, which in chapter 2 was mentioned as a

good measure of the hydrogen bond donating ability of the ionic liquid. The standardised scale of measurement is E_T^N, which has no units. For the ionic liquids, the ability of hydrogen bond donation increases in exactly the same order as before, [bmim][CH_3SO_3]< [bmim][Tf_2N]< [bmim][OTf]. The E_T^N values are 0.62, 0.64 and 0.65 (lit. 0.67[27]) respectively.

Since these ionic liquids have the same cation, their intrinsic ability to hydrogen bond donate must be the same, yet they exhibit different abilites to hydrogen bond to the solute. Hence the anion must somehow be playing a part. This will discussed in more detail later on in this chapter. However, for now we can say, on the data given that the trends seen with the ionic liquids in the last section of this chapter are being followed. As the hydrogen bond donating ability of the ionic liquid as a whole increases, so too does the N/X value of the reaction in that solvent. These ionic liquids all have ready hydrogen-bond accepting sources (the oxygen lone pairs in $[OTf]^-$ and $[CH_3SO_3]^-$, and the nitrogen lone pairs in $[Tf_2N]^-$.

Comparing the other ionic liquids in this study, [bmim][BF_4] has an E_T^N value of 0.67, [bmim][NO_3] has a value of 0.64, [bmim][ClO_4] has a value of 0.68, and [bmim][PF_6] has a value of 0.67. The differences are smaller than have been observed so far. However, they still follow a trend when compared to the N/X ratios. The lowest N/X ratio for the probe reaction belongs to the run carried out in [bmim][NO_3]. This ionic liquid also has the lowest E_T^N value. Although the experiment carried out in [bmim][PF_6] has a lower N/X value than for the run in [bmim][ClO_4], they are very nearly similar, as their E_T^N values suggest, being very similar too. However, both give an N/X value that is appreciably higher than that of the reaction carried out in [bmim][NO_3]. The same applies to [bmim][BF_4] in relation to [bmim][NO_3]. The higher E_T^N value of the former results in a higher N/X ratio. The rise in N/X in changing the solvent from [bmim][NO_3] to either of the others is far more significant than the increase in E_T^N values. However, we can still conclude, based on our findings of how the other studies have been affected by the changing E_T^N values of the solvent, that the solvent polarity is telling us about how

readily the solvent hydrogen bonds to itself and therefore to what extent it can cause a solvophobic environment for the reaction to take place in.

Again, none of the cations were changed during this run of experiments. Hence, the anion must have some part to play in the reaction process. This will be discussed later on. However, the amount of change in E_T^N does not truly reflect the amount of change in N/X (although they both change in the same direction), and as this is so, we can begin to appreciate that the anion does indeed have some influence on the N/X ratio. There are 3 ways that this could happen. The anion might be altering the solvent structure or characteristics in some way, or it could be interacting with the reacting substrates in some way; either directly onto the substrates themselves, or indirectly through affecting some influence the cation on the substrates.

6.2.1.3. A combination of the above results

Table 6.3: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) in a selection of moisture-stable ionic liquids

Ionic Liquid	E_T^N (where available)	Yield	N/X	Prods/DiCp
[emim][BF_4]	-	90.7%	4.46	16.86
[bmim][BF_4]	0.673[a]	84.6%	4.56	22.26
[hmim][BF_4]	0.657[b]	86.0%	4.26	18.23
[bmmim][BF_4]	0.654[b]	83.6%	3.26	10.24
[bmim][OTf]	0.655[c]	87.4%	4.49	13.71
[bmim][CH_3SO_3]	0.620[c]	88.5%	3.88	12.16
[bmim][Tf_2N]	0.642[a]	89.9%	4.32	12.16
[bmim][NO_3]	0.637[b]	81.2%	3.27	8.26
[bmim][ClO_4]	0.680[c]	74.4%	4.75	9.99
[bmim][PF_6]	0.667[a]	92.9%	4.78	11.20

[a] Data obtained from work by Gordon and co-workers[2.28]

[b] Data obtained by work carried out from this project

[c] Data obtained from another member of the Welton research team

NB: All reactions were carried out at 25 °C for 72 hours
Cyclopentadiene was always used at 1.270 M concentration
Methyl acrylate was always used at 1.110 M concentration

The results shown in table 6.3 are the combined results of the reactions in moisture-stable ionic liquids that were included in our studies. The E_T^N values for each solvent (where known) is included. Figure 6.2 (below) is a graph of the E_T^N value of each individual ionic liquid plotted against the N/X ratio for the probe reaction, when carried out in that solvent.

Figure 6.2: Solvent polarity vs N/X illustrated as a linear relationship for a selection of moisture-stable ionic liquids used in the Diels-Alder probe study

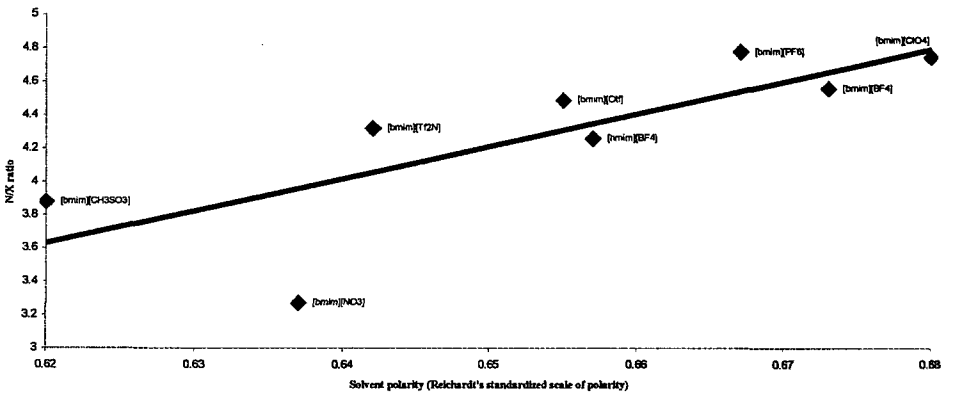


Figure 6.2 does not include the ionic liquid [emim][BF_4] since E_T^N value was not available at the time of writing. [bmmim][BF_4] is also not included in this study. It will be discussed below. All data points, except that for [bmim][NO_3] lie in a zone that obeys a linear relationship. As there are two variables (E_T^N and N/X) that control its position on the graph, there are two possible explanations.

The E_T^N value for [bmim][NO_3] was calculated by us during the course of this work, and not taken from the literature, as some other data values were. It could be possible, that some uncertainty might rest on the value and the way it was calculated, as the process to obtain E_T^N depends on an ultra-dry solvent system. If even slightly wet, the dye will prefer to bind itself to water, giving a result that does not reflect the polarity of the solvent system but the water trapped in it.

Alternatively, the [bmim][NO_3] may be contaminated with chloride anions. The most common method of preparation of the liquids featured in table 6.3 is via salt metathesis of the imidazolium chloride with (normally) a group I metal salt of the desired anionic part of the ionic liquid. The resulting mixture contains the ionic liquid and a group I metal

chloride, which is separated from the ionic liquid. During its preparation, [bmim][NO_3] is particularly difficult to obtain free of chloride ions. In addition, of all the ionic liquids studied here, it was found to be particularly difficult to make and purify. It will be demonstrated later that these chloride anions act to hinder the Diels-Alder probe reaction, and lower the N/X ratio.

If plotted, the other result that would lie off the linear range belongs to [bmmim][BF_4]. In fact, if plotted it would lie at about the same point on the y-axis (measuring N/X) as [bmim][NO_3], but to the right (i.e. even further off the linear range than [bmim][NO_3]). Of all the ionic liquids used, only [bmmim][BF_4] does not have a proton on the imidazolium ring position two. This is significant as it reduces the hydrogen bonding potential of the cation. However, it seems that the numerical value that relates to hydrogen bonding (E_T^N) is not reduced as significantly as the N/X ratio. Of course, hydrogen bonding can still take place from the protons on ring positions four and five, and from the E_T^N value of this solvent (table 6.5) it is fair to assume that these two protons are stronger, in terms of hydrogen bonding ability, than they would be were there a proton on ring position two. So it seems that there is a greater lack of reactivity in this case (in terms of the N/X ratio) than the E_T^N data suggests. This will be dealt with later on in this section.

Figure 6.2 also shows a linear best fit line. If it were assumed that hydrogen bonding interactions that are strong (according to the E_T^N values) are applied within the solvent structure, between the cation and anion. This backs up the theory of solvophobicity that results in internal pressure. However, there are discrepancies that do not fully fit into this theory. These can be seen in figure 6.2.

If, for example we compare the data points for [bmim][CH_3SO_3] and [bmim][OTf] it is possible to find doubts over the full validity of this theory. The anions in both ionic liquids share very similar structures. The main difference between them is that the former has a methyl group, and the latter a trifluoromethyl group in its place. We would expect the trifluoromethyl group on the triflate anion to be strongly electron withdrawing

whereas the methyl group on the $[CH_3SO_3]^-$ anion is electron donating. The most likely location for hydrogen bonding to take place from on both anions is one of the oxygen atoms on the SO_3 function. However, with a strongly electron withdrawing group adjacent to this function on the triflate anion, it would be logical to assume that the lone pairs of electrons on the oxygen atoms that are associated with forming a hydrogen bond to the H^2 proton on the $[bmim]^+$ cation are less available for this to occur. We would still expect hydrogen bonding to occur between the cation and anion, but to less of a degree and more weakly, resulting in a solvent with less solvophobic power and thus a lower N/X ratio for the probe reaction (less *endo*-product formed). Conversely, the methyl group on the $[CH_3SO_3]^-$ anion, would be expected to make the lone pairs of electrons on the oxygen atoms of the SO_3 function more available for hydrogen bonding between the anion and cation. Therefore we would expect hydrogen bonding between these two species to occur to a higher a degree and more strongly, resulting in a solvent with more solvophobic power and thus a higher N/X ratio for the probe reaction (more *endo*-product formed).

The results in figure 6.2 show the opposite of this situation is true. Solvophobicity may well be helping ionic liquids in a completely general and non-discriminatory way to a point, but when we compare individual ionic liquids against each other we see a linear relationship forming. This indicates that a relationship or pattern is followed for these solvents, but that it is probably not caused by solvophobicity. Indeed, if solvophobicity (caused by hydrogen bonding interactions within the ionic liquids), were the only contributing factor in these systems, then we would expect the best fit line in figure 6.2 to travel in a different direction; starting at high N/X with low E_T^N values, and ending at low N/X with high E_T^N values.

It should be remembered that ionic liquids are made up of two separate but co-dependent entities; an anion and a cation. When a measurement is taken using the Reichardt's dye, what is effectively being observed is the ability of the cation to donate a proton to hydrogen bond with the dye. In terms of hydrogen bonding, the ionic liquid anion is basically being replaced by the solute dye molecule, and the E_T^N value indicates how

easy it is for the dye to do this, in relation to the anion. Therefore it is also necessary to build up some sort of picture as to how the anion involved can influence the hydrogen bonding ability of the cation (since all the cations with the exception of [hmim][BF_4] are exactly the same), and how hydrogen bonding really affects the probe reaction. We can be certain that hydrogen bonding does influence the probe reaction in some form (in terms of the N/X ratio) since there is a linear relationship based on the E_T^N scale of polarity.

Recently, Kristiansson and Schuisky[2.29] have used vibrational spectroscopy to measure the strength of hydrogen bonds formed by some of the anions used in this study. Ionic liquids were not used, but ammonium salts of the anions. The interaction studied was between the anion and methanol in solutions of dichloromethane. It is well known that as the hydrogen bond gets stronger, a shift to lower wavenumbers is observed, along with increase in the bandwidth and intensity. Their results are shown below in table 6.4.

Table 6.4: Determination of hydrogen bonding strengths of various anions, from work by Kristiansson and Schuisky,[2.29] compared with results from this study.

Anion	Position of band / cm^{-1}	Shift of band relative to monomeric methanol molecules / cm^{-1}	E_T^N of [bmim][anion] ionic liquid	N/X ratio of probe reaction in [bmim][anion]
PF_6^-	3618	9	0.667	4.78
BF_4^-	3571	56	0.673	4.56
ClO_4^-	3545	87	0.680	4.75
OTf	3500	127	0.655	4.49
NO_3^-	3402	225	0.637	3.27

Kazarian and co-workers,[2.30] in a currently unpublished work, have investigated the molecular state of water in some of the $[bmim]^+$ ionic liquids used in this study also by IR spectroscopy. Water has three IR active vibrations; a symmetric shift (ν_1), a bending mode (ν_2) and an antisymmetric shift (ν_3). From the IR data they obtained of the vibrations ν_1 and ν_3 of absorbed water in ionic liquids they were able to estimate the strength of hydrogen bonding between water molecules and the ionic liquid anions. Their results are shown below in table 6.5.

Although the ionic liquid for the anion $[Tf_2N]^-$ is not included in their numerical study in table 6.5, Kazarian and co-workers estimated that its hydrogen bond accepting strength lies in between those of the $[BF_4]^-$ and $[ClO_4]^-$ anions. The $[Tf_2N]^-$ anion has been included in the table as it has been used in this study.

It can be seen that both pieces of work by Kristiansson and Schuisky, and Kazarian and co-workers are in total agreement over the order of strength of hydrogen bond formation of the various anions, whether they be in the form of part of a dissolved salt or a room temperature ionic liquid. It can also be seen in general terms that as the strength of the hydrogen bond formed to the anion increases, so the observed strength of the hydrogen bond formed by the cation to the Reichardt's dye decreases, and the N/X ratio of the Diels-Alder probe reaction also decreases.

Table 6.5: Determination of hydrogen bonding strengths of various ionic liquid anions, from work by Kazarian and co-workers,[2.30] compared with results from this study

Anion	$-\Delta H$ / kcal/mol	E_T^N of [bmim][anion] ionic liquid	N/X ratio of probe reaction in [bmim][anion]
PF_6^-	1.8	0.667	4.78
BF_4^-	2.3	0.673	4.56
Tf_2N^-	(2.4 - 2.9)[a]	0.642	4.32
ClO_4^-	3.0	0.680	4.75
OTf^-	3.8	0.667	4.49
NO_3^-	5.0	0.637	3.27

[a] Estimate only

Although hydrogen bonding appears to affect the probe reaction, it does not appear to be in terms of the anion-cation interactions within the ionic liquid that would cause increased solvophobicity. A clue as to what could actually be taking place lies in the fact that the Reichardt's dye study (as discussed earlier in this section) depends on the cation hydrogen bonding to the dye molecule itself in preference to the anion. This cannot be classed as an absolute measure of hydrogen bonding, only a relative indication of how the same cations act with different anions.

In order to comprehend the environment of the probe reaction taking place in the ionic liquid, it is necessary to think in terms of a relative hydrogen bond. With the data assembled, it is known that the dye molecules are in competition with the anions of the ionic liquid. It is also known that the strengths of hydrogen bonds formed by a selection of the anions to hydrogen bond donor species. It has been shown that the order of increasing hydrogen bond strength displayed by the anions of the ionic liquid results in a converse trend of hydrogen bond strength of the cation and the N/X ratio of the probe reaction.

When the probe reaction is taking place in any given ionic liquid that is discussed in this section, there are naturally no Reichardt's dye molecules present to hydrogen bond with the ionic liquid cation. However, it is possible that the Diels-Alder substrates could be involved in hydrogen interactions with the ionic liquid itself. In the reaction between cyclopentadiene and methyl acrylate in the ionic liquids used so far, the methyl acrylate can act as a hydrogen bond acceptor. This is shown in figure 6.3, below.

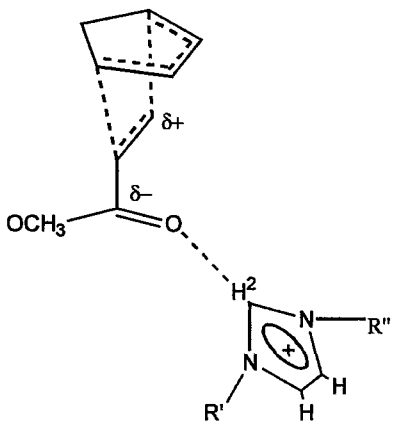


Figure 6.3: The proposed manner in which an imidazolium cation can act as a Lewis acid in the case of the probe reaction between cyclopentadiene **(4)** and methyl acrylate **(12)**

This hydrogen bond donation to the methyl acrylate is, of course, also a Lewis acid interaction. The effect of Lewis acids on this reaction is well-known (see chapter 4), giving an increase in the rate of reaction. With the highly electronegative carbonyl oxygen partially donating a lone pair of electrons into the bond with the imidazolium salt, the carbon-carbon double bond would become more polarised as its electron density was pulled towards the carbonyl function. This, in turn would make the dienophile more susceptible to attack from a cyclopentadiene molecule. This effect has already been discussed in chapter 4. Any Lewis acid that can interact with the carbonyl group of the dienophile will lower the energy of its LUMO, enhancing its possible overlap with the

HOMO of the diene. This leads to an increase in the rate of reaction. As the polarity of the double bond is increased, so too is the amount of *endo*-selectivity, raising the value of N/X.

The carbonyl function on methyl acrylate is certainly a good hydrogen bond acceptor. However, as most of the cations on the ionic liquids used in this study are the same, the factor of hydrogen bonding to the dienophile should not be thought of in absolute terms, but relatively. As the dienophile is able to form these interactions with the ionic liquid cation, it immediately places itself in a position of competition with the ionic liquid anion, which is also capable of accepting the same hydrogen bonds.

Therefore, the higher the strength of the hydrogen bond formed by the anion, the stronger the competition faced by the dienophile to form a hydrogen bond with the cation. This means that the cation is less available to form hydrogen bonds with the dienophile. In this situation, dienophile-cation hydrogen bonds will be relatively rarer and weaker, leading to a lower N/X ratio as the dienophile double bond is less strongly polarised. Conversely, ionic liquid anions that form weaker hydrogen bonds offer less competition to the dienophile. The cation will become more available to interact with the dienophile. In this situation, dienophile-cation hydrogen bonds will be relatively more common and stronger, leading to a higher N/X ratio as the dienophile double bond is more strongly polarised.

The general trends that have been observed in the results to this section do confirm this hypothesis. As the hydrogen bonding ability of the anion increases, we see lower E_T^N values, meaning the cation is less available to form hydrogen bonds with the Reichardt's dye. We also see the value of the N/X ratio decrease due to the same effect. The opposite applies for the situation where the hydrogen bonding ability of the anion decreases. The E_T^N values of the solvent increase and the N/X ratio also increases.

In qualitative terms we can look at the situation in terms of the example used earlier which appeared to contradict the theory of solvophobicity being solely responsible for the

change in N/X over different ionic liquids. The comparison of [bmim][OTf] and [bmim][CH_3SO_3] can now be reassessed. The triflate anion has a strongly electron withdrawing trifluoromethyl group adjacent to the SO_3 function whereas the [CH_3SO_3]$^-$ anion has an electron donating methyl group in the same position. Although there is no data in the literature for [bmim][CH_3SO_3] and the ability of the [CH_3SO_3]$^-$ anion to form hydrogen bonds, we would expect it to form stronger hydrogen bonds than the triflate anion. This is simply because the lone pairs of electrons on the oxygen atoms that are used for such interactions on the [CH_3SO_3]$^-$ anion are more available for hydrogen bonding than those of the triflate anion. As this limits the ability of the triflate anion to form hydrogen bonds to the ionic liquid cation, we would expect the cation to form stronger hydrogen bonds with the carbonyl oxygen on methyl acrylate, resulting in a larger N/X ratio. As the anion-cation hydrogen bonds are relatively strong in [bmim][CH_3SO_3] we would expect weaker hydrogen bonds to be formed to the dienophile, giving a lower N/X ratio. Indeed this is the case as figure 6.2 shows.

When the anion is kept constant but the cation changed for a series of ionic liquids, (as has been seen in section 6.2.1.1) then hydrogen bonding is still of importance. As the anion is unaltered it can be said that the characteristics that make the cation more strongly hydrogen bonding can be directly applied to the probe reaction undergoing an increase in N/X. Although hydrogen bonding within the solvent to strengthen the local structure may be of importance, the increasing ability of the cation to form hydrogen bonds increases its Lewis acidity towards the dienophile.

The example whose data that was omitted from figure 6.3 study is [bmmim][BF_4]. In fact this is a very useful case to observe. Since it has no H^2 proton (the imidazolium ring 2 position is blocked by a methyl group) it has much less ability to hydrogen bond. This is not reflected as a big decrease in the E_T^N value for [bmmim][BF_4] (0.654) relative to [bmim][BF_4] (0.673) for example. However the N/X value is dramatically reduced (3.26 for [bmmim][BF_4] and 4.56 for [bmim][BF_4]).

6.2.1.4. A further investigation of the effects of Lewis acidity on the Diels-Alder probe reaction

Table 6.6: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) in [bmim][BF_4] with added [bmim]Cl

Label	Ionic Liquid	Identity of added substrate	Conc diene / M	Conc dienophile / M	Yield	N/X	Prods/DiCp
1	[bmim][BF_4][a]	None	1.270	1.110	84.6%	4.56	22.26
2	[bmim][BF_4]	0.5 M [bmim]Cl[b]	1.270	1.110	52.2%	4.62	10.36
3	[bmim][BF_4]	1.0 M [bmim]Cl[b]	1.270	1.110	50.3%	4.62	26.02
4	[bmim][BF_4]	2.0 M [bmim]Cl[b]	1.270	1.110	48.8%	3.72	7.93

[a] This is a reaction run from table 6.1

[b] The concentrations shown were made according to the volume of solvent used

NB: All reactions were carried out at 25 °C for 72 hours

The hypothesis that the methyl acrylate hydrogen bond acceptor is in competition with other hydrogen bond acceptors in the reaction mixture led us to attempt the probe reaction in the presence of an excess of a good Lewis base. If hydrogen bond donor ability is indeed the controlling factor in the performance of the Diels-Alder probe reaction in these solvents, then we would expect the presence of the Lewis base to hinder or slow down the reaction process. The solvent chosen for this study was [bmim][BF_4]. The species containing the Lewis base was [bmim]Cl. The chloride anion is a good hydrogen bond acceptor, and to ensure that upon introduction into the reaction system, it would be the only new species, [bmim]Cl (i.e. the same imidazolium cation as is present in the solvent) was used. Reaction 1 in table 6.6 shows the results of the chosen solvent alone, whereas reactions 2, 3 and 4 are runs carried out in the solvent with increasing concentrations of [bmim]Cl. It is important to note that samples more concentrated than

2.0 M were impossible to prepare at room temperature, as not all of the added [bmim]Cl would dissolve to form a solution.

It can be seen that although the yield is lowered to a significant degree, it stays at around this level even as the concentration of added [bmim]Cl increases. It can therefore be said that the yield after a set time is not concentration dependant. The value of the N/X ratio is quite a different matter. Staying at around the same level as the solvent-only reaction (reaction 1) in reactions 2 and 3, it is only at the maximium concentration that we see a significant reduction in N/X.

Although both the yield and N/X ratio show the consequences of the predicted effects of adding a Lewis base to the solvent system, they seem to be affected in different ways. The yield drops immediately on additions of low concentrations of [bmim]Cl and stays constant, but N/X stays constant and then drops at a higher concentration of [bmim]Cl. It is not understood why this occurs, but a more detailed study of the effects of concentration could perhaps clarify why this occurs.

However, at higher concentrations of [bmim]Cl it certainly hinders the pathway of *endo*-formation over *exo*-formation. The cations that can to some degree (in the solvent only reaction) hydrogen-bond to the carbonyl function of methyl acrylate, are less available to do this in these systems since the presence of a Lewis base in the reaction system causes more competition in terms of where the cation can form such interactions.

6.2.2. Moisture-sensitive ionic liquids composed of anions with flexible Lewis acidity/basicity

6.2.2.1. Moisture-sensitive ionic liquids

Table 6.7: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) in a selection of moisture-sensitive ionic liquids

Ionic Liquid	Conc diene / M	Conc dieneophile / M	Yield	N/X	Prods/DiCp
[bmim]Cl-$AlCl_3$ - acidic[a]	1.270	1.110	89.5%	10.11	20.28
[bmim]Cl-$AlCl_3$ - neutral[b]	1.270	1.110	69.2%	5.67	99.00
[bmim]Cl-$AlCl_3$ - basic[c]	1.270	1.110	63.0%	4.95	16.59
[bmim]Cl-$FeCl_3$ - acidic[a]	1.270	1.110	90.4%	5.62	44.45
[bmim]Cl-$FeCl_3$ - neutral[b]	1.270	1.110	89.1%	5.02	12.26
[bmim]Cl-$FeCl_3$ - basic[c]	1.270	1.110	86.1%	5.10	50.28
[bmim]Cl-$SnCl_2$ - acidic[a]	1.270	1.110	95.4%	5.25	99.00
[bmim]Cl-$SnCl_2$ - neutral[b]	1.270	1.110	91.6%	6.04	43.22
[bmim]Cl-$SnCl_2$ - basic[c]	1.270	1.110	71.4%	5.01	124.0

[a] All acidic ionic liquids were prepared by adding a 51 % molar ratio of metal chloride

[b] All neutral ionic liquids were prepared by adding an equal molar ratio of components, and buffering with dry NaCl

[c] All basic ionic liquids were prepared by adding a 51 % molar ratio of [bmim]Cl

NB: All reactions were carried out at 25 °C for 72 hours

The terms acidic, neutral and basic are used to describe the Lewis acidity of the ionic liquids. By altering the molar composition of the components added that make up the ionic liquids, it is possible to alter the Lewis acidity or basicity of the solvents. These ionic liquids work slightly differently to the others that have been seen so far that have

only one possible composition. Whereas the same components are always present in the liquids that we have studied up until now, these melts can exhibit vast structural changes from basic to acidic. In neutral form the chloride from the imidazolium salt will be used to form the anion shown in equation 6.1.

$$[bmim]Cl + MCl_x \rightarrow [bmim]^+ + [MCl_{x+1}]^- \quad (6.1)$$

However, with a molar excess of [bmim]Cl, there will be an excess of the chloride anion, which is Lewis basic (hence the term, basic ionic liquid). In the acidic ionic liquid, with a molar excess of the MCl_x species, an ionic liquid with a composition like that in equation 6.1 is formed, but with an added species, formed from the excess of MCl_x, as described in equation 6.2.

$$[MCl_{x+1}]^- + MCl_x \rightarrow [M_2Cl_{2x+1}]^- \quad (6.2)$$

It is this species that is responsible for the Lewis acidic nature of the melt, and causes us to give the name acidic to the resulting ionic liquid.

Table 6.7 shows that the solvents chosen for this study exhibit a descending yield and N/X ratio as the corresponding ionic liquid turns from acidic to neutral to basic. The exception to this rule is the ionic liquid [bmim]Cl-$SnCl_3$, whose N/X for the reaction carried out in the acidic variant of the ionic liquid is lower than for the neutral variant. Of all the ionic liquids, the acidic version of [bmim]Cl-$AlCl_3$ gives the most dramatic results, with a good yield, and an N/X ratio of over ten (the highest by far seen so far in this study). This indicates that $[Al_2Cl_7]^-$ is the strongest Lewis acid, compared to $[Fe_2Cl_7]^-$ and $[Sn_2Cl_5]^-$. This would be expected since $AlCl_3$ is a better Lewis acid than $SnCl_2$ or $FeCl_3$.

However, despite being so favourable, a recent study of the same reaction in a very similar melt by Lee[2.22] (which has been discussed in chapter 4) revealed an N/X ratio in the acidic version of the melt ([emim]Cl-$AlCl_3$) of 19. The neutral melt was not studied, but an N/X ratio of 5.25 of the same reaction carried out by Lee in the basic melt was comparable with our corresponding result.

It is not clear why the result in our acidic chloroaluminate melt is lower than that of Lee. The conditions used (the composition of the acidic melt) appear identical.

Small structural changes in the cation seem very unlikely to be able to cause such an increase in N/X, since we have seen earlier in this chapter that although they contribute to changes in the outcome of reactions, they do not do so to such a degree as we are seeing here. Also, since the Lewis acidity of these melts is directly attributable to the anion and not the cation, it seems that changing the length of an alkyl side chain would have even less effect than has been observed in previous ionic liquids where this is more significant to the overall Lewis acidity.

Lee's study used 0.42 M concentrations of diene and dienophile, whereas ours were nearly three times higher. The initial investigations of the reaction carried out in [emim]BF_4 in chapter 5 show that this may have some contribution. Table 5.3 shows that for that solvent system, the best N/X results achieved at room temperature used lower concentrations. However the increase in N/X for that system was not double, as we can see here, so maybe this reason is not enough to completely explain the difference in our results.

The most likely reason is a third possibility, the fact that small variations in the melt composition could affect the results of the reaction quite radically. Although our acidic melt is apparently of the same composition of Lee's, a small error in the relative amounts of $AlCl_3$ and [bmim]Cl added could lead to large changes in the concentration of the acidic species $[Al_2Cl_7]^-$. This has been demonstrated, and can be calculated with ease.[2.30] Consider equation 6.3 below.

$$a[bmim]Cl + bAlCl_3 \rightarrow (2a-b)[bmim][AlCl_4] + (b-a)[bmim][Al_2Cl_7] \quad (6.3)$$

In the acidic chloroaluminate ionic liquid used in this study, it is assumed that a 51 % molar percentage of $AlCl_3$ was used (therefore a = 0.49 and b = 0.51). According to equation 6.3, the molar ratio of $[bmim][Al_2Cl_7]$ present is 0.02 (or 2 %). $[bmim][Al_2Cl_7]$ is directly responsible for introducing the $[Al_2Cl_7]^-$ ion into the system. If, for example, the melt used in Lee's study was composed of a 51.5 % molar percentage of $AlCl_3$ (therefore a = 0.485 and b = 0.515). According to equation 6.3, the molar ratio present is 0.03 (or 3 %), which is exactly one and a half times the amount to be found in our acidic chloroaluminate ionic liquid. This could give rise to the fact that Lee's N/X ratio is almost double ours. However, this error must rely on the fact that we have added less $AlCl_3$ than Lee did. Also, we cannot assume (as in the numerical example above) where the error came from. This is a likely explanation, since only small changes in the relative amount of $AlCl_3$ added would give rise to large changes across the ionic liquid system.

This also gives us an insight into the amount of the strongly acidic Lewis acidic species present in the melt. At such low concentrations, we would assume it was acting as a catalyst. This is significant, since all the ionic liquids used in our previous studies that could affect the reaction made use of general properties that applied across the whole solvent system. Here, we see that although the solvent is classed as Lewis acidic, the strongest Lewis acid is present in catalytic quantities. This makes the third explanation to how our results differ so considerably from those of Lee more plausible. As the species $[Al_2Cl_7]^-$ is acting as a catalyst, only small concentration changes would be required to allow it to vary the effects it has on this reaction to a large extent, as we have already seen above.

In our study, it was found that altering the composition of our chloroaluminate melts to make them more Lewis acidic than indicated in table 6.7 led to the polymerisation all the cyclopentadiene present. As these solvents are air-sensitive and highly Lewis acidic, the presence of traces of water leads to the formation of a combined Lewis acid-Brønsted

acid superacid system. It is well-known that cyclopentadiene will undergo catalytic polymerisation in such systems.

6.2.2.2. Further investigations of the effects of Lewis acidity on the Diels-Alder probe reaction

Table 6.8: Results of the reaction between methyl acrylate (**12**) and cyclopentadiene (**4**) in a selection of moisture-stable ionic liquids with added Lewis and Bronsted acids

Label	Ionic Liquid	Identity of added substrate	Conc diene / M	Conc dienophile / M	Yield	N/X	Prods/DiCp
1	[bmim][OTf][a]	None	1.270	1.110	87.4%	4.49	13.71
2	[bmim][OTf]	$Sc(OTf)_3$[b]	1.270	1.110	85.8%	13.71	16.24
3	[bmim][OTf]	Dry $Sc(OTf)_3$[b]	1.270	1.110	95.6%	16.86	7.55
4	[bmim][Tf_2N]	None	1.270	1.110	89.9%	4.32	12.16
5	[bmim][Tf_2N]	$Sc(OTf)_3$[b]	1.270	1.110	polymer	-	-
6	[bmim][OTf]	HOTf[b]	1.270	1.110	polymer	-	-

[a] This is a reaction run from table 6.2

[b] 5 mol% (with respect to methyl acrylate) of catalyst was used in the reaction

NB: All reactions were carried out at 25 °C for 72 hours

Having investigated ionic liquids with strongly Lewis acidic anions, it was decided to investigate the addition of Lewis acids to the ionic liquid environment. The results are shown in table 6.8. Reaction 1 has already been discussed, but since it consists of the same ionic liquid to be used with the added salts it has been decided to include it as a means of comparison.

In chapter 4 the use of the lithium cation as a Lewis acid for Diels-Alder reactions was discussed,[2.19] when it made up part of the solvent known as LPDE (lithium perchlorate – diethyl ether solution). The introduction a strong Lewis acid into the reaction mixture was chosen as a route in the evolution of elucidating to what extent a catalyst could actually improve the Diels-Alder probe reaction. The Lewis acid and solvent system chosen were scandium triflate in [bmim][OTf]. As the solvent is already made up of triflate anions, the only new species to be introduced would be the scandium cation, the proposed Lewis acid. Scandium triflate has been used extensively as a catalyst in organic synthesis, especially as a Lewis acid catalyst for C-C bond formation reactions.[2.32] Recently it has been employed in ionic liquids, as a catalyst for Diels-Alder[2.33a] and Friedel-Crafts alkylation reactions.[2.33b] In this example, we would expect the scandium cation to act as a strong Lewis acid towards the carbonyl group on methyl acrylate. Figure 6.3 (above) shows the imidazolium cation acting as a Lewis acid in this manner *via* its H^2 proton. If the imidazolium cation were substituted with a scandium anion, this is how we would imagine it to be able to influence the reaction. Thus the mechanism is identical to figure 6.3, but it would be expected that the dominant Lewis acid is different.

Reactions 2 and 3 in table 6.8 show just how much scandium triflate can influence the reaction. Although the yield of reaction 2 is very similar to the uncatalysed version (reaction 1), the N/X ratio shows a dramatic improvement, not only compared to reaction 1, but over all the solvents systems attempted so far. The only solvent that has come close to producing an N/X of this value is the acidic version of [bmim][$AlCl_4$], which is known to be a strong Lewis acid.

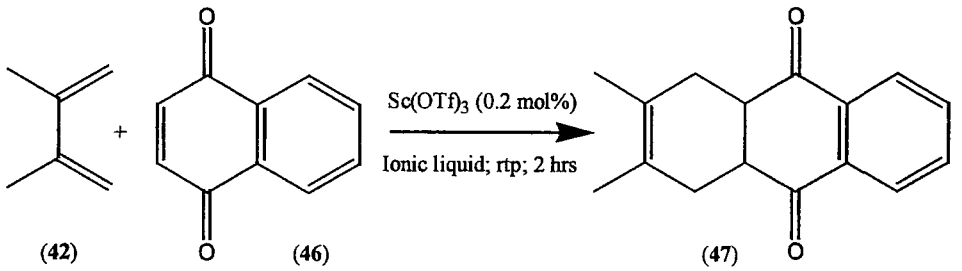
After this, it was decided to use pre-dried scandium triflate. Reaction 2 used commercially available scandium triflate which is known to be hydrated. Scandium triflate has a coordination sphere with approximately seven water molecules around it. It was thought that the removal of as much of or all of the coordinated water molecules would result in a more reactive scandium cation. Without the water molecules coordinated, it was hoped that Lewis acidity would become more pronounced. Run 3

shows this to be the case. As well as a very high yield, the N/X ratio is now the highest recorded in an ionic liquid in this study.

The next solvent system to be tried with scandium triflate was the imide ionic liquid [bmim][Tf_2N]. The commercially available hydrated version of scandium triflate was used. A suspected polymerisation reaction took place as soon as the reactants came into contact with the ionic liquid/added Lewis acid combination. The reaction took place in less than a minute, generating heat and forming a brown/black solid. The reaction could be a polymerisation of any of the cyclopentadiene, the methyl acrylate, the ionic liquid cation, or a combination.

Song, Choi and co-workers have also carried out the Diels-Alder reaction in ionic liquids with the use of scandium triflate as a Lewis acid catalyst.[2.33a] Studying the reaction between 1,4-napthaquinone (**46**) and 2,3-dimethyl-1,3-butadiene (**42**) (scheme 6.1, below) in a variety of solvents, they found that using [bmim][PF_6] and 10 mol% of scandium triflate caused a reaction to proceed in seconds with high exothermicity and a colour change of the reaction to dark brown.

They did not report any identification of the product. Neither were any possible causes for it discussed by them. Despite a different reaction and ionic liquid, the results of reaction 4 in table 6.8 appear to be the same. [bmim][PF_6] and [bmim][Tf_2N] are both classed as "hydrophobic" ionic liquids. That is, they form biphasic mixtures with water. It should be noted that they are not water-free. Only on lowering the concentration of scandium triflate in the ionic liquid by 100 times did Song, Choi and co-workers observe a Diels-Alder reaction in the ionic liquid.



Scheme 6.1: The Diels-Alder reaction between 2,3-dimethyl-1,3-butadiene (**42**) and 1,4-napthaquinone (**46**), carried out by Song, Choi and co-workers[2.33a]

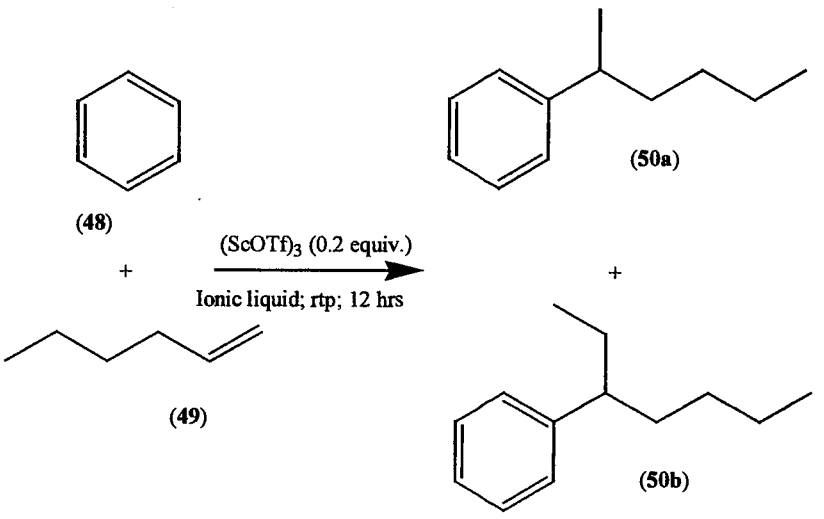
It should be noted that, strangely enough, Song, Choi and co-workers did not attempt the Diels-Alder reaction from scheme 6.1 in their chosen ionic liquids without the presence of scandium triflate. Therefore, despite the fact that the reaction proceeded with high yield for them, the reader has no indication as to whether this is due to the fact that the catalyst was at a suitable concentration to affect the reaction positively, or whether the catalyst was at too low a concentration to even affect the reaction. Thus we have no idea whether the substrates are reactive on their own in ionic liquids or not. A useful study of this would have been to run the same Diels-Alder reaction in solvent only and compare the results with those for the corresponding solvent and 0.2 mol% scandium triflate systems.

Although there is no study for this in Song, Choi and co-workers' report, a very similar reaction has been carried out in this study (section 5.2.3.2) between 1,4-benzoquinone (**39**) and 2,3-diemthyl-1,3-butadiene (**42**). No catalyst was used, and the reaction solvent was [emim][BF_4]. It was shown (by GC mass spectroscopy) that attack of both double bonds on 1,4-benzoquinone was taking place, which resulted in the formation of compound (**41**) (see figure 5.1). This indicates that the substrates used are reactive in the ionic liquid, since the level of reactivity could not be controlled in our study for this reaction. These results could be extrapolated to this case. We can be fairly certain that on their own, the starting materials used by Song, Choi and co-workers are also highly reactive in ionic liquids alone. This would lead to a lack of certainty as to whether the

reaction they studied is even being catalysed at such low concentrations of scandium triflate. Since the reaction we studied is highly reactive in the ionic liquid alone, we would expect a similar outcome for the reaction of Song, Choi and co-workers. This puts any possible benefits derived by the use of such low concentrations of scandium triflate into doubt.

The same research group have also used other ionic liquids with dissolved scandium triflate to catalyse the same Diels-Alder reaction.[2.33a] The only suggestion they have made regarding the reaction in [bmim][PF_6] with 10 mol% scandium triflate is that it is "too fast to control". Also, there is no mention of whether the higher concentration of scandium triflate was attempted in other ionic liquids, and if this was more succesful. As one of the other ionic liquids used in their study was [bmim][OTf], a hydrophilic ionic liquid, this would have been a useful comparison.

Another scandium triflate-catalysed reaction that Song, Choi and co-workers have attempted in ionic liquids is the Friedel-Crafts alkylation of aromatic compounds with alkenes.[2.33b] In particular, the reaction between benzene (**48**) and hex-1-ene (**49**) (scheme 6.2, below) exhibited some interesting results that can be used to further our discussion. Again, the reaction was carried out in a variety of ionic liquids, some "hydrophilic" and some "hydrophobic".

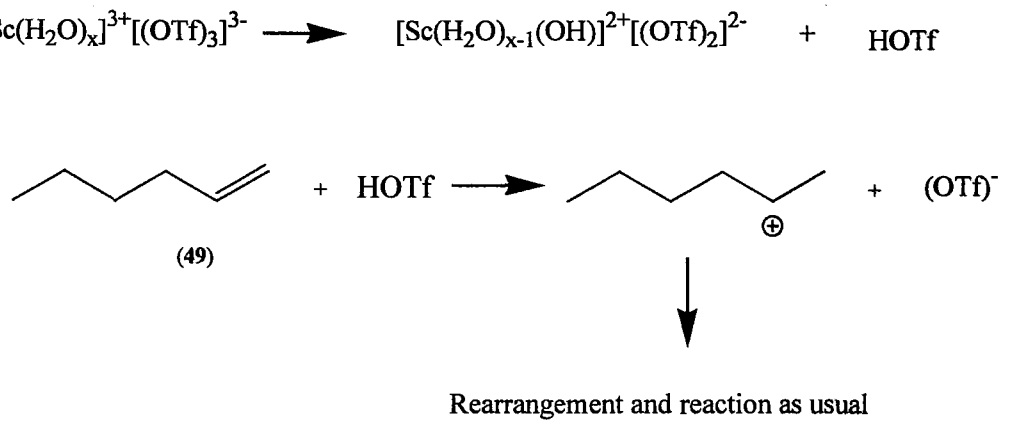


Scheme 6.2: The Friedel-Crafts alkylation of benzene (**48**) with hex-1-ene (**49**), carried out by Song, Choi and co-workers[2,33b]

Alkyl chain rearrangements occur in this reaction, giving a mixture of products. This is an indication that the species that attacks the benzene ring is a free carbonium ion. What is particularly noteworthy is that using the conditions described, no reaction was observed in the "hydrophilic" ionic liquids used ([emim][BF_4], [emim][OTf] and others with variations of the imidazolium cation but the same anions). The "hydrophobic" ionic liquids ([emim][PF_6], [emim][SbF_6] and others with variations of the imidazolium cation but the same anions) gave good results. The only suggestion that Song, Choi and co-workers made regarding any differences in the system observed between the two types of ionic liquid was the solubility of scandium triflate. In the "hydrophobic" ionic liquids (which support the reaction) the Lewis acid catalyst is only slightly soluble, and in the "hydrophilic" ionic liquids (where no reaction occurs) the Lewis acid catalyst is highly soluble. In general terms, the expected outcome would be for the catalyst to be more active in the ionic liquid that it is more soluble in. Although the observed outcome does not reflect this, it does not appear to be a coincidence that these two very different reactions occur in only one type of the ionic liquid (when scandium triflate is used as a catalyst), and moreover the type that the other reaction does not work in.

The results from Song, Choi and co-workers that have been described have led us to re-investigate our results using scandium triflate as a Lewis acid catalyst for the Diels-Alder probe reaction in ionic liquids. As shown in table 6.8, our study used two ionic liquids; [bmim][OTf] which is "hydrophilic" and [bmim] [Tf_2N] which is "hydrophobic". The reaction worked in [bmim][OTf] but gave a polymeric product in [bmim][Tf_2N]. However the results for the Friedel-Crafts reactions carried out by Song, Choi and co-workers show that the reaction only works in "hydrophobic" ionic liquids. Their results also show that alkene rearrangement occurs prior to ring substitution. This indicates that the carbonium ion is formed before it attacks a benzene molecule. The formation of a carbonium ion in the Friedel-Crafts reaction requires that a proton be supplied to the alkyl reagent. This can supplied by the solvent, when traditional organic solvents are used. It is very unlikely that the ionic liquid itself could donate a proton to the reaction, as this would lead to an unstable species. Another possible proton source would be the benzene molecule, but this too is not the case here, since the carbonium ion is formed before attacking benzene. Commercially available scandium triflate is in fact a hydrated salt $[Sc(H_2O)_7]^{3+}[OTf_3]^{3+}$. This is the most likely source of the proton (see scheme 6.3).

The proton source, according to our proposal, is the water of hydration that forms a shell around the scandium anion. Scheme 6.3 shows that triflic acid can be formed if a water molecule dissociates into a proton and a hydroxide ion, and the proton associates with one of the triflate anions. The hydroxide ion would be expected to stay bonded to the scandium cation, so reducing the overall charge on the complex. In our view, it is the this proton that attacks the hex-1-ene, in order to allow rearrangement of the carbonium ion before it attacks benzene. This is also shown in scheme 6.3.



Scheme 6.3: Proposed mechanism for the formation of the carbomiun ion in the Friedel-Crafts alkylation of benzene (**48**) with hex-1-ene (**49**)[2.33a]

The products of the Friedel-Crafts alkylation would be the alkylated benzene molecule and a proton, which would lead to the regeneration of triflic acid. In this way, triflic acid would be acting as a catalyst for the reaction. We can deduce that the process to produce triflic acid, seen in figure 6.3 does not need to happen on a large scale. If scandium trflate is added in catalytic quantities, then the amount of triflic acid produced will be relatively small (even if all three of the triflate anions on scandium triflate form triflic acid, leaving the species scandium hydroxide).

The combination of Lewis acids with Brønsted acids leads to the formation of superacids.[2.34] It is possible that the combination of the triflic acid with the scandium complex will have this effect in ionic liquids. This will be investigated in the future.

It is interesting that in their study of the Friedel-Crafts reaction,[2.33b] Song, Choi and co-workers observed that using even larger amounts of scandium triflate in organic solvents (dichloromethane, acetonitrile, nitromethane and nitrobenzene) gave no reaction. We can also deduce that this is an effect that is only seen in "hydrophobic" ionic liquids. It is not known why this effect is not observed in the "hydrophilic" ionic liquids. Evidently, more

study is needed to deduce why this effect only takes place in one specific type of ionic liquid.

The consequences of this study on Friedel-Crafts reactions have important implications for Diels-Alder reactions catalysed by scandium triflate in ionic liquids. The fact that the probe reaction we studied, and the reaction studied by Song, Choi and co-workers[2.33a] did not work in the "hydrophobic" ionic liquids (with polymer formation taking place instead, see below), and that they did work with very satisfactory results in the "hydrophilic" ionic liquids has already been mentioned. Our "hydrophobic" ionic liquid was [bmim][Tf_2N]. The model postulated above can give us some information as to what is actually happening. Although it is not known why, the results obtained show that we would not expect the formation of triflic acid in the "hydrophilic" ionic liquids. Instead, the scandium cations should be acting as a strong Lewis acid and interacting with the carbonyl function of the dienophile to speed up and improve the selectivity of the reaction.

However, in considering what takes place in the "hydrophobic" ionic liquids, we should again consider the first step of scheme 6.3, namely the formation of triflic acid. Our assumption is that it is the triflic acid that causes the formation of the unwanted polymer and the breakdown of any possible reaction between methyl acrylate and cyclopentadiene. We would expect the polymer to be made up solely of either one of the starting materials of the Diels-Alder reactions. In order to test this, we would need to know whether a system with a known quantity of triflic acid could cause such a polymerisation (since scheme 6.3 is merely a hypothesis of what could be happening in these systems), and whether the polymer formed was indeed of the composition that we would expect. Both these tests have been carried out with positive results.

The same solvent, substrate concentrations and conditions as run 2 in table 6.8 were used to test whether triflic acid hindered or accelerated the probe reaction. Scandium triflate was not used in the reaction, but the same quantity (5 mol% with respect to methyl acrylate) of triflic acid was used in its place (see table 6.8, entry 6). The starting materials

for the probe reaction were pre-dried and added (in the order dienophile and then diene). On the addition of cyclopentadiene, a sudden exothermic reaction, resulting in the formation of a brown/black solid was observed. As this reaction had worked with exactly the same conditions but scandium triflate in the place of triflic acid, it is logical to conclude that the presence of triflic acid does in fact cause the formation of the suspected polymeric compound. We can conclude that triflic acid is not produced from scandium triflate in the "hydrophilic" ionic liquids, but we could assume that its presence in any solvent would have the same effects upon the probe reaction, since it is a strong proton donor.

The second test involved the analysis of the polymer. ^{1}H NMR studies of the polymer were taken. As two starting materials were present in the reaction mixture that could have potentially been polymerised, this was to confirm whether both, or just one of the substrates had undergone this process. Comparison with the literature[2.35] showed the species formed to be made up of poly(cyclopentadiene) only, with a mixture of both 1,2-addition and 1,4-addition.

We can assume, therefore, that the addition of a proton to cyclopentadiene from a strong proton donor source (triflic acid) causes cationic polymerisation to take place in preference to the desired Diels-Alder probe reaction. Again, it is not yet known why the formation of triflic acid from scandium triflate only appears to occur to a noticeable degree in the "hydrophobic" ionic liquids.

It has already been discussed that the Diels-Alder reaction that Song, Choi and co-workers studied in these systems[2.33a] did work in a "hydrophobic" ionic liquid when the concentration of scandium triflate was reduced by 50 times (from 10 to 0.2 mol%). As was concluded, at such low concentrations, it would not be sure whether the catalyst is actually present in a large enough quantity to actually catalyse the reaction effectively. At such concentrations it could well be the ionic liquid that is playing the main role in improving the reaction. No comparison is given in their study to the performance of the reaction in the ionic liquid alone.

The hypothesis and evidence to back it up that was put forward above does explain what is most likely to be happening in the "hydrophobic" ionic liquids when scandium triflate is used as a catalyst. However, it is not yet known why this process of triflic acid generation (that hinders the Diels-Alder reaction yet aids the Friedel-Crafts reaction) does not occur in the "hydrophilic" ionic liquids. In order to test this further it would be useful for future work in this area to exploit the fact that it is possible to pre-dry scandium triflate, and thus remove the hydration sphere. Using this species in a "hydrophobic" ionic liquid as the catalyst would be able to confirm whether the proton source is indeed the water molecules around the scandium cation, as we believe.

6.3. Kinetic studies of ionic liquid systems already used as solvent systems for the Diels-Alder probe reaction

Table 6.9: Second order rate constants for the probe reaction in a selection of solvents with added Lewis and Bronsted acids

Label	Ionic Liquid	Identity of added substrate	$k_2 \times 10^5 / M^{-1} s^{-1}$
1	[bmim][BF_4]	None	12.98
2	[bmim][OTf]	None	12.40
3	[bmim][OTf]	$Sc(OTf)_3$[a]	32.57
4	[bmim][OTf]	$Sc(OTf)_3$[a]	20.04
5	[bmim][OTf]	$Sc(OTf)_3$[a]	79.77
6	[bmim][OTf]	Dry $Sc(OTf)_3$[a]	113.66
7	[bmim][OTf]	HOTf[a]	Polymer
8	[bmim][Tf_2N]	None	10.95
9	[bmim][Tf_2N]	$Sc(OTf)_3$[a]	Polymer
10	[bmim]Cl-$AlCl_3$ - basic[b]	None	125
11	[bmim]Cl-$AlCl_3$ - acidic[c]	None	297
12	EAN[d]	None	17
13	EAN[d]	LiCl[e]	16
14	EAN[d]	LiI[e]	54
15	water[d]	None	300
16	1-chlorobutane[f]	None	5.3
17	SDS[g]	None	100
18	Dioxane[g]	None	1.18

[a] 5 mol% (with respect to methyl acrylate) of catalyst was used in the reaction

[b] Result from ref. 2.22 - composition 48 mol% $AlCl_3$

[c] Result from ref. 2.22 - composition 51 mol% $AlCl_3$

[d] Results from ref. 2.20

[e] A 1.0 M solution of the added salt was used in the reaction

[f] Result from ref. 2.36

[g] Results from ref. 2.37

NB: All reactions were carried out at 20 °C except for run 15 which is reported to be carried out at 35 °C.

Table 6.9 shows the results from the kinetic studies of the Diels-Alder reaction in a variety of ionic liquids, some containing additional Lewis and Brønsted acids. Entries 1-9 are all results from this study. The plots of the runs that worked can be found in the appendix. Entries 10-18 are from the literature, and are included as a comparison of the results we obtained to similar studies carried out in other solvents. Where the k_2 result is simply described as polymer (entries 7 and 9), the desired reaction did not proceed due to the formation of poly-cyclopentadiene. The reasoning for this has already been discussed in section 6.2.2.2).

Entries 3-5 are simply repeat runs of the same reaction, where methods of stirring were altered. As can be seen, this gave radically different results. Entry 3 was the first attempt. Stirring was set at medium, and two layers were observed to have formed on addition of the starting materials to the ionic liquid. Sampling was taken exclusively from the top layer, which was organic in composition. Entry 4 was the first repeat, stirring was constant and medium, until the time of reaction reached 70 minutes, at which point it was made vigourous. When this happened, the two layers were observed to merge, and sampling was continued from the single reaction layer. Entry 5 was the final repeat of this reaction. Stirring was vigourous from the beginning, and kept constant to ensure that only one layer was present from the commencement of the reaction.

It is the third run of this reaction (entry 5) that has given the fastest rate of reaction by far (according to k_2). From this data, we can assume that the presence of a biphasic system decreases the rate of reaction, presumably due to the fact that the organic reactants must cross the resultant phase boundary in order to react in the ionic liquid. This adds an additional step to the reaction process, which doen not exist in a monophasic system. A biphasic system was not observed in any of the other reactions attempted, except when the same ionic liquid and dry $Sc(OTf)_3$ were used (entry 6). In this case, as with entry 5, vigourous stirring was employed from the start of the reaction.

The three ionic liquids used in this study without any added catalyst exhibit very similar results ([bmim][BF_4] – entry 1, [bmim][OTf] – entry 2, and [bmim][Tf_2N] – entry 8). However, a slight variation in the rate of reaction k_2 is observed, in the order [bmim][Tf_2N]<[bmim][OTf]<[bmim][BF_4]. If we compare the E_T^N values for these ionic liquids then we see a pattern emerging. These also follow a pattern according to the order we see in k_2, namely [bmim][Tf_2N] (0.642)<[bmim][OTf_3] (0.667)<[bmim][BF_4] (0.673).

It has previously been discussed (section 6.2.1.3) how the E_T^N value (which is a direct measure of the hydrogen bond donating ability of the ionic liquid cation) would tell us very little, if anything about the hydrogen bond accepting strength of the anion in these systems. Table 6.5 ilustrated how the strength of the hydrogen bonds formed by these three anions varied in the order [bmim][Tf_2N]<[bmim][OTf_3]<[bmim][BF_4]. Again, this follows the same order as the two relationships shown above. Section 6.2.1.3 discussed how these factors probably cause an effect in the value of the N/X ratio. However, the rate will also depend on this relationship. As [bmim][Tf_2N] forms the weakest hydrogen bonds, in terms of both the cation and anion, it would not be expected to act as a strong Lewis acid towards the dienophile methyl acrylate (see figure 6.3). As has already been seen this would lower the N/X ratio.

However, a relatively weak Lewis acid interaction with the carbonyl group on methyl acrylate would also be expected to increase the rate of reaction. This is because any Lewis acid that can interact with the carbonyl group of the dienophile will lower the energy of its LUMO, enhancing its possible overlap with the HOMO of the diene (see figure 6.4, below). This leads to an increase in the rate of reaction. The order of rate of reaction shown between the three ionic liquids above is thus explainable in terms of the strength of the hydrogen bond accepting ability of the anion. As the strength of the possible hydrogen bonds formed by the anion increases, so too does the rate of reaction.

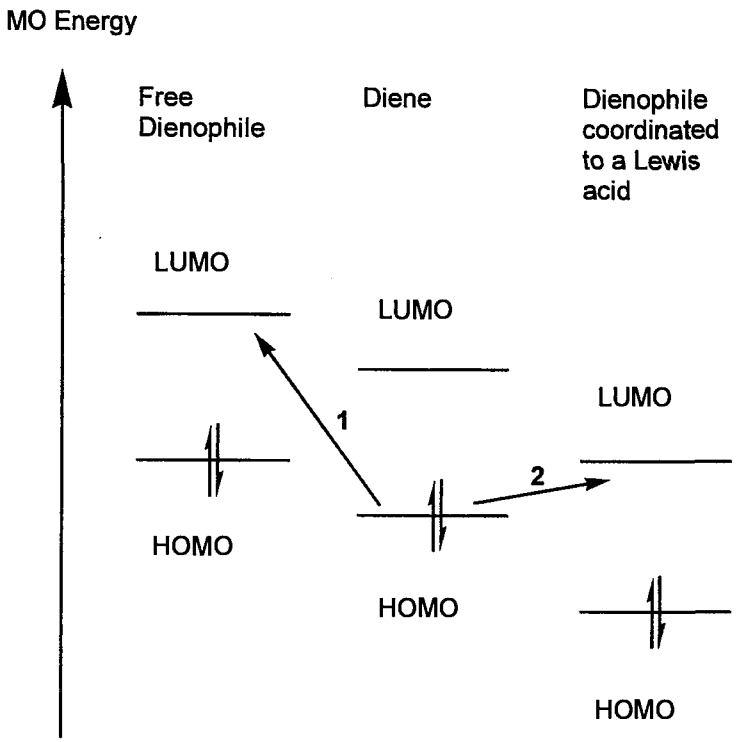


Figure 6.4: Representation of the overlap between the HOMO of the diene, and the LUMO of the dienophile, for free dieneophiles and dienophiles with Lewis acid/base interactions. Pathway 1 is energetically more unfavourable than pathway 2, since the energies of the orbitals are closer for any overlap.

The addition of scandium triflate (entries 3-5 in table 6.9) to these systems gives a strong Lewis acid species that, too, can bind to the carbonyl group of the dienophile. It has already been seen that scandium triflate can increase the N/X ratio, when used as a catalyst (see section 6.2.2.2). Entry 5, which was mixed into one phase from the beginning of the reaction, shows more than a six-fold increase in the rate of reaction k_2, than the equivalent uncatalysed ionic liquid. This is a more dramatic effect than the N/X ratio underwent with the addition of the same catalyst in the same solvent system.

As with the study into the effects on the N/X ratio using scandium triflate, the pre-dried version of the salt was next used. Commercially available scandium triflate has a

coordination sphere of seven water molecules around the scandium cation. It was hoped that by removing them, the scandium cation would be rendered more reactive, in terms of its ability to act as a Lewis acid and coordinate to the carbonyl group on methyl acrylate. Whether this had actually occurred would be known by the outcome of the kinetic study on the probe reaction in this environment. The results of this reaction (entry 6 in table 6.9) do indeed confirm this. The rate of reaction k_2, is seen to rise by over one and a half times from using the undried scandium triflate. As the only change between entries 5 and 6 is the removal of the water of coordination from the scandium cation (i.e. not a major change in the reaction system or the Lewis acid used), we would not expect this to be reflected in a huge increase in the rate. Rather, this can be seen as a fine-tuning of the existing reaction environment.

Finally, some indication to where these results stand in comparison to similar studies carried out in other solvent systems should be given. Entries 10-18 in table 6.9 have been collected from the literature. The results from this study for the three uncatalysed ionic liquids (entries 1, 2 and 8) are all far better than organic solvents such as 1-chlorobutane (entry 16), and even non-aqueous solvophobic solvent systems such as dioxane (entry 18). They are also comparable with the ionic liquid ethylammonium nitrate. The scandium triflate catalysed reaction (entry 5) compares well to that of ethylammonium nitrate with added lithium iodide (entry 14 – addition of LiI is to increase the solvophobicity of the system, see chapter 4 for discussion). The reaction catalysed by predried scandium triflate shows the highest k_2 value (and thus fastest rate of reaction).

It is perhaps surprising that not only the Lewis acidic version of [bmim]Cl-$AlCl_3$ (entry 10), but also the Lewis basic version of the same liquid (entry 11) show an improvement in rate over all the results of this study. We would expect the Lewis acidic liquid to improve the reaction rate over the Lewis basic one, and this is indeed the case. However, even the most Lewis acidic system from this study (entry 6) shows an unfavourable rate of reaction in comparison to the Lewis basic ionic liquid (entry 10). This is because the molar ratio of [bmim]Cl used to make the ionic liquid in entry 10 is only 0.52. This is not highly Lewis basic. We would expect this liquid to be mainly composed of $[AlCl_4]^-$ ions,

with only a slight excess of chloride ions (the Lewis basic species) present. Although this will hinder the reaction relative to the Lewis acidic version of the same liquid, it should be stressed that this is relative to that version and a gradual change as the concentration of chloride ion is increased. Section 6.2.1.4 illustrated this point. As the chloride ion concentration is increased in a solution of [bmim][BF_4], so the yield and N/X decrease gradually.

7. EXPERIMENTAL FOR SECTION 2

7.1. General

All manipulations were carried out using standard vacuum and Schlenk techniques under an atmosphere of dry nitrogen, or in a drybox under an atmosphere of dry nitrogen.

Dried methyl acrylate was used in all cases. Methyl acrylate was dried by distillation from the appropriate drying agent ($CaCl_2$).

Dicyclopentadiene was cracked by distillation through a column packed with glass beads. Dry cyclopentadiene was used in all cases. Cyclopentadiene was dried during the cracking process by distillation from the appropriate drying agent ($Mg(ClO_4)_2$).

^1H NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transform spectrometer. Cas chromatography fast atom bombardment mass spectra (GC Mass Spectra) were recorded by the mass spectrometry laboratory of the Department of Chemistry of Imperial College, University of London.

GC measurements were performed using an Agilent 4890D GC spectrometer. The column fitted was a Hewlett Packard HP-5 (Crosslinked 5 % PH ME Siloxane) column, of length 15 m, diameter 0.53 mm, and with a 1.5 μm film thickness. The conditions used for all runs were as follows:

- **Flow rate:** 100 mL/min of argon
- **Inlet temperature:** 200 °C
- **Detector temperature:** 250 °C
- **Total run time:** 14 min

- **Oven conditions:** maintained at 50 °C for 6 mins, then ramped at +15 °C/min for 4 mins, then maintained at 110 °C for 1 min.

7.2. Ionic Liquid Preparation

The ionic liquids used in this project were as follows:

[emim][BF_4], [bmim][BF_4], [hmim][BF_4], [bmmim][BF_4], [bmim][PF_6], [bmim][ClO_4], [bmim][NO_3], [bmim][CF_3SO_3], [bmim][CH_3SO_3], [bmim][$(CF_3SO_2)_2N$], [bmim][$CH_3CH(OH)CO_2$], [bmim]Cl-$AlCl_3$ slightly Lewis acidic {$X(AlCl_3)$ = 0.51}, [bmim]Cl-$AlCl_3$ neutral buffered {$X(AlCl_3)$ = 0.50}, [bmim]Cl-$AlCl_3$ slightly Lewis basic {$X(AlCl_3)$ = 0.48},[bmim]Cl-$FeCl_3$ slightly Lewis acidic {$X(FeCl_3)$ = 0.51}, [bmim]Cl-$FeCl_3$ neutral buffered {$X(FeCl_3)$ = 0.50}, [bmim]Cl-$FeCl_3$ slightly Lewis basic {$X(FeCl_3)$ = 0.48}, [bmim]Cl-$SnCl_2$ slightly Lewis acidic {$X(SnCl_2)$ = 0.51}, [bmim]Cl-$SnCl_2$ neutral buffered {$X(SnCl_2)$ = 0.50}, [bmim]Cl-$SnCl_2$ slightly Lewis basic {$X(SnCl_2)$ = 0.48}.

All ionic liquid preparations have been fully described and characterised in chapter 3.

7.3. Diels-Alder Reactions

In many cases, only one typical procedure has been given. The reactants are displayed in the results and discussion chapters 5 and 6 in terms of the concentrations they were used in. In this chapter they are referred to in terms of the relative amount that was added to

the volume of ionic liquid used for the reaction. In many cases where multiple runs of one reaction were performed, the initial concentration (and thus the amount of reactants used) was varied. In some cases the time of reaction was varied. In some cases the temperature of reaction was varied. The typical procedures described in this chapter do not reflect this. Cross-reference with the results in chapters 5 and 6 should clarify this point.

7.3.1. 3-Methyl-bicyclo-[2.2.1]-hept-5-ene-2-carbaldehyde (31a/b)

Typical Procedure

Trans-crotonaldehyde (1.00 cm^3; 0.012 mol) and freshy cracked cyclopentadiene (1.04 cm^3; 0.013 mol) were added to 10 cm^3 [emim][BF_4] and stirred for 72 hours at 25 °C. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, and the product ratio determined by gas chromatography.

- GC analysis: *Exo*-product appears at 5.230 mins; *Endo*-product appears at 5.578 mins.

7.3.2. 2-Methyl-bicyclo-[2.2.1]-hept-5-ene-2-carbaldehyde (33a/b)

Typical Procedure

Methacrolein (1.00 cm^3; 0.012 mol) and freshy cracked cyclopentadiene (1.04 cm^3; 0.013 mol) were added to 10 cm^3 [emim][BF_4] and stirred for 72 hours at 25 °C. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, and the product ratio determined by gas chromatography.

- GC analysis: *Exo*-product appears at 5.064 mins; *Endo*-product appears at 5.391 mins.

7.3.3. 2-Methyl-bicyclo-[2.2.1]-hept-5-ene-2-carboxylic acid methyl ester (17a/b)

Typical Procedure

Methyl methacrylate (3.08 cm^3; 0.029 mol) and freshy cracked cyclopentadiene (3.08 cm^3; 0.037 mol) were added to 10 cm^3 [emim][BF_4] and stirred for 72 hours at 25 °C. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, and the product ratio determined by gas chromatography.

- GC analysis: *Exo*-product appears at 9.862 mins; *Endo*-product appears at 10.435 mins.

7.3.4. Bicyclo-[2.2.1]-hept-5-ene-2-carboxylic acid methyl ester (13a/b)

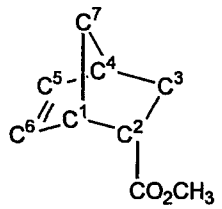
Typical Procedure

Methyl acrylate (3.08 cm^3; 0.029 mol) and freshy cracked cyclopentadiene (3.08 cm^3; 0.037 mol) were added to 10 cm^3 [emim][BF_4] and stirred for 72 hours at 25 °C. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, and the product ratio determined by gas chromatography. An analysis of the *endo-* and *exo-* products is included below.

- GC analysis: *Exo*-product appears at 12.673 mins; *Endo*-product appears at 13.015 mins.

Endo-Product

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 6.16 (1H, m, $C^6\underline{H}$), 5.90 (1H, m, $C^5\underline{H}$), 3.60 (3H, s, $CO_2C\underline{H_3}$), 3.17 (1H, m, $C^1\underline{H}$), 2.93 (1H, m, $C^4\underline{H}$), 2.88 (1H, m, $C^2\underline{H}$), 1.89 (2H, m, $C^3\underline{H_2}$), 1.27 (2H, m, $C^7\underline{H_2}$). (see figure 7.1)



endo **(13a)**

Figure 7.1: Diagram of the *endo*-product of the reaction between methyl acrylate and cyclopentadiene. The carbon atoms are numbered to aid analysis of the ^{1}H NMR spectrum. **NB:** The *exo*-product (**13b**) is identical to this figure, except for the CO_2CH_3 group, which points upwards

Exo-Product

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 6.06 (1H, m, $C^6\underline{H}$), 5.92 (1H, m, $C^5\underline{H}$), 3.66 (3H, s, $CO_2C\underline{H_3}$), 3.12 (1H, m, $C^1\underline{H}$), 2.89 (1H, m, $C^4\underline{H}$), 2.38 (1H, m, $C^2\underline{H}$), 1.42 (2H, m, $C^3\underline{H_2}$), 1.24 (2H, m, $C^7\underline{H_2}$). (see figure 7.1)

Other Procedures

In cases where the ionic liquid was varied, 10 cm^3 of the appropriate ionic liquid was used.

In cases where the reaction was carried out at elevated temperatures, the apparatus was modified to incorporate a reflux setup. The temperature was adjusted accordingly.

In cases where additional reagents were added to the ionic liquid, this was done before the introduction of the starting materials.

Kinetic measurements were carried out using the same amounts of starting materials in the same volume of the appropriate ionic liquid, with the exception of cyclopentadiene, which was added in excess (4.00 cm^3; 0.049 mol). The internal standard used was chlorobenzene (0.80 cm^3). In general, 2 μL readings were taken by microsyringe every 5 minutes for the first hour, every ten minutes for the second hour, and every 30 minutes after that. Approximate results and curves for the dissipation of methyl acrylate were plotted simultaneously, and the reaction terminated when five half-lives had been achieved. This could vary quite considerably in time.

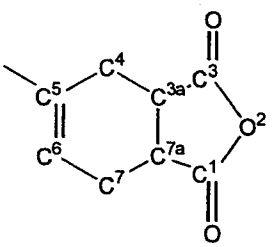
7.3.5. 5-Methyl-3a,4,7,7a-tetrahydro-isobenzofuran-1,3-dione

Typical Procedure

Maleic anhydride (1.35 g; 0.014 mol) was dissolved in 10 cm^3 [emim][BF_4] and isoprene (6.90 cm^3; 0.069 mol) added. The reaction vessel was stirred for 72 hours at 25 °C, under a closed system. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, leaving a white crystalline solid (Yield: 2.00 g; 86.0 %).

- GC mass spectrum: Peak at 14:51 mins in the GC confirmed to be the desired product by mass spectrometry, (EI+) m/z: 166 $(M)^+$.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 5.64 (1H, m, $C^6\underline{H}$), 3.37 (2H, m, $C^{3a}\underline{H}$ and $C^{7a}\underline{H}$), 2.55 (2H, m, $C^7\underline{H}$ (underside) and $C^4\underline{H}$ (underside)), 2.29 (2H, m, $C^7\underline{H}$ (topside) and $C^4\underline{H}$ (topside)), 1.79 (3H, s, $C\underline{H}_3$).



(38)

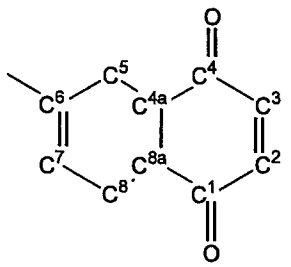
Figure 7.2: Diagram of the product of the reaction between maleic anhydride and isoprene. The carbon atoms are numbered to aid analysis of the ^{1}H NMR spectrum

7.3.6. 6-Methyl-4a,5,8,8a-tetrahydro-[1,4]napthoquinone

1,4-Benzoquinone (0.60 g; 0.0055 mol) was dissolved in 10 cm^3 [emim][BF_4] at 70 °C. The solution was cooled to 55 °C and isoprene (2.76 cm^3; 0.028 mol) was added. The reaction vessel was stirred for 72 hours at 55 °C, under a closed system. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, leaving an orange crystalline solid (Yield: 0.75 g; 77.0 %).

- GC mass spectrum: Peak at 20:23 mins in the GC confirmed to be the desired product by mass spectrometry, (EI+) m/z: 172 $(M\text{-}4H)^+$, 157 $(M\text{-}O)^+$, 144 $(M\text{-}2O)^+$, 129 $(M\text{-}2O\text{-}CH_3)^+$.

- ^{1}H-NMR (270 MHz, Acetone-d_6) δ/ppm: 6.49 (2H, s, $C^2\underline{H}$ and $C^3\underline{H}$), 5.56 (IH, m, $C^7\underline{H}$), 3.21 (2H, m, $C^{4a}\underline{H}$ and $C^{8a}\underline{H}$), 3.11 ($C^5\underline{H}$ (underside) and $C^8\underline{H}$ (underside)), 2.04 (2H, m, $C^5\underline{H}$ (topside) and $C^8\underline{H}$ (topside)), 1.78 (3H, s, $C\underline{H_3}$).



(40)

Figure 7.3: Diagram of the product of the reaction between 1,4-benzoquinone and isoprene. The carbon atoms are numbered to aid analysis of the ^{1}H NMR spectrum

7.3.7. 4-Methyl-cyclohex-3-enecarboxylic acid methyl ester (attempted)

Typical Procedure

Methyl acrylate (0.81 cm^3; 0.010 mol) and isoprene (1.00 cm^3; 0.010 mol) were added to 10 cm^3 [emim][BF_4] and stirred for either 4.5, 48, 72 or 120 hours 25 °C. No product was observed upon extraction with diethyl ether (3x20 cm^3).

7.3.8. 5,6-Dimethyl-3a,4,7,7a-tetrahydro-isobenzofuran-1,3-dione

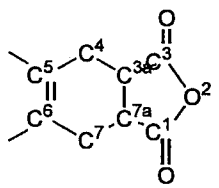
Typical Procedure

Maleic anhydride (1.76 g; 0.018 mol) was dissolved in 10 cm^3 [emim][BF_4] and 2,3-dimethyl-1,3-butadiene (2.03 cm^3; 0.018 mol) added. The reaction vessel was stirred for 20 hours at 25 °C, under a closed system. The product mixture was extracted from the

ionic liquid with diethyl ether (3x20 cm^3). The diethyl ether was removed by rotary evaporation, leaving a white crystalline solid (Yield: 2.30 g; 71.0 %).

- GC mass spectrum: Peak at 15:53 mins in the GC confirmed to be the desired product by mass spectrometry, (EI+) m/z: 180 $(M)^+$, 152 $(M\text{-}2O)^+$, 137 $(M\text{-}2O\text{-}CH_3)^+$.

- ^{1}H-NMR (270 MHz, Chloroform-*d*) δ/ppm: 3.29 (2H, s, $C^{3a}\underline{H}$ and $C^{7a}\underline{H}$), 2.24 (2H, m, $C^7\underline{H}$ (underside) and $C^4\underline{H}$ (underside)), 2.12 (2H, m, $C^7\underline{H}$ (topside) and $C^4\underline{H}$ (topside)), 1.67 (6H, s, $2C\underline{H_3}$).



(43)

Figure 7.4: Diagram of the product of the reaction between 1,4-benzoquinone and 2,3-dimethyl-1,3-butadiene. The carbon atoms are numbered to aid analysis of the ^{1}H NMR spectrum

7.3.9. 6,7-Dimethyl-4a,5,8,8a-tetrahydro-[1,4]napthoquinone (attempted)

1,4-Benzoquinone (0.60 g; 0.0055 mol) was dissolved in 10 cm^3 [emim][BF_4] at 70 °C. The solution was cooled to 55 °C and 2,3-dimethyl-1,3-butadiene (3.13 cm^3; 0.028 mol) was added. The reaction vessel was stirred for 72 hours at 55 °C, under a closed system. The product mixture was extracted from the ionic liquid with diethyl ether (3x20 cm^3).

The diethyl ether was removed by rotary evaporation, leaving a brown oil that, did not, by GC mass spectrometry, indicate the formation of the desired product.

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SECTION 3

STRUCTURE IN IONIC LIQUIDS

8. THE DIMERSOL® PROCESS AND THE USE OF EXAFS SPECTROSCOPY TO DETREMINE THE STRUCTURES OF ACTIVE CATALYTIC SPECIES

8.1. The Dimersol® Process

8.1.1. Definition

It has been demonstrated during the course of this work, and in the literature, that room temperature ionic liquids have proved to be useful in the laboratory as solvent systems and catalysts for a variety of chemical processes. This field is still very much in its infancy, and information still needs to be gathered concerning how exactly ionic liquids behave and affect reactions that are already known. However, one reaction that has worked well in ionic liquids and on an industrial scale is the Dimersol® process.

The industrial synthesis of higher number carbon backbone olefins is generally performed *via* oligomerization of lower olefins by transition metal catalysts. The starting materials are obtained as unwanted side-products after the cracking of hydrocarbons from crude oil. Many types of olefins can be produced in this way, all of great importance to manufacturing and industrial processes. They are used as polythene co-monomers or as intermediates in the synthesis of detergents, surface active compounds, lubricating oils and plasticizers. The Dimersol® process is the nickel-catalysed dimerisation of propene into hexenes or of butenes into octenes. Thus, it is of great industrial importance, since it ensures less wastage of the components of crude oil.

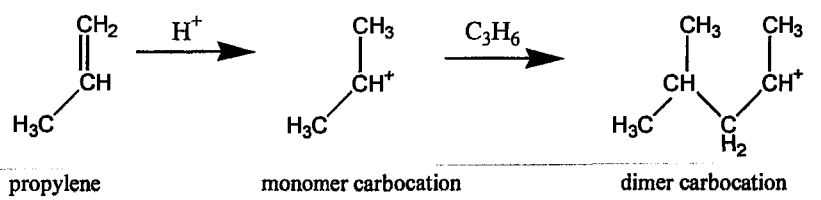
The end products are of use in several industrial applications. For example, the octenes produced from the dimerisation of butenes are usually hydroformylated, giving C_9 alcohols that can be used in the manufacture of plasticizers. Chauvin and co-workers[3.1] discovered this process in the 1960's. Like other lower olefin dimerisation processes, it was carried out in aromatic or chlorinated hydrocarbons in the laboratory, but without a solvent when applied industrially.[3.2]

The original Dimersol® process was envisaged to be a homogeneous process at its conception, taking place in a single liquid phase.[3.3] The original catalytic system used was similar to that of the Ziegler-Natta process of polymer formation, being composed of a transition metal complex associated with an organometallic compound. The term homogenous system can be used for any reaction system when the catalytic system is totally miscible with the reactants (lower olefins) and the products (higher olefins). This was indeed the case for the Dimersol® process when it was first used. In fact, it was one of the first homogeneous reaction systems to be applied commercially.

8.1.2. History of Catalytic Systems Used in the Dimersol® Process

8.1.2.1. Acid Catalysis[3.3]

The catalysis in this case occurs via the addition of a proton to the olefin double bond, resulting in the formation of a carbocation. This is followed by the addition of the carbocation to the olefin double bond of a second olefin. The typical case, in the example of the dimerisation of propylene is illustrated below, in scheme 8.1.



Scheme 8.1: The dimerisation of propylene *via* acid catalysis proposed by Chauvin and co-workers[3.3]

Once the dimer carbocation is evolved, there are three choices available for the next step.

1. Proton elimination, giving the olefinic dimer.
2. Continuation of the addition reaction of the monomer, resulting in an oligomerisation reaction.
3. Methyl group migration and/or breaks of the hydrocarbon chain.

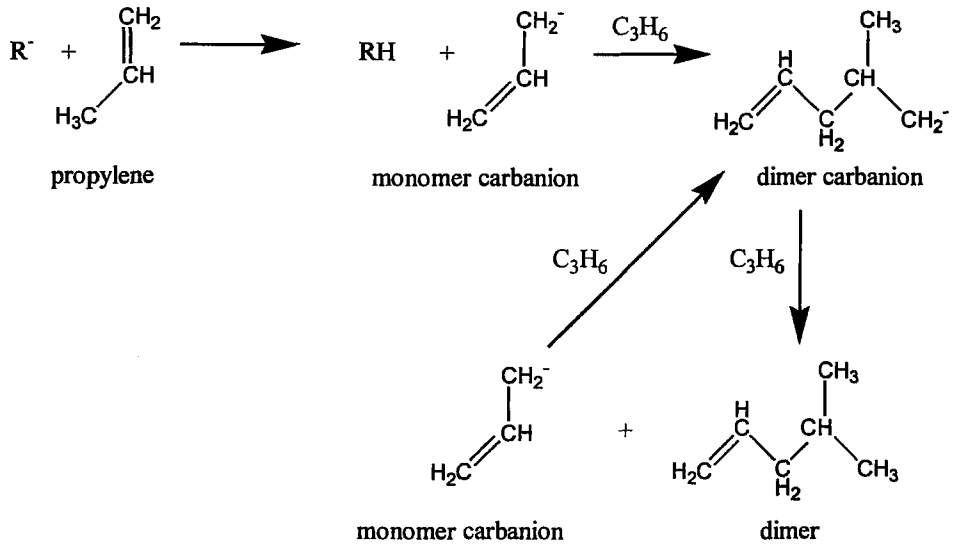
All of these options are likely, which means that the acid catalysed reaction is not selective, and can lead to the formation of a variety of products (in terms of further oligomerisation or isomeric variations of the dimer).

Acidic catalysts normally employed for this process are in the solid phase. A typical example is phosphoric acid on silica or alumina. These catalysts are difficult to handle, due to their sensitivity to water.

8.1.2.2. Main Group Metal Catalysis[3.3]

In this case, the reaction intermediates are carbanions. The dimerisation of propylene in this manner is illustrated below in scheme 8.2. Such a mechanism would be expected to be seen with very electropositive metals such as sodium or potassium. Carbanionic intermediates are relatively stable compared to the intermediates seen in acid catalysis. This eliminates the chance of rearrangement once the intermediate is formed. The growth of the chain can also be controlled by choosing the temperature at which the reaction is carried out. This leads to a higher product selectivity.

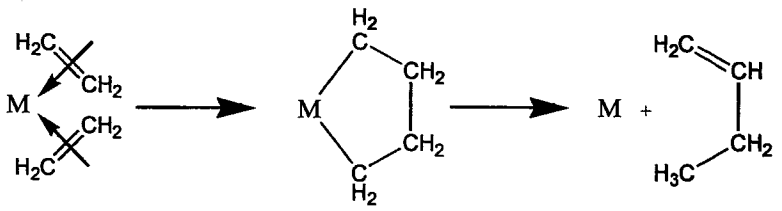
Despite these favourable aspects to the process, the relatively weak reactivity of organometallic agents and the high prices of these metals make these reactions quite costly.



Scheme 8.2: The dimerisation of propylene *via* metal catalysis proposed by Chauvin and co-workers[3.3]

8.1.2.3. Transition Metal Catalysis[3.3]

Chauvin and co-workers have proposed a mechanism for the catalysis of the diemerisation of olefins by transition metals, which is illustrated below, in scheme 8.3.

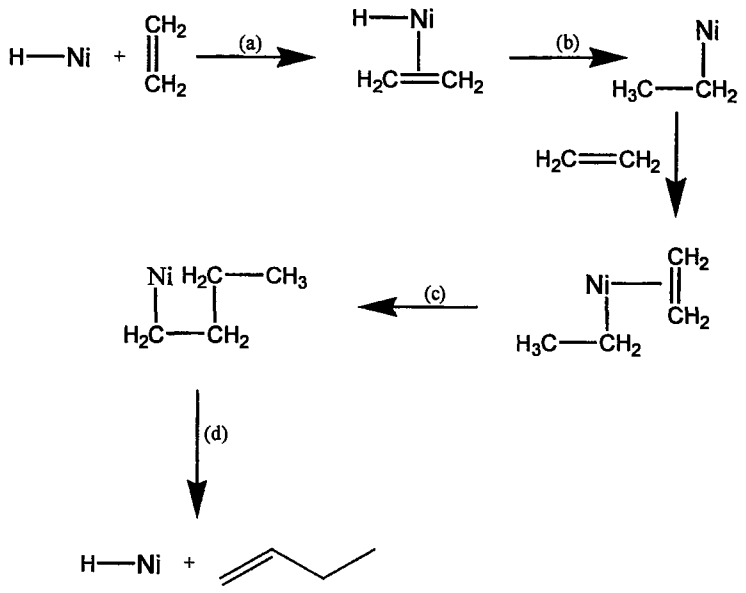


Scheme 8.3: The dimerisation of ethylene *via* transition metal catalysis proposed by Chauvin and co-workers[3.3]

Using this method, the product selectivity is high, and the formation of unwanted isomers is generally avoided. Chauvin and co-workers used this mechanism as a general way of describing the process when catalysed by transition metals. Different transition metal catalysts have been used in this way, including solutions of metal salts (such as $PdCl_2$, $RhCl_3$, $RuCl_3$ and $IrCl_3$), titanium salts TiX_4 (where X=Cl or OR) with halogenalkyl-aluminates, nickel complexes in solution (to be covered in more detail later), and heterogeneous catalyst systems such as nickel oxide on an inorganic support (these were quickly discounted since they are not active enough, and they deactivate with time).

8.1.2.4. Nickel catalysts[3.3]

Scheme 8.4 illustrates the catalysis of the dimerisation of ethylene by a typical nickel complex in solution. This process can broadly be divided into four steps, which are described below.



Scheme 8.4: The dimerisation of ethylene *via* catalysis by nickel metal, proposed by Chauvin and co-workers[3.3]

a) Coordination of the olefin to the nickel hydride.

b) Cis-migration of the nickel-coordinated hydrogen to ethylene.

c) Insertion of a second monomer molecule into the nickel-carbon bond generated in (b), to propogate the oligomer chain.

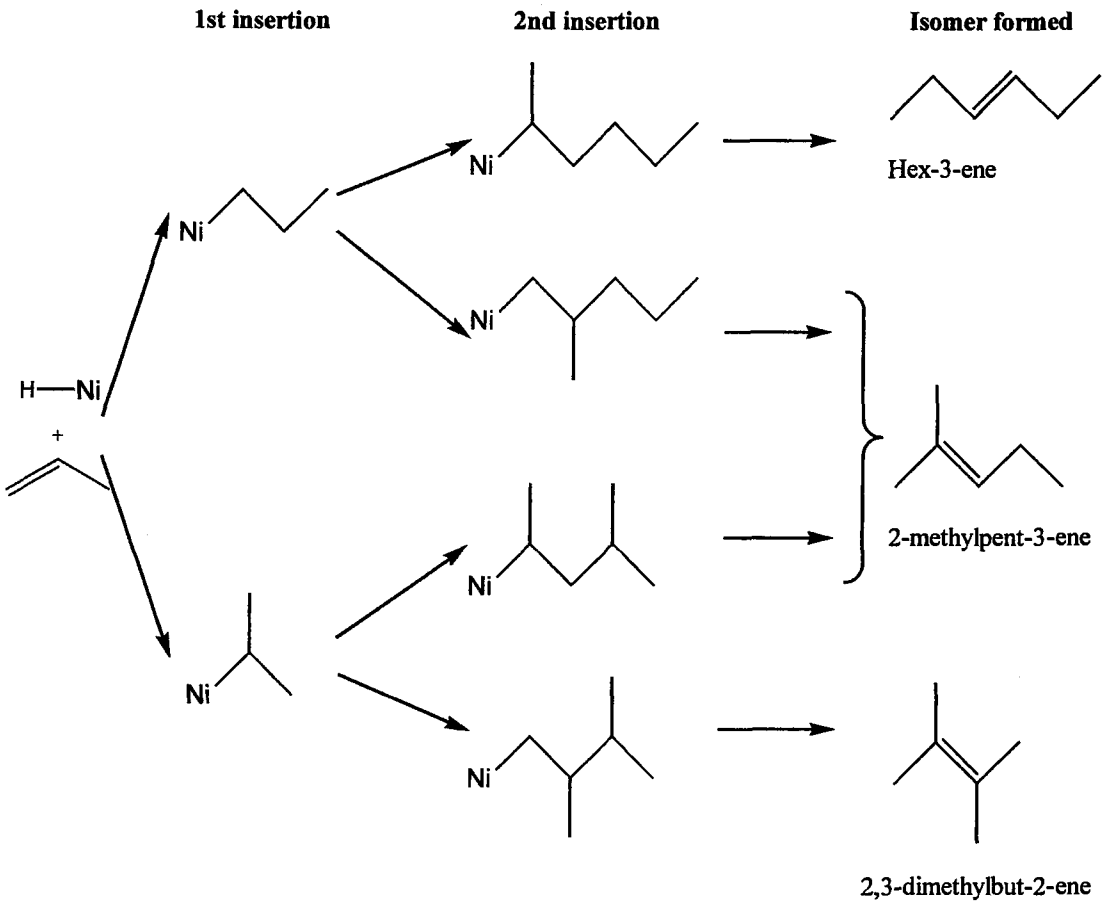
d) Liberation of the oligomeric dimer by β-elimination of a hydrogen (which also results in the regeneration of the nickel hydride catalytic species).

The steps above follow the classic Ziegler-Natta polymerisation reaction mechanism. The selectivity of this reaction is therefore dependant on the rate of β-elimination once the dimer bound to the nickel centre is formed against the rate of insertion of another monomer. Unlike the catalysts mentioned in section 8.1.2.2, the temperature of the reaction plays no part in determining this.

What is important to this process is the structure of the active catalytic species. As with classic Ziegler-Natta type catalysts, the placement and size of the ligands around the nickel centre will decide the reactivity of the catalyst, as well as the relative amounts of each isomeric structure that can be formed.

Scheme 8.5 below shows the case for the isomers possible in the dimerisation of propylene. Heavier monomers, such as butene, would show a more complicated scheme since there is the added possibility of the monomer itself undergoing self-isomerisation (or rearrangement) once it is coordinated to the nickel, but before it undergoes dimerisation. As can be seen from scheme 8.5, two separate pathways reach the same product (2-methylpent-3-ene), meaning that if all four pathways had equal weighting, the chance of forming this isomer would be twice as great as that of each of the other two.

Since the conception of the Dimersol® process, it has been the aim of the chemist to control the product distribution of the reaction. This can be achieved by changing the size of the ligands on the nickel centre (to alter the steric hindrance encountered by the monomers), changing the electron donating or accepting abilities of the ligands, or altering the charge on the metal centre.



Scheme 8.5: Nature of the dimers formed during the dimerisation of propylene by nickel complexes, proposed by Chauvin and co-workers[3.3]

It is not deemed relevant for the background of this study to discuss in detail the different studies attempted in order to find a suitable catalyst system. However, the catalyst system that was in use industrially at this time was made up of two components; a nickel allyl phosphine complex, together with an excess of an aluminium alkyl halide (the co-catalyst). The origins of this have been discussed extensively by the Max Planck group.[3.4]

8.1.3. Room Temperature Organochloroaluminate Molten Salts as Solvents for the Dimersol® Process

In 1990, Chauvin and co-workers published a study that not only changed the accepted method of the Dimersol® process, but also brought the field of ionic liquids to the attention of industrial chemistry.[3.5] They found that propene dimerisation could be succesfully performed in a room temperature ionic liquid. Until then, the major problem that had been experienced by chemists working on the Dimersol® process was the question of homogeneous *versus* heterogeneous reaction systems. The dimerisation of lower olefins was carried out in homogeneous systems, which meant that the reactions were faster because both the substrates and the catalyst were in the same phase. With no phase boundary to cross for reaction to occur, a potential rate limiting step is eliminated from the process, resulting in quicker reactions.

However, one major drawback with homogeneous systems (especially on an industrial scale) is the fact that when one phase contains all of the reaction components, it becomes difficult to separate the products from the reaction mixture. In many cases, the catalyst can leave the reactor even though it is still active. As these species are expensive to buy or make, this is a major problem.

Normally, the role of a solvent in such reactions is to solubilise and stabilise the active catalytic species. However, in order to act as a good solvent system it should not be reactive towards the transition metal carbon-bond intermediate, nor should it coordinate to the metal centre in preference to the reactant. In many homogeneous processes, no solvent is used, and the catalyst is dissolved into the reactants/products mixture.

Another solution to this problem is to use what are known as liquid-liquid two-phase systems.[3.6] This involves employing a solvent for the catalyst that acts as a poor solvent towards the reactants and products. Factors associated with homogeneous reaction systems, such as mild conditions and the use of solvent effects, are still relevant. Certain

advantages associated with heterogeneous reaction systems, such as more efficient and long-lasting use of the catalyst and better separation of the products, are also in effect.

Two-phase systems appear to marry the most appealing factors of each reaction type. However, most organic solvents do not meet the physical and chemical requirements discussed above, and so are unable to be used in this way. Aqueous-organic systems are an example of one such system that has been used in this way, but the use of water itself presents many problems. It may be necessary to alter the ligand design around the active species to allow catalyst solubility but not to the extent of the removal of active sites due to the binding of water. The ligand design also has to allow the catalyst to dissolve in the solvent phase and not the reactants/products phase or the benefits of the two-phase system are rendered useless. Another major problem experienced by the use of aqueous systems is that many catalytic compounds are water-sensitive. In order to make liquid-liquid two phase systems work effectively for the Dimersol® process, a new type of solvent was needed.

The class of organochloroaluminate ionic liquids was studied for this process. The type typically used was a mixture of 1,3-dialkylimidazolium chloride with aluminium trichloride. Their properties were deemed suitable for this type of application (high ionic mobility, a broad range of room temperature liquid compositions, negligable vapour pressure, and good chemical and thermal stabilities). On top of this, the fact that their Lewis acidity can be varied with the composition of the liquid proved to be another attractive feature.

If a molar excess of the imidazolium salt is used to prepare the ionic liquid, the resulting melt contains a mixture of $[AlCl_4]^-$ and the Lewis basic (and highly complexing) Cl^- anions. When a molar excess of the aluminium trichloride is used, the resulting melt contains a mixture of $[AlCl_4]^-$ and the polynuclear, weakly coordinating $[Al_2Cl_7]^-$ and $[Al_3Cl_{10}]^-$ anions, both strong Lewis acids. Hence, the former liquid is called Lewis basic, and the latter Lewis acidic. Both are variations of the same melt. These liquids are highly sensitive to water. In the course of this study, other ionic liquids that are water stable

have been encountered and used. Examples include [bmim][BF_4], [bmim][PF_6] and [bmim][OTf]. Chauvin and co-workers knew of the existence of these liquids, but chose not to use them for the Dimersol® process since they do not combine with their Lewis acids (as the chloroaluminate liquids do) and hence do not form polynuclear anions of the type described above.

Using their experience of the Dimersol® process, Chauvin and co-workers attempted the reaction in chloroaluminate ionic liquids. It had long been known[3.4a] that the active species in the reaction is a cationic nickel complex $[LNi\text{-}CH_2R']^+[AlCl_4]^-$ (where L = PR_3 – see figure 1, below).

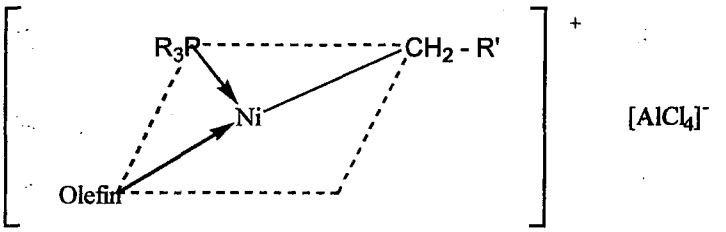


Figure 8.1: The active nickel complex present in the Dimersol® process[3.4a]

Ionic liquids favour the dissociation of transition metal complexes and show poor solubility of aliphatic hydrocarbons. In view of this, Chauvin and co-workers thought that they would be suitable solvents for stabilising active nickel catalysts.

The only variation of the ionic liquid that Chauvin and co-workers were able to demonstrate the reaction taking place was the Lewis acidic version. Chauvin and co-workers found that at low temperatures (-15 to 5 °C) and atmospheric pressure, propene is converted into a mixture of hexenes with high activity. As well as this, the problems associated with homogeneous reaction systems (discussed above) were eradicated, since

the products formed a top layer that could be separated by simple decantation, and the catalyst was left in the ionic liquid and could be reused several times.[3.6] This meant that a continuous process was possible in an industrial reactor. As the dimer is formed it is removed, and monomers can be continuously introduced into the reactor. Also, in terms of the economical usage of nickel complexes, aluminium compounds and costly phosphine ligands, this is of great benefit to the process. The solvent system even showed improvements over organic solvents, in terms of the productivity of the reaction. In the ionic liquid used, over 250 kg of dimer mixture was produced per gram of nickel.

Another advantage of the reaction system was the fact that a much greater dimer product selectivity was observed (in terms of the chain length of the oligomer). As the dimer has a low solubility in the ionic liquid, it is unlikely to stay in the reaction phase long enough to undergo further monomer insertions once it is formed.

A recent article from the same group[3.7] also claims that in these solvent systems, the ligands around the nickel can alter the regioselectivity of the dimer products. When the nickel complexes contain no phosphine ligands, dimers and oligomers are produced with uncontrolled regioselectivity. However, in the presence of sterically demanding phosphine ligands, the dimerisation regioselectivity is directed towards the formation of 2,3-dimethylbutenes.

Another refinement that Chauvin and co-workers made to this process was to slightly alter the anionic part of the ionic liquid.[3.5] Instead of using only $AlCl_3$ to make the melt, they used $AlCl_3$ and $AlEtCl_2$. In section 8.1.2.1 it was seen that acid catalysis, although giving a reaction, provides very little selectivity in terms of the oligomer chain length formed or the distribution of isomers. Traces of protons present in the reaction system when [bmim]Cl-$AlCl_3$ was used as the solvent could cause cationic side reactions to take place. As the protons act as catalysts, only a small amount present is needed to form a significant amount of unwanted side products. However, it is known that $AlEtCl_2$ acts as a proton scavenger in chloroaluminate systems.[3.8] Hence, when $AlEtCl_2$ is added, the product selectivity is greatly improved. When the catalyst used was $NiCl_2(PPr^i_3)_2$ the 2,3-

dimethylbutene content was found to be high, demonstrating that the validity of the 'phosphine effect'[3.9] in molten salts, and also the fact that there is no displacement of the trialkylphosphine group bound to nickel by any anionic species present in the ionic liquid. Their results with selected solvent and catalyst systems are shown in table 8.1.

Table 8.1: Dimerisation of propene by nickel complexes in molten salts, by Chauvin and co-workers[3.5]

Entry	Molten salt		Ni complex		T/ °C[f]	Dimer			
	Composition	Al molar fraction	Type	Conc./ mmol dm^{-3}		Yield, g/g Ni	Composition (%)		
							DMB[g]	M2P[h]	nH[i]
1	$AlCl_3$-MBI[a]	0.60	None	-	-15	0[j]	-	-	-
2	$AlCl_3$-MBI	0.60	$[Ni_2Br_2L_2]$[d]	67	-15	1500	1	67	32
3	$AlCl_3$-MBI	0.45	$[Ni_2Br_2L_2]$	42	-15	0	-	-	-
4	$AlEtCl_2$-MBI	0.70	$[Ni_2Br_2L_2]$	34	-15	6600	6	76	18
5	$AlEtCl_2$-MBI	0.70	$[Ni(acac)_2]$[e]	61	-15	1400	16	46	38
6	$AlEtCl_2$-MBI	0.70	$[Ni_2Cl_2(PPr^i_3)_2]$	12	-15	3300	76	21	3
7	$AlEtCl_2$-BP[b]	0.70	$[Ni_2Cl_2(PPr^i_3)_2]$	10	0	5300	69	28	3
8	$AlEtCl_2$-MBI	0.70	$[Ni_2Cl_2(PPr^i_3)_2]$	7	-10	4900	40	48	12
9	$AlEtCl_2$-TBP[c]	0.65	$[Ni_2Cl_2(PPr^i_3)_2]$	82	50	900	44	48	8

[a] MBI: 1-butyl-3-methylimidazolium chloride
[b] BP: 1-butylpyridinium chloride
[c] TBP: tetrabutylphosphonium chloride
[d] L: 2-methylallyl
[e] acac: pentane-2,4-dione
[f] All pressures at 0.1 MPa, except run 8 at 0.3 MPa and run 9 at 0.6 MPa
[g] DMB: 2,3-dimethylbutenes
[h] M2P: 2-methylpentenes
[i] nH: n-hexenes
[j] 5.2 g of various cationic type oligomers were obtained

As can be seen from entry 1, with no nickel catalyst, some oligomerisation did take place (catalysed by the acidic melt, and due to the presence of trace amounts of protons). However, as with acid catalysis, the product distribution was very broad, so no observable product was noted.

In the basic melt, the nickel catalyst was also seen to be inactive (entry 3), whereas in the acidic version (entry 2) a reaction was observed. However, it should be noted that again, due to the presence of trace amounts of protons, an amount of trimer product was observed in entry 2, originating from a cationic side reaction. The active species in the basic melt was examined by Chauvin and co-workers by UV spectroscopy. It was found that, according to the theory discussed above, Cl^- anions were indeed coordinating strongly to the metal centre, giving $[NiCl_4]^-$ or $[NiLCl_3]^-$ complexes.

Due to the presence of cationic side-reactions, the ionic liquid was changed to include $AlEtCl_2$. Entries 4 onwards showed no product formation from cationic side-reactions. As well as this, catalytic activity could be observed in the presence of nickel complexes not containing a Ni-C bond, such as $[Ni(acac)_2]$ (entry 5) and $[NiCl_2(PPr^i_3)_2]$ (entries 6-9).

Chauvin and co-workers have also conducted Raman spectroscopy measurements on the acidic ionic liquid typically found in entry 4 to more clearly understand the speciation within the melt. They found it to consist of $[AlEtCl_3]^-$ and $[Al_2Et_2Cl_5]^-$ anions associated with $[bmim]^+$ cations.[3.10]

However, since this study was completed, very little work has been carried out to deduce how the various nickel catalysts actually behave once dissolved in the ionic liquid. It seems clear that the presence of the Lewis acid $[Al_2Cl_7]^-$ in the ionic liquid itself must be playing a part somehow. However, one cannot assume that these complexes behave in exactly the same way as in organic solvents. It appears that in the acidic melt the phosphine ligands (where applicable) stay attached to the nickel centre, but in the basic melt they are displaced by the strongly coordinating Cl^- anions.

Also of importance is the observation[3.5] that catalysts which normally produced no reaction in organic solvents (namely those with no Ni-C bond) did work succesfully in the ionic liquid systems. This indicates that different effects are present in these systems.

In their reviews, Chauvin and co-workers mention solvent tailoring[3.6] in the same way as was mentioned with the Diels-Alder reaction in this study (chapter 6). However, this can only become a reality if the systems that have so far worked are studied, and data gained as to why and how these catalysts behave when dissolved in these solvents. This can then be applied to other systems, until enough data exists so that choices can be made regarding a specific solvent for a specific catalyst, or *vice versa*. It appears that as far as the Dimersol® process goes, this has not yet been fully done. It does seem strange, given that this was the first process involving the use of room temperature ionic liquids as solvent systems which was accepted and succesfully performed by industrial organisations.

The process of understanding how the nickel complex, when dissolved in the ionic liquid actually arranges itself structurally the reaction is not easy. This is because liquid phase active species cannot easily be isolated for observation. However, the technology and the means do exist to further our understanding of these processes, as shall be seen in the next section.

8.2. Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS)

8.2.1. Background

Extended X-Ray Absorption Fine Structure (or EXAFS) is a spectroscopic technique. It works by bombarding an atom of a selected element (known as the absorbing atom) with X-rays. The atom absorbs the X-rays, exciting a core electron in the process. The excited electron is ejected from the nucleus. Figure 8.2 shows the spectroscopic representation of

this process occurring for a non-specified system. The peak labelled EDGE represents the sudden absorption in energy as an electron is ejected from the atom.

Every element has different electron configurations, and nuclear sizes and nuclear compositions. Therefore the X-ray energy needed to excite an electron from one element to another varies, making EXAFS an element specific process. This is a beneficial factor of the procedure since, for example, transition metal organometallic complexes invariably contain complex ligand systems that are composed of different elements. Thus the absorption edge of the atom being studied (normally the central transition metal) will be free from interference from the absorption edges of other elements present in the system. The separation between the X-ray energies required to excite inner core electrons from different elements is usually large, which also aids the element specificity of the EXAFS process.

In EXAFS, it is the area immediately to the right of the EDGE that is of interest. This region is known as the EXAFS region of the spectrum. The EDGE peak is comprised of sharp features which can also give useful data (known as XANES). These are caused by the excited electron's transitions to higher orbitals, and are therefore also characteristic of a particular metal environment.

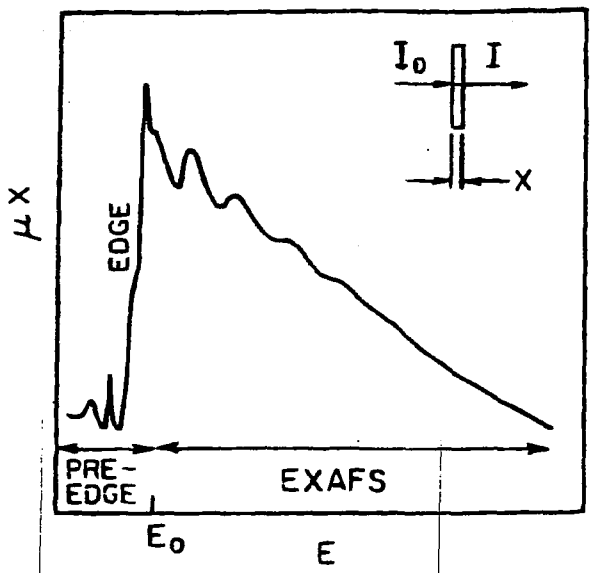


Figure 8.2: X-ray absorption spectrum illustrating the absorption edge for an absorbing atom

At higher energies to the XANES region the spectrum is comprised of weaker oscillations, called the extended X-ray absorption fine structure (EXAFS). It is best to visualise the ejected electron in terms of a spherical wave function which travels outwards from the nucleus of the absorbing atom. Figure 8.3 below shows this analogy.

Figure 8.3A shows the idealised spectrum for the case of a single isolated atom of a monotomic gas (krypton). As the excited electron moves away from the nucleus, the peak caused by the edge can be seen to decay smoothly (right hand side of figure 8.3A).

Figures 8.3B shows the spectrum for the case of a single isolated molecule of a diatomic gas (bromine). In this case the central absorbing atom is in the proximity of another atom (also an absorbing atom, but nonetheless irrelevant as we are focussing on the events taking place after electron excitation and dissociation). As the electron wave function passes the neighbouring atom, it will experience interference. In EXAFS terminology, this phenomena is known as backscattering. This can be observed as a series of

oscillations on the decay pattern of the EXAFS region of the edge peak (right hand side of figure 8.3B).

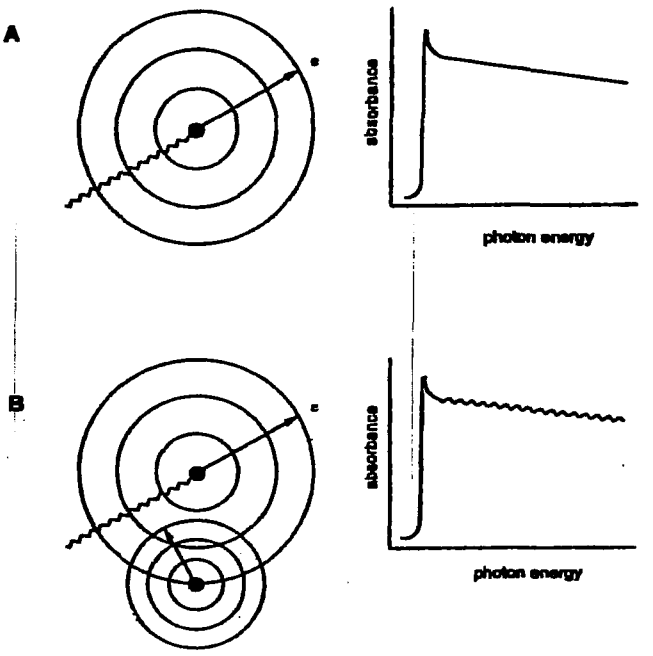


Figure 8.3: Qualitative rationalisation of the absence and presence, respectively, of EXAFS in a monoatomic gas such as krypton (A), and in a diatomic gas such as bromine (B)

The frequency of the oscillations in the EXAFS region indicates the interatomic distance, and the intensity gives the atomic number and coordination number of the neighbouring atoms. This makes EXAFS a very useful method of establishing bonding (and some non-bonding) distances. Unlike X-ray crystal structures, bond angles are not given by this method. However the fact that the identities of atoms in the proximity of the absorbing atom and their coordination numbers can be found from this process means that when combined with other forms of spectroscopy (for example UV, NMR and IR), EXAFS can be a very powerful tool in the determination of molecular structures.

In this study, EXAFS spectroscopy weas used to study the structures of catalysts in solution. The characteristics of EXAFS spectroscopy make it a very powerful tool for *in situ* studies of this kind. Not only is it element specific (as discussed above), but it is also available for a wide range of sample environments, in that structural data is obtainable even for amorphous solids and solutions (which is beyond the scope of X-ray crystallography).

As has been seen in figure 8.2, the EXAFS region of the spectrum is relatively weak in comparison to the absorption edge. Therefore, EXAFS spectroscopy demands a high signal to noise ratio in the original spectrum. Normal X-ray sources cannot provide beams of the right power and intensity to carry out EXAFS. Synchotron radiation was first discovered in 1947[3.11] as an unwanted side effect produced in particle accelerators (it caused the accelerating particles to lose energy). Now it is regarded as a source of light with valuable properties. The radiation has a wide range of wavelengths (so not only X-ray studies can be carried out with it) and has high brilliance, which means that very dilute solutions can be studied with it. Dedicated synchotron radiation sources can generate X-rays with at least 10,000 times more intensity than the average laboratory source. This is the intensity needed to succesfully perform EXAFS studies on dilute solution samples.

One disadvantage of EXAFS is that it will only give a population weighted mean of the species present. Minor components, which may be of great importance to the catalytic process, can be missed. However, for most systems, EXAFS spectroscopy is a powerful means of structural determination.

8.2.2. Examining *in situ* catalyst systems using EXAFS spectroscopy

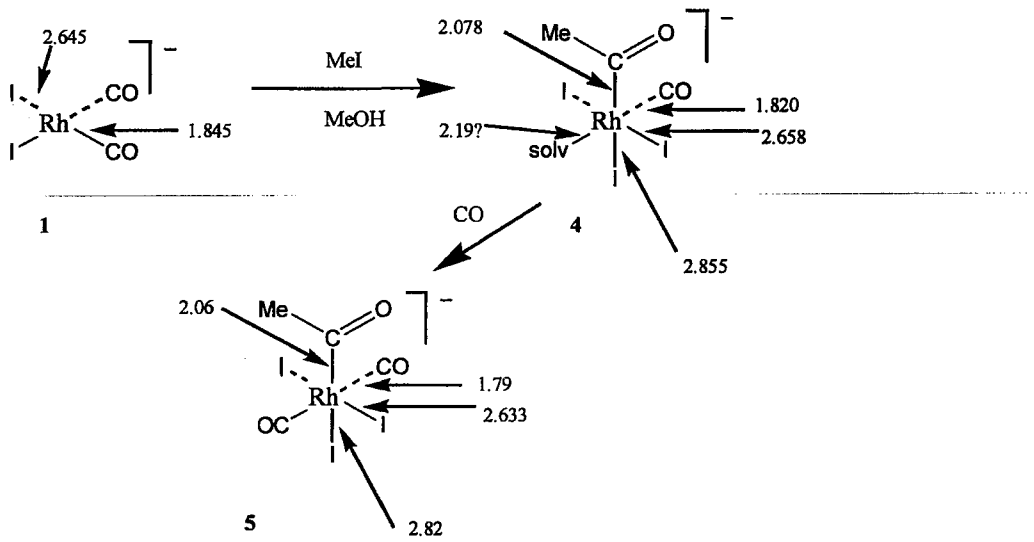
8.2.2.1. General Examples

EXAFS spectroscopy was widely accepted by the chemical community after it had been succesfully applied to heterogeneous catalysis and metalloenzymes.[3.12] An early study of homogeneous catalytic systems was carried out by Goulon, Chauvin and co-workers[3.13] on nickel and cobalt precursors of Ziegler-Natta type hydrogenation catalysts. Not only were they attempting to deduce these structures, but also validate the EXAFS method for this type of work. The nickel (II) salt of 2-ethyl-hexanoic acid was used in benzene and reduced with aluminium trichloride (which leads to the precursor used in the catalytic system). Similar cobalt solutions were also prepared. They found that the EXAFS results for the solutions before and after reduction were very different. The lengths of the Ni-C and Ni-O bonds of the nickel salt solution before reduction were compared to known crystal structures of the complex being studied and showed very good agreement. By comparing their results of the reduced solutions to the EXAFS spectra of the relevant metal foil, they deduced that when reduced and in solution, these complexes form disordered amorphous-like metal clusters. They also found evidence of an increase in the number of metal-carbon bonds which would almost certainly play an important role in the catalytic activity of the complexes.

Evans and Corker used EXAFS spectroscopy to investigate the structures of liquid phase $Cu(acac)_2/ZnEt_2$ syngas conversion catalysts (involved in catalysing the synthesis of C_2-C_6 alkenes from CO and H_2).[3.14] The question being asked was whether these systems were truly homogeneous or in fact more complex systems containing metallic clusters. Both copper and zinc EXAFS studies were undertaken on the same catalyst system to determine its structure from the point of view of both metals. Comparing the copper EXAFS spectrum to one of copper foil showed that small metal cluster particles with a face-centred cubic lattice local structure had been formed. They also deduced that in

different solvents, different cluster particle sizes were formed. This was based on the fact that average coordination numbers around the absorbing copper atoms are a good measure of the particle size).

Cruise and Evans[3.15] carried out an EXAFS study on a rhodium catalyst (in tetrahydrofuran solution) used in the carbonylation of methanol, a well-established industrial process. Their results are shown below in scheme 8.6. The initial catalytic complex is known to be $[RhI_2(CO)_2]^-$ (**1**). Kinetic and spectroscopic studies had already shown the first transformation to be the oxidative addition of iodomethane to form $[Rh(Me)I_3(CO)_2]^-$ (**2**), which is then followed by a rapid migration step. The resulting acyl complex had been identified by crystallography to be a dimeric species $[\{Rh(COMe)I_3(CO)\}_2]^-$ (**3**). The work carried out by Cruise and Evans showed that species (**3**) goes on to form complexes (**4**) and (**5**).



Scheme 8.6: Results of EXAFS data analysis of solutions of (**1**), (**3**) giving (**4**) and (**5**) in methanol solution; distances in Å.; study by Cruise and Evans[3.15]

The presence in solution of a mixture of (**4**) and (**5**) was deduced due to the increase in the Rh-CO coordination number, and a decrease in the Rh-I distance (less steric hindrance from the relatively bulky solvent molecule to the relatively compact CO group allowed the iodide anion to move closer to the metal centre). Not only can the presence of these species be detected by EXAFS studies, but the mechanism of the reaction can be deduced and clarified by using the information from the scans. Although the complexes (**4**) and (**5**) had been hypothesised by kinetic and mechanistic studies, they were now clearly shown to exist in the reaction environment.

8.2.2.2. Examples Involving Catalytic Systems Used in the Dimersol® Process

As mentioned in section 8.1.3, the Dimersol process in chloroaluminate ionic liquids has received little attention in terms of structural determination of the active nickel species in solution. Some studies that have used nickel complexes dissolved in organic solvents are included in this section.

Corker and Evans[3.16] have examined solutions of $NiCl_2(PEt_3)_2$ with $Al_2Me_3Cl_3$ and $AlEt_3$ in diethyl ether. The aim was to discover the role of the Lewis acid co-catalyst in activating the nickel complex to dimerise alkenes. Their results indicated the presence of a first coordination sphere of C and P atoms (indicating the phosphine to still be intact and methyl addition to the metal centre). They also found aluminium in the proximity of nickel, but a longer distance of about 2.97 Å. As the sum of the nickel and aluminium covalent radii is 2.4 Å (considerably less than the distance they were observing), they deduced that this could not be due to a Ni-Al bond, but instead caused by a Ni-C-Al interaction, which would form the complex shown in figure 8.4, below.

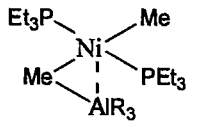
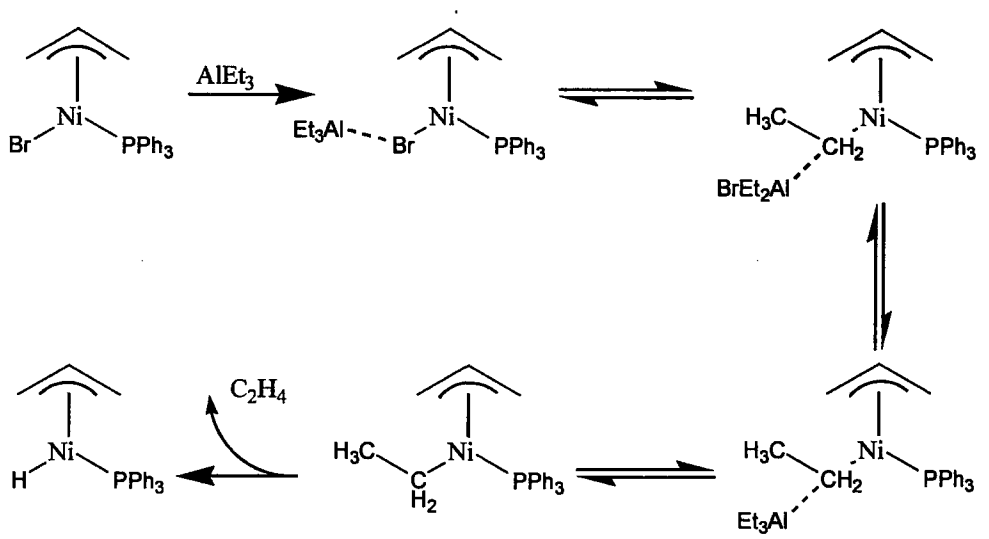


Figure 8.4: Proposed structure of the active nickel complex in the EXAFS study carried out by Corker and Evans[3.16]

They suggested the hypothesis that the Ni-C-Al interactions would probably serve to stabilise the nickel centre. This bridging unit would also serve to allow alkyl groups to transfer between the two metals. This would make for an ideal environment in which to carry out oligomerisation reactions.

Evans and co-workers[3.17] have also studied another nickel catalyst used for the same process in organic solvents, namely $AlEt_3$ added to $[Ni(\eta^3\text{-}C_3H_5)(PPh_3)Br]$. The structure of the nickel complex alone had already been determined by X-ray crystallography and variable temperature NMR spectroscopy. EXAFS spectroscopy showed an inner coordination sphere of 3.9 carbons at 1.93 Å and 1.0 phosphorus at 2.19 Å, with a more distant aluminium being present at 3.21 Å. These results implied that Ni-Al interactions occurred via alkyl bridges in the predominant species during catalysis. This directly contradicted mechanistic studies proposed earlier, that claimed that the Ni-Al interaction occurred via a halide bridge. Evans and co-workers claimed the bridge was alkyl based, because their EXAFS studies clearly showed halide loss from the nickel centre. The results did show the presence of a distant aluminium about the nickel, but only with evidence of carbon and phosphorus coordination. The purpose of the Lewis acid is widely believed to be to decrease the charge on the nickel in order to facilitate the coordination of electron donors to the metal centre.

From their results, Evans and co-workers deduced the mechanism for the reaction, shown below in scheme 8.7.



Scheme 8.7: Proposed activation reaction of $[Ni(\eta^3\text{-}C_3H_5)(PPh_3)Br]$ with $AlEt_3$, deduced from NMR and EXAFS spectroscopic studies. **NB:** The final species has not been detected spectroscopically. Work by Evans and co-workers[3.17]

9. THE STRUCTURES OF NICKEL COMPLEXES IN CHLOROALUMINATE IONIC LIQUIDS

9.1. Research aims

The industrial importance of the Dimersol® process was discussed in chapter 8. This is not only because it ensures a more complete usage of the otherwise wasted lower olefins found in crude petroleum as starting materials in the synthesis of industrially useful chemicals. This is also the first process of interest to the manufacturing industry that has been used with room temperature ionic liquids as effective solvent systems. This signifies a new commercial interest in these materials. The homogeneous *versus* heterogeneous debate appears (in this case) to have been solved and replaced with liquid-liquid two phase reaction systems which are able to bring the advantages of both the reaction types to the Dimersol® process.

Despite this major breakthrough from the research laboratory to commercial application for ionic liquid chemistry, very little work has been done to understand how and why these systems affect the active catalytic species. For the future usage of ionic liquids in other catalytic reactions to be developed, there is a requirement to fill this gap in the literature, and thus our knowledge. Chapter 8 showed that there is clear evidence that the use of chloroaluminate ionic liquids have given rise to new, previously unseen effects in the reaction system.

This work will study the structural differences between a selection of model nickel complexes in the solid form, and the same substrates when dissolved in the Lewis basic and acidic forms of the [bmim]Cl-$AlCl_3$ ionic liquids. The complexes under observation are $[bmim]_2[NiCl_4]$, $[Ni(acac)_2]$, $[NiCl_2(PPh_3)_2]$, $[NiCl_2(dppe)]$, and $[NiCl_2(PMe_3)_2]$. It should be noted that these were used to create a model system in the ionic liquids that would behave as the complexes used in the actual dimerisation process. EXAFS spectroscopy (discussed in chapter 8) and other methods have been used to understand what happens to these complexes in solution. It is hoped that this data can be used to further our understanding of this process when carried out in ionic liquids, and in the long term to start building up a library of information on the effects that ionic liquids can have

on solute species. In this way, the concept of 'solvent tailoring' to suit reaction or catalyst types can begin to become a distinct reality.

9.2. Determination of the Structures of Nickel Complexes in Solid Form and in Solution

As described above, the five chosen nickel complexes have been studied in three different forms; as solids, and as solutions in Lewis acidic and Lewis basic ionic liquids respectively. For ease of layout, each form of each complex will be discussed separately, but all five complexes in the same environment will be arranged together in the same section.

9.2.1. Analysing EXAFS data

9.2.1.1. The Appearance and Terminology of EXAFS Data

Figure 9.1 shows the resolved EXAFS spectrum for one of the complexes studied ($[bmim]_2[NiCl_4]$). On the left hand side, the top diagram is the EXAFS derived from the X-ray absorption information as the excited electron moves away from the absorbing atom and its wavefunction is distorted as backscattering occurs. From this information, computer software can read the frequency and intensity of the pattern, and fit this data as closely as possible (*via* least squares iterations) to any predicted atomic arrangement or configuration that the user chooses to input. It is possible to fit chemically absurd

molecular formulae to a high degree of accuracy with the software, which is totally non-discriminatory in its approach. Therefore the human interface is vital in EXAFS data treatment. In other words, chemists must be careful to supply careful estimates to assign EXAFS.

The top left diagram shows two lines following the same pattern. One is solid and the other broken. The solid line represents the experimental data that has been collected. The broken line represents a theoretical EXAFS pattern, based on the data inputted by the user and mathematically refined by the computer software. The numerical data that the computer software has fitted to the theoretical scan is arranged along the right hand side. The value labelled R is of great importance since it tells us the accuracy of the fit between the theoretically generated and experimentally collected EXAFS. In general (also depending on the quality of the sample), an R-value of under 25-30 is considered satisfactory.

EXAFS are processed by the summation of as many repeat scans of the sample as time permits. In general, the more repeat scans that can be summed, the greater the signal to noise ratio will become (as random noise peaks will be eliminated by summation), giving more accurate data.

There are other parameters displayed alongside the R-value that are of great importance to understanding the EXAFS. N1 is the number of atoms in shell 1. Using the example in figure 9.1, the nickel centre is known to be surrounded by 4 equidistant chloride anions, so only 1 coordination shell is programmed into the computer software. Where it is believed that more than 1 type of atom exists around the close proximity of the central absorbing atom (even if more than 1 atom type are equidistant from the centre), or the same atom type exists at different distances from the centre, multiple shells must be set up. The type of atom in shell 1 is listed after the value of N1. R1 refers to the calculated distance from the centre of the first shell. Finally A1 refers to the amount of vibrational motion (or variation in distance from the source of the excited electron) that the shell undergoes. This is known as the Debye-Waller factor, and can be treated as an indication

of the standard deviation of any numerical bond length that it refers to. This value would be expected to increase in solution, since the atoms are more free to move.

The bottom left hand diagram is a Fourier transform representation of the EXAFS pattern. This provides the user with a more understandable diagramatic representation of the EXAFS results. The x-axis refers to the contact distance (in Ångstroms). The coordination number is indicated by the y-axis. As with the EXAFS pattern, two lines are generated. The solid line represents the experimental data that has been collected. The broken line represents the theoretical pattern. It is important to stress that the fit is made to the actual EXAFS spectrum and not the Fourier transform.

9.2.1.2. Note on EXAFS Data Refinement

The user can input a suggested atomic configuration for the studied complex, and can also instruct the software as to which parameters can be refined mathematically and which should be left as fixed. Sometimes, to obtain the optimum results from this software, it is recommended that parameters are changed in gradual steps and individually by the user. For example in more complex examples than the one shown in figure 9.1, where more than one coordination shell is situated around the absorbing atom it would be recommended to refine each shell individually, leaving the other shells fixed as refinements are made. Once a refinement has been carried out by the software then more changes can be made. This ensures that the software can avoid making huge refinement steps that could result in chemically illogical complexes being suggested as solutions. However, this suggests that data manipulation can, in theory occur, by setting and then fixing certain parameters so that they agree with the user's theoretical ideas of how the complex should appear. Care must be taken to avoid this.

In this study, all EXAFS data were refined as normal until a solution was obtained. Once the solution was believed to be correct, a refinement of all the parameters was carried out, using the determined parameters as first values. The reasoning behind this was to see if the solution still held true, or if indeed the fixing of certain parameters has suppressed the true solution.

9.2.2. Solid Samples of Nickel Complexes

The study of the chosen complexes in the solid state may seem unnecessary, since enough crystal data and information exists on them already, and more importantly because the active complexes are only found in solution. However, the use of EXAFS for the determination of structures in solution is relatively new, and has received limited usage in terms of *in situ* catalyst structural determination. It was decided to determine the structures of the nickel complexes in the solid state as a control. Comparing the data received from the EXAFS process with structural data that is already well-established and exists in the literature will reveal how accurately EXAFS can determine the structures of solid state nickel complexes. As there is no way of checking the accuracy of the EXAFS data (especially information about bond lengths) obtained in solution, it is hoped that the data concerning the solid samples will give us an indication of the accuracy of the results from this study. These data were also used in the initial fitting of the solution EXAFS.

9.2.2.1. Solid $[bmim]_2[NiCl_4]$

In its solid form this is structurally the simplest of all the nickel complexes used for this study. However it is relevant and useful to study since Chauvin and co-workers[3.5] have

mentioned that when catalysed in ionic liquids, the Dimersol® process is able to proceed using nickel complexes with no metal-carbon bonds, which are required in organic solvents. The imidazolium cation $[bmim]^+$ was chosen to be the countercation for this complex, simply because the ionic liquids it will be dissolved in have the same cation as this complex. It was thought that the introduction of a countercation that was also a new species for the system could result in unpredicted structural changes. Figure 9.1 below shows the refined EXAFS data for this complex in the solid state.

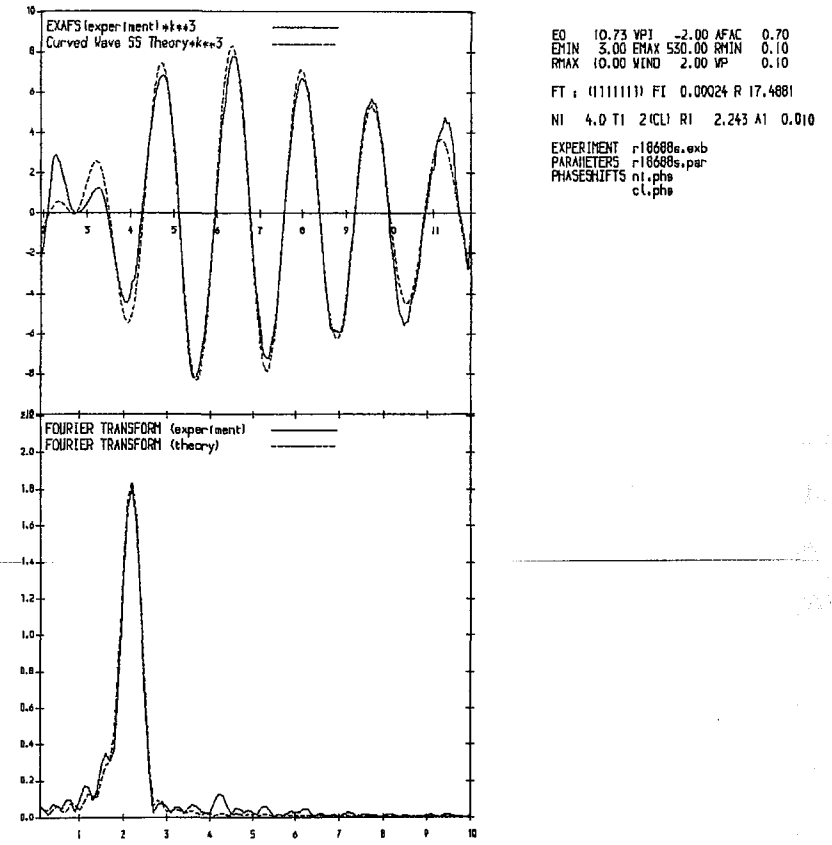


Figure 9.1: EXAFS data for $[bmim]_2[NiCl_4]$ in solid state

The EXAFS data clearly shows that the nickel atom is surrounded by 4 chloride anions at a distance of 2.243 Å. The fitting parameter, R, is about 17, which is a good fit to the experimental data.

It has been mentioned that the reasoning behind carrying out EXAFS scans for solid nickel complexes is to compare the results obtained against literature data as a test to measure the reliability and accuracy of the method. Crystal structure data for the complex $[emim]_2[NiCl_4]$[3.18] shows that the bond length for the four chloride anions is 2.254 Å. This shows a good level of agreement between the two methods, well within experimental error. An EXAFS study has also been carried out on the same slightly modified complex.[3.19] The bond lengths recorded here were 2.25 Å, which is also in good agreement. They show that the chloride anions form the main coordination shell of ligands around the nickel, and that the $[emim]^+$ or $[bmim]^+$ countercations are not closely associated with the nickel.

EXAFS can yield information concerning bond lengths, but not bond angles. With four identical groups about the nickel atom, two main symmetrical configurations could be expected, tetrahedral or square planar. One method of deduction in this case could be to compare the bond lengths obtained from this EXAFS study to those from the crystal structure data. The bond lengths would be expected to change from the relatively spacially limited square planar configuration (where the four groups only have two dimensions to arrange themselves in) to the tetrahedral one (where the four group have three dimensions to arrange themselves in). The good agreement between the EXAFS bond lengths and the crystallographic values show the tetrahedral configuration.

It has been mentioned that when used with other forms of spectroscopy, EXAFS can be trusted to come into its own as a powerful tool to deduce the structures of such compounds. The structure was confirmed using solid state UV-VIS spectroscopy. Peaks at 2500 nm, 1330 nm, and 600 nm corresponded to the electronic transitions $^3\Gamma_1(F) \rightarrow {}^3\Gamma_2$, $^3\Gamma_1(F) \rightarrow {}^3\Gamma_2$ and $^3\Gamma_1(P) \rightarrow {}^3\Gamma_2$ respectively. This defines the complex as tetrahedral

in structure, which is consistent with the literature. Figure 9.2 shows the structural solution for this complex in the solid state.

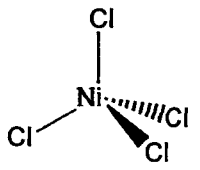


Figure 9.2: The local structure of $[bmim]_2[NiCl_4]$ in solid state

9.2.2.2. Solid $[Ni(acac)_2]$

The solid structure of this complex is known from the literature,[3.20] but in terms of using the EXAFS process, was more complex to define. As will be seen it provided a sterner test of the process. $[Ni(acac)_2]$ forms a trimer in solid state as shown below in figure 9.3.

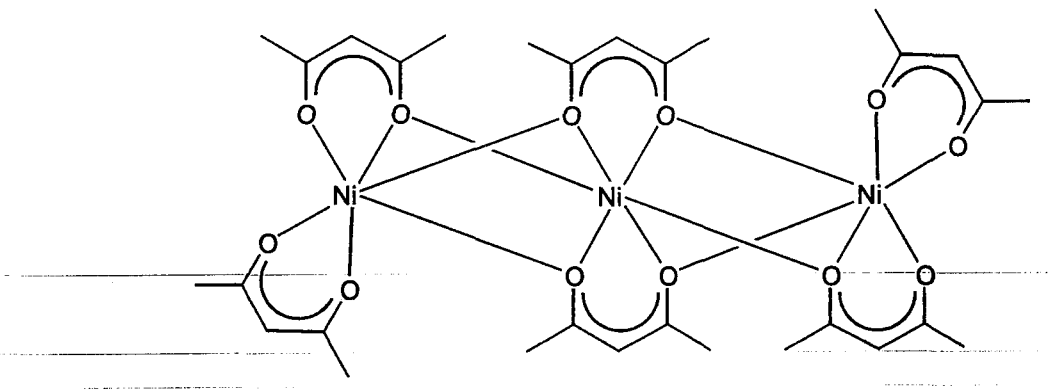


Figure 9.3: $[Ni(acac)_2]$ trimer in solid state[3.20]

Although each nickel is in the close proximity of two acac ligands, a trimer species is formed, effectively placing the nickel in an octahedral site. Each nickel forms Ni-O associations of two types. There are the atomic bonds between a nickel atom and either of the two acac ligands directly bonded to it, and there are also associations between a nickel atom and an acac ligand that is directly bonded to an adjacent nickel atom. It is expected that the former bond types would be shorter than the latter ones, giving four short Ni-O bonds and two longer Ni-O bonds. However, crystallographic data indicates three shorter bonds and three longer ones. This must be due to some sort of spacial arrangement caused by the formation of the trimer. The three shorter bonds, in each case, are not identical but all happen to be shorter than 2.0 Å. Conversely, the three longer bonds are all longer than 2.0 Å.

In order to be accurate and consistent, the EXAFS data would not only have to show a distinction in the Ni-O bonds formed, but also at least one nickel atom in the proximity of each absorbing nickel centre. Figure 9.4 shows the refined EXAFS data for this complex in the solid state.

As EXAFS can only see an average environment for the collective absorbing atoms (in this case nickel), it was necessary to define the parameters of the model as such to the software. Two oxygen shells were defined. As the software would be used to calculate and refine the model, they were specified as consisting of three oxygen atoms each. The first shell was specified as having a distance of 2.1 Å from the nickel centre and the second a distance of 1.9 Å. Figure 9.3 shows that the two nickel atoms on the extremity of the trimer model are surrounded by one nickel atom each, and that the central nickel atom is surrounded by two nickel atoms. Therefore the average nickel atom environment has 1.3 nickel atoms surrounding it.

When these parameters were refined, the model did not alter itself (i.e. the two Ni-O shells did not attempt to equilibrate themselves to the same distance). Both of the Ni-O shells solved by EXAFS showed good agreement when all the crystal data of the corresponding Ni-O bond lengths was averaged. The Ni-Ni bond lengths, and importantly

coordination shell size, also showed good agreement. Unfortunately the original spectrum contained a high amount of noise. Due to the quality of the sample, the fit was not ideal (R=31.8). However, when the refinement was attempted with the parameters set up to incorporate a single [Ni(acac)$_2$] unit (i.e. not taking the trimeric model into consideration), a worse fit (R>40) was observed. The agreement was considered close enough to validate the use of EXAFS to solve models with more complex symmetries.

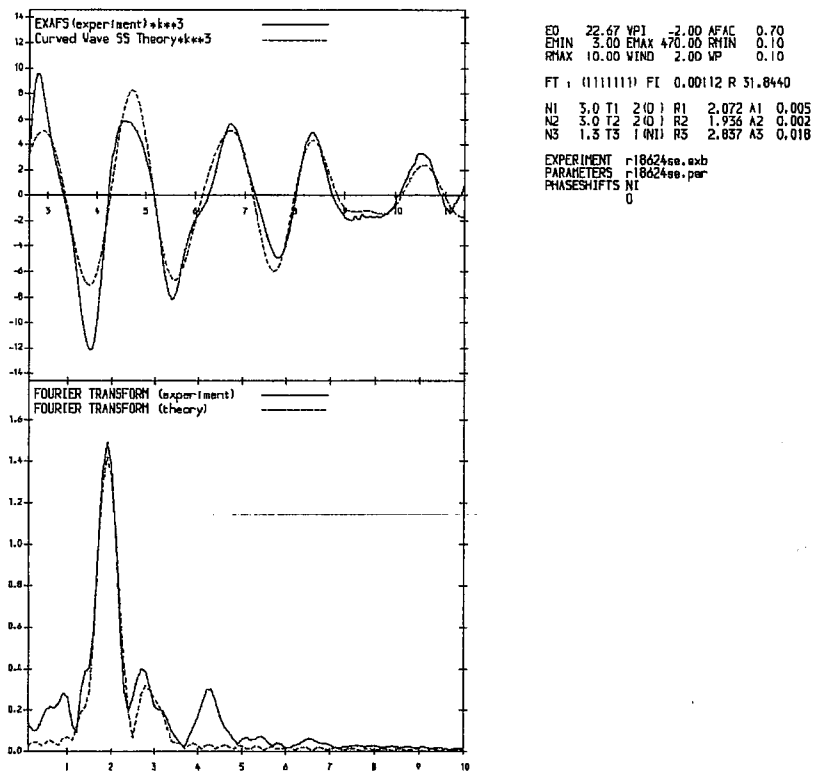


Figure 9.4: EXAFS data for [Ni(acac)$_2$] in solid state

In order to check the symmetry of the complex, solid state UV-VIS spectrometry was used. Peaks at 1150 nm, 665 nm and 390 nm corresponded to the electronic transitions $^3A_{2g} \rightarrow {}^3\Gamma_{2g}$, $^3A_{2g} \rightarrow [{}^3\Gamma_{1g}, {}^1E_g]$ and $^3A_{2g} \rightarrow {}^3\Gamma_{1g}$ respectively. This defines the complex as octahedral in structure. Although the EXAFS data shows the presence of either one or two nickel atoms around the absorbing nickel atom in the trimer state, these are non-bonding, and so do not show in the UV-VIS spectrum.

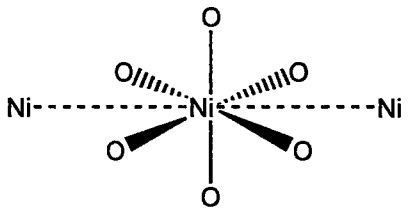


Figure 9.5: The local structure of $[Ni(acac)_2]$ in solid state

The structure would not be expected to be a perfect octahedron, since three of the Ni-O bond lengths are slightly longer than the other three. Also to accommodate the strain caused by the steric requirements of the trimeric species, some further distortion would be expected. Figure 9.5 shows the structural solution for this complex in the solid state (from the view of the central nickel atom).

9.2.2.3. Solid $[NiCl_2(PPh_3)_2]$

This phosphine model is similar to those often used in the Dimersol® process as catalysts. Figure 9.6, below shows the refined EXAFS data for this complex in the solid state.

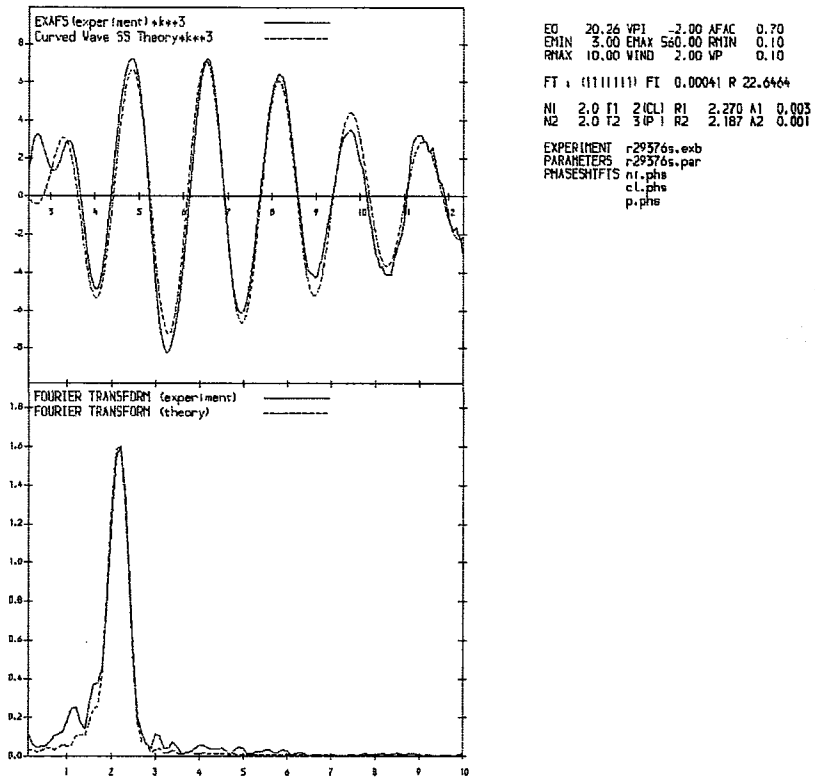


Figure 9.6: EXAFS data for $[NiCl_2(PPh_3)_2]$ in solid state

As can be seen, two coordination shells were created according to the model. The first consists of two chloride anions, and the second of two phosphorus atoms (relating to the phosphine ligands). The nearest carbon atoms from the phenyl groups directly attached to the phosphine ligands were briefly attempted as a third coordination shell, but were not able to be fitted. This is presumably because they are out of the EXAFS range, and also because they are, to some extent shielded from the path of the outgoing excited electron by the phosphorus atoms and chloride anions.

After refinement, a Ni-Cl bond length of 2.270 Å and Ni-P bond length of 2.187 Å were recorded. The fit between theoretical and experimental data was good (R=22.6). This was in excellent agreement with crystal structure data from the literature,[3.21] which showed a Ni-Cl bond length of 2.270 Å, and a Ni-P bond length of 2.187 Å.

It is known that this complex forms a distorted tetrahedral complex.[3.22] Solid state UV-VIS studies confirmed this to be true. Peaks at 875 nm, 560 nm and 434 nm, and shoulders at 1050 nm and 663 nm confirmed this when compared to the literature.[22] It was expected that the tetrahedral shape would be distorted since the phosphine ligands are more sterically demanding than the chloride ligands. Figure 9.7 shows the structural solution for this complex in the solid state.

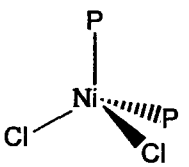


Figure 9.7: The local structure of $[NiCl_2(PPh_3)_2]$ in solid state

9.2.2.4. Solid $[NiCl_2(dppe)]$

This complex is similar to $[NiCl_2(PPh_3)_2]$, although it should be noted that that the phosphine ligand contains an ethylene bridge between the two phosphine atoms. This would be expected to impose a rigid stereochemistry, since the phosphine groups cannot act as separate ligands and position themselves anywhere around the nickel.

Crystal structure data from the literature[3.23] claims that there are two possible solid state forms of this compound (referred to only as forms A and B). Both have the same symmetry but slightly different Ni-Cl and Ni-P bond lengths. They are prepared by different methods of recrystallisation. Form A has an Ni-Cl bond length of 2.205 Å, and an Ni-P bond length of 2.157 Å. Form B has an Ni-Cl bond length of 2.195 Å, and an Ni-P bond length of 2.145 Å. The coordination shells around the nickel centre were set up very similarly to that for $[NiCl_2(PPh_3)_2]$. Figure 9.8, below, shows the refined EXAFS data for this complex in the solid state.

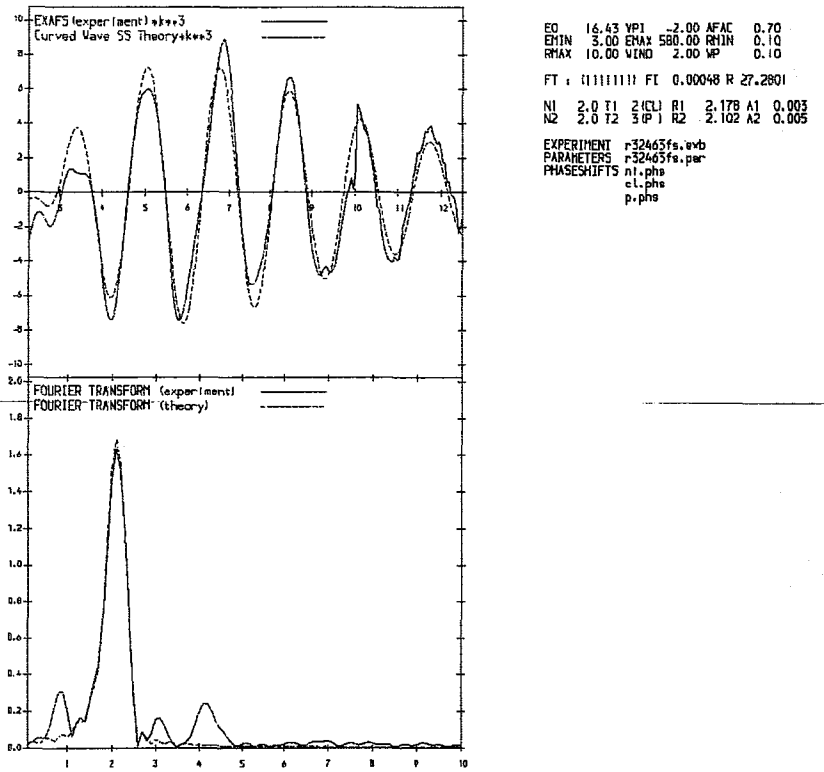


Figure 9.8: EXAFS data for $[NiCl_2(dppe)]$ in solid state

After refinement, the EXAFS data showed that the Ni-Cl bond length was calculated at 2.178 Å, and the Ni-P bond length at 2.102 Å. The data had a good fit (R=27.3). Although the bond lengths do not agree perfectly with either crystal structure, it more closely agrees with that of form B. In the event that a mixture of both forms exists, one possible reason could be the method by which the sample in this study was prepared, which was from an older paper in the literature where the existence of two forms of this complex were as yet unknown.

As can be seen from figure 9.8, the Fourier transform plot contains two low intensity peaks in the region between 3-5 Å. There are two reasons that these could exist. Firstly, the ethylene bridge carbon atoms (further away from the nickel centre than the phosphorus atoms) could be causing some weak backscattering of the excited electron, or the carbons of the phenyl groups directly bonded to the phosphorus atoms may be backscattering. The latter would be a possibility, but less likely since it is the ethyl bridge that spans the gap between the two phosphorus atoms (and is less hidden by the them), and thus more likely to be seen by the EXAFS process.

However, when a third shell containing an unfixed number of carbon atoms at an unfixed distance was refined, the value of the fit went up and the number of carbon atoms at the distance rose to an unfeasible value (about four). It might be that the EXAFS was combining the carbons of the bridge and the closest carbon atoms on the phenyl groups of the phosphine ligand. However, this is not logical, since the scan for $[NiCl_2(PPh_3)_2]$ showed no such carbon atoms, and it would be expected to if this were the case.

The second, and thus more likely reason is due to the quality of the data. The EXAFS patterns shows some jagged curves to the right of the spectrum that indicate a loss of resolution (or an increase in noise) at this part. This is also likely to make the fit much greater than it could have been. Hence no further fitting was attempted and the signal was attributed to noise.

Due to the geometry of the phosphine ligand, it is unlikely that this complex would form a tetrahedron, since this would provide stress on the bridge. The other possible configuration would be *cis*-square planar. A broad peak at 460 nm in the solid state UV-VIS spectrum confirmed this, in agreement with the literature.[3.24] Figure 9.9 shows the structural solution for this complex in the solid state.

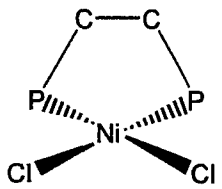


Figure 9.9: The local structure of $[NiCl_2(dppe)]$ in solid state

9.2.2.5. Solid $[NiCl_2(PMe_3)_2]$

The last of the complexes to be studied is similar to the triphenylphosphine nickel complex, except for the vastly reduced bulk of the phosphine ligands. The coordination shells for the EXAFS model were set up very similarly to those of $[NiCl_2(PPh_3)_2]$ as a starting point. Figure 9.10, below, shows the refined EXAFS data for this complex in the solid state.

The EXAFS scan was straightforward to refine, due to the collective experience of the other compounds analysed. Unfortunately, no crystal structure data was available in the literature for comparison. The sample studied showed a Ni-Cl bond length of 2.176 Å and an Ni-P bond length of 2.380 Å.

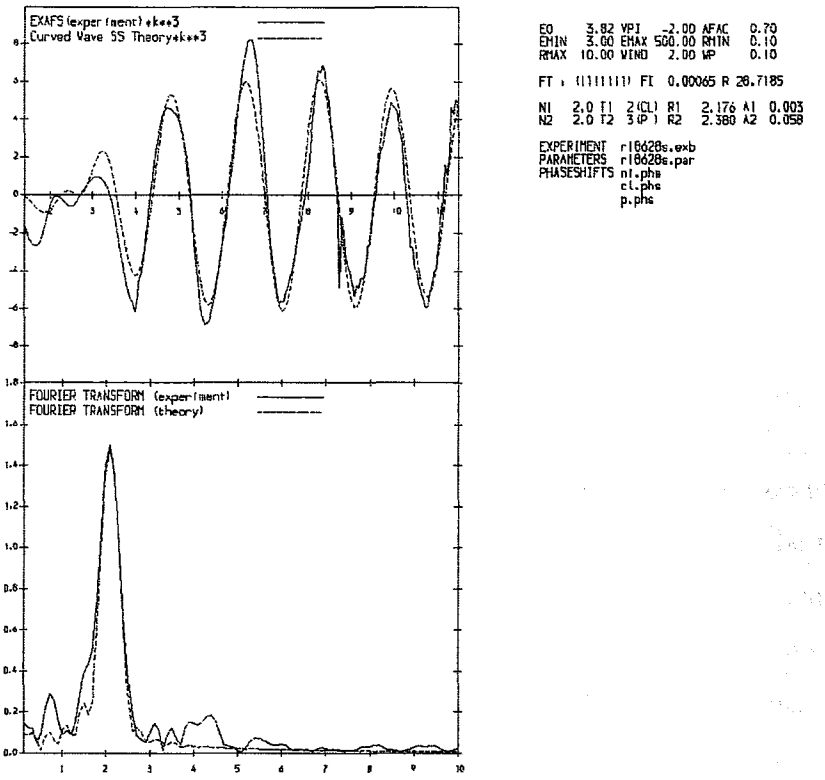


Figure 9.10: EXAFS data for $[NiCl_2(PMe_3)_2]$ in solid state

The presence of four coordinating atoms means that a tetrahedral or square planar structure could be expected. The literature[3.25] states that the configuration is definitely *trans*-square planar. Solid state UV-VIS studies confirmed this, due to the presence of a broad band at 520 nm, which was consistent with the literature.[3.25] Figure 9.11 below shows the structural solution for this complex in the solid state.

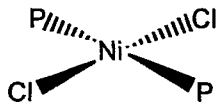


Figure 9.11: The local structure of $[NiCl_2(PMe_3)_2]$ in solid state

9.2.2.6. Conclusions of Solid-State EXAFS Studies

The EXAFS studies carried out for all five samples were deemed to be a success, with good agreement when compared to the literature. As there will be no comparison once dissolved in the ionic liquids, this study was important in order to establish the validity of EXAFS as a method of structural determination for these complexes. The fact that other forms of spectroscopy used in conjunction with the EXAFS scans also led to a clearer structural picture for each complex bodes well for the work to come.

9.2.3. Nickel Complexes dissolved in the Lewis basic [bmim]Cl-$AlCl_3$ ionic liquid

The ionic liquid was made as strongly Lewis basic as possible, with a 0.35 molar ratio of [bmim]Cl used.

9.2.3.1. $[bmim]_2[NiCl_4]$, $[Ni(acac)_2]$, $[NiCl_2(PPh_3)_2]$ and $[NiCl_2(PMe_3)_2]$

When dissolved in the Lewis basic ionic liquid, all of these complexes showed very similar results in the compounds that they formed. The fact that the Dimersol® process does not proceed in the Lewis basic ionic liquid has already been discussed in chapter 8. This was believed to be because an inactive species is formed by the nickel complexes in these solvents. It is known that these chloroaluminate melts, when Lewis basic, contain an excess of strongly coordinating chloride anions. Figure 9.12 shows the refined EXAFS data for the complex $[bmim]_2[NiCl_4]$ in the Lewis basic ionic liquid.

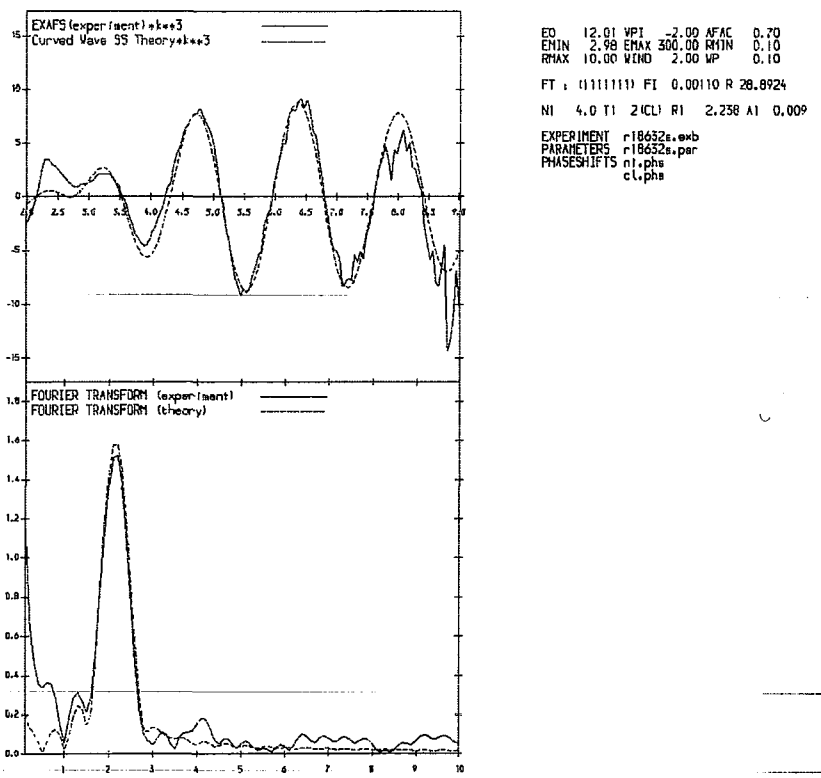


Figure 9.12: EXAFS data for $[bmim]_2[NiCl_4]$ dissolved in Lewis basic version of [bmim]Cl-$AlCl_3$

It was found that after refinement, the complex had an identical structure in solution as in the solid state. The Ni-Cl bond length is 2.238 Å, which compares well with the data for the solid version, and agrees with literature data for this species in the Lewis basic ionic liquid.[3.19] The R value also shows an acceptable fit at 28.89.

As discussed earlier, the starting parameters used to fit all of these complexes were those obtained from the EXAFS of the solid state versions. The structural solution for $[bmim]_2[NiCl_4]$ in the Lewis basic ionic liquid exhibited a high similarity to the solid state version, with only a slight refinement necessary to obtain a good fit. However, the other three complexes showed a bad fit when the solid state parameters were applied to and refined to the EXAFS of the Lewis basic solution scans. So alteration of the parameters was required to arrive at a suitable solution in each case.

Table 9.1 shows the EXAFS results for all the complexes mentioned in this section. After finding a solution to the EXAFS data for each complex, it was found that they corresponded exactly to $[NiCl_4]^{2-}$ in solution. The (acac) or various phosphine ligands had been displaced by chloride anions. It would be assumed that the chloride anions are so strongly coordinating to the nickel that they form bonds to the ligands already present. This could be observed, even in simple terms, as the variously coloured nickel complexes all became the same colour on being dissolved in Lewis basic [bmim]Cl-$AlCl_3$, giving four identically coloured deep blue solutions. Table 9.1, below shows the refined EXAFS results for all four samples in the Lewis basic ionic liquid.

Table 9.1: EXAFS results for $[NiCl_4(bmim)_2]$, $[Ni(acac)_2]$, $[NiCl_2(PPh_3)_2]$ and $[NiCl_2(PMe_3)_2]$ dissolved in the Lewis basic ionic liquid [bmim-Cl][$AlCl_3$]

Compound	Ni-Cl length / Angstroms	A1 value	N1 value	Fit (R)
$[bmim]_2[NiCl_4]$	2.238	0.009	4.0	28.89
$[Ni(acac)_2]$	2.232	0.009	4.0	27.60
$[NiCl_2(PPh_3)_2]$	2.243	0.009	3.9	26.13
$[NiCl_2(PMe_3)_2]$	2.237	0.009	4.0	25.54
$[emim]_2[NiCl_4]$[a]	2.25	0.008	4	22

[a] This result is from work carried out by Seddon and co-workers[3.19]

As can be seen, the data for all four complexes is virtually identical and also agree closely with literature data for $[emim]_2[NiCl_4]$ in the same ionic liquid proposed by Seddon and co-workers.[3.19] To test that all of these samples had the same structures, UV-VIS spectrometry was used. Again, the results were virtually identical, showing that the same complex whose composition had been identified from the EXAFS was present. Peaks were present at 705 nm ($^3\Gamma_1 \rightarrow {}^1\Gamma_5$) and 657 nm ($^3\Gamma_1 \rightarrow {}^3\Gamma_3$), with a shoulder at 618 nm ($^3\Gamma_1 \rightarrow {}^3\Gamma_4$) for all samples. This identifies the solution sample as tetrahedral, just as the solid version of $[NiCl_4]^-$ was. Therefore, the local structure for all four compounds $[bmim]_2[NiCl_4]$, $[Ni(acac)_2]$, $[NiCl_2(PPh_3)_2]$ and $[NiCl_2(PMe_3)_2]$ dissolved in the Lewis basic version of [bmim]Cl-$AlCl_3$ is in no different than previously shown in figure 9.2.

9.2.3.2. $[NiCl_2(dppe)]$

The only complex that showed any structural difference in the Lewis basic version of the ionic liquid was $[NiCl_2(dppe)]$. Although no quantitative study was undertaken, it turned out to be noticeably less soluble in the ionic liquid, and unlike the other samples, its

solution was not blue, but an orange/red, in fact the same colour as the solid. Figure 9.13 shows the refined EXAFS data for the complex $[NiCl_2(dppe)]$ in the Lewis basic ionic liquid.

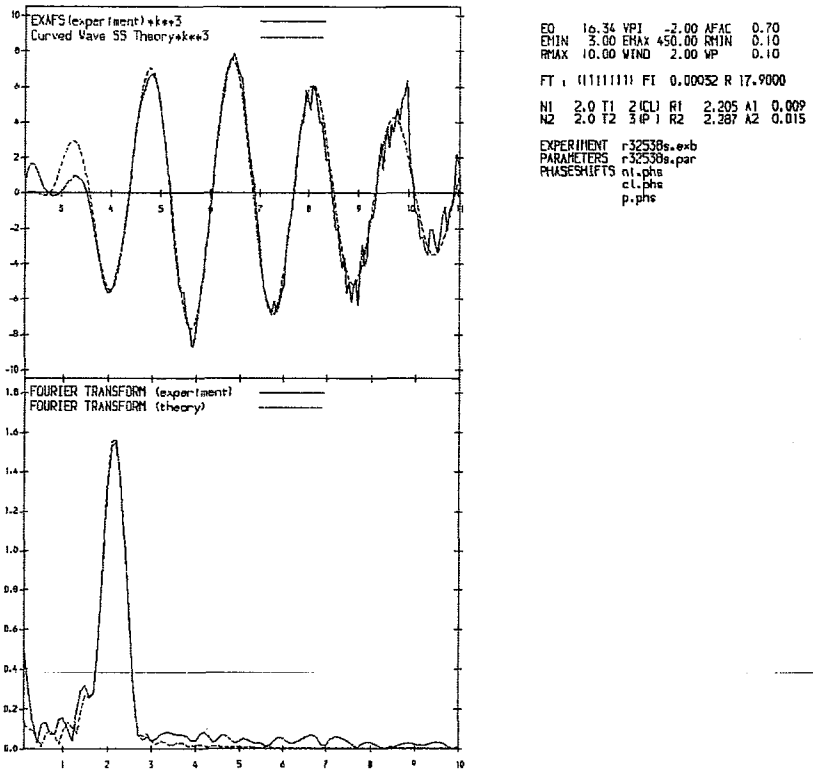


Figure 9.13: EXAFS data for $[NiCl_2(dppe)]$ dissolved in Lewis basic version of [bmim]Cl-$AlCl_3$

The starting parameters used were those of solid state complex. After refinement the fit was such that it was found that the soluble species was in fact unchanged from the solid one. Again, two coordination shells were present; one containing two chloride anions at a distance of 2.205 Å, and one containing two phosphorus atoms at a 2.287 Å. These

figures compare well with the EXAFS data for the solid version of this compound (2.178 Å and 2.102 Å respectively). As the sample is in solution, it could be expected that the ligands are no longer locked in a crystal structure and have more space to move slightly outwards from the nickel centre, as can be seen from these results. The value of R is also the best seen so far (17.90), which validates this result, even though it shows a major difference to other nickel complexes.

To verify completely that this structure was indeed the same as the solid version a UV-VIS analysis was carried out on the solution. Not only did the result indicate a square planar complex, as had been observed for the solid version, but the peaks for both complexes were observed at exactly the same wavelength (460 nm). This is significant. Although the EXAFS scan showed the presence of the four ligands around the nickel centre, it cannot be assumed that the molecule is intact. For example, the ethylene bridge might be disconnected in solution, or phenyls from the phosphine ligand may be lost. Although this is highly unlikely, it cannot be discounted because the EXAFS can only give a picture of the local structure immediately around the nickel centre. In section 9.2.2.4 the ethylene bridge on (dppe) could not be seen in the EXAFS data. However, the fact that UV-VIS spectrometry indicates exactly the same configuration as the solid version when dissolved in solution reveals that there is no distortion. If the ethylene bridge were to "fall off" in solution then the phosphine groups would be able to move more freely and would no longer have the rigid support that the short bridge provides. This would be observed one of in two ways. Either by a small shift by the peak in the UV-VIS spectrum to indicate the formation of a complex with a different degree of distortion than is seen in the solid version, or indeed by a change in symmetry to, for example, a tetrahedral structure, indicating a great degree of freedom for the phosphine groups to position themselves at will around the nickel centre.

Whichever effect were seen would be an indication of some structural change that EXAFS cannot pick up. However, using the two spectroscopic methods in tandem (along with comparisons to previous data from the solid sample) allowed complete elucidation of the structure of the complex in solution. So now it can be assumed that the complex in

Lewis basic ionic liquid solution has exactly the same configuration and structure as the solid sample, the local structure of which can be seen in figure 9.9.

It is interesting to note that even in this chloride rich environment no further coordination of chloride anions to give, for example, $[NiCl_4]^{2-}$ occurs. This can be directly attributed to the chelate effect, which states that entropy effects make a major contribution to the stabilities of complexes. In order to understand this it should be remembered that the equilibrium constant of any substitution process is related to the standard free energy of a reaction, as shown in equation 9.1 below.

$$\Delta G^{\circ} = -RT\ln K \tag{9.1}$$

The free energy is related to the enthalpy and entropy changes, as shown in equation 9.2, below.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{9.2}$$

Thus the stability constant for the formation of a complex depends on the enthalpy and entropy changes in the complexing process. In such cases as the one being discussed, enthalpy changes are usually small, and so entropy contributions can become significant. If the ligand dppe in $[NiCl_2(dppe)]$ were substituted by chloride anions in the Lewis basic ionic liquid, then more free molecules would be seen in the system before the process than afterwards, thus decreasing the overall randomness of the system. This would result in an overall decrease in entropy. If a chelating ligand replaces two or more unidentate ligands, then more free molecules would be produced than had been present at the start. This would increase the overall randomness of the system, resulting in an increase in the overall entropy of the system. After muliplication with the absolute temperature T, this

would lead to a negative contribution to the free energy, and hence a positive contribution to the equilibrium constant *K*, meaning a more stable product. Thus the complex $[NiCl_2(dppe)]$ will remain as it is, even in a solution that is rich in highly coordinating chloride anions. If it were to substitute its bidentate phosphine ligand, or even coordinate to more chloride anions, or even both, an overall and entropically unfavourable reduction in the number of free molecules after complexation would be observed.

It should be noted that although the chelate effect applies to the case of the bridged phosphine ligand, we saw that the acac ligand came off the nickel centre in the same ionic liquid. This can be attributed to it being a poorer ligand than the dppe.

9.2.4. Nickel Complexes dissolved in the Lewis acidic [bmim]Cl-$AlCl_3$ ionic liquid

The ionic liquid was made as strongly Lewis acidic as possible, with a 0.65 molar ratio of $AlCl_3$ used.

9.2.4.1. $[bmim]_2[NiCl_4]$ and $[Ni(acac)_2]$

When dissolved in the Lewis acidic ionic liquid, both of these complexes showed very similar results in the compounds that they formed. As with the solutions in the Lewis basic ionic liquid, the starting parameters used were those of the solid state complexes. The refinement gave a poor fit, so alteration of the parameters and further refinement was necessary in order to arrive at a solution. Figure 9.14, below shows the refined EXAFS data for the complex $[bmim]_2[NiCl_4]$.

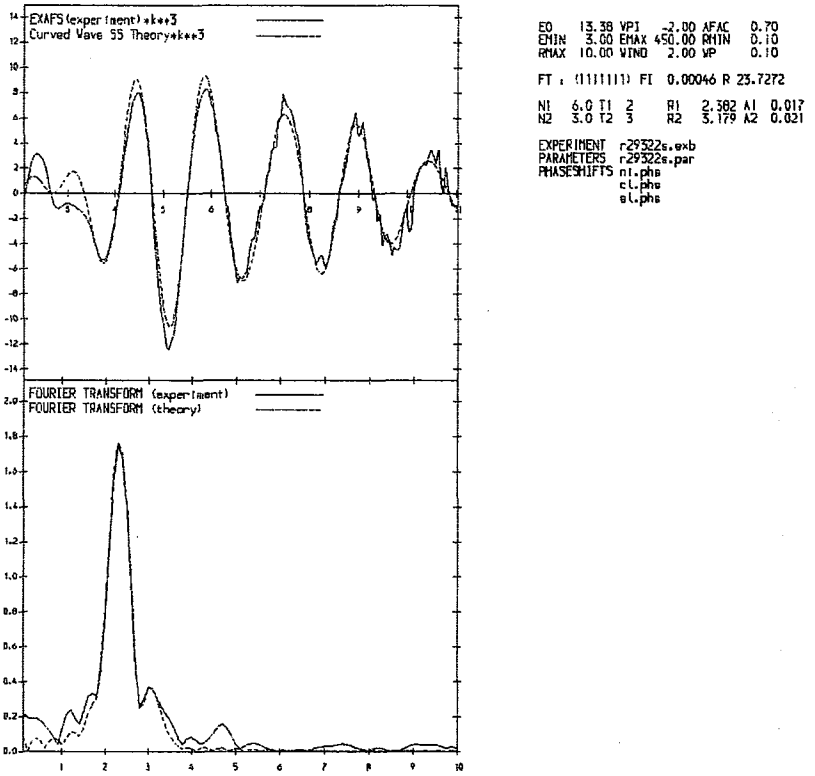


Figure 9.14: EXAFS data for $[bmim]_2[NiCl_4]$ dissolved in Lewis acidic version of [bmim]Cl-$AlCl_3$

In this version of the ionic liquid, there are no highly coordinating chloride anions present. Instead, the main species present are $[AlCl_4]^-$ and $[Al_2Cl_7]^-$, which although less strongly coordinating than chloride anions, are able to coordinate to the nickel centre. The only structural solution that gave an acceptable fit (R=23.73) was one where two coordination shells were present. The first shell contained six chlorides at a distance of 2.382 Å from the nickel centre, and the second contained three aluminiums at a distance of 3.179 Å from the nickel centre.

Two structural arrangements could be imagined from the configuration of the atoms around the nickel, and are illustrated in figure 9.15 below. The first (9.15a), proposed by

Seddon and co-workers[3.19] who worked in the same ionic liquid, is an octahedral arrangement of the chloride anions about the nickel centre, with the aluminium atoms bonded to the chlorides and forming a second coordination shell, but not directly bonded to the nickel itself. The second (9.15b) has been discussed in chapter 8, and was proposed by Corker and Evans[3.16] in an EXAFS study they carried out on the nickel complex $[NiCl_2(PEt_3)_2]$ in the presence of $Al_2Me_3Cl_3$ and $AlEt_3$ using diethyl ether as the solvent. Their conclusion from the data they assembled was that one of the alkyl groups formed a bridge between the aluminium and nickel atoms, but that the aluminium atom itself also formed a bond to the nickel.

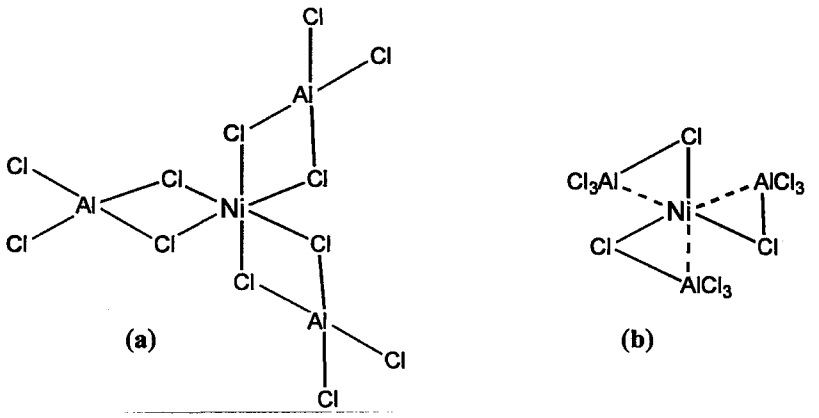


Figure 9.15: Proposed structures for $[bmim]_2[NiCl_4]$ dissolved in the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$

The data assembled makes it quite easy to discount the complex (b) in this case. Although enough chlorides are present to allow a coordination shell of six chlorides, the structural arrangement means that the aluminium atoms would need to be closer than are observed from this EXAFS study, and also that two coordination spheres of chloride anions would need to be present. The first at about the same distance observed in this study, but containing only three atoms, and the second further out with up to nine atoms present.

This data was entered as part of the study, but a very poor fit was observed, indicating that the complex (b) was not formed.

Confirmation of the formation of a complex consisting of $[Ni(AlCl_4)_3]^-$ in the Lewis acidic ionic liquid was obtained by FAB$^-$ mass spectrometry. A signal cluster centred around 564 indicated the presence of the named species. The isotopic distribution pattern obtained from the analysis perfectly matched a theoretical computer generated isotopic distribution pattern based on the named complex being present. This is illustrated below in figure 9.16. Another signal observed at 396 confirmed the fragmentation of this species into $[Ni(AlCl_4)_2]$.

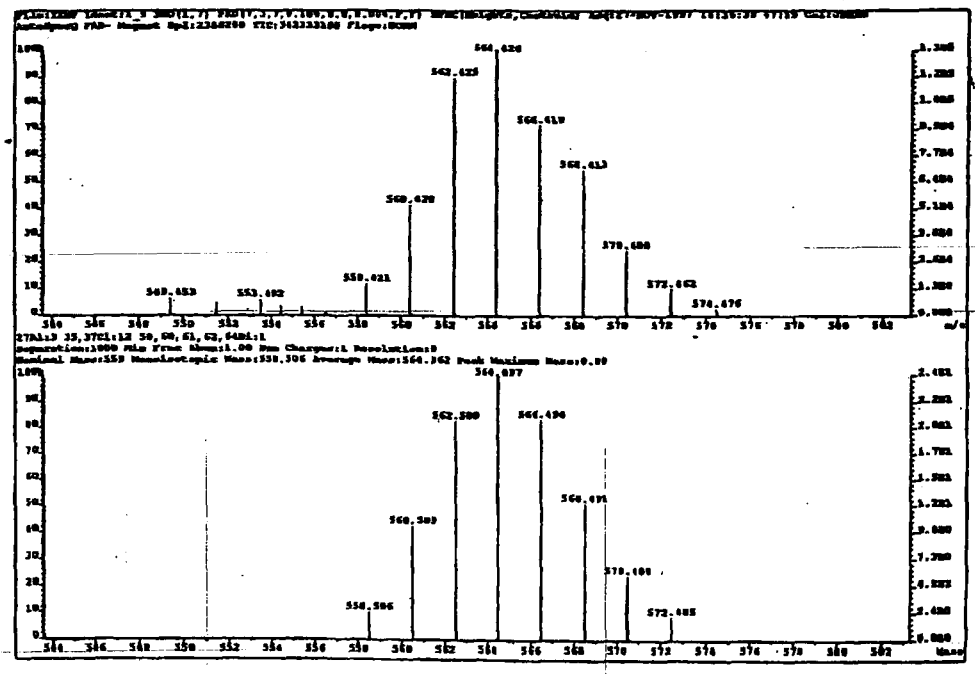


Figure 9.16: Experimentally derived (top) and theoretical (bottom) isotopic distribution patterns for the FAB$^-$ mass spectrum of the species $[Ni(AlCl_4)_3]^-$

To confirm the symmetry of the complex, UV-VIS spectrometry was carried out. A peak at 462 nm ($^3\Gamma_5 \rightarrow {}^3\Gamma_3$) confirmed the presence of an octahedral complex. The proposed structure is thus the one illustrated in figure 9.15a, above.

The fact that the $[AlCl_4]^-$ ligand is known to be less strongly coordinating than the chloride ligand would not allow the prediction of the existence of $[Ni(AlCl_4)_3]$ in this species. However it must be recognised that the situation in the acidic environment must be a dynamic one, and that EXAFS is a technique that detects the predominant species present. It could well be the case that any chloride anions present will rapidly react with $[Al_2Cl_7]^-$ to give $[AlCl_4]^-$. In other words the chlorides present as ligands on the nickel complexes are strongly coordinating as would be expected, but more so towards aluminium than nickel. This would result in the removal of chloride anions, leaving the species $[AlCl_4]^-$ free to coordinate with the nickel.

The data for the complex $[Ni(acac)_2]$ dissolved in the same ionic liquid gave very similar results to $[bmim]_2[NiCl_4]$. The presence of the acac ligand was not observed at all, which led to the conclusion that the complex $[Ni(AlCl_4)_3]^-$ had been formed. The refined EXAFS data for $[Ni(acac)_2]$ in the Lewis acidic ionic liquid showed a coordination shell consisting of six chlorides at a distance of 2.384 Å, and a second coordination shell of three aluminiums at a distance of 3.190 Å. The fit for these results was good (R = 25.35). The same fragmentation pattern seen in figure 9.16 was observed in the FAB^- mass spectrum of the sample, and the UV-VIS spectrum yielded the same data seen for $[bmim]_2[NiCl_4]$. Thus the structural solution was deduced to be the same as for $[bmim]_2[NiCl_4]$ (see figure 9.15a). The acac ligand is not known to be as strongly coordinating as the chloride ligand, which was observed to displace it in the Lewis basic version of the ionic liquid. The spectroscopic evidence shows that the acac ligands are displaced by $[AlCl_4]^-$ groups in the Lewis acidic version of the ionic liquid.

9.2.4.2. [$NiCl_2$(dppe)]

As was seen in section 9.2.3.2, the dppe ligand on this complex was not substituted by the chloride anions in the Lewis basic version of the ionic liquid. The major species present in this liquid are $[AlCl_4]^-$ and $[Al_2Cl_7]^-$, and it would be interesting to observe how the complex behaves in this environment.

Figure 9.17 below shows the refined EXAFS data for the complex [$NiCl_2$(dppe)].

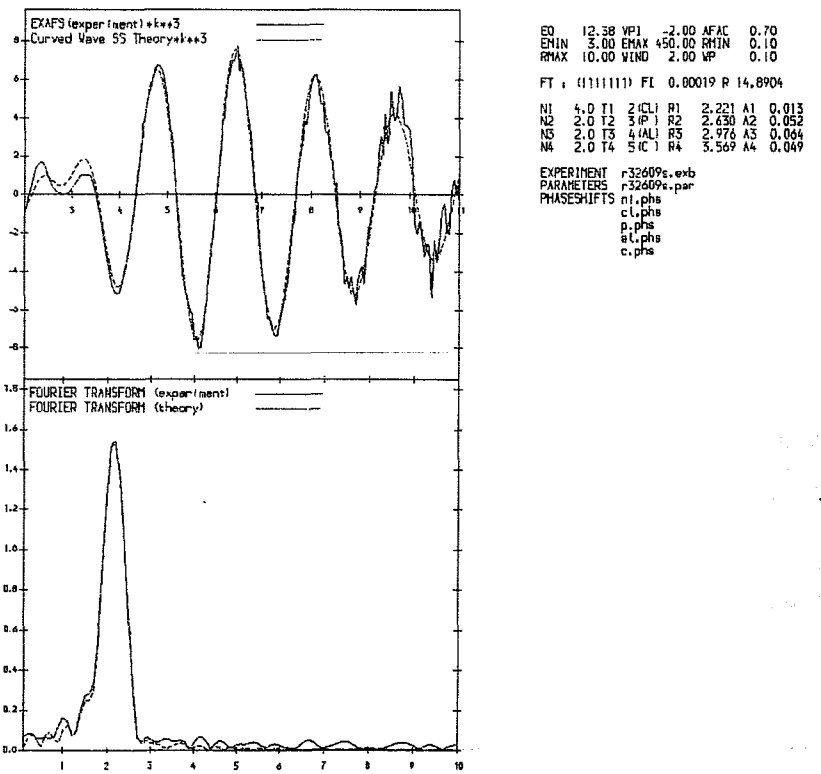


Figure 9.17: EXAFS data for [$NiCl_2$(dppe)] dissolved in Lewis acidic version of [bmim]Cl-$AlCl_3$

Again, the initial parameter values used were those of the same complex in the solid state. However, upon refinement to fit the experimental data a poor fit was obtained. Thus the parameters had to be changed and refitted. It can be seen that four coordination shells are present for this complex. The first consists of four chlorides at a distance of 2.221 Å, the second of two phosphorus atoms at 2.630 Å, the third of two aluminium atoms at 2.976 Å, and the fourth of two carbon atoms at 3.569 Å. The fit of the observed data to the theoretical EXAFS is in excellent agreement (R = 14.89).

The first thing to be noted is that the carbon shell must refer to the ethylene bridge between the two phosphorus atoms. Unlike the EXAFS spectra for the solid state and basic ionic liquid solution state versions of this complex, the bridge could be identified and fitted to the experimental data. The most likely explanation is not a structural change between the samples, since the UV-VIS data does not confirm this, but instead the quality of the raw EXAFS data. The elimination of unwanted noise occurs by summing repeatedly collected spectra of the same complex. In this case, unlike the other EXAFS spectra for the same complex in the other environments, the number of repeated spectra to sum was high (about 30, compared to up to about 10 for the other two spectra). This would mean that the data is likely to have been of a higher resolution than previously observed. In this way, the signal which corresponds to the carbon atoms, which is a weak signal due to its distance from the nickel centre, would have been relatively free of noise in comparison to previous. It is almost certain that the signal for the ethylene bridge carbons has been observed in the two previous EXAFS spectra for this complex, but was unable to be fitted to any degree of accuracy as so much noise was present.

The other bond lengths in the spectra confirm that the phosphine ligand (dppe) is still intact. However the presence of four chloride groups and two aluminium atoms at the same relative positions from the nickel centre as seen for the previous complex $[bmim]_2[NiCl_4]$ in section 9.2.4.1 indicates that, again, the chloride anions of the solid species are no longer present, but instead replaced with $[AlCl_4]^-$ groups from the ionic liquid. The presence of a peak at 463 nm in the UV-VIS spectra, again confirms the

presence of an octahedral complex. Figure 9.18 shows the structural solution for this complex in a solution of the Lewis acidic version of the ionic liquid.

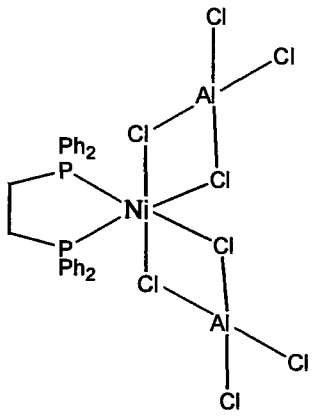


Figure 9.18: The local structure of $[NiCl_2(dppe)]$ in a solution of the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$

It is known that the configuration will be *cis*-octahedral since the presence of the ethylene bridge forces the phosphorus atoms into this arrangement. This could prove useful as a model if the bond lengths can be compared to the two nickel complexes with *bis*-monodentate phosphine ligands (assuming that in the forthcoming examples, both the phosphine ligands stay attached to the nickel) to discover whether they are *cis*- or *trans*-octahedral in configuration.

9.2.4.3. $[NiCl_2(PPh_3)_2]$ and $[NiCl_2(PMe_3)_2]$

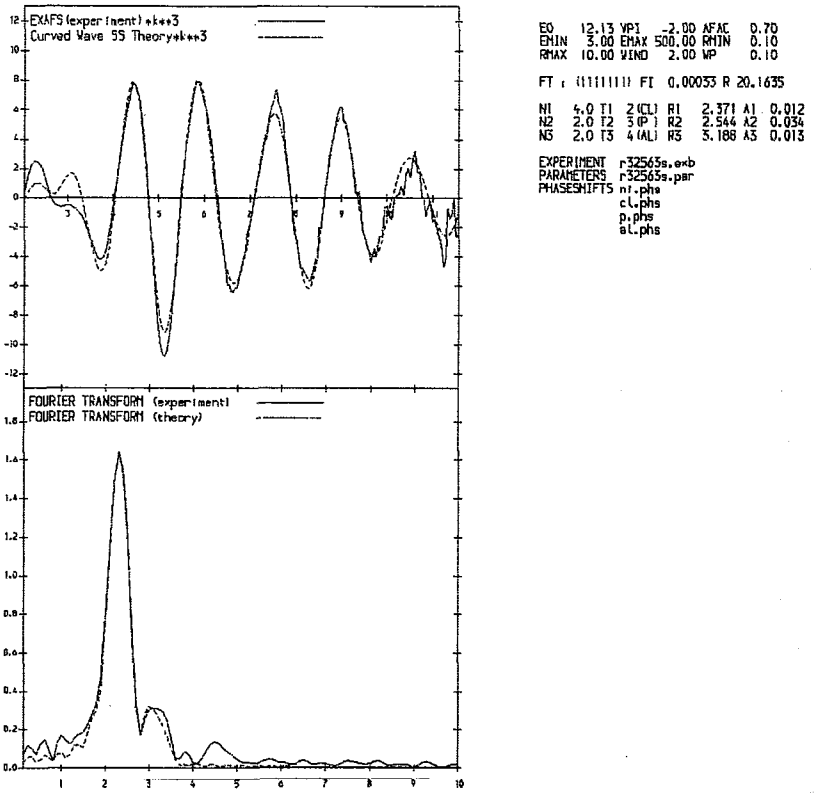


Figure 9.19: EXAFS data for $[NiCl_2(PPh_3)_2]$ dissolved in Lewis acidic version of [bmim]Cl-$AlCl_3$

In section 9.2.3.1 it was observed that both these complexes (unlike the other nickel phosphine complex [$NiCl_2$(dppe)]) lost their phosphine ligands in the presence of the highly coordinating chloride anions, found in the Lewis basic version of the ionic liquid [bmim]Cl-$AlCl_3$. Although the major species in this ionic liquid ($[AlCl_4]^-$ and $[Al_2Cl_7]^-$) are known to be more weakly coordinating than the chloride anions, it was of interest to see whether they would be able to display the phosphine ligands in this case. The

complex [$NiCl_2$(dppe)] showed no phosphine displacement in the Lewis acidic ionic liquid, but this should give no indication of what will happen in these cases since it also exhibited the same behaviour in the Lewis basic ionic liquid. Figure 9.19 above shows the refined EXAFS data for the complex [$NiCl_2(PPh_3)_2$].

Again, the initial parameter values were those of the same complex in the solid state. However, upon refinement to fit the experimental data a poor fit was obtained. Thus the parameters had to be changed and refitted. Two major forms were attempted in the fitting process. The first assumed that the phosphines had been substituted by $[AlCl_4]^-$ groups, giving a complex similar to that illustrated in figure 9.15a. The second assumed that the phosphines were intact, but that a similar situation to that for [$NiCl_2$(dppe)] (shown in figure 9.18) had occurred, whereby the octahedral nickel sites around the phosphorus nickel bonds were occupied by two $[AlCl_4]^-$ groups. The latter showed a good fit (R=20.16), whereas the former displayed a poor fit that was out of the range of an acceptable EXAFS fit.

Three coordination shells were fitted to the data. The first contained four chloride ions at a distance of 2.371 Å, the second two phosphorus atoms at a distance of 2.544 Å and the third two aluminium atoms at a distance of 3.188 Å. The UV-VIS spectrum showed a strong peak at 463 nm, consistent with the species being octahedral, as would be expected. However, the exact structure could not be given at this stage, since it was unclear whether the complex was *cis*- or *trans*-octahedral.

Figure 9.20 below shows the refined EXAFS data for the complex [$NiCl_2(PMe_3)_2$].

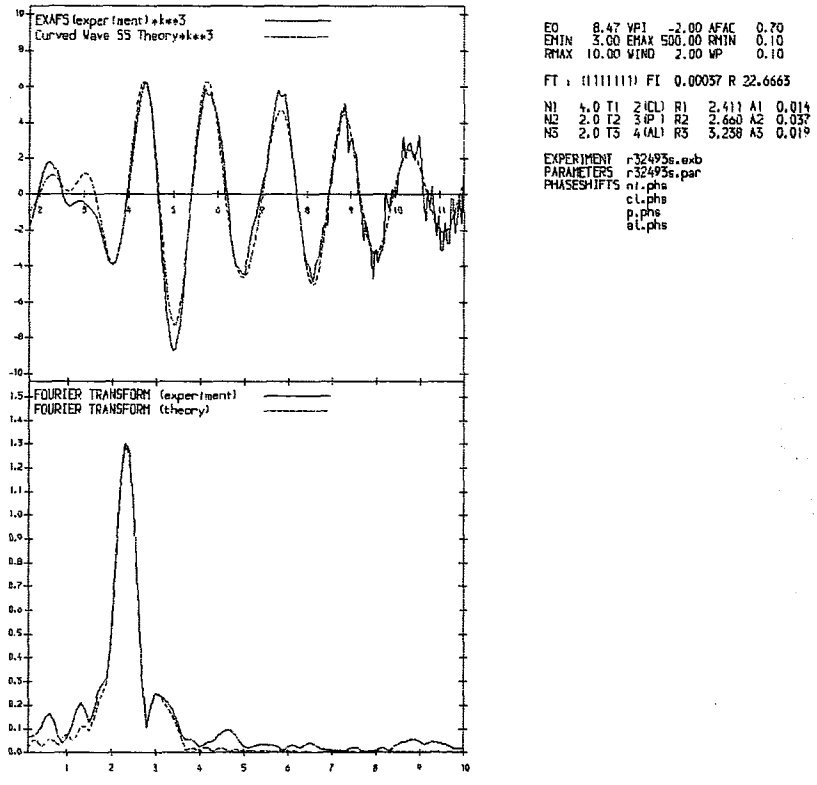


Figure 9.20: EXAFS data for $[NiCl_2(PMe_3)_2]$ dissolved in Lewis acidic version of [bmim]Cl-$AlCl_3$

Again, the initial parameter values was of the same complex in the solid state. However, upon refinement to fit the experimental data a poor fit was obtained. Thus the parameters had to be changed and refitted. The same two models that were previously attempted in the EXAFS fit for the complex $[NiCl_2(PPh_3)_2]$ were also used as the new starting points in this case. Again, it was shown that the phosphine ligands stayed attached to the nickel centre, but that the complex became octahedral in solution with two $[AlCl_4]^-$ groups binding to the metal. Three shells were fitted to the EXAFS data. The first consisted of four chloride groups at a distance of 2.411 Å, the second of two phosphorus atoms at a distance of 2.660 Å, and the third of two aluminium atoms at a distance of 3.238 Å. The UV-VIS spectrum confirmed the octahedral structure with a peak at 471 nm. Again, the

exact structure of the complex could not be given at this stage, since it was unclear whether the complex was *cis*- or *trans*-octahedral.

In order to determine which conformation each complex chose in the Lewis acidic ionic liquid, it had been planned to compare the bond lengths of these complexes with those of the complex $[NiCl_2(dppe)]$ in the Lewis acidic ionic liquid (see section 9.2.4.2). It was hoped that any change in the Ni-P bond lengths could indicate which isomer had been formed. Since the complex $[NiCl_2(dppe)]$ is known to be *cis*-octahedral in the Lewis acidic ionic liquid (due to the ethylene bridge on the phosphine ligand which constricts the phosphorus atoms from moving too far apart and thus forming the *trans*-isomer), it was hoped that some small difference in bond length could yield information regarding the conformation of the complex. However, all three complexes displayed similar Ni-P and Ni-Cl bond lengths. This either means that both complexes under study in this section are also in the *cis*-conformation, or that the data is not conclusive. It was decided that the latter hypothesis was true, and so an alternative method to deduce the structures of these compounds was searched for.

In order to state which of the two possible isomeric forms had been generated in the Lewis acidic ionic liquid in each case, ^1H NMR spectroscopy was utilised. Take the complex $[NiCl_2(PMe_3)_2]$. In such an NMR experiment, the protons on the methyl groups will give a peak. However, due to a phenomena known as virtual coupling,[3.26] the splitting of this signal can indicate whether the methyl groups on the two phosphines are adjacent (*cis*) or opposite (*trans*) to each other. If a 1:1 doublet is observed, then the *cis*-isomer is present, and if a 1:2:1 triplet is observed, the *trans*-isomer is present.

The fact that one of the complexes contains the triphenylphosphine ligand is a potential problem to this strategy. The signal provided by the methyl groups in the complex $[NiCl_2(PMe_3)_2]$ would be a clean peak. However the corresponding signal for the phenyl protons in $[NiCl_2(PPh_3)_2]$ would be a multiplet, and any further splitting due to virtual coupling would be almost impossible to detect. The obvious reason for assuming that the geometries of the two complexes might be different is of course the bulk of the

triphenylphosphine ligand. In order to avoid steric crowding around the nickel centre, it is likely that the triphenylphosphine ligands would be forced into forming the *trans*-isomer. However, it is quite likely that the less bulky trimethylphosphine ligands could form the *cis*-isomer. Therefore, it is important to measure the ^{1}H NMR spectra of both compounds in the ionic liquid. In view of this, the complex $[NiCl_2(PPh_2Me)_2]$ was made for this study. The presence of the single methyl group on each phosphine ligand would allow a signal in the ^{1}H NMR spectrum, while retaining the overall bulk of the ligand (thus allowing it to act as the triphenylphosphine ligand would). Figure 9.21 below, shows the ^{1}H NMR spectra for both complexes in the Lewis acidic version of the ionic liquid. Only the appropriate areas that refer to the methyl signal and its appropriate splitting pattern have been shown.

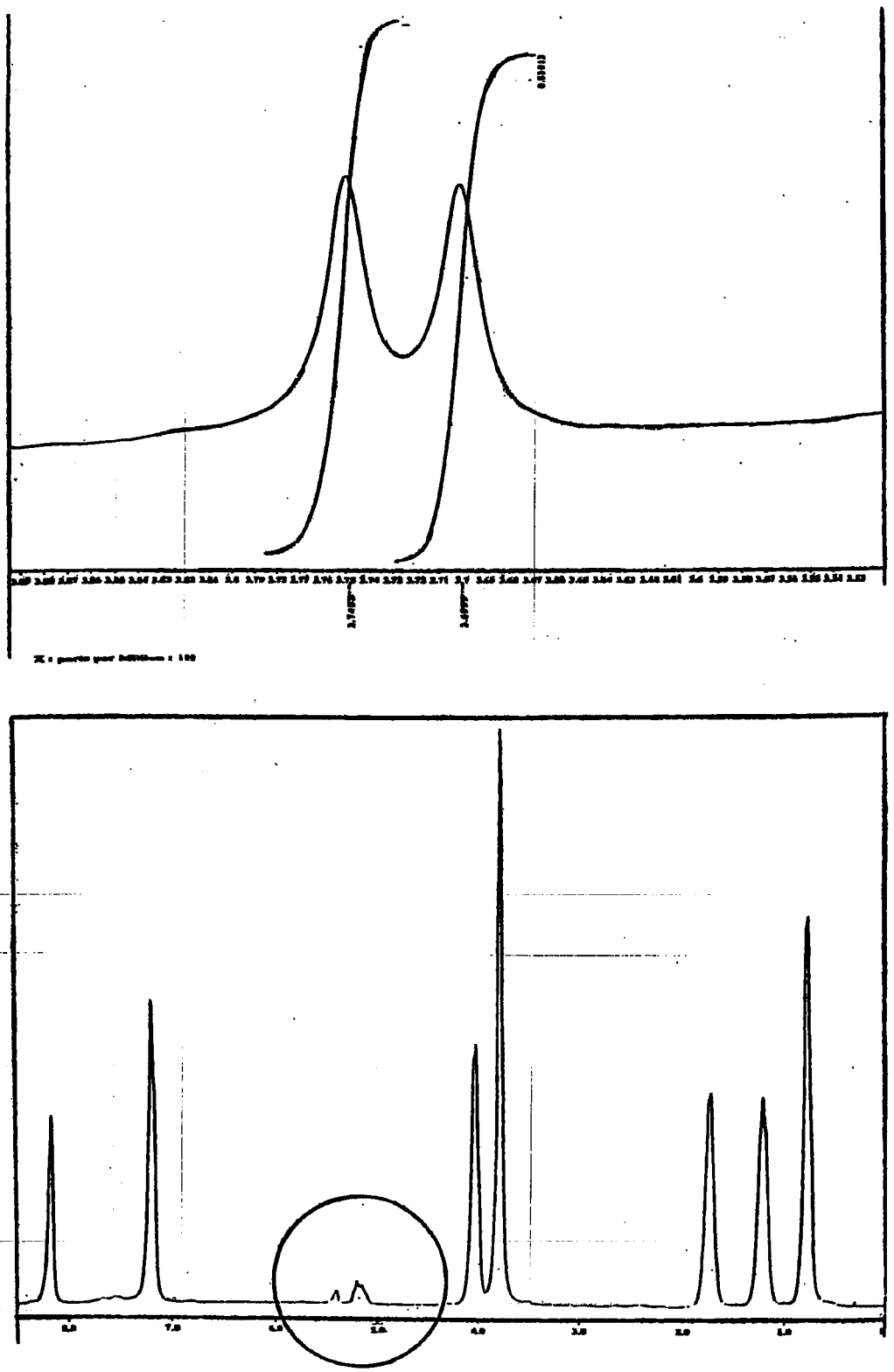


Figure 9.21: ^{1}H NMR spectra of (a) $[NiCl_2(PMe_3)_2]$ and (b) $[NiCl_2(PPh_2Me)_2]$ dissolved in the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$

The complex $[NiCl_2(PMe_3)_2]$ shows a very clear 1:1 doublet signal that indicates the formation of the *cis*-isomer. Whilst the results for the complex $[NiCl_2(PPh_2Me)_2]$ are less clear, they do indicate the formation of a triplet peak, which is indicative of the presence of the *trans*-isomer. The main reason this result is unclear stems from the fact that the resolution that the machine was able to give these peaks was extremely small, owing to the presence of peaks in the spectrum referring to the protons on the imidazolium part of the solvent. These latter peaks dwarfed the phosphine peaks, since they belonged to the solvent, and the nickel complexes only have a limited solubility. However, the ^1H NMR data shows that the complex $[NiCl_2(PPh_2Me)_2]$ is not in the *cis*-form since a 1:1 doublet would have been observed. Since it is assumed that this complex is in the *trans*-form, it is likely that the $[NiCl_2(PPh_3)_2]$ complex (containing the slightly bulkier triphenylphosphine ligand) would also be found in the *trans*-isomeric form in this ionic liquid. Figure 9.22 shows the structural solutions for these complexes in solutions of the Lewis acidic version of the ionic liquid.

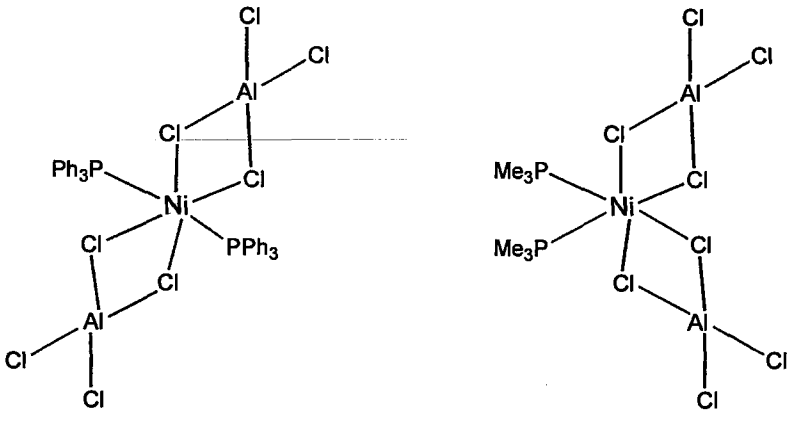


Figure 9.22: The local structures of (a) $[NiCl_2(PPh_3)_2]$ and (b) $[NiCl_2(PMe_3)_2]$ in solutions of the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$

9.2.4.4. Summary of Lewis Acidic Melt Work

Table 9.2: $[NiCl_2(PPh_3)_2]$ and$[NiCl_2(PMe_3)_2]$ dissolved in the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$

Compound	Ni-Cl length / Angstroms (r1)	N1	Ni-Al length / Angstroms (r2)	N2	Ni-P length / Angstroms (r3)	N3	Fit (R)
$[bmim]_2[NiCl_4]$	2.382	6.0	3.179	3.0	-	-	23.73
$[Ni(acac)_2]$	2.384	6.0	3.190	3.0	-	-	25.35
$[NiCl_2(PPh_3)_2]$	2.371	4.0	3.188	2.0	2.544	2.0	20.16
$[NiCl_2(PMe_3)_2]$	2.411	4.0	3.238	2.0	2.660	2.0	22.67
$[NiCl_2(dppe)]$[a]	2.221	4.0	2.976	2.0	2.630	2.0	14.89

[a] $[NiCl_2(dppe)]$ also shows a shell made up of 2.0 carbon atoms with Ni-Cl = 3.569 Angstroms

9.3. Application of Structural Data to the Dimersol® Process

It was shown throughout section 9.2.2 that the use of EXAFS for the structural determination of the model compounds studied was an accurate and reliable method. Where appropriate, other forms of spectroscopy have been used in tandem with the EXAFS procedure to either support or provide further information on the data obtained.

The data obtained from the samples of each complex dissolved in the Lewis basic version of the ionic liquid [bmim]Cl-$AlCl_3$ (a chloride rich environment) showed that in all cases except one ($[NiCl_2(dppe)]$), $[NiCl_4]^-$ was formed. For complexes which had previously contained phosphine or acac ligands, this meant substitution by the highly coordinating chloride anions. $[NiCl_2(dppe)]$ did not undergo these substitutions due to the chelate effect.

The data obtained from the samples of each complex dissolved in the Lewis acidic version of the ionic liquid [bmim]Cl-$AlCl_3$ (a solvent system rich in $[AlCl_4]^-$ and $[Al_2Cl_7]^-$) showed coordination of the more weakly coordinating $[AlCl_4]^-$ group, but not at the expense of the phosphine ligands. Apart from the case of $[Ni(acac)_2]$, no substitution was observed.

This data provides a greater understanding of the workings of the active nickel complexes in solution during the Dimersol® process. Unlike suggestions in the literature,[16] it is now known (through the EXAFS data) that no direct Ni-Al bond is formed in these complexes in this environment. Due to the fact that the ligand $[AlCl_4]^-$ is weakly coordinating in its nature, and that the most favourable catalytic species contains a Ni-H bond, it is now possible to apply this data to the practical example of the Dimersol® process.

The ionic liquid used in the industrial process consists of the acidic version of [bmim]Cl-$AlEtCl_2$. The anionic species $[AlEtCl_3]$ would also be weakly coordinating. Figure 9.23 below shows how the active complex for $[bmim]_2[NiCl_4]$ might be expected to look in such a Lewis acidic ionic liquid solution.

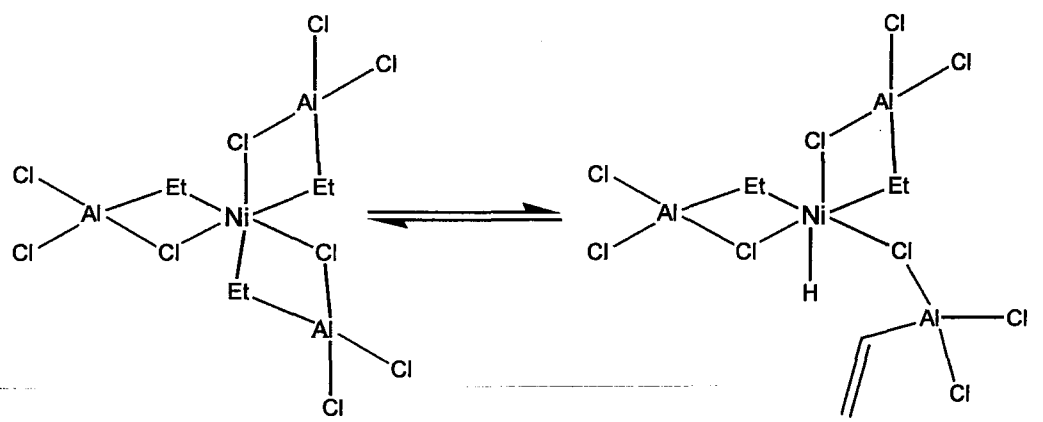


Figure 9.23: Proposed active species when $[bmim]_2[NiCl_4]$ is dissolved in the Lewis acidic version of the ionic liquid [bmim]Cl-$AlEtCl_2$

It should be stressed that the complex to the right is only found in a dynamic equilibrium. However, in this way, a complex containing a Ni-H bond is formed which can go on to dimerise propenes or butenes. Where complexes containing phosphine ligands are used, these will stay intact on the active complex. Thus the high product selectivities that have been observed using these systems would be attainable according to the phosphine effect.

It appears that the property of the ionic liquid that gives rise to this ability to cause the nickel species to act as an effective catalyst is simply chemical. The key here would be the ability of the $[AlCl_4]^-$ species to weakly coordinate to the nickel centre, thus giving it the ability to form the active complex. Evidence for this lies in the fact that no reaction is seen in the Lewis basic version of the same ionic liquid, an environment that is known to be rich in strongly coordinating chloride anions. Their inability to leave the nickel centre with any degree of ease would discourage the $[AlEtCl_3]^-$ species (that is also present in these systems) from coordinating to nickel and allowing the vital Ni-H bond to form. So effective are the chloride anions in doing this, that the literature states that no reaction at all is seen in these systems.[3.5] This is consistent with the structural results for complexes dissolved in these systems.

10. EXPERIMENTAL FOR SECTION 3

10.1. General

All manipulations of moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of dry nitrogen, or in a drybox under an atmosphere of dry nitrogen.

The Lewis acidic and Lewis basic versions of the ionic liquid [bmim]Cl-$AlCl_3$ were prepared as described in sections 3.2.4.1.1. and 3.2.4.1.5. respectively.

Anhydrous nickel(II)chloride was prepared from the hydrated version ($NiCl_2.6H_2O$). About 50 g of the hydrated version was placed into a round-bottom flask equipped with a reflux condenser and a dropping funnel. 100 cm^3 of thionyl chloride was added with care under an atmosphere of dry nitrogen. The mixture was heated under reflux for 12 hours. On cooling, excess thionyl chloride was removed *in vacuo*, and the remaining solid stored under an atmosphere of dry nitrogen.

Dry solvents were obtained as follows. Nitromethane was dried over CaH_2 for 24 hours and then distilled. Acetonitrile was distilled from CaH_2, as was tetrahydrofuran (THF). Diethyl ether was distilled from $CaCl_2$. Ethanol was distilled from $CaSO_4$, and pentane was distilled from P_2O_5.

^1H NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transform spectrometer. Elemental analysis and fast atom bombardment (FAB) mass spectra were recorded by the microanalytical and mass spectrometry laboratories of the Department of Chemistry of Imperial College, University of London. Infrared spectra were recorded on a Mattson Satellite FTIR machine.

10.2. Preparation of Nickel (II) Complexes

10.2.1. $[NiCl_4][bmim]_2$

Anhydrous nickel(II)chloride (2.00 g; 0.0154 mol) was added (in 30 cm^3 dry acetonitrile) to [bmim]Cl (5.38 g; 0.0309 mol). The reaction mixture was heated under reflux for 12 hours in which time a blue oils was observed to form. The mixture was then cooled and the solvent removed *in vacuo* until a thick blue oil remained. This was left at 0 °C for 24 hours. Dry pentane (30 cm^3) was added to aid the crystallisation process. On observinhg the formation of blue crystals from the oil, the pentane was removed by decantation, and a recrystallisation carried out from dry THF (35 cm^3). On dissolving in THF, the mixture was left for 24 hours at -20 °C, after which time blue crystals were observed to have formed. The solvent was removed by decantation, and the remaining blue solid (Yield: 4.98 g; 79.8 %) dried.

- Elemental analysis: Found: %C 41.25, %N 12.35, %H 3.02. Calc.: %C 40.08, %N 11.69, %H 3.13.

- Infrared spectrum (nujol mull) cm^{-1}: 3135 (m, aromatic C-H), 2724, (m, aliphatic C-H), 2672 (m, aliphatic C-H), 1788 (w, aromatic C-H), 1569 (m, Im ring), 1461 (st, Im ring), 1376 (st, Me C-H), 1337 (m, Im ring), 1167 (m, Im ring), 1091 (m, Im ring C-H), 1031 (m, Im ring C-H), 956 (m, Im ring C-H), 289 (m, Ni-Cl).

- Mass spectrum (FAB +ve) m/z: 617 $(M+bmim)^+$, 139 $(M-NiCl_4)^+$, 109 $(M-NiCl_4-2CH_3)^+$, 96 $(M-NiCl_4-CH_3-CH_2CH_3)^+$, 83 $(M-NiCl_4-CH_3-(CH_2)_2CH_3)^+$, 69 $(M-NiCl_4-CH_3-(CH_2)_3CH_3)^+$, 55 $(M-NiCl_4-CH_3-(CH_2)_3CH_3-N)^+$. (FAB -ve) m/z: 467 $(M-bmim+NiCl_2)^-$, 339 $(M-bmim)^-$, 295 $(M-2bmim-NiCl)^-$, 209 $(M-bmim-NiCl_2)^-$, 165 $(M-2bmim-Cl)^-$.

10.2.2. $Ni(acac)_2$

Three separate solutions were prepared separately; nickel(II)chloride hexahydrate (9.27 g; 0.039 mol) in 40 cm^3 distilled water, acetylacetone (5.94 g; 0.060 mol) in 20 cm^3 methanol and sodium acetate (7.00 g; 0.085 mol) in 30 cm^3 distilled water. The acetylacetate solution was added to the stirred solution of nickel(II)chloride hexahydrate. Then the sodium acetate solution was added to this mixture. A bright green solution was observed to form at this point. This was heated for 10 minutes at 100 °C, abd then cooled at 0 °C for 12 hours, allowing the formation of turquoise crystals. The whole mixture was reduced *in vacuo* until more green crystals appeared from the solution. The reaction solution was eliminated *in vacuo* until only the green crystals were left. These were the hydrated version of the desired product, and were heated to 50 °C *in vacuo* until a constant mass was recorded, indicating the removal of all water of crystalisation. A colour change occurred, from a darker to paler shade of green. The crystals were recrystallised from dry toluene and dried *in vacuo*, giving the anhydrous form of the desired product (Yield: 8.15 g; 81.50 %).

- Melting point: 232 °C (lit.[3.27] 229-230 °C).
- Elemental analysis: Found: %C 42.35, %H 5.38. Calc.: %C 46.69, %H 5.45.
- Infrared spectrum (nujol mull) cm^{-1}:
- Mass spectrum (FAB +ve) m/z: 413 $(M+Ni(acac))^+$, 257 $(M)^+$.

10.2.3. $NiCl_2(PPh_3)_2$

Two separate solutions were prepared; nickel(II)chloride hexahydrate (2.38 g; 0.010 mol) was dissolved in 25 cm^3 dry ethanol, and triphenylphosphine (5.24 g; 0.020 mmol) was also dissolved in 25 cm^3 dry ethanol. The solution containing triphenylphosphine was heated under reflux, and the other solution added to it slowly. A purple precipitate was observed to form almost immediately. The reaction mixtue was maintained at reflux for a further 20 minutes, and then cooled. The precipitate was washed with cold (0 °C) ethanol (2 x 20 cm^3) and diethyl ether (2 x 20 cm^3). Each wash was removed by filtration. The dark purple precipitate was dried *in vacuo*, giving crystals of the same colour (Yield: 3.701 g; 37.05 %).

- Melting point: 246-8 °C (lit.[3.28] 247-250 °C).
- Elemental analysis: Found: %C 65.93, %H 4.43. Calc.: %C 65.93, %H 4.59.
- Infrared spectrum (nujol mull) cm^{-1}: 533 (st, Ni-P), 497 (st, Ni-P), 439 (m, Ni-P), 341 (m, Ni-Cl), 304 (m, Ni-Cl).
- Mass spectrum (FAB +ve) m/z: 617 $(M\text{-}Cl)^+$, 582 $(M\text{-}2Cl)^+$, 505 $(M\text{-}2Cl\text{-}Ph)^+$, 279 $(M\text{-}NiCl_2\text{-}PPh_3\text{+}O)^+$, 262 $(M\text{-}NiCl_2\text{-}PPh_3)^+$. (FAB -ve) m/z: 130 $(M\text{-}2PPh_3)^-$.

10.2.4. $NiCl_2(dppe)$

The same method as in the preparation of $NiCl_2(PPh_3)_2$ (see section 10.2.3, above) was used, with separate solutions of nickel(II)chloride hexahydrate (2.38 g; 0.010 mol) and 1,2-bis(diphenylphosphino)ethane (3.98 g, 0.010 mol) being prepared in 25 cm^3 dry

ethanol each. The solutions were combined and treated as before. An orange precipitate was observed to form, which was washed as before, and dried *in vacuo*, giving an orange crystalline solid (Yield: 3.33 g; 63.21 %).

- Melting point: 270 °C (lit.[3.29] 271 °C).
- Elemental analysis: Found: %C 58.90, %H 4.25. Calc.: %C 59.12, %H 4.55.
- Infrared spectrum (nujol mull) cm^{-1}: 550 (st, Ni-P), 487 (st, Ni-P), 478 (m, Ni-P), 341 (m, Ni-Cl), 325 (m, Ni-Cl).
- Mass spectrum (FAB +ve) m/z: 1019 $(M+NiCl(dppe))^+$, 528 $(M)^+$, 491 $(M-Cl)^+$. (FAB –ve) m/z: 130 $(M-dppe)^-$.

10.2.5. $NiCl_2(PMe_3)_2$

The same method as in the preparation of $NiCl_2(PPh_3)_2$ (see section 10.2.3, above) was used, with separate solutions of nickel(II)chloride hexahydrate (2.38 g; 0.010 mol) and trimethylphosphine (1.52 g, 0.020 mol) being prepared in 25 cm^3 dry ethanol each. The solutions were combined and treated as before. A red/brown precipitate was observed to form, which was recystallised from 20 cm^3 dry ethanol, and dried *in vacuo*, giving a dark red crystalline solid (Yield: 2.17 g; 77.00 %).

- Melting point: 195-197 °C (lit.[3.30] 180-190 °C).
- Elemental analysis: Found: %C 26.36, %H 6.47. Calc.: %C 25.53, %H 6.38.

- Infrared spectrum (nujol mull) cm^{-1}: 549 (st, Ni-P), 475 (st, Ni-P), 468 (m, Ni-P), 348 (m, Ni-Cl), 325 (m, Ni-Cl).

- Mass spectrum (FAB +ve) m/z: 283 $(M)^+$, 209 $(M\text{-}PMe_3)^+$, 147 $(M\text{-}NiPMe_3)^+$, 135 $(M\text{-}2Cl\text{-}PMe_3)^+$, 73 $(M\text{-}NiCl_2(PMe_3))^+$. (FAB –ve) m/z: 204 $(M\text{-}PMe_3)^-$, 130 $(M\text{-}2PMe_3)^-$.

10.2.6. $NiCl_2(PPh_2Me)_3$

A solution of nickel(II)chloride hexahydrate (1.076 g; 0.0027 mol) in 20 cm^3 dry ethanol was made up. To it was added (with extreme care) methyldiphenylphosphine (1.00 cm^3; 0.0054 mol). The mixture was heated under reflux for 12 hours, giving a red/brown precipitate. The solvent wwas removed *in vacuo*, and the resulting product recrystallised from dry pentane, giving a red/brown crystalline solid (Yield: 0.987 g; 69.31 %).

- Elemental analysis: Found: %C 59.93, %H 4.78. Calc.: %C 58.87, %H 4.91.

10.3. EXAFS Studies

10.3.1. Sample Preparation

All manipulations of moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of dry nitrogen, or in a drybox under an atmosphere of dry nitrogen.

Solid samples for EXAFS studies were prepared by thoroughly grinding the solid. A thin layer was attatched to the middle 2 cm of a 10 cm length of plastic tape. This was stuck across the hole of a stainless steel plate so that the sample was visible through the hole. This process was repeated ten times using the same plate, until a sample thickness of roughly 1 mm had been achieved. The metal plate was used as the sample carrier for the EXAFS scan.

Solution samples were prepared by dissolving the appropriate solid sample into the appropriate ionic liquid. When saturation point was reached, the mixture was left stirring for 12 hours, and filtered through a plug of glass wool in a column of diameter of 5 mm. Approximately 1 cm^3 of the sample was injected into a small (50 mm by 50 mm) polyethylene bag, which was double sealed, and used as the sample carrier for the EXAFS scan.

10.3.2. EXAFS Acquisition and Analysis

The EXAFS data were obtained using the synchatron radiation source at the SRS in Daresbury UK, at station 7.1. Experiments for solid samples were carried out on the Ni K edge in transmission mode under dry inert gas conditions. Experiments for solution samples were carried out on the Ni K edge in fluorescence mode under dry inert gas conditions. Background subtraction of the EXAFS spectra was carried out using EXCALIB and EXBROOK programs, and the spectra were fitted using the EXCURVE92 program.[3.31] These programs are all available on the Daresbury Convex.

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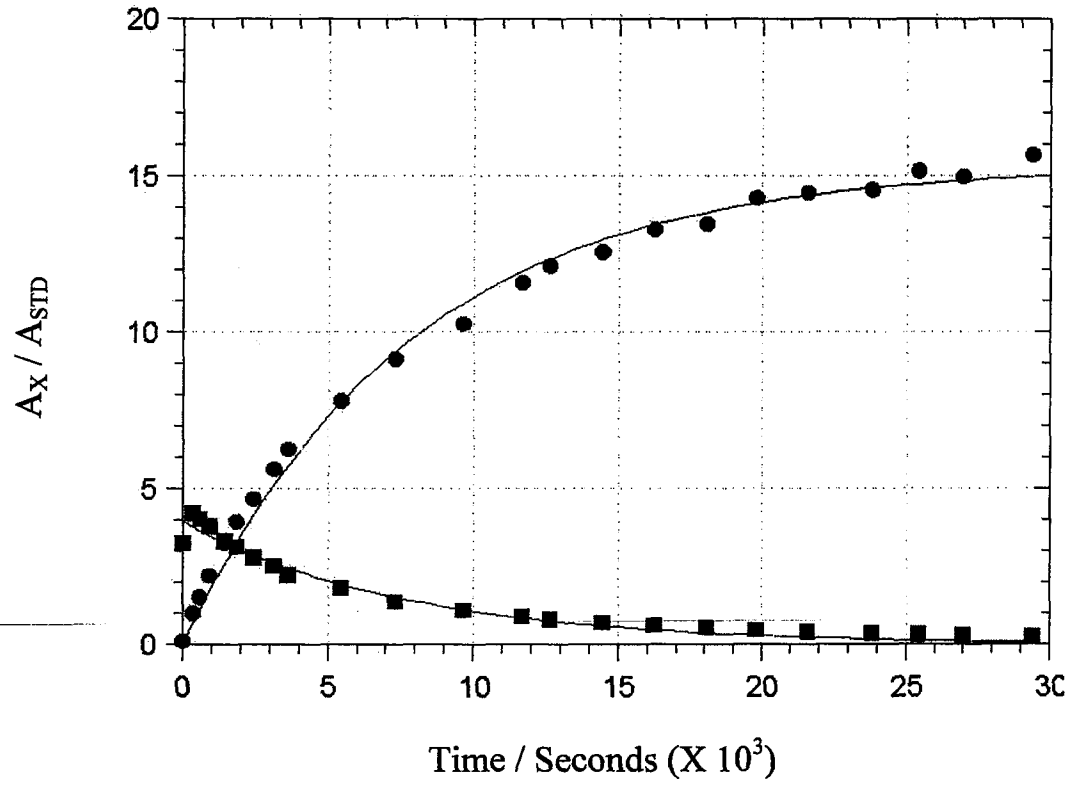
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SECTION 4

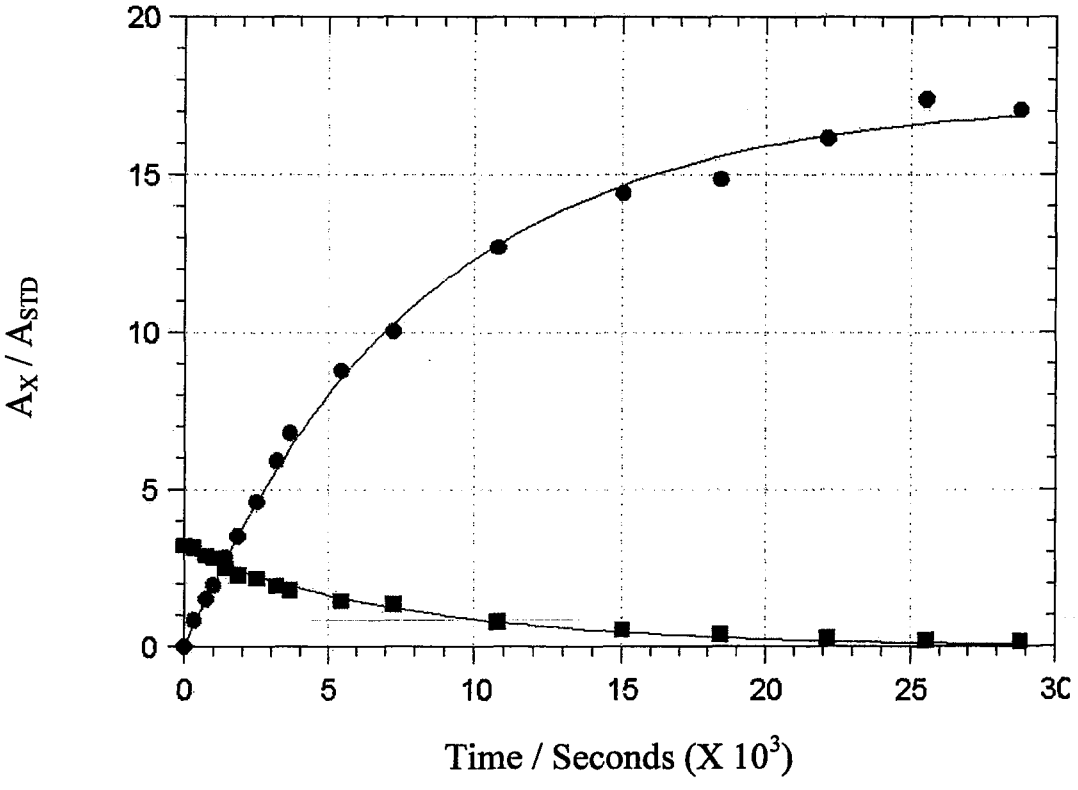
APPENDIX

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][BF_4]



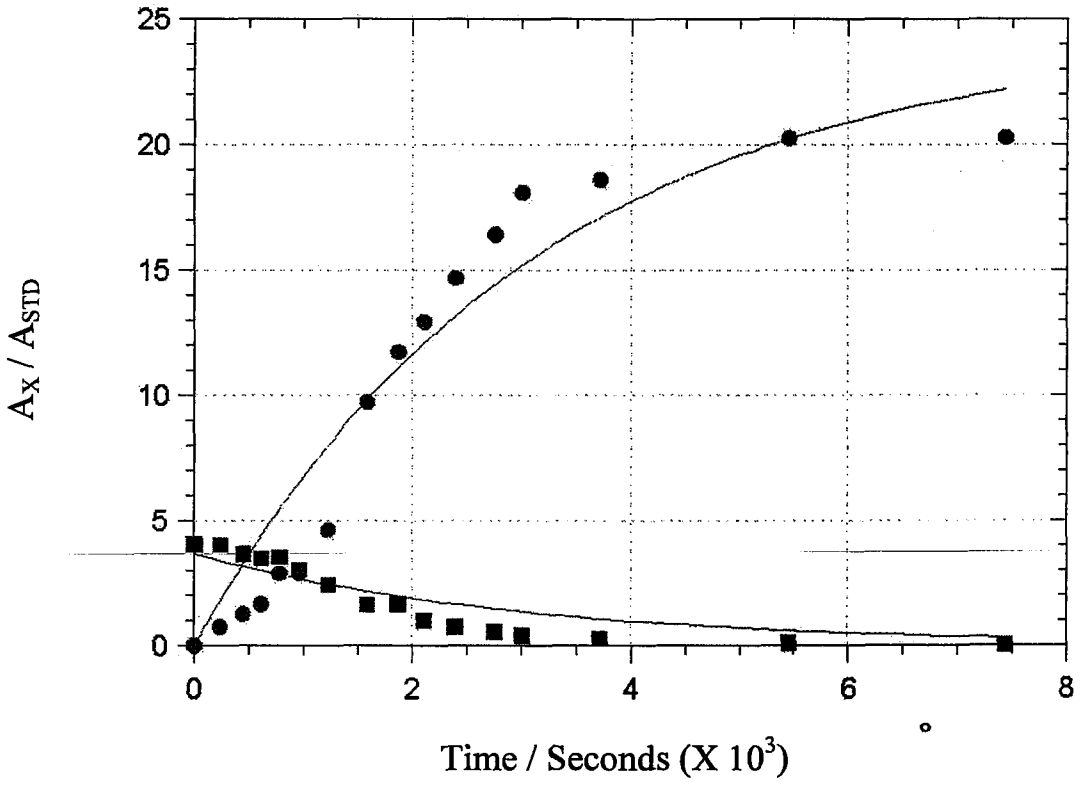
- **See Table 6.9 – Entry 1**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][OTF]



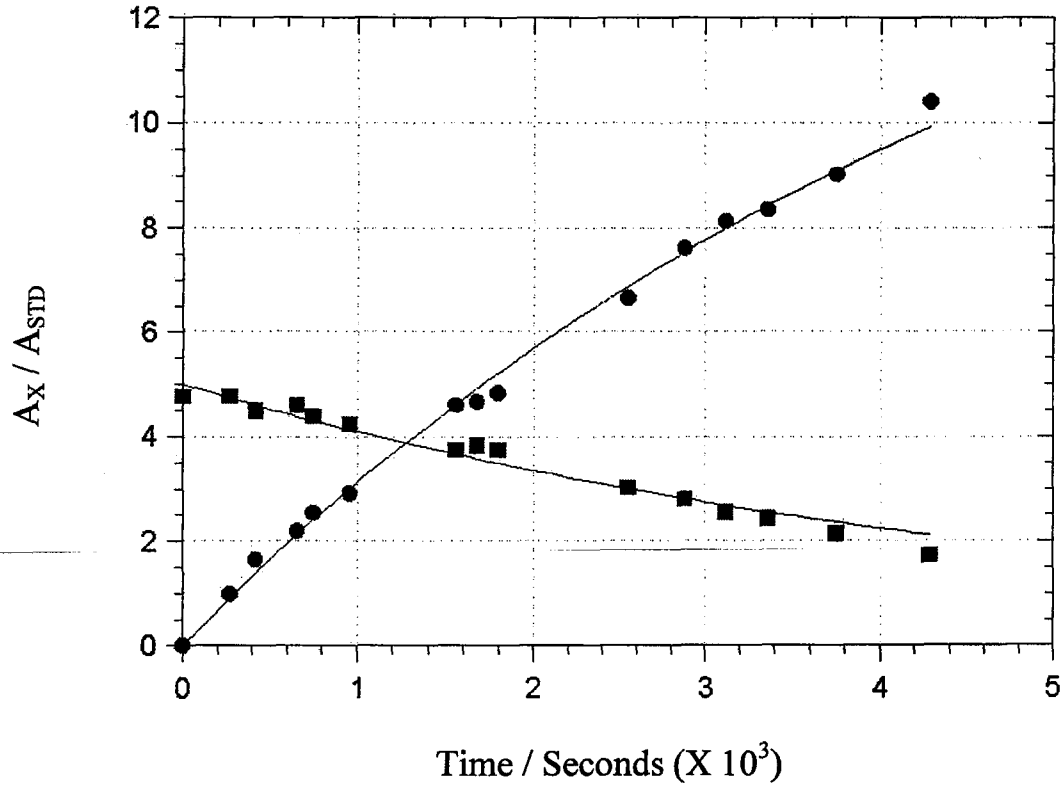
- **See Table 6.9 – Entry 2**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][OTF] WITH THE ADDITION OF SCANDIUM TRIFLATE – RUN 1



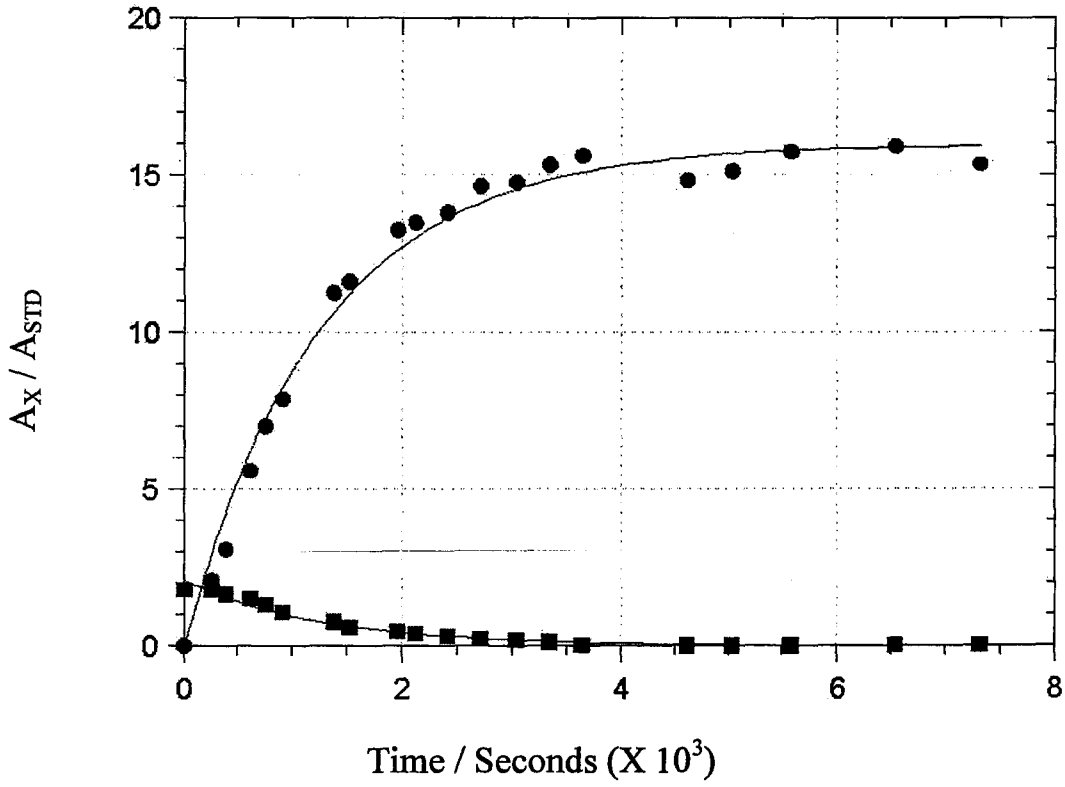
- **See Table 6.9 – Entry 3**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][OTF] WITH THE ADDITION OF SCANDIUM TRIFLATE – RUN 2



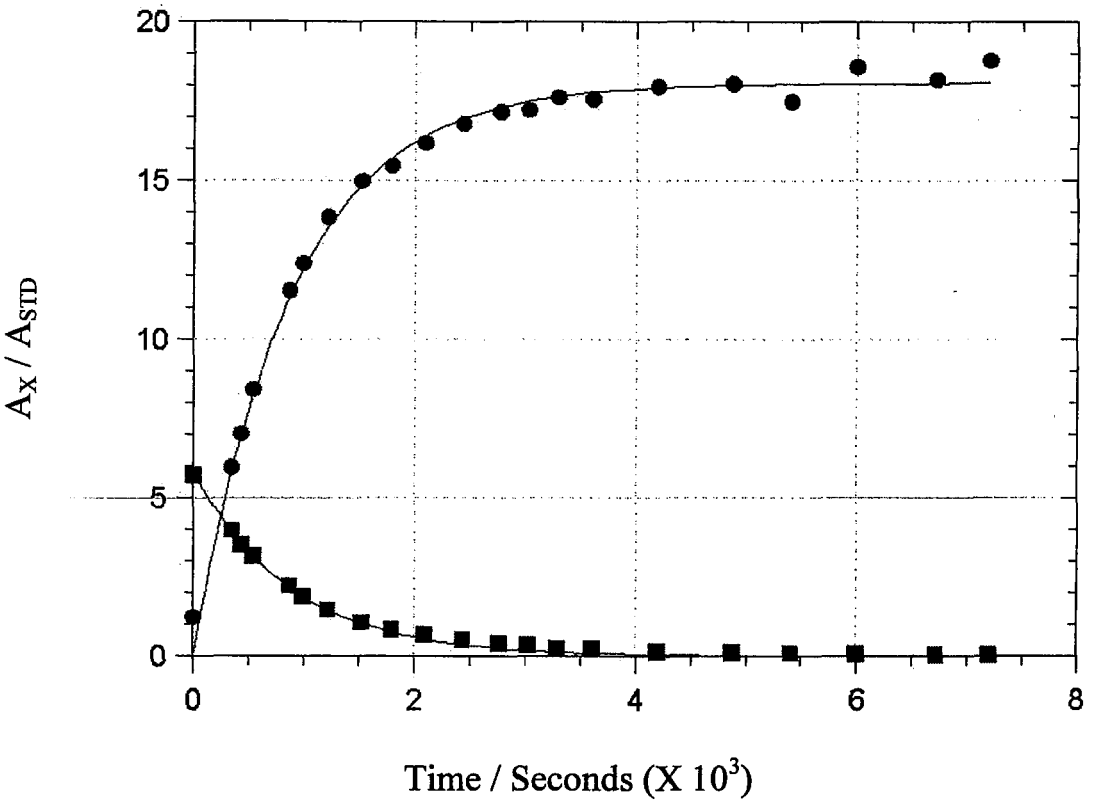
- **See Table 6.9 – Entry 4**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][OTF] WITH THE ADDITION OF SCANDIUM TRIFLATE – RUN 3



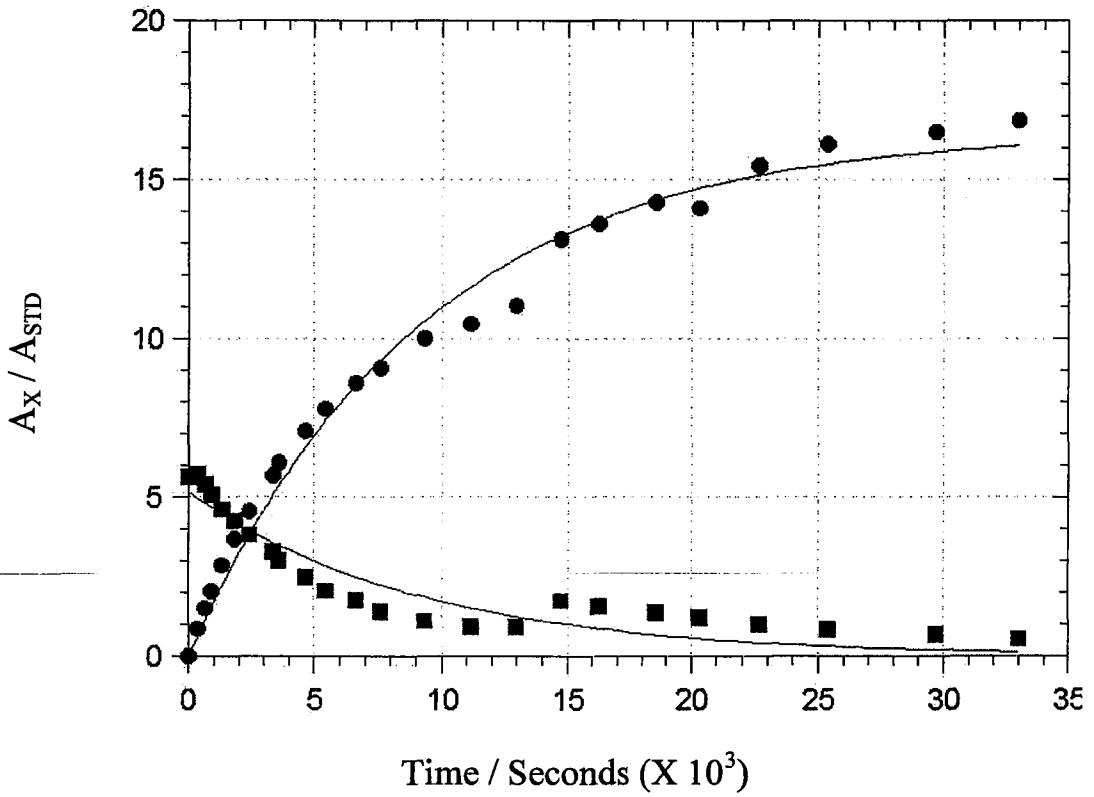
- **See Table 6.9 – Entry 5**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][OTF] WITH THE ADDITION OF DRY SCANDIUM TRIFLATE



- **See Table 6.9 – Entry 6**

KINETIC PLOT FOR THE REACTION BETWEEN CYCLOPENTADIENE (4) AND METHYL ACRYLATE (12) IN [BMIM][Tf_2N]



- **See Table 6.9 – Entry 8**