

Metathesis and hydroformylation reactions

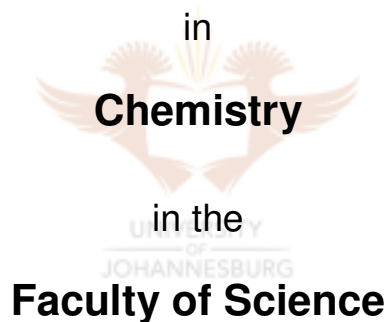
in ionic liquids

by

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REFERENCES

APPENDIX: NMR spectra of ionic liquids





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Abbreviations

acac	acetyl acetonate
ADMET	Acyclic diene metathesis
BASIL	Biphasic Acid Scavenging Ionic Liquid process
[beim]	1-butyl-3-ethylimidazolium
[bmim]	1-butyl-3-methylimidazolium
BTA	bis(trifluoromethane sulfonimide) or bistriflimide
CFC	chlorofluorocarbon
DA	detergent alcohol
DCM	dichloromethane
[eeim]	1-ethyl-3-ethylimidazolium
[emim]	1-ethyl-3-methylimidazolium
[edmim]	1-ethyl-2,3-dimethylimidazolium
eq	equivalents
FT	Fischer-Tropsch
GC	gas chromatography
H ₂ IMes	1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazoline
H ₂ IPh ⁱ Pr ₂	1,3-bis(2,6-di <i>i</i> sopropylphenyl)-4,5-dihydroimidazoline
[hmim]	1-hexyl-3-methylimidazolium
IFP	Institut Français de Pétrole
IL	Ionic Liquid
LABS	linear alkyl benzene sulfonates
MDA	methyl-branched detergent alcohols
MLAB's	Modified linear alkyl benzenes
NHC	<i>N</i> -heterocyclic carbene
NMP	<i>N</i> -methylpyrrolidone
NMR	Nuclear Magnetic Resonance
OCT	Olefin conversion technology
[omim]	1-octyl-3-methylimidazolium
Py	pyridinium

RCM	Ring-closing metathesis
ROM	Ring-opening metathesis
ROMP	Ring-opening metathesis polymerisation
SAE	Secondary alkylethoxylates
SCF	Supercritical fluid
ScCO ₂	Supercritical carbon dioxide
SHOP	Shell Higher Olefin Process
SMP	Secondary metathesis products
STY	Space time yield
TBHP	<i>tert</i> -butyl hydroperoxide
TGA	Thermogravimetric analysis
TSIL	Task-specific Ionic Liquid
TOF	Turnover frequency
VA	Vinyl acetate
VOS	Volatile organic solvents



Abstract

Ionic liquids (ILs), consisting of ions that are liquid at ambient temperatures, can act as solvents for a broad spectrum of chemical processes. These ionic liquids are attracting increasing attention from industry because they promise significant environmental as well as product and process benefits. ILs were used as solvents for two industrially important homogeneous reactions namely metathesis of 1-octene and the hydroformylation of vinyl acetate.

In the metathesis of 1-octene, several reaction parameters were investigated, including temperature, catalyst (type and concentration) and influence of ionic solvent and conventional solvents. Temperature and catalyst concentration were found to be rate-determining factors, but played smaller roles in determining the outcomes of the reactions compared to the influence of individual ILs. It was discovered that more polar ILs were favourable in producing high rates and selectivities. Imidazolium-based cations and tetrafluoroborate anions were superior in activity when compared to other combinations of cations and anions. The addition of catalyst promoters such as phenol and tin(II) chloride were also investigated and found to enhance metathesis rates in “neat” reactions. These catalyst promoters inhibited metathesis rates when used in combination with ILs.

In the hydroformylation of vinyl acetate, several reaction parameters were investigated, including temperature, catalyst concentration, vinyl acetate concentration, ligand concentration, syngas pressure and influence of ionic solvent and conventional solvents. It was shown that high $n : i$ ratios of aldehyde products were formed with specific IL systems. Also, low ligand concentrations and low vinyl acetate concentrations increased selectivities, although rates of reactions were somewhat compromised. Lower syngas pressure and lower temperatures afforded enhanced selectivities, again at the expense of reaction rates. Depending on whether fast reaction rates or high regioselectivity is required, the IL and general reaction conditions can be tailored to fit the needs of the reaction. It was discovered that aromatic-containing ammonium-based ILs

afforded high rates at low selectivity. Bulkier ammonium cations tended to give lower rates but the selectivity was significantly enhanced. Impurities present in ILs have also been shown to have a marked effect on hydroformylation rates and selectivity.

The reader will be accompanied along a path designed to discover an optimised set of reaction conditions, the path of which will take the reader from reactions providing low selectivities, low turnover numbers and low yields to a much brighter picture, namely extremely high selectivities, turnover numbers and yields.



Chapter 1

Introduction

Olefins are the fundamental building blocks of the petrochemical industry. Olefins are isolated from the Fischer-Tropsch process being operated in South Africa. The South African chemical industry therefore has an abundance of olefin streams, which are underutilised. These readily available reactive olefins can be converted to a range of versatile chemicals using various processes. Olefin metathesis represents one of the interesting possibilities to convert less desirable olefins to more useful olefins. Homogeneous metathesis is an emerging technology and represents an interesting field to investigate for future use due to its highly selective and active catalyst systems and mild operating conditions required. Due to the high cost of some of the homogeneous catalyst systems, catalyst recovery and recycle would have a significant impact on the economic viability of the technology.

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Ionic liquids (ILs) are emerging as an exciting alternative solvent technology and represent an ideal system for the recycling of homogeneous catalyst systems. They provide a unique solvent environment to the catalyst system, unlike that of the conventional organic solvents and form biphasic systems with most olefins. The use of room temperature ionic liquids (RTILs) as alternative solvent systems for olefin metathesis was investigated in order to add value to locally sourced olefin feedstreams. The metathesis of olefins using ILs has been described in the literature, although it has not been studied in full detail.

This chapter is separated into two sections. Section 1 in this chapter deals with a literature review on olefin metathesis. Section 2 deals with a literature overview of ILs in order to give a broader picture of the potential of ILs.

Section 1

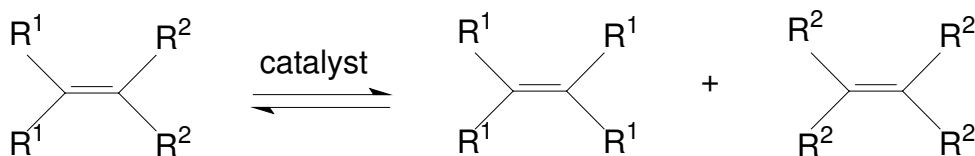
Olefin Metathesis - A Literature Review

1.1 Introduction

Metathesis has become one of the most important carbon-carbon bond forming chemical reactions known.¹ It is an extremely versatile and productive reaction in industry.² The word metathesis comes from the Greek μεταθεσις (metathesis) meaning transposition. Metathesis, for instance, involves the exchange of ions in a solution containing two ion pairs to produce the thermodynamically most stable ion pairs (Scheme 1.1). In the same way, olefin metathesis is a catalytic reaction in which the carbon-carbon double bonds of olefins are broken and then rearranged to form new products (Scheme 1.2).³



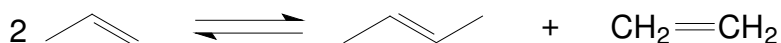
Scheme 1.1



Scheme 1.2

Metathesis reactions are under thermodynamic control, which means they are equilibrium controlled and reversible and can form both *cis* and *trans* isomers. Many metathesis reactions are also under kinetic control.

Banks and Bailey at Dupont serendipitously discovered the first catalytic metathesis reaction of olefins in 1964.⁴ They used a supported heterogeneous molybdenum oxide catalyst with propene to produce ethylene and 2-butenes and called their reaction olefin disproportionation. This process was commercialised as the Phillips Trioлеfin Process (Scheme 1.3).



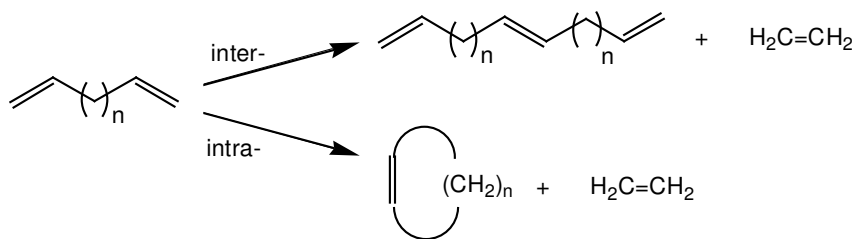
Scheme 1.3

Calderon made use of a homogeneous catalyst system, $\text{WCl}_6/\text{EtAlCl}_2/\text{EtOH}$ (1:4:1), to perform the disproportionation of 2-pentene into 2-butene and 3-hexene. They introduced the reaction type with the widely recognised name metathesis in 1967.⁵

1.2 Scope of the metathesis reaction

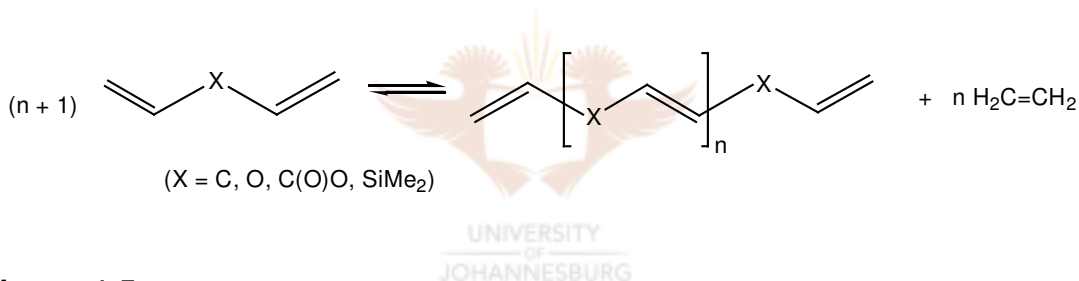
The metathesis of pure, single compound α -olefins essentially yields ethylene and a symmetrical internal olefin. Removal of the volatile ethylene product can allow the reaction to be driven to completion. The starting olefins need not be identical; they can be two different olefin molecules reacting with each other. This type of reaction is called **Cross-Metathesis (CM)**.⁶ The reverse reaction where the ethylene reacts with the internal olefin produces linear α -olefins, is a reaction known as ethenolysis.

The metathesis of acyclic dienes could follow an inter- or intramolecular pathway. For example, an intramolecular metathesis of an α,ω -diene produces ethylene and a cyclic olefin, whereas an intermolecular metathesis of α,ω -diene produces ethylene and a symmetrical triene (Scheme 1.4). The relative stability of the cyclic *versus* the linear products will be responsible for whether the inter- or intramolecular pathway will dominate.



Scheme 1.4

Interestingly, the triene produced during the acyclic version of the reaction can react further with the starting diene *via* an intermolecular metathesis reaction to form a tetraene and so forth. This reaction could result in unsaturated polymers forming in the presence of the correctly chosen catalyst system. This step-growth condensation polymerisation is known as **Acyclic Diene MET**athesis (ADMET) (Scheme 1.5).⁷



Scheme 1.5

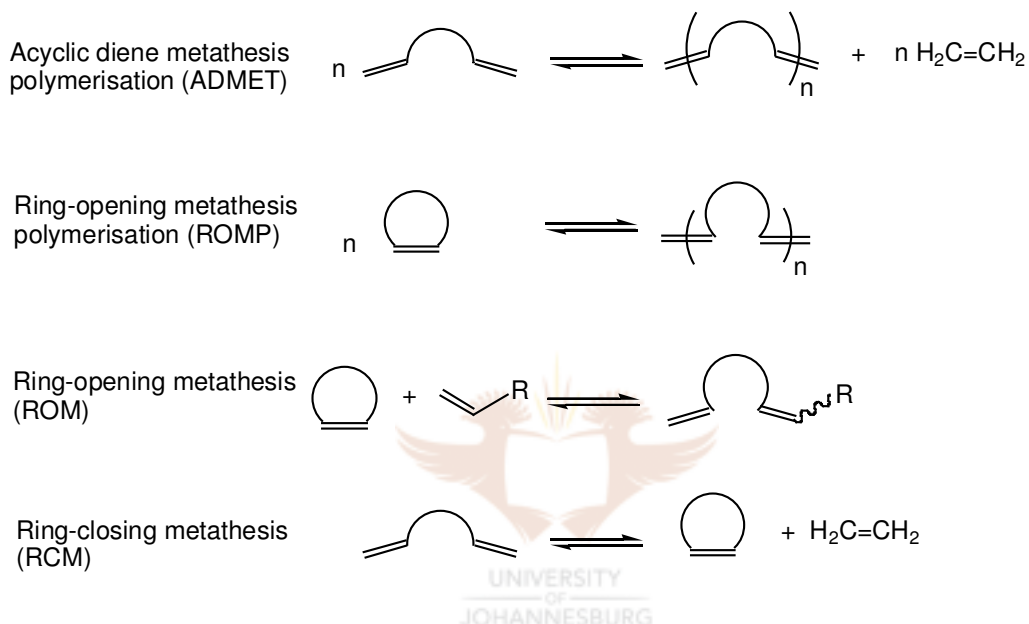
Ring-Opening Metathesis Polymerisation (ROMP) is a reaction where strained cyclic olefins are used to produce polymers and co-polymers.⁸ The reaction is irreversible if the cyclic olefin is highly strained (e.g. norbornene).

The cross-metathesis of an acyclic and a cyclic olefin yields interesting polyunsaturated substances that can be used as cross-linking agents in polymers or precursors for α,ω -difunctional substances.⁹ This reaction is called **Ring-Opening Metathesis (ROM)**.

A promising application for the metathesis reaction is the **Ring-Closing Metathesis (RCM)** of functionalised linear dienes, diene-ethers, diene-amines,

etc. to produce a variety of cyclic olefins and heterocycles.¹⁰ This is the reverse of the ROM reaction. RCM could lead to the production of a number of interesting substances including insect pheromones, fragrances, *etc.*

Of all the metathesis reactions (See Scheme 1.6 for comparisons), RCM and ROMP have received the most attention.



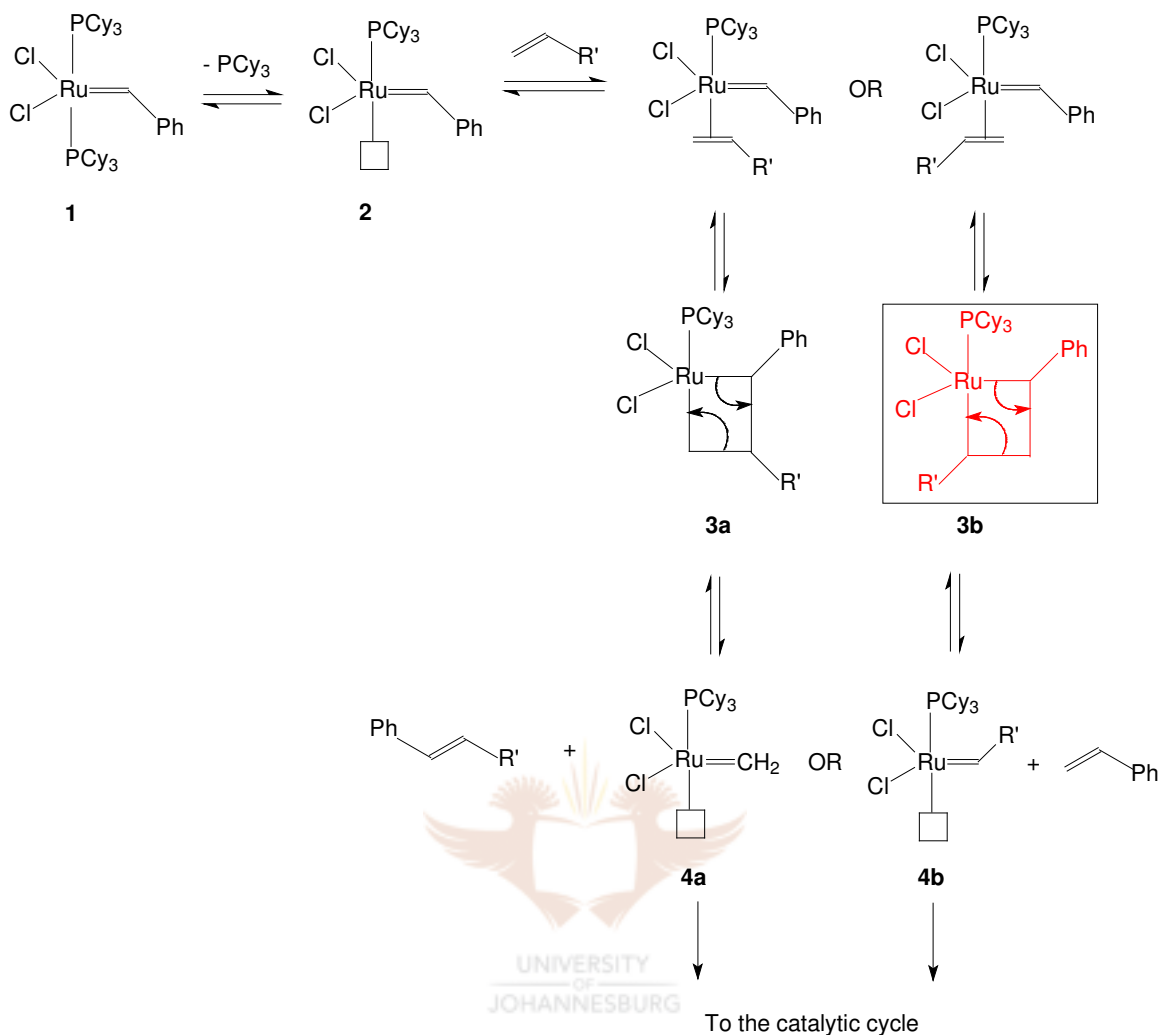
Scheme 1.6

These different olefin metathesis reactions essentially provide a route to molecules that would otherwise have been challenging and difficult to synthesise using other means. The ROMP reactions, in particular, provide a means to synthesise important new functionalised polymers while the RCM reactions can be used to synthesise large heterocyclic molecules from small ones and RCM of olefins can result in molecules with important pendant functional groups.¹¹ Metathesis is also an extremely useful and productive reaction in industry, producing important compounds such as antibiotics,¹² anti-tumour agents¹³ and immunostimulants.¹⁴

1.3 Reaction mechanism

Olefin metathesis proceeds *via* the so-called metal-carbene chain mechanism as first proposed by Jean-Louis Hérisson and Yves Chauvin from the Institut Français du Pétrole in 1971.¹⁵ Chauvin's metathesis mechanism is not only important in the olefin metathesis reaction but has been generalised to many organometallic reactions such as σ -bond and single and double π -bond metathesis and the β -elimination reactions.

The mechanism (Scheme 1.7), is specifically based on a ruthenium carbene catalyst, involves loss of one of the ligands from ruthenium alkylidene **1** to create an intermediate **2** with a vacant site. This is the active species. The vacant site allows co-ordination of an olefin in one of two orientations, followed by a [2+2] cycloaddition reaction to generate metallocyclobutane intermediate **3a** or **3b** which ultimately releases the propagating alkylidene species **4a** or **4b**. These two species can then co-ordinate any of the olefins in solution to keep the cycle going: **4a** can undergo productive metathesis with the olefin substrate to generate **4b** and release ethylene, while **4b** can undergo productive metathesis with the olefin substrate to generate **4a** and release the desired internal olefin product. Unproductive metathesis can also occur through co-ordination and reaction of the internal olefin product or ethylene.



Scheme 1.7

1.4 Industrial applications of olefin metathesis

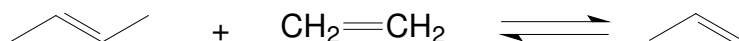
In the field of petrochemicals, the most important industrial applications of olefin metathesis are the olefin conversion technology (OCT) process and the Shell higher olefins process (SHOP). Other industrial processes involving the production of linear polymers using ring-opening metathesis polymerisation (ROMP) of cycloalkenes (such as cyclooctene, norbornene and dicyclopentadiene) do exist,¹⁶ but will not be discussed here. Due to the efficient catalyst systems (with regard to activity and selectivity as well as functional group

tolerance) now available, it seems inevitable that this chemistry will eventually lead to commercial applications for the production of polymers, agrochemicals, pheromones, fragrances, pharmaceutical intermediates and many other interesting materials.²

a) Olefin conversion technology (OCT) process

There is a strong global demand for propene and presently the demand exceeds the supply. Propene is used to make 60% of the world's polypropylene and also to produce acrylonitrile, 1-butanol and acrylic acid. Propene is mainly obtained from naphtha steam crackers (65%) and relatively small amounts are obtained by propane dehydrogenation and by coal gasification using Fischer-Tropsch chemistry. An alternative route to produce propene is *via* the metathesis of ethylene and 2-butene (reversed Phillips triolefin process). The Phillips triolefin process,⁴ using a heterogeneous catalyst, was originally developed by Phillips Petroleum Co. and dealt with the conversion of propene into ethylene and 2-butene. The reverse process (Scheme 1.8), known as the olefin conversion technology (OCT), for the production of propene using a WO_3/SiO_2 metathesis catalyst is now available for licensing by ABB Lummus Global, USA.

A number of chemical companies have already licensed this technology to increase their propene output capacities.¹⁷



Scheme 1.8

Another process to produce propene is called Meta-4 and was a joint development by the Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Taiwan).¹⁸ This process deals with reacting ethylene and 2-butene in the presence of a Re_2O_7/Al_2O_3 catalyst at 35 °C and 60 atmospheres of pressure to produce propene. The Meta-4 process is not yet commercialised

mainly due to the high cost of the catalyst system and the requirement for a high purity feedstream.¹⁹

b) The Shell Higher Olefin Process (SHOP)

The Shell Higher Olefin Process (SHOP) was designed to meet the market demand for linear α -olefins for detergents.²⁰ Today, the SHOP process produces about one-half of the world-wide output of linear α -olefins *via* oligomerisation. This process takes place in three stages involving oligomerisation, isomerisation and metathesis steps. The first step involves the oligomerisation of ethylene in the presence of a homogeneous nickel-phosphine catalyst to produce a mixture of linear even-numbered α -olefins in the range C_4 to C_{40} . The olefins undergo fractionation and in the second step, the lighter ($<C_6$) and heavier ($>C_{18}$) olefins undergo isomerisation over a solid potassium metal catalyst to give a mixture of internal olefins. The third key step involves the cross-metathesis of internal olefins with ethylene over an alumina-supported molybdate catalyst. The products consists of approximately 11 – 15% of the desired C_{11} – C_{14} linear olefins which are then converted into detergent alcohols using a hydroformylation process. The first commercial plant was built in Geismar, LA, in 1977, and was followed by the construction of a plant at Stanlow, UK, in 1982.

1.5 Homogeneous *versus* Heterogeneous Metathesis

The olefin metathesis reaction can be catalysed by both heterogeneous and homogeneous catalysts.²¹ A wide variety of transition metal compounds can catalyse the olefin metathesis reaction, the most important ones being ruthenium, molybdenum, tungsten and rhenium.²¹ Other catalyst systems based on osmium, iridium, tantalum and titanium can also be used.²²

Much research has gone into developing a catalyst that would be more tolerant towards polar and basic functional groups on functionalised olefins since the most common metathesis catalysts are poisoned by these entities. A number of

applications for olefin metathesis have been developed in organic chemistry and polymer chemistry by the availability of efficient catalyst systems.²³

Heterogeneous metathesis is a well-established technology and is applied on a commercial basis. The catalyst systems normally used in commercial applications consist of at least one of the metal oxides of rhenium,²⁴ molybdenum²⁵ or tungsten²⁶ and are usually supported on alumina,²⁷ silica²⁸ or combinations thereof.²⁹ The supported metal catalysts normally show significant activity enhancements upon the addition of additives and promoters such as Lewis acids.³⁰ Heterogeneous metathesis allows for ease of separation of the catalyst and products, ease of regeneration of the catalyst if it has become deactivated, and greater thermal stability. Due to the degree of acidity required for catalyst activity, isomerisation of the feed and product could pose a significant problem. In some applications, extensive feed preparation is required as the feed contains branched species and/or oxygenated compounds. These types of species cannot be tolerated by the catalyst systems.³¹ High temperatures are also required with most heterogeneous catalyst systems. Molybdenum, rhenium and tungsten based-catalysts have received wide attention as heterogeneous catalysts.³² Rhenium, in particular has been a focal point because of its greater tolerance to functional groups and milder reaction conditions.³³

Homogeneous metathesis, on the other hand, is an emerging technology which is rapidly developing but has not been applied in large scale industrial processes as yet. Many of the applications of homogeneous metathesis are found in fine chemical and pharmaceutical production and in the preparation of speciality polymers. Catalyst systems used for homogeneous metathesis can in principle be almost any metal capable of forming a metal carbene *in situ* or *ex situ*. The main metals employed in practice for homogeneous catalysts are ruthenium³⁴ (Grubbs-type), molybdenum³⁵ (Schrock-type) or tungsten^{34,36} and these catalysts do not require promoters such as Lewis acids. Molybdenum and tungsten catalysts were initially used in homogeneous metathesis.³⁷ However, these

conventional homogeneous catalysts are extremely air- and moisture-sensitive.³¹ The new generation homogeneous catalysts, which are well-defined metal alkylidene complexes such as ruthenium carbene catalysts (known as Grubbs and second-generation Grubbs catalysts), are much more efficient, with some catalysts even performing well in air and water.³⁸ These catalyst systems have attracted a lot of interest due to their high catalyst activities, selectivities and turnover numbers (TON's), as well as their remarkable tolerance towards air, water and oxygenates.³⁹ Also, these specific catalysts display robustness to a wide range of substrates with different functional groups.⁴⁰

Other metals that can be used as catalysts in homogeneous metathesis include osmium,⁴¹ rhodium,⁴² iridium, cobalt,⁴³ iron⁴⁰ and rhenium.⁴⁴ These systems have not found much use due to their low activity and selectivity, instability of the catalyst precursors, or sensitivity to functional groups.

Functional groups present in the substrate or solvent can interfere with catalyst activity by binding competitively to the active metal centre and consequently deactivating the catalyst, or directly bind to the metal centre and therefore prevent the formation of the active catalyst.^{1,45}

A catalyst that reacts preferentially with olefins (from Table 1.1, the ruthenium metal is the best catalyst system) in the presence of various other functional groups should be the best catalyst with broad functional group tolerance. The trend for reactivity with various functional groups with different transition metals is shown in Table 1.1.³⁸

Titanium and tungsten catalysts prefer to olefinate ketones and esters (*cf.* The Tebbe reagent).⁴⁶ Molybdenum, on the other hand, is more reactive towards olefins, although it also reacts with aldehydes and alcohols. Ruthenium reacts with olefins in preference to most other compounds, which makes catalysts

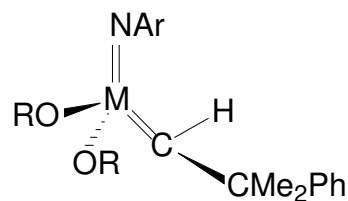
based on this metal stable to compounds containing alcohol, amide, aldehyde and carboxylic acid functional groups.

Table 1.1: Functional group tolerance of different metals as olefin metathesis catalysts³⁸

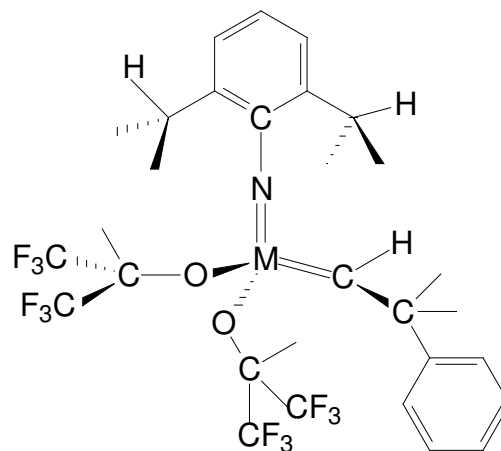
Titanium	Tungsten	Molybdenum	Ruthenium	Increased Reactivity
Acids	Acids	Acids	<u>Olefins</u>	↑
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids	
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water	
Ketones	Ketones	<u>Olefins</u>	Aldehydes	
Esters, Amides	<u>Olefins</u>	Ketones	Ketones	
<u>Olefins</u>	Esters, Amides	Esters, Amides	Esters, Amides	

1.6 Grubbs and Schrock-type Metathesis Catalysts

Before the early 1980s, all olefin metathesis reactions were accomplished using poorly defined multi-component homogeneous or heterogeneous catalyst systems. These catalyst systems consisted of a transition metal salt with a main group alkylating agent or one supported on silica or alumina. The following are classical examples of this type of early catalyst system: WCl_6/Bu_4Sn , $WOCl_4/EtAlCl_2$, MoO_3/SiO_2 and Re_2O_7/Al_2O_3 amongst others.⁴⁷ They are easily prepared, have a low cost and therefore have great importance in commercial processes such as the SHOP procedure. The use of these catalysts, however, requires harsh conditions and the presence of strong Lewis acids, which renders them incompatible with most functional groups.⁴⁸ In the late 1970s and early 1980s, Chauvin's proposed mechanism led to the discovery of the first single-component homogeneous catalysts for olefin metathesis. The tungsten and molybdenum alkylidenes (with general formula $(NAr)(OR')_2M=CHR$) developed by Schrock were the first of these catalysts to be widely used in particular the molybdenum complex (Figure 1.1).⁴⁹



General formula for the family of Schrock's metathesis catalysts (M = Mo or W; R and Ar are bulky substituents)



Commercial version of Schrock's metathesis catalyst

Figure 1.1: Schrock's metathesis catalyst systems

Schrock's molybdenum catalysts are air and moisture-sensitive and incompatible with aldehydes and alcohols but they are effective in the presence of phosphanes, thioethers and nitriles (Ru-based catalysts are decomposed by these substrates), sterically protected free alcohols, metal carbonyls and amines.⁵⁰ Schrock's commercial molybdenum catalyst produced high activity and could be used in a number of metathesis applications.⁵¹

Grubbs-type (ruthenium-based) catalysts for olefin metathesis have attracted considerable attention over the past few years. This is largely due to their excellent functional group tolerance towards those containing O and N atoms,⁵² ease of use in air and water, mild reaction conditions and high selectivity. However, they are relatively expensive catalysts. Most of the catalyst systems consist of a carbene moiety⁵³ although other simple salts⁵⁴ have shown to be effective metathesis catalysts with certain substrates. Ring closing metathesis of highly functionalised organic molecules is one of the common applications of ruthenium catalysts.⁵⁵

First generation Grubbs catalysts have a limited lifetime, particularly at elevated temperatures but tend to show extremely high selectivities.⁵⁶ Second generation Grubbs catalysts where one or both of the phosphine ligands has been replaced by an electron-donating, sterically demanding carbene ligand (highly basic imidazolium based ligands), have received much attention due to enhanced catalyst lifetime and activities.^{38,57} These carbene ligands are typically based on nitrogen-containing heterocycles such as substituted imidazoles.⁵⁸ The activities of the first- and particularly second-generation Grubbs catalysts make them interesting for commercial applications, but the catalysts do deactivate over time.

Much research and development with respect to the catalyst backbone has been performed to enhance activity, selectivity and stability. The catalytic activity of these ruthenium complexes (See Figure 1.2) is highly dependent on the identity of the X- and L-type ligands. Catalyst activity increases with the use of a larger, and more basic, strongly electron-donating phosphine ligand.⁵⁹ The catalyst activity of complexes increases with the basicity of the phosphines in the order $\text{PPh}_3 \ll \text{P}^i\text{Pr}_2\text{Ph} < \text{PCy}_2\text{Ph} < \text{PPr}_3^i < \text{PCy}_3$. Phosphines with larger cone angles result in catalysts with greater activity.³⁸ For example, PPr_3^i has a slightly smaller cone angle than PCy_3 , but similar electronic properties.⁶⁰ The ligands $\text{P}^i\text{Pr}_2\text{Ph}$ and PCy_2Ph , on the other hand, have similar or slightly smaller cone angles but have substantially different electronic properties.⁵⁷

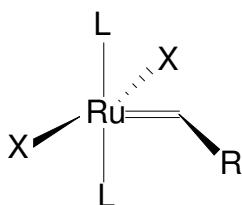


Figure 1.2: The model ruthenium complex

In the proposed metathesis mechanism, the phosphine ligands allow σ -donation to the metal centre, which promotes the formation of the mono-phosphine complex by facilitating phosphine dissociation and stabilising the active species.

The 14-electron metallacyclobutane intermediate is stabilised by the σ -donation. The steric bulk of the ligands may aid in increasing phosphine dissociation by destabilising the crowded *bis*(phosphine) olefin complex. Catalyst activity decreases with larger and more electron-donating halides in the order Cl > Br >> I.³⁸ This trend is exactly opposite to that observed when varying the phosphine ligands. This is due to the fact that a more electron-donating halide could weaken the ruthenium-olefin bond if the incoming olefin binds *trans* to the halide thereby disfavoured olefin co-ordination.

Table 1.2 shows the potential advantages of using homogeneous ruthenium-based catalysts.

Table 1.2: Advantages of homogeneous ruthenium based catalyst systems⁶¹

Homogeneous metathesis	Explanation
High selectivities	Isomerisation of the substrate and resultant formation of secondary metathesis products is often problematic with heterogeneous catalysts.
Mild operating conditions	Typically ambient temperature to 80 °C and ambient pressure.
Tolerance to oxygenates	Ruthenium-based catalysts have a greater tolerance towards oxygenates, unlike tungsten and molybdenum catalysts.
Tolerance towards branched feeds	Several heterogeneous catalysts are poisoned by 2-methyl-1-alkenes (vinylidenes). Ruthenium-based catalysts are unaffected.
Catalyst cost	Ruthenium is more expensive than cobalt, but cheaper than metals such as palladium and rhodium; catalyst cost relative to many other homogeneous processes is relatively inexpensive.
High activities and lifetimes	Some of the ruthenium-based homogeneous catalysts display remarkable TON's and TOF's.

1.7 Metathesis in the Sasol context

Sasol uses synthesis gas (from either coal or natural gas) to perform the Fischer-Tropsch reaction, amongst others producing olefins. Sasol, therefore, has an abundance of olefin streams (particularly odd numbered olefins such as C₅, C₇ and C₉ since Sasol is the only producer of these odd numbered olefins), many of which are underutilised and therefore regarded as fuel alternative value. Of Sasol's wide range of olefin streams, only a few such as 1-hexene and 1-octene have a high market value. Also, there are many higher value olefins which are either in short supply or not available at all. There is, therefore, a significant drive to add value to Sasol's olefin feedstreams, which provides an opportunity to use homogeneous metathesis as a fundamental technology to allow the conversion of low value olefins to high value olefins which can be employed in further downstream processes. High value olefins include the following:

- C₆, C₈ and C₁₀ α- or internal olefins
- C₁₀ – C₁₄ linear α- or internal olefins for the production of detergent alcohols, linear alkyl benzenes (LABs) and secondary alkylethoxylates (SAE)
- C₁₅ and α- or linear internal olefins for use on long chain alcohols after hydroformylation
- C₁₀ – C₁₃ branched olefins

Metathesis essentially shifts the carbon number of the feedstream, which allows facile separation of the olefins from impurities such as paraffins, aromatics and oxygenates, thereby removing potential catalyst poisons from downstream processes and providing essentially pure olefin streams.

So far, the application of homogeneous metathesis in large-scale processes has not yet been developed in the chemical industry. A potential application for metathesis within Sasol is the conversion of low value C₇ α-olefins to internal C₁₂ olefins which can then be utilised as detergent alcohol (DA) feedstocks, linear

alkyl benzene sulfonates (LABS), secondary alkylethoxylates (SAE), modified linear alkyl benzenes (MLAB's) or methyl branched detergent alcohols (MDA).

The highly active ruthenium complexes could potentially be used due to their robustness to air, water and oxygenates as well as their high activities and selectivities. However, the high cost of some of these olefin metathesis homogeneous catalyst systems, limited catalyst lifetime and difficulty of recovery, especially for these ruthenium alkylidene catalysts, poses major problems for future use in industrial applications. For this reason, alternative solvents such as ionic liquids that would facilitate the separation of catalyst from the reactants and products with the catalyst selectively dissolved in the ionic liquid whilst the reactants and products form a separate biphasic layer, and with the ionic liquid stabilising the catalyst while maintaining catalyst integrity would be a major advantage.

1.8 Ionic Liquids

ILs are classified as a new, unique and exciting class of solvents that could potentially replace the volatile organic solvents currently being used in large volumes.⁶² They have attracted lots of attention since their discovery as reaction media for catalytic reactions.⁶³ ILs essentially consists of a combination of an organic cation and an anion (Figure 1.3) that are a liquid at room temperature (melting point typically below 100-150 °C). The fact that they are liquid at room temperature distinguishes them from classical molten salts. They are liquids at room temperature largely due to the large, asymmetrical cations preventing close packing of the ions.

ILs consist of two main categories;

- Binary ILs (also referred to as first-generation ILs) consisting of several different ionic species usually in equilibrium. For example mixtures of aluminium(III) chloride and 1,3-dialkylimidazolium chlorides.⁶⁴
- Simple ILs (also referred to as second-generation ILs) consist of a single anion and a single cation.⁶⁵

Given the variability of the imidazolium parent compound (or the pyridinium or phosphonium as the case may be), taken together with combinations and permutations around the alkyl groups attached thereto, as well as possible variability of the associated anions, it is, in theory, possible to generate a vast number of ILs possessing a range of physical characteristics. Seddon speaks of about one trillion (10^{18}) possible cation/anion combinations to produce RTILs.^{62c}

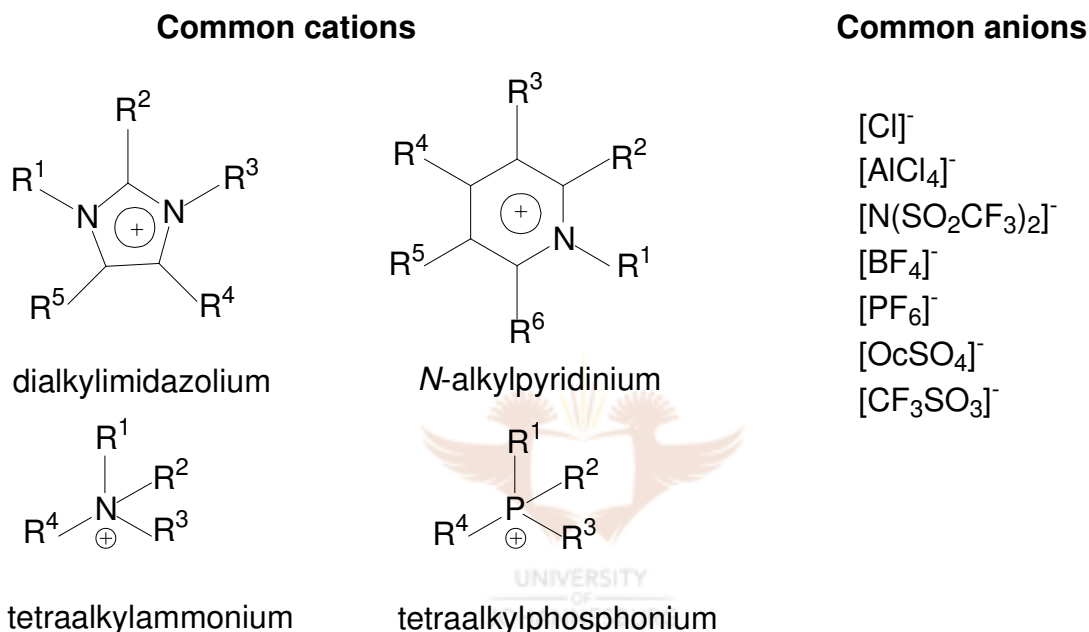


Figure 1.3: Examples of common cations and anions used to form ILs

Properties of ILs that make them attractive include:

- ✓ Highly polar, non co-ordinating solvents
- ✓ Negligible vapour pressure
- ✓ Wide liquid range
- ✓ Immiscible with a wide range of common organic solvents
- ✓ High electrical conductivity
- ✓ Tunable physicochemical properties (“Designer Solvents”)⁶⁶

ILs are justifiably classified as “green solvents” mainly due to their negligible vapour pressure meaning that they are not volatile organic compounds.⁶⁷ They

are not as flammable as the volatile organic solvents therefore making process safety and environmental concerns less of an issue. The thermodynamics and kinetics of reactions carried out in ILs can possibly be different to those in traditional volatile organic solvents and therefore creates great interest amongst chemists in their use as solvents.

ILs are immiscible with a number of common organic solvents and therefore provide a polar alternative for biphasic systems. This allows for catalyst recovery, possible recycling of the IL as well as separation of products from the IL system. Liquid-liquid biphasic catalysis represents a popular approach to heterogenise a homogeneous catalyst in one phase normally a polar phase (in this case the IL) and the organic products in another phase without necessarily hindering the efficiency and selectivity of the process. The product is separated from the catalyst solution by simple decantation and the catalyst can then be re-used. Recycling of the expensive catalyst and ligands in catalytic reactions has always been a major problem. The need to find novel reaction media to enable efficient recovery and recycling of homogeneous catalyst is of utmost importance. ILs are, therefore, attractive solvents for biphasic catalysis.

A catalyst that is ionic can easily be retained in the IL phase without the need for specially designed ligands. In this case, significant enhancement of catalyst activity, selectivity and stability is possible with re-use of the catalyst. When the catalyst is non-charged, leaching of the expensive transition metal into the organic phase can be limited by using functionalised ligands that can be specially tuned to the IL.

These ILs are attracting increasing attention from industry because they promise significant environmental as well as product and process benefits. Making changes to the cation or anion of the IL can result in significant changes to properties such as solubility, density, refractive index and viscosity to suit the needs for a specific application.⁶⁸

Using ILs as an alternative solvent in transition metal catalysed biphasic catalysis has many advantages;

- Most transition metal complexes are quite soluble in ILs with no need to modify the IL, ligand or catalyst as is often needed for aqueous and fluorous biphasic systems.
- The IL provides a polar yet weakly co-ordinating medium. The active site of the catalyst is therefore only accessible to the organic substrate.
- The biphasic system can be optimised with regard to solubility of the reactants and products by “tuning” the IL to fit the needs of the reaction. ILs can also improve selectivity due to preferential solubility of reactants and the removal of reaction products out of the IL/catalyst layer.
- Engineering advantage due to their non-volatile character.

1.9 Metathesis of 1-octene in ionic liquids

The role of the solvent in homogeneous catalysis is to dissolve, stabilise the substrate, ligand and catalyst without reacting with the catalyst or competing with the substrate for a vacant co-ordination site. ILs as solvents offer a unique way with weak co-ordination abilities. The co-ordination ability of ILs towards the catalyst complex depends on the nature of the anion. ILs which display low nucleophilic character will not compete with the organic substrate for the co-ordination to the electrophilic active metal centre. In some cases, the role of the ionic liquid is to merely provide a polar, weakly co-ordinating medium for the organometallic catalyst complex (as an “innocent” solvent) or as a co-catalyst (for example the chloroaluminate⁶⁹ or chlorostannate⁷⁰ ILs). ILs can therefore be used as both a solvent and a catalyst or co-solvent.⁶⁷

In some cases, reactants and products are not soluble in the IL, but catalyst systems do dissolve in the IL. Interestingly, most ILs form biphasic mixtures with most olefins. These biphasic systems offer the benefits of both homogeneous and heterogeneous catalysis (*i.e.* the mild conditions and high efficiency /

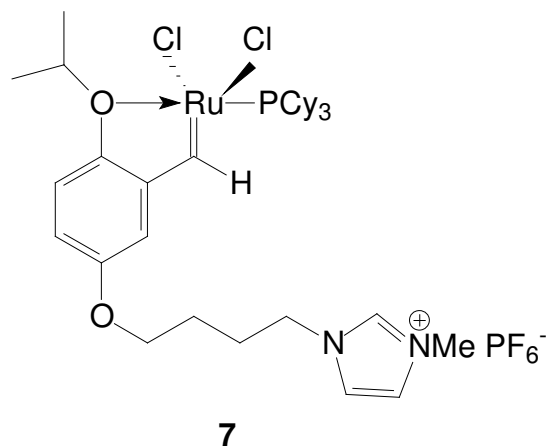
selectivity of homogeneous catalysts with the easy separation and optimal use of heterogeneous catalysts).

Although there are distinct advantages in using biphasic systems, there are also certain significant problems that might arise namely:

- ❖ Catalyst leaching into the organic phase;
- ❖ Mass transfer problems leading to low reaction rates.

In order to overcome these problems, there would be a need to tailor the catalyst and/or IL to prevent possible leaching of the catalyst into the organic phase. Furthermore, changing the cation or anion of an IL would give further opportunities to tailor the IL of a specific application. The solvent can potentially be designed to optimise a reaction with control over yield and selectivity.

A number of reports have dealt with the use of ILs for olefin metathesis.⁷¹ These focus mainly on RCM using W, Ru and Mo catalysts in [1-butyl-3-methylimidazolium]-type IL where the anion has been varied.⁷² The RCM reaction in ILs produced high activities and selectivities, although upon recycling rates decreased and this is most probably due to catalyst deactivation and leaching.⁷² Grubbs catalyst^{72b}, second-generation Grubbs catalyst^{72c} and ruthenium allenylidene salt^{72a} catalysts has been investigated in great detail for RCM. Many research groups have therefore added an “ionic liquid tag” **7** to the ligand of the catalyst in order to enhance solubility of the catalyst in the IL and improve recyclability of the catalyst system.^{72b,d}

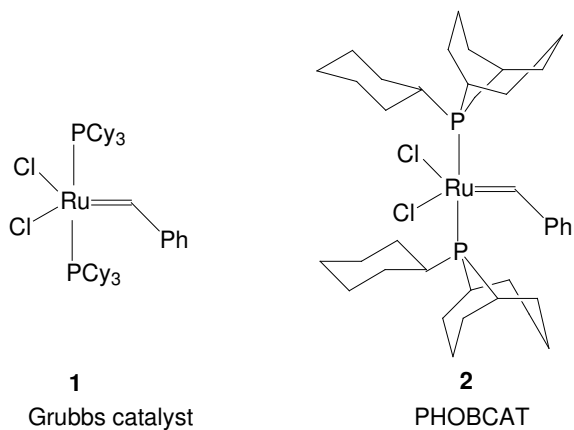


The cross- and self-metathesis of olefins have been less studied in these reaction media. The research group at IFP studied the metathesis of olefins using $W(OAr)_2Cl_4$ complexes where (ArOH = 2,6-diphenylphenol or 2,4,6-triphenylphenol) dissolved in acidic ILs such as [bmim][AlCl₃/EtAlCl₂].^{71c} They showed that the catalyst/IL system can be recycled several times.^{71c}

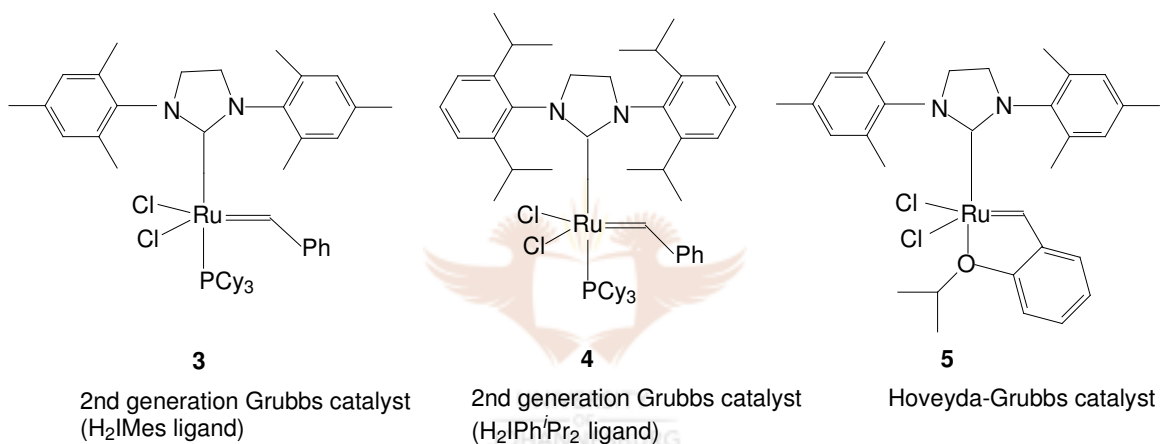
ILs have, therefore, been proven to be suitable solvents for olefin metathesis with similar activities and improved selectivities, together with less by-product formation when compared to conventional solvents. Leaching of the catalyst from the IL, as well as deactivation of the catalyst in both IL and conventional solvents is still a problem. Future work could possibly deal with modifications of the catalyst and/or IL to reduce leaching of the catalyst in a biphasic system.

The metathesis of 1-octene without the use of an additional solvent has been studied using (1, 3 and 4) these ruthenium-based catalysts (Figure 1.4).³⁹

First generation Grubbs catalysts



Second generation Grubbs catalyst



Cationic Ruthenium allenylidene catalyst

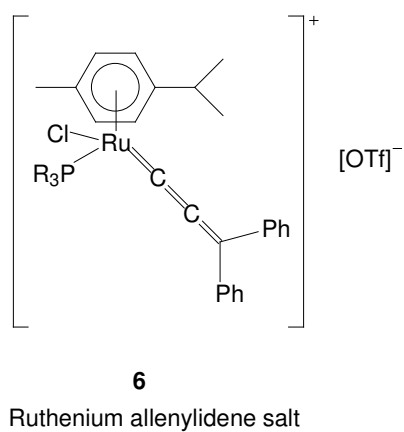


Figure 1.4: Ruthenium-based catalyst systems

An important side reaction occurs when using all metathesis catalysts is olefin isomerisation.⁷³ Olefin isomerisation is a well-known process when using ruthenium catalysts and results in double bond migration.⁷⁴ It has been reported that it is the decomposition products of the ruthenium catalyst that results in the isomerisation.⁷⁵ It is only when the ruthenium-based catalyst deactivates that significant by-product formation is observed during the metathesis of 1-octene. This is due to the formation of internal octenes by isomerisation, and the resultant cross metathesis of 1-octene with 2- and 3-octene to form tridecene or dodecene (Figure 1.5).

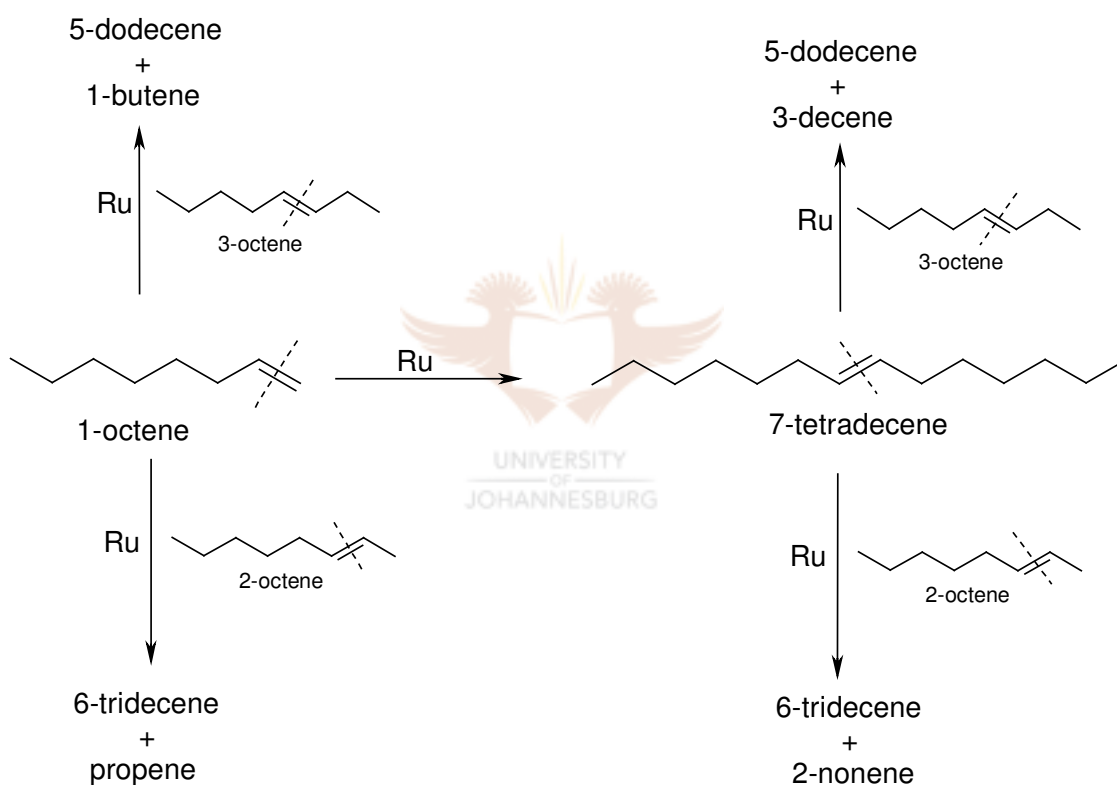


Figure 1.5: Formation of secondary metathesis products from 1-octene⁷⁶

It is believed that the deactivated ruthenium catalyst becomes an isomerisation catalyst while at the same time being metathesis inactive. The second generation ruthenium-based catalysts are more likely to produce isomerised products compared to the first generation Grubbs catalyst. ILs as solvents for the metathesis of 1-octene tend to show less formation of SMPs.

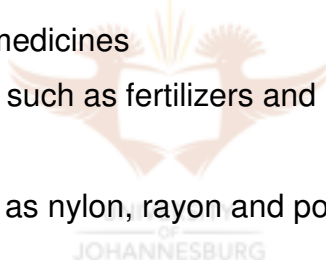
Section 2

Ionic Liquids – A Deeper Look

2.1 Introduction

A perception that pervades society regarding the chemical industry is that it (the chemical industry) has only been responsible for a number of devastating health and environmental issues, including those relating to thalidomide, the pesticide DDT, polychlorinated biphenyls (PCBs), chlorofluorocarbons (CFCs) and many more. It is only due to a lack of appropriate marketing and public awareness campaigns that society is generally unaware of the manifold advances that improve so many aspects of human life. These include:

- ✓ antibiotics and other medicines
- ✓ agricultural chemicals such as fertilizers and pesticides
- ✓ plastics
- ✓ synthetic fabrics such as nylon, rayon and polyester.



What is concurrently true is that the manufacture of these useful materials that society depends on frequently uses chemicals or technologies that are harmful to our health and the environment. The impact that the chemical industry has on the environment has led to a massive surge in awareness of “green chemistry” in the last decade. This sub-discipline deals with pollution prevention, especially the reduction of waste in industrial chemical processes. The term “green chemistry” has been coined by Paul Anastas of the U.S. Environmental Protection Agency (EPA) and essentially deals with how the chemical industry can produce products necessary to human life and also protect the environment at the same time.⁷⁷

The Green chemistry mission as stated by the U.S. EPA reads as follows:

“To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products.”

This mission is aimed at the idea of developing new (or improving existing) chemical technologies making them less hazardous to human health and the environment. Among these is the need to employ clean, “greener”, safer solvents and reduce the use of damaging volatile organic solvents (VOS), especially halogenated solvents such as carbon tetrachloride and 1,1,1-trichloroethane. Chemical industries rely heavily on these toxic, hazardous, often flammable, organic solvents for the industrial synthesis of petrochemicals and pharmaceuticals. The environmental impact of these solvents is significant and many industrial chemical processes need to be re-evaluated. By offering environmentally benign alternatives to these toxic, hazardous chemicals used by industry, we are promoting the idea of green chemistry and thereby preventing pollution to our environment.

Other key ideas to promote clean green chemistry as stipulated in Paul Anastas’ “The twelve principles of green chemistry” is to develop processes with lower energy input, economise on atoms where only the desired product is formed without waste by-products, use renewable resources such as substances derived from plants rather than petrochemical feedstocks and produce products that are benign and easily biodegradable (easily digested by microorganisms in the environment to less harmful products).⁷⁷

Roger Sheldon defined the *E*-factor of a process as the ratio (by weight) of the by-products to the desired products. Chemical processes with high *E*-factors need to be re-evaluated since they produce more waste. Table 1.3 shows the *E*-factor of different industries.⁷⁸

Table 1.3: Production and *E* factors of different chemical industries

Industry	Production /tons p.a.	<i>E</i> -factor
Oil refining	$10^6 - 10^8$	0.1
Bulk chemicals	$10^4 - 10^6$	1-5
Fine chemicals	$10^2 - 10^4$	5-50
Pharmaceuticals	$10^1 - 10^3$	25-100

From the table it can be seen that the oil refining and bulk chemical industries produce less waste and therefore have the highest selectivity towards the desired product when compared to the fine chemical and pharmaceutical companies, contrary to popular belief. The fine chemical and pharmaceutical companies, although producing chemicals on a smaller scale have processes that are inefficient and produce more undesired by-products and spent solvents. There is, therefore, an increasing demand for new cleaner technologies, especially in the pharmaceutical industry.

The role of chemical research should essentially be to advance global environmental protection and sustainable development. Adopting green chemistry is a way of ensuring economic and environmental prosperity. While chemistry and other related sciences have brought society lifesaving drugs, improved nutrition, extra food, mobility, shelter and an improvement to the world economy as well as an increased human lifespan, chemicals are still characterised often incorrectly so) as hazardous and toxic.

Alternative reaction media to the toxic VOS are at the heart of green chemistry. Reaction media can be used to produce cleaner chemical technologies. Chemistry had always been studied in water as a solvent until the use of organic solvents such as alcohols, chlorinated hydrocarbons, arenes, *etc.* in the nineteenth century came into play. Most common chemical reactions are

performed in organic solvents; these are the traditional VOS. All of our basic understanding of reactive chemistry in solution has been derived from the use of molecular solvents and not ionic solvents. Recently, there has been a great need to minimise the usage of these often toxic VOS and replace them with “greener” solvents.

Properties of an ideal “green” solvent would include the following:

- ✓ low volatility
- ✓ chemically and physically stable
- ✓ recyclable and reusable
- ✓ easy to handle
- ✓ enhanced activity and selectivity

There are five possible alternative routes that can possibly be used to replace the traditional VOS and include:

- i) solvent-free synthesis
- ii) the use of water as a solvent
- iii) the use of perfluorinated hydrocarbons as a solvent
- iv) the use of supercritical fluids as a solvent
- v) the use of ILs as a solvent.

2.2 Alternative reaction media to ionic liquids

The use of these alternative reaction media is mainly aimed at replacing the toxic volatile organic solvents that have a negative impact on the environment.

i) Solvent-free synthesis

It seems that the easiest way to prevent any form of solvent emission is to use no solvent at all. There have been many attempts to perform various reactions using no solvent at all.⁷⁹ Advantages of solvent-free synthesis include reduced pollution, low costs, easy handling and simple processes. These advantages are quite important especially for industry. There are however also many

disadvantages in performing solvent-free synthesis, for one strong exotherms can occur which can be difficult to deal with.

ii) Water

In the last 20 years, water has been used as a medium for organic reactions. It has major advantages such as low cost, non-toxicity and abundance.⁸⁰ There has been significant attention to aqueous-organic biphasic systems in particular.⁸¹ The disadvantage of these systems is that the ligands have to be modified in order to solubilise the catalyst in the aqueous phase. Its use is also limited due to the low solubility of organic substrates often resulting in low reaction rates. Water is also a protic co-ordinating solvent and could react with organometallic compounds by co-ordinating the active metal centre or it may react with metal-carbon bonds that are present, thereby deactivating the catalyst and/or producing by-products.

iii) Perfluorinated solvents

The perfluorinated solvents are attractive solvents because they allow for easy product separation and are chemically inert and non-flammable. Perfluorinated solvents have recently been used for many organic and catalytic reactions.⁸² Special ligands containing perfluoroalkyl chains are, however, required to solubilise the catalyst in the fluoruous phase.⁸³ These tailor-made ligands are often difficult to synthesise and relatively expensive. Another disadvantage of perfluorinated solvents is that they produce toxic substances at high temperatures and fluoruous substances are often found present in the organic phase. Currently it is doubtful whether perfluorinated solvents will emerge as a new technology in the near future.

iv) Supercritical fluids

Supercritical fluids, especially supercritical carbon dioxide (scCO₂) (31.1 °C, 73 atm), have been described as solvents for organic and catalytic reactions.⁸⁴ ScCO₂ is non-toxic, easily recycled, non-polar, inflammable and inexpensive. Its

use as a solvent is, however, limited due to the critical conditions needed in order for scCO_2 to operate as a solvent.⁸⁵ Other commonly used supercritical fluids include ethylene, water and dinitrogen oxide.

Combinations of scCO_2 and ILs have successfully been used as solvents.⁸⁶ ILs are insoluble in scCO_2 whilst the supercritical carbon dioxide is reasonably soluble in the IL phase.⁸⁷ Additionally, the viscosity of the IL decreases significantly when scCO_2 is dissolved in the IL phase. Due to the complementary properties scCO_2 has with ILs, such combinations have been used as biphasic solvent systems in hydrogenation and hydroformylation reactions.⁸⁸

ScCO_2 has also been successfully used for extracting products from ILs, although it is technically demanding.⁸⁹ The use of scCO_2 could prevent the loss of the catalyst from the IL/catalyst system by extracting the products only. Using a solvent that is immiscible with the IL to extract products out of the IL phase will lead to loss of catalyst by leaching which gives the use of scCO_2 a huge advantage in this case.

Seddon refers to these two solvents, ILs and scCO_2 , as neoteric solvents meaning recent, new, modern and novel solvents with exciting properties. These two solvents represent the most promising solvent systems required to clean up the chemical industry.

ScCO_2 has also successfully been used for dry-cleaning (rather than using the toxic solvent perchloroethylene which is a human carcinogen and a groundwater contaminant), extraction of natural products such as caffeine from coffee, metal cleaning and textile processing.

v) Ionic liquids

ILs are the least investigated alternative solvent system of these five options. However, increased interest and research on ILs have dramatically increased in the past few years. These solvents were assessed in the present study as an alternative solvent system for the metathesis of 1-octene and the hydroformylation of vinyl acetate. ILs will be discussed in more detail in the following pages.

2.3 Ionic liquids

2.3.1 Ionic Liquid Nomenclature

ILs have also been referred to as “room temperature molten salts”, “low temperature molten salts” and “liquid organic salts”. ILs are named as all common salts with the following format: [cation][anion]. Ionic liquids employed in the present study are based on 1-alkyl-3-methylimidazolium, *N*-alkylpyridinium, tetraalkylphosphonium and tetraalkylammonium cations.

The 1-alkyl-3-methylimidazolium cations are abbreviated as [Rmim]⁺ where the R is replaced by the first letter of the name of the alkyl chain length. For example, [emim]⁺ and [bmim]⁺ are referred to as [1-ethyl-3-methylimidazolium]⁺ and [1-butyl-3-methylimidazolium]⁺ respectively. Merely altering the chain length of only one of the alkyl groups of the imidazolium cation produces a different IL. Other combinations exist where the methyl group on the imidazolium cation can also be replaced by other alkyl chain groups, although the focus was mainly on [Rmim]⁺ type cations. Imidazolium cations where the C2 position has been methylated were also investigated as potential solvents in this study. These cations are abbreviated as [Rdmim]⁺. For example, [1-ethyl-2,3-dimethylimidazolium]⁺ is abbreviated as [edmim]⁺.

The pyridinium, ammonium and phosphonium cations are abbreviated in a different way to that of the imidazolium cations. For example [*N*-alkylpyridinium]⁺ is abbreviated as [C_{*n*}py]⁺ where *n* accounts for the number of carbons in the alkyl chain attached to the nitrogen of the pyridinium ring. An abbreviated example of the [tetraalkylammonium]⁺ and [tetraalkylphosphonium]⁺ are [(C_{*n*})_{*m*}N]⁺ and [(C_{*n*})_{*m*}P]⁺ respectively where *m* accounts for the number of alkyl chain groups attached to the nitrogen or phosphorus.

The anions are given as their molecular formulas. The ionic liquids used in this study are classified by their anions. For example, hexafluorophosphates,

tetrafluoroborates or bistriflimide ILs were used. Representative structures and their names are presented in Figure 1.6.

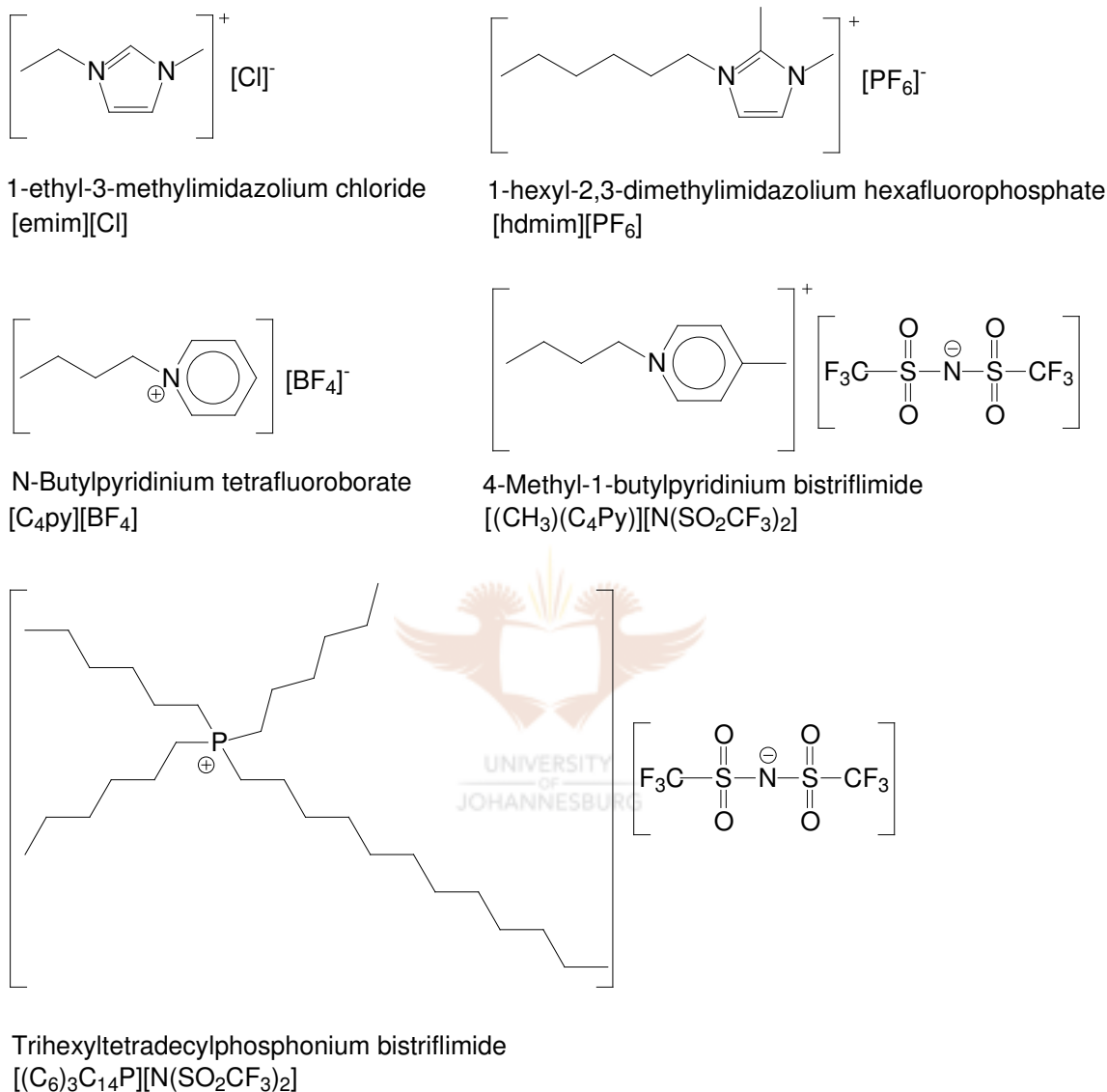


Figure 1.6: Representative structures of ILs and their names

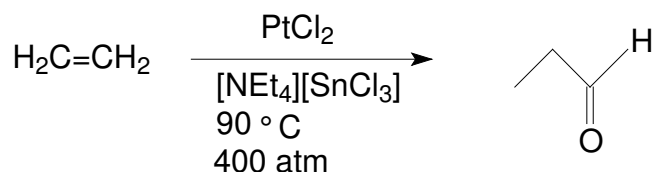
2.3.2 History of Ionic Liquids

ILs may be considered as a new class of remarkable solvents, but they have been around for many years dating back to the 1900s.⁹⁰ There has been an increased interest in them due to their capability of being used as reaction solvents. ILs were initially discovered by electrochemists many years ago while

looking for ideal electrolytes for batteries.⁶² The first recorded IL, ethylammonium nitrate [EtNH₃][NO₃], that is a liquid at room temperature was discovered by Walden in 1914.⁹¹ It was developed by the military for use in liquid propellants.⁹¹ It is now widely used in the structuring of surfactants and the study of protein folding.⁹² The modern history of ILs started with the development of aluminium chloride based salts for electroplating in 1948.⁹³ ILs were later rediscovered by US scientists Frank Hurley and Tom Weir at the Rice Institute in Texas in 1951 while looking for a cheaper and easier way to electroplate aluminium. The IL they produced was an alkylpyridinium chloroaluminate.⁹⁴ The imidazolium cations were discovered by Hussey and Wilkes at the US Air Force Academy while looking for a replacement for the alkylpyridinium cations since they were relatively easy to reduce, both chemically and electrochemically.⁹⁵ Their particular favourite, [emim][AlCl₄] had a melting point below room temperature.⁹⁵ The chloroaluminate ILs act as both catalyst and solvent in many processes.⁹⁶ Chemical reactions in the chloroaluminate ILs, including Friedel-Crafts⁹⁶ and oligomerisation reactions⁹⁷ have been tested successfully. However, they suffered a major drawback: they are air and water sensitive and therefore their use as solvents in transition metal catalysis is limited. Before the mid 1980s, ILs were mainly used in electrochemical applications and have only recently been used as solvents in catalytic reactions.

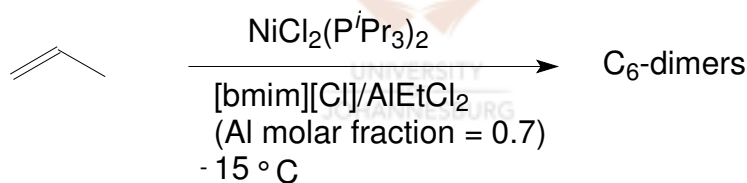
The air and water-stable ILs based on dialkylimidazolium cations were discovered in 1992 by Zaworotko and Wilkes by combining the cation with water-stable anions.⁶⁵ These ILs were based on anions such as halide, tetrafluoroborate, hexafluorophosphate, nitrate, sulfate and trifluoromethanesulfonate, to name but a few. The tetrafluoroborate and hexafluorophosphate ILs are the common “workhorses” for transition metal catalysis using ILs. The hexafluorophosphate ILs are, however, less stable to moisture and are known to hydrolyse in the presence of water and heat to form HF and/or phosphoric acid.

ILs were used for the first time as a solvent for homogeneous transition metal catalysis by Parshall in 1972 in which platinum catalysed hydroformylation of ethylene (Scheme 1.9) was performed in tetraethylammonium trichlorostannate (mp. 78 °C).⁹⁸



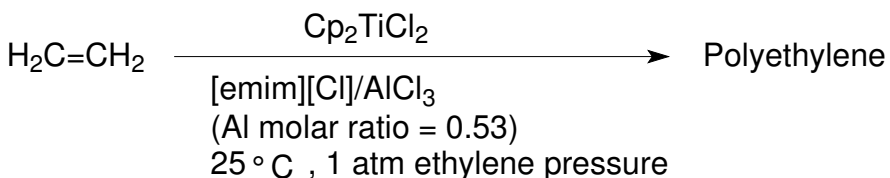
Scheme 1.9

ILs were later also used as solvents for homogeneous metal catalysts by Chauvin *et al.*⁹⁹ and Wilkes *et al.*¹⁰⁰ in the 1990s. The dimerisation of propene in weakly acidic chloroaluminate ILs (Scheme 1.10) were investigated by Chauvin's group.⁹⁹



Scheme 1.10

Wilkes' group investigated the polymerisation of ethylene (Scheme 1.11) using Ziegler-Natta catalysts in weakly acidic chloroaluminate ILs.¹⁰⁰



Scheme 1.11

2.3.3 Physicochemical Properties of Ionic Liquids

ILs have been dubbed “designer solvents” because the properties of the IL can be fine-tuned to favour certain needs of a respective reaction.⁶⁷ The solvent can be designed to optimise a reaction with control over both yield and selectivity.¹⁰¹ Varying the cation or anion, or both, could alter the properties of the IL such as melting point, solubility, acidity, density, viscosity, hydrophobicity and refractive index to fit the needs of a specific reaction. The unique properties of an IL are determined by its structure and interactions of ions present in the IL. The anion of the IL determine the chemical properties of ILs to a large extent.¹⁰² The purity of the IL is an extremely important factor when measuring the physical properties of an IL.¹⁰³ A recent review by Wilkes deals with the crucial properties of ILs required to be known for catalysis.¹⁰⁴

2.3.3.1 Negligible vapour pressure

ILs are known to have negligible vapour pressure (due to the non-existence of ion pairs) thereby minimising solvent losses by evaporation into the environment. They are therefore potentially recyclable. Due to their negligible vapour pressure and non-flammable nature, ILs have been developed recently as so-called green solvents, since there is currently an increasing need to develop environmentally friendly alternatives to replace VOS – a class of molecular solvents. These are the common industrial solvents for industrial synthesis in petrochemical and pharmaceutical industries. The known problems with VOS are that they are quite volatile, highly flammable, toxic and they tend to damage the Earth’s atmosphere.

The fact that ILs are non-volatile allows for easy product separation by distillation/sublimation and pervaporation. However, this also means that the ILs cannot be purified by distillation.

2.3.3.2 Wide liquid range and thermal stability

An interesting feature of ILs that common molecular solvents do not possess is their exceptionally wide liquid range. A solvent's liquid range is the span of temperatures between its melting point and boiling point. For example, water has a liquid range of 100 °C (0 to 100 °C), dichloromethane (145 °C) and dimethyl sulfoxide (170 °C). In comparison, [bmim][BF₄] has a liquidus range of 400 °C. ILs also possess a high thermal stability, which is dependent on both the anion and cation.¹⁰⁵ The upper limit of the liquid range for ionic liquids normally signifies thermal decomposition rather than vaporisation since ILs are non-volatile. The thermal decomposition temperature of ILs generally range from 250 °C to 450 °C. The decomposition temperature of an IL varies with anion type.

A range of [Rmim]⁺ salts with varying anions has been tested for decomposition using thermogravimetric analysis (TGA) and the general stability order is as follows with regards to anion type:

[Cl]⁻ < [BF₄]⁻ ~ [PF₆]⁻ < [N(SO₂CF₃)₂]⁻.

ILs based on the trifluoromethylsulfonylamide anion are particularly thermally stable salts (up to 400 °C).¹⁰⁶ For example, [emim][BF₄] has been reported to be stable to about 300 °C and [emim][N(SO₂CF₃)₂] is stable to more than 400 °C.¹⁰⁷ The thermal stability of ILs therefore depends on the nucleophilicity of the anion. The more weakly co-ordinating anions are more stable to high temperature decomposition.¹⁰⁸

ILs based on 1,3-dialkylimidazolium cations are generally preferred since they are thermally more stable than the quaternary ammonium cations. The quaternary ammonium salts have limited thermal stability due to decomposition via the Hoffmann elimination.¹⁰⁹

2.3.3.3 Melting points

Both the cation and anion affects the melting point of the IL. The main factors that influence the melting points of ILs are the charge, size, the distribution of charge on the ions, the symmetry of the ions, H-bonding ability and van der Waals interactions.¹¹⁰

Increasing the size of the anion or the cation results in a decrease in the melting point of the IL. Large cations tend to reduce the melting points of the IL. The cation symmetry is also important in determining the melting point of an IL. The more unsymmetrical the cation is, the more difficult it is to have efficient ion-ion packing into a solid thereby decreasing the melting point of the IL. Substitution at the C2-position of the imidazolium ring increases the melting point of the IL. This may be due to aromatic stacking or methyl- π stacking between cations. Adding other functionalities such as ether groups around the ions increases the melting points due to an increase in the number of interactions between the ions. An increase in alkyl chain length on the imidazolium cation initially causes a decrease in melting point of the IL. On increasing the alkyl chain length beyond a certain point (e.g. 8-10 carbons for 1-alkyl-3-methylimidazolium cations) the melting point of the IL tends to increase due to an effect on the efficiency of ion packing.

The effect of changes in the cation for different chloride salts is shown in Table 1.4. Alkali metal salts are known to have high melting points and these melting points are reduced to temperatures at or below room temperature by replacing the simple inorganic cations with unsymmetrical organic cations.¹¹¹

Table 1.4: The effect of cation size on the melting point

Cation	Melting point (° C)	Reference
NaCl	803	111
KCl	772	111
[mmim]Cl	125	63c
[emim]Cl	87	63c
[bmim]Cl	65	63c

An increase in anion size reduces the melting point of the IL. However, not all ILs follow this rule of decreasing melting point with increasing anion size (e.g. [emim][PF₆]). The effect of anion size on the melting point of [emim]X ILs is seen in Table 1.5.

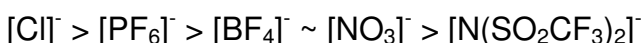
Table 1.5: Effect of anion size on the melting point of [emim]X ionic liquids

Anion (X)	Melting point (° C)	Reference
[Cl] ⁻	87	63c
[BF ₄] ⁻	15	112
[PF ₆] ⁻	62	113
[CF ₃ SO ₃] ⁻	-9	107b
[N(SO ₂ CF ₃) ₂] ⁻	-3	107b

2.3.3.4 Viscosity

ILs are generally more viscous (comparable to viscosities of oils) than most common molecular solvents, varying over a range of <10 to >1000 cP at room temperature. For example, water and ethylene glycol have viscosity values of 0.89 cP and 16.1 cP respectively. The viscosity of the ILs is strongly dependent on the temperature, their tendency to form hydrogen bonds and the strength of their van der Waals interactions.^{107b} An increase in formation of hydrogen bonds between ions results in a higher viscosity of the IL. The influence of hydrogen bonding can be diminished by fluorinating the IL.¹¹⁴ A stronger van der Waals interaction between ions results in a higher viscosity. The purity of ILs is important when determining accurate values for viscosity.¹⁰³ Small amounts of impurities present in ILs have dramatic effects on the viscosity of the IL. Water tends to decrease the viscosity while high chloride impurities increase the viscosity.¹⁰³

The viscosity of an IL is determined by both the cation and anion. For the same cation the viscosity decreases as follows:



For ILs with the same anion, the viscosity increases using longer or fluorinated alkyl chains on the imidazolium ring due to stronger van der Waals interactions.^{107b} The more asymmetrical the cation, the lower the viscosity of the IL. It has been shown that the viscosity of imidazolium based ILs can be decreased by using highly branched and compact alkyl chains.¹¹⁵ Phosphonium ILs also tend to have higher viscosities than imidazolium-based ILs. ILs based on the dicyanamide anions have been found to have the lowest viscosity of all the ILs.

Also, the addition of co-solvents to the ILs can dramatically decrease the viscosity of the IL without changing the cation or anion of the IL.¹¹⁶ Higher temperatures could also result in a dramatic decrease in the viscosity of ILs.¹¹⁷

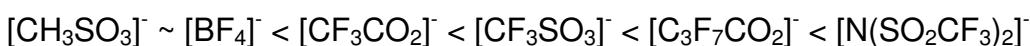
2.3.3.5 Density

The density of ILs is generally greater than that of water with values ranging between 1 and 1.6 g/cm³. Both cation and anion of the IL affect the density.

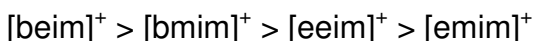
For ILs with the same cation, an increase in the mass of the anion leads to an increase in the density of the IL.



The general order of increasing density with respect to the anion is:



In contrast, for ILs with the same anion, the density decreases with increasing cation mass.



Increasing the alkyl chain length on the cation results in a decrease in density preventing close packing of ions.¹¹⁸ Phosphonium-based ILs tend to have lower densities than imidazolium-based ILs. Impurities present in the ILs have a less dramatic effect on the density of ILs compared to their effect on viscosity.¹⁰³ An increase in temperature results in a decrease in density of the IL.

2.3.3.6 Surface tension

The surface tensions of ILs (*e.g.* [bmim][PF₆] = 48.8 Nm⁻¹ and [bmim][BF₄] = 46.6 Nm⁻¹) are lower than that of water (72.7 Nm⁻¹ at 20 °C) but higher than the surface tensions of *n*-alkanes (*e.g.* hexane = 18 Nm⁻¹).¹¹⁹ Increasing the alkyl chain length on the cation results in a decrease in the surface tension value.¹²⁰

2.3.3.7 Polarity

ILs are considered to be highly polar due to their ionic character. ILs have a polarity that lies between those of water and chlorinated organic solvents.¹¹⁰ Due to the presence of the cation and the anion in the IL, there is most likely to be a much wider range of solvent-solute interactions than with conventional organic solvents. Different solvent-solute interactions in ILs using solvatochromic dyes such as Nile Red and Reichardt's dye have been reported.¹²¹ The results indicate that the polarities of 1,3-dialkylimidazolium salts based on the [PF₆]⁻, [BF₄]⁻, [CF₃SO₃]⁻ and [N(SO₂CF₃)₂]⁻ anions can be compared to those of short chain primary alcohols (such as ethanol and methanol) and other polar, aprotic solvents such as DMSO (dimethylsulfoxide), DMF (dimethylformamide) *etc.* and therefore can be regarded as being relatively polar.¹²² ILs containing the [N(SO₂CF₃)₂]⁻ anion have a slightly lower polarity. Also, the polarity of the IL decreases as the alkyl chain length increases.

In another study using Reichardt's dye, it was shown that tetraalkylammonium cations are relatively non-polar while the cations of type [NH_xR_(4-x)]⁺ (*x* ≥ 1) are much more polar.¹²²

2.3.3.8 Water miscibility

The solubility of ILs in water is dependent on the nature of the anion, the length of alkyl chain on the dialkylimidazolium cation as well as temperature.

Figure 1.7 shows the anions (for the same 1-butyl-3-methylimidazolium cation) responsible for water miscibility and immiscibility. The anions mainly afford water miscibility.

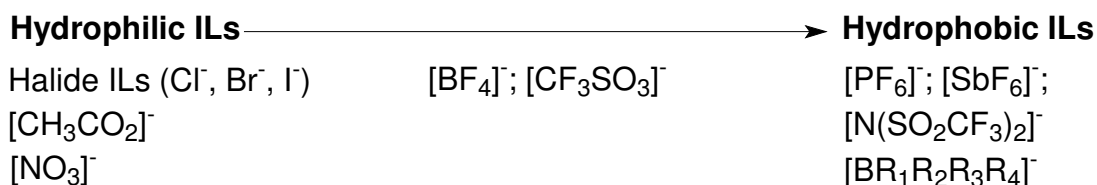


Figure 1.7: Different anions determining water immiscibility and miscibility

In general, an increase in the organic character of the cation results in a decrease of water solubility in the IL.¹²³ The solubility of water in ILs increases with using more co-ordinating anions.

Increasing the alkyl chain length of the 1,3-dialkylimidazolium cations as well as anions increases the lipophilicity/hydrophobicity of the IL. For example, 1-alkyl-3-methylimidazolium tetrafluoroborates salts with alkyl chain length less than six are miscible with water at 25 °C, but with chain length greater than six, the ILs are immiscible with water.⁶²

2.3.3.9 Solubility characteristics

The solubility properties of ILs can be fine-tuned by careful choice of anion and cation.⁶² Varying the alkyl chain length on the dialkylimidazolium cation or the nature of the anion can alter the miscibility of organic compounds or substances with ILs. Aromatics (such as benzene) have better solubility in ILs than do olefins. Alkanes and non-polar organic solvents are generally not miscible in ILs. Polar and ionic substances are very soluble in ILs.

In general, olefins have poor solubility in ILs. However, increasing the nonpolar character of the cation by increasing the alkyl chain length results in an increase in the solubility of alkenes in the IL.

The anion also plays a substantial role. For example, the solubility of hexene in ILs changes in accordance with the following order of anions;



2.3.3.10 Co-ordination ability and acidity

The nature of the anion essentially determines the acidity, basicity and co-ordination ability of the IL. Table 1.6 shows the co-ordination ability of various anions.

Table 1.6: Co-ordination abilities of various anions^{63c}

Basic/strongly Co-ordinating	Acidity/co-ordination neutral/weakly co-ordinating	Acidic/non- co-ordinating
$[\text{Cl}]^-$	$[\text{AlCl}_4]^-$	$[\text{Al}_2\text{Cl}_7]^-$
$[\text{AcO}]^-$	$[\text{CuCl}_2]^-$	$[\text{Al}_3\text{Cl}_{10}]^-$
$[\text{NO}_3]^-$	$[\text{SbF}_6]^-$	$[\text{Cu}_2\text{Cl}_3]^-$
$[\text{SO}_4]^{2-}$	$[\text{BF}_4]^-$	$[\text{Cu}_3\text{Cl}_4]^-$
	$[\text{PF}_6]^-$	

From the table, halides, $[\text{NO}_3]^-$, $[\text{SO}_4]^{2-}$ and other anions not classified in the table (such as $[\text{CF}_3\text{CO}_2]^-$ and $[\text{CF}_3\text{SO}_3]^-$) are co-ordinating anions *i.e.* they will co-ordinate to the active site of a catalyst.

2.3.4 Applications of Ionic Liquids

2.3.4.1 Organic and Catalytic reactions in Ionic Liquids

ILs seem to be attractive suitable replacements for commonly used solvents for many applications. ILs have already been used for a large number of organic and catalytic reactions.⁶³ Using ILs as reaction media often affords accelerated activity and improved selectivity when compared to organic solvents. In some cases, increased catalyst stability is also observed in the IL. ILs provide a unique solvent environment. The main objective for using an IL in a reaction is to enhance reaction activity and selectivity. Additional benefits of using an IL in a

reaction would be for easy separation of reaction products and recovery of the catalyst due to their nonvolatile nature.

An ideal case for using ILs in catalytic reactions would be when the catalyst and substrate are soluble in the IL and the reaction product is insoluble in the IL. Additionally, the reaction product should not extract the catalyst, thereby allowing the products to be removed by simple decantation and the catalyst to be recovered and re-used. However, if the reaction products are miscible with the IL, separation is much more complicated often requiring distillation, which is facilitated due to the IL's negligible vapour pressure. This method is, however, limited to volatile products and is dependent on the thermal stability of the catalyst. Possible extraction of the product with a co-solvent that is immiscible with the IL but miscible with the product is possible but often leads to cross-contamination. A number of transition metal-catalysed reactions have been successfully tested in ILs and these include hydrogenation,¹²⁴ oxidation,¹²⁵ hydroformylation,¹²⁶ Heck reaction,¹²⁷ oligomerisation,¹²⁸ carbonylation,¹²⁹ Suzuki cross-coupling,¹³⁰ Diels-Alder reaction¹³¹ and many others.

2.3.4.2 Ionic liquids as extractant in separation technology

ILs have not received much attention as a substitute for volatile organic solvents for separation technology, scope but this idea represents an interesting field attracting increasing attention nowadays.¹³² ILs are receiving growing interest as a replacement for organic solvents in the aqueous/organic two-phase separation systems for the removal of metals from mining waste water.¹³³ ILs with hydrophobic cations are normally preferred, to increase their hydrophobicity and extracting agents such as crown ethers that complex with metal cations are added to ensure complete removal of the metal ions from the aqueous phase.¹³⁴

The term Task-specific Ionic Liquid (TSIL) introduced by Davis essentially refers to ILs that have a complexing functionality incorporated into their backbone to increase the IL affinity of the extractants.¹³⁵ The functional group can be

covalently tethered to the cation or the anion of the IL. Many TSIL have ligated groups attached to the cationic moiety of the IL to increase metal ion partitioning to the IL phase. For example, thioether, urea and thiourea-based imidazolium ILs (Figure 1.8) have been investigated as extractants of Hg^{2+} and Cd^{2+} from aqueous phases.¹³⁶

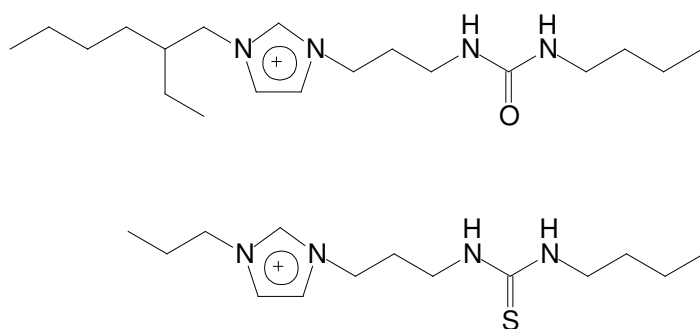


Figure 1.8: Examples of Task-specific Ionic Liquids

It is known that polar compounds or compounds containing strong proton donor functionality (such as phenols, carboxylic acids, diols as well as ionised compounds) interact strongly with ILs.¹¹⁰ Compounds such as ketones, aldehydes and esters with weak proton donor/acceptor functionality interact with ILs through induced ion dipole or weak van der Waals interactions.¹¹⁰

2.3.4.3 Ionic Liquids for Electrochemical Devices

ILs are excellent materials for use in electrochemical devices including batteries, supercapacitors, fuel cells, photovoltaic cells, electroplating and many more.¹³⁷ ILs have a large window of electrochemical stability (electrochemical window > 4 V), high conductivities, wide liquid range and greater thermal stability, which make them excellent materials for this particular application. ILs have been proven to be good electrolytes for lithium rechargeable batteries. A review on the electrochemical investigations in ILs has been published.¹³⁸

2.3.5 Cost and Availability of ILs

The success of ILs eventually will lie in their commercial availability and ultimate cost. ILs are significantly more expensive than traditional organic solvents. There are a number of commercial suppliers of ILs such as Solvent Innovation, Cytec, Merck, Sigma-Aldrich, Acros-Organics who are willing to supply ILs in larger quantities.¹³⁹ The price of an IL produced on large scale is determined by the price of the cation and the anion source. Table 1.7 shows the relative price of typical cations and anions making up ILs.

Table 1.7: Cost outline of typical cations and anions used to prepare ionic liquids¹²³

Cheap	Expensive
Cations:	
[HNR ₃] ⁺ , [NR ₄] ⁺ [HPR ₃] ⁺ , [PR ₄] ⁺	alkylmethylimidazolium- dialkylimidazolium-
alkylpyridinium-	
Anions:	
[Cl] ⁻ , [AlCl ₄] ⁻ [MeSO ₄] ⁻ [acetate] [NO ₃] ⁻	[PF ₆] ⁻ [BF ₄] ⁻ [CF ₃ SO ₃] ⁻ , [SbF ₆] ⁻ [(CF ₃ SO ₂) ₂ N] ⁻

From Table 1.7, it can be seen that anions such as [BF₄]⁻, [PF₆]⁻ and [N(SO₂CF₃)₂]⁻ used in combination with dialkylimidazolium cations form quite expensive ILs.

The cost of the IL ideally can be regarded as a once-off investment since the IL used for any particular application can in theory be recycled and reused. It has been estimated that manufacturers should be able to supply ILs containing the cheaper anions at a price between 25 and 50 Euros per kilogram.¹⁴⁰

2.3.6 Commercial Processes using Ionic Liquids

In 1998, the Institut Francias du Petrole (IFP) in France launched a commercial process based on ILs.¹⁴¹ It is known as the *Difasol* process where butenes are dimerised to iso-octenes in a slightly acidic imidazolium aluminate ILs ([bmim]Cl/AlCl₃/EtAlCl₂ = 1/1.2/0.25) using a nickel-based *Dimersol* catalyst.¹⁴² The iso-octenes are used to produce isononanols, which are converted into dialkylphthalate for use as PVC plasticisers. Existing *Dimersol* units can be retrofitted to the *Difasol* units. The *Dimersol* process produces an 85% octene selectivity and 80% conversion of *n*-butene. The *Difasol* process is much more efficient with a dimer selectivity in the range of 90–95% due to the differences of solubility of the monomers and dimers (dimers have a low solubility in the IL) in the IL. The conversion of butenes for the *Difasol* process is in the range of 70–80% even when using dilute butene feedstocks.

The process is widely used in 25 plants worldwide and is available for licensing. The biphasic *Difasol* process is an improvement over the conventional homogeneous, monophasic, solvent-free *Dimersol X* process since it has an improved iso-octene yield and reduces catalyst consumption thereby reducing catalyst disposal and cost.

Recently, BASF commercialised a process using ILs in the manufacture of alkoxyphenylphosphines.¹⁴³ Alkoxyphenylphosphines are used as precursors for the production of photoinitiators used in the manufacture of printing inks, glass fibre and wood coatings. Alkoxyphenylphosphines are produced by the reaction of phenylchlorophosphines with alcohols. Hydrochloric acid is formed as a by-product.

BASF uses *N*-methylimidazole to scavenge the acid formed in the process, forming an IL, *N*-methylimidazolium chloride which has a melting point of 75 °C. The IL separates from the pure product and is recycled. The process has a name termed the BASIL process (**b**iphasic **a**cid **s**cavenging utilising **i**onic **l**iquids). In

many industrial processes, acids need to be removed to prevent the product from either decomposing or to prevent possible contamination of the product. Conventional acid scavengers such as triethylamine form solids which are difficult to remove from the product making the IL process advantageous since it produces a liquid-liquid phase.

These commercial processes clearly show that handling ILs on a large industrial scale is not an issue.

2.3.7 Drawbacks of Ionic Liquids

There have been questions raised as to whether the ILs really are “green” solvents.¹⁴⁴ The corrosivity of the acidic chloroaluminate ILs is an obvious example and the lack of toxicity and biodegradability studies makes it premature to classify ILs as “green” solvents. Until recently, very few toxicity and biodegradability data of ILs were available, which could pose a problem in the future since it is quite expensive as well to generate these toxicity data. These data are however a pre-requisite for the industrial scale use of ILs. It is also important to know the impact it would have on the environment. Wasserscheid and Hilgers believe that the best prediction of the toxicity of an IL ([cation][anion]) can be derived from the toxicity data of the salts [cation]Cl and Na[anion]. An academic group in Germany recently reported toxicological tests that were performed on a series of ILs based on imidazolium cations and varying anions such as [PF₆]⁻, [BF₄]⁻, [Cl]⁻, [Br]⁻ and tosylate.¹⁴⁵ The results showed that the most toxic IL has the same toxicity as the least toxic traditional volatile organic solvents namely methanol, acetone and acetonitrile. They found that most of the ILs were less toxic than the organic solvents.¹⁴⁵

ILs are relatively expensive when compared to the traditional volatile organic solvents but this is unlikely to always be the case with more universities and industries becoming interested in using ILs in their processes. The availability of ILs at a tonnage scale is slowly becoming a reality. Knowledge of the physical-

chemical property data is required by the engineers to better understand the nature of ILs if they are to be used in a large scale to design a chemical plant and these data is slowly growing in the IL field but are not as well-established as with conventional organic solvents. Also, studies show that impurities present in the IL can significantly affect the physical properties of the IL.¹⁰³

Long-term recyclability of ILs also still has to proven and is unknown. Another unknown is the issue of disposal of ILs, since ILs containing halide ions will liberate corrosive and toxic acids such as HF and HCl when undergoing thermal incineration. The supplier could possibly take back the spent IL and recycle it.

2.4 Preparation, Characterisation and Purification of ILs

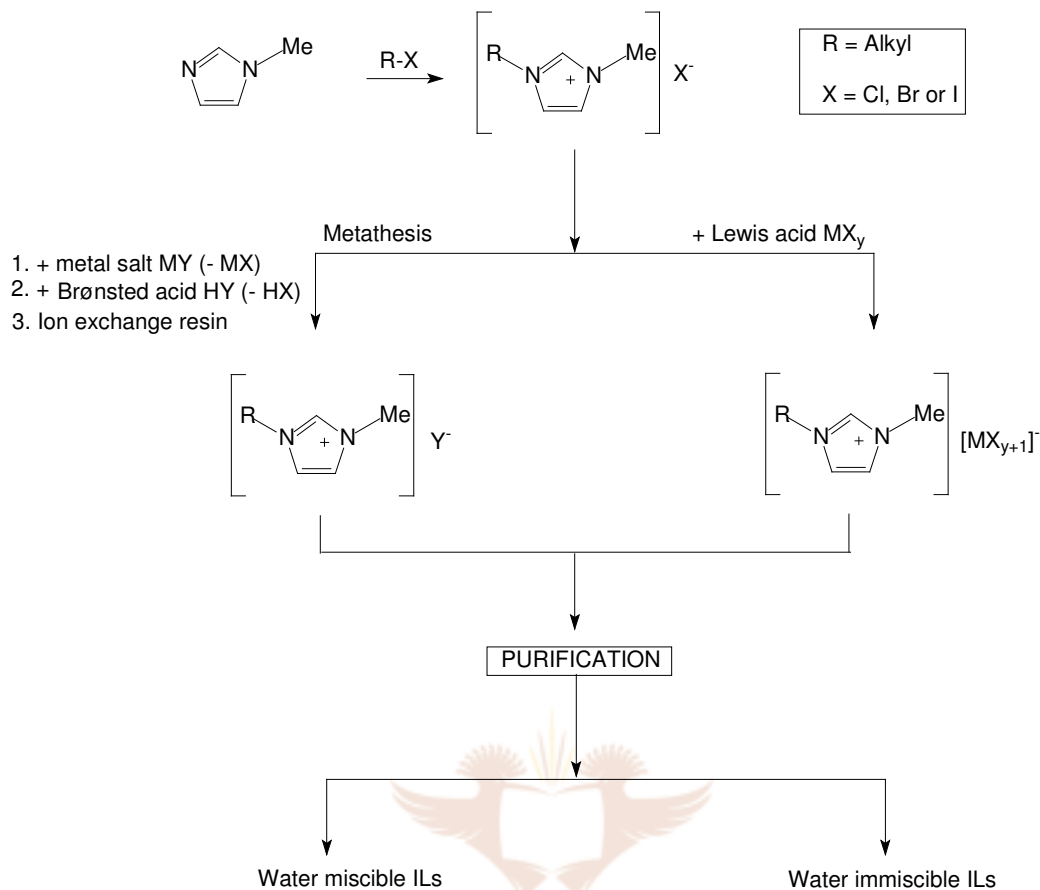
2.4.1 Preparation of ILs

2.4.1.1 Introduction

In general, the synthesis of ILs can be divided into three parts:

- The formation of the precursor cation (normally a halide salt), and then
- Anion exchange to produce the desired IL, or
- Lewis acid reaction to produce the desired IL.

A reaction scheme (Scheme 1.12) for the basic synthesis of ILs is shown below using the imidazolium cation as an example.



Scheme 1.12

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In some instances, the precursor cation (especially tetraalkylammonium salts) is commercially available therefore requiring only an anion exchange reaction or a Lewis acid reaction.

The preparation of ILs is relatively simple. The anion exchange reaction normally occurs by a metathesis exchange reaction. The major problem with the metathesis anion exchange reaction is the stoichiometric amount of waste (MX, HX) that is formed. The Lewis acid reaction is normally used to prepare chloroaluminate-based ILs.

ILs can also be prepared directly by alkylating 1-alkylimidazoles, trialkylamines and trialkylphosphines with methyl triflate or methyl tosylate.^{107b} The alkyl triflates and tosylates are sensitive to hydrolysis and should therefore be worked with

under an inert atmosphere. This method has a major advantage since the desired IL is produced with no by-products, especially no halide impurities which could hinder catalysis by strongly co-ordinating to transition metal catalysts.

2.4.1.2 Preparation of the precursor cation

The formation of the precursor cation is normally performed by quaternisation of an amine or phosphine with a haloalkane. These halide salts can then be converted to the desired ILs by reacting them with salts or acids containing the desired anion. The common amines used are 1-alkylimidazoles but others such as pyridine, isoquinoline, 1-methylpyrrolidone and trialkylamines can also be used for quaternisation. Haloalkanes include chloroalkanes, bromoalkanes and iodoalkanes with reaction conditions being milder in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ with the chloroalkanes being the least reactive and the iodoalkanes being most reactive. For example, a quaternisation reaction of 1-methylimidazole and an alkyl chloride can take 2-3 days at 80 °C whereas the reaction with an alkyl bromide takes about 1 day at 50–60 °C.¹⁴⁶ The reactions with the alkyl bromides are exothermic and lead to highly coloured ILs forming. In general, the reactivity of the haloalkane decreases with increasing alkyl chain length.

The precursor cation is formed by simply stirring the amine or phosphine with the haloalkane under nitrogen (to exclude water and oxygen) while heating. The reaction is normally not carried out with a solvent since the reagents are miscible with one another and the halide salt is immiscible forming a lower phase. Overheating the reaction mixture to temperatures greater than 80 °C could result in the reversal of the quaternisation reaction. The halide salts should be kept free of moisture as they are hygroscopic.

Purification of the halide salt is normally performed by recrystallisation from a mixture of dry acetonitrile and ethyl acetate in the case of a solid halide salt or in the case of an oil washing with an immiscible solvent such as dry acetonitrile, or ethyl acetate.

Recently, the use of microwave irradiation as an alternative approach to produce the halide salts with high yields and short reaction times have been reported.¹⁴⁷

2.4.1.3 Preparation of the desired IL by anion metathesis reactions

In this approach, the desired IL is obtained by performing an anion metathesis reaction of the halide salt with a salt (normally silver, group 1 or ammonium salts) or an acid containing the desired anion (acid-base neutralisation reactions). Using the acid (where available) is normally preferred since it produces HCl, HBr or HI as a by-product which is easily removed by washing the IL with water. The metathesis anion exchange reaction, when using a free acid, is normally performed by cooling the aqueous halide mixture since the reaction is exothermic. Where the acid is not available, metal or ammonium salts can be used without any difficulty.

ILs that are immiscible with water are more straightforward to prepare than the water miscible ILs. With water-immiscible ILs, the free acid or metal salt is washed out with water to give the final IL product. Water-miscible ILs are normally extracted out of the aqueous phase with dichloromethane.¹⁴⁸ In both cases, the ILs are then dried under vacuum. Table 1.8 below shows the examples of ILs that can be prepared from an anion source using the anion metathesis reaction.

Table 1.8: Anion sources to prepare different ILs using metathesis reaction¹²³

Ionic Liquid	Anion source	Reference
[cation][PF ₆]	HPF ₆	149, 150, 151
[cation][BF ₄]	HBF ₄ , NH ₄ BF ₄ , NaBF ₄	150, 151
[cation][N(SO ₂ CF ₃) ₂]	Li[N(SO ₂ CF ₃) ₂]	107b, 150
[cation][CF ₃ SO ₃]	CF ₃ SO ₃ CH ₃ , [NH ₄ [(CF ₃ SO ₃)]	107b, 152
[cation][NO ₃]	AgNO ₃ , NaNO ₃	107b, 150
[cation][N(CN) ₂]	Ag[(N(CN) ₂)]	153

The use of ion-exchange resins to prepare a desired IL has also recently been reported.^{63c,154} All of the methods should ideally produce high purity ILs.

2.4.2 Purification of ILs

Since the purification of ILs by distillation is not possible due to their negligible vapour pressures, it is important to purify starting materials efficiently, thereby reducing the amount of impurities to be removed in the desired IL. This protocol results in the highest purity possible in the produced IL.

ILs should in theory be colourless liquids but in practise this is hardly the case. The coloured impurities present in ILs are probably due to oxidation products, thermal degradation impurities from the starting materials, or traces of compounds from the starting material. It is therefore important to use freshly distilled starting materials (1-methylimidazole is normally distilled prior to use under vacuum from calcium hydride and stored under nitrogen while the haloalkanes could be washed with acid, neutralised and distilled) and low-temperature synthesis and drying methods to avoid extreme colouration of the IL. Coloured impurities present in ILs normally do not affect most applications using ILs.

2.4.2.1 Types of Impurities

The common impurities present in ILs after the anion metathesis reaction are halide ions, free acids (protic impurities), water and unreacted 1-methylimidazole. The presence of these impurities can be extremely detrimental to transition metal catalysts leading to their deactivation.¹⁵⁵ Additional to this, impurities present in the IL significantly alter their physical properties.¹⁰³ Purification of ILs, is therefore, essential before using it in any application.

Water-immiscible ILs are normally much easier to purify than water-miscible ILs by simply washing the IL with water.

a) Volatiles and reagents

Volatile impurities present in ILs could be due to unreacted starting materials or organic solvents used. Residual reaction solvents are readily removed by heating the IL under vacuum. These volatile impurities can easily be removed by evaporation from the non-volatile IL. Unreacted 1-methylimidazole is extremely difficult to remove due to its relatively high boiling point of 198 °C and strong interaction with the IL. 1-Methylimidazole is a co-ordinating base and will frequently irreversibly co-ordinate to an electrophilic catalyst thereby deactivating the catalyst. A colourimetric method implemented by Holbrey allows for the determination of 1-methylimidazole present in the IL in the 0-3 mol % concentration range. This method is based on the formation of the blue $[\text{Cu}(\text{mim})_4]^{2+}$ ion from the reaction of 1-methylimidazole with copper (II) chloride.¹⁵⁶ Free acids (protic impurities) remaining after the metathesis reaction are normally removed by washing with water. In water-immiscible ILs, shaking up with water and then testing the aqueous phase with a pH test will confirm the presence of acid in the IL.

b) Halide impurities

Halide impurities adversely affect the physicochemical properties of an IL. Additionally, they can act as catalyst poisons, as stabilising ligands and as nucleophiles. The presence of halide ions in the wash solutions can be detected by testing them with a silver nitrate solution which will become white and murky showing the presence of silver chloride. Halide content in ILs is normally measured using an ion-sensitive electrode or using a wet chemical method (Volhard method).¹⁵⁷ Alternative methods of IL preparation have also been proposed to avoid halide impurities present in ILs which entails direct alkylation of 1-alkylimidazole.

c) Water

Residual water present in ILs (more problematic to remove than organic solvents probably due to the existence of hydrogen bonding with IL) can normally be

removed by heating the IL under vacuum at 70-80 °C for several hours. For example, even a hydrophobic IL such as [bmim][N(SO₂CF₃)₂] can be saturated with about 1.4 wt % water. Hydrophilic ILs tend to contain a more significant amount of water. Water present in the IL can also affect the physico-chemical properties of ILs, the stability of the IL (IL could undergo hydrolysis forming acidic protons), and catalyst inhibition. The water content in ILs can be determined by Karl-Fischer titration or even IR spectroscopy.

With [PF₆]⁻ and [BF₄]⁻ based ILs, traces of water present result in the decomposition of the anion producing HF and phosphoric acid or boric acid. This poses a problem, since these by-products are corrosive and they can act as poisons and deactivate the catalyst.

For further purification of the IL, they can be dissolved in dichloromethane, acetonitrile or THF and treated with activated charcoal and stirring for 24 hours. The IL can then be filtered through a short column of acidic or neutral alumina and dried under vacuum.

2.5 Conclusions

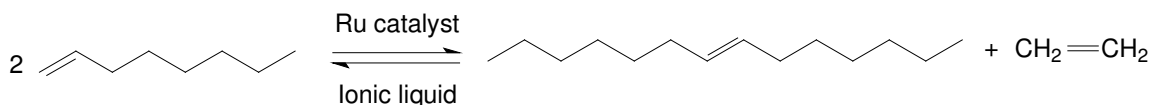
Carbon-carbon bond-forming (C-C) transformations remain the foundation of organic chemistry and of all C-C transformations olefin metathesis is one of the major reactions undergoing an exciting renaissance. Many new metathesis applications have become possible mainly due to the development of excellent, structurally defined catalyst systems which are robust and stable to air and water but most importantly tolerant to a wide range of functional groups. Of these catalyst systems, ruthenium-based catalysts (Grubbs-type) are of particular importance due to their ability to produce high activities and selectivities. Olefin metathesis has shown to produce many useful materials and also opened up industrial routes to important petrochemicals, polymers as well as speciality chemicals.

From the discussion on ILs, it is clear that this class of solvents possesses a range of characteristics that can be varied. These characteristics range from viscosities and melting points to polarity and miscibility with water. It is clear that these solvents lend themselves to tuning, and the judicious selection of cation-anion pairs can provide a desirable confluence of variables.

This study will focus mainly on the olefin metathesis reaction. The literature survey has shown that there is ample scope for carrying out catalysed transformations in ILs. The use of ILs as solvents allows for new, innovative and exciting chemistry, with possibly better selectivities and conversions, and frequently enhancing the stability of transition metal catalysts. The olefin metathesis reaction, specifically the cross-metathesis of olefins, has not yet been fully studied in ILs and the present study attempts to investigate the metathesis of α -olefins in ionic liquids as solvent media. The reader will note that the coverage of metathesis catalysts is fairly extensive and that, for practical reasons, the ILs employed here were selected to provide a manageable but sufficiently broad range of variables.

A study of the self-metathesis of 1-octene to 7-tetradecene (Scheme 1.13) as a feedstock for the production of linear alkyl benzene sulfonates (LABS) was undertaken in ILs as solvents. 1-Octene was used as a model substrate, since it is inexpensive and readily available.

Model reaction:



Scheme 1.13

The ruthenium catalyst ideally should selectively be dissolved in the IL phase and the 1-octene and 7-tetradecene not soluble in that phase, instead forming a

separate second phase that can be easily separated. This set-up should allow efficient recycling of the IL/catalyst phase. A comprehensive study was undertaken here on different ruthenium-based catalysts (Figure 4) to determine the effect of reaction parameters, additives and different IL systems on catalyst activity, selectivity and lifetime. Of the catalysts, first (**1** and **2**) and second generation (**3**, **4** and **5**) Grubbs-type catalysts were investigated for 1-octene metathesis in ILs. It was believed that an ionic catalyst would be more soluble in the ionic liquid phase, and therefore an ionic ruthenium allenylidene catalyst system (**6**) was also tested for metathesis of 1-octene in ILs.

Suitable IL systems were identified and reaction conditions optimised to deliver maximum rates and favourable selectivities for the metathesis of 1-octene. The effect of the counterion and the length of the alkyl chains of the ILs on the metathesis activity and selectivity were investigated. ILs represent a good system for the recycling of these homogeneous catalysts, and have been evaluated for application in homogeneous metathesis.

To broaden the scope of reactions tested in ILs, hydroformylation reactions were also investigated using ILs as solvents and is presented in the chapter three. The study deals with the hydroformylation of vinyl acetate, in particular. Definite advantages have been noted in using ILs as solvents for hydroformylation which include enhanced selectivity to the desired product and similar hydroformylation activities when compared to conventional organic solvents.

In order for industry to adopt IL processes and technologies, it is essential to show that they are better than existing processes. The IL technology should not only be cleaner but also cheaper and safer. The IL should essentially give process improvements such as enhanced reactivity and selectivity, easy product separation (by decantation or gravity separation) and stabilisation of catalyst in order to recycle the catalyst much more efficiently. Product benefit (such as significantly improved quality and stereochemical purity), major process

simplifications (such as reduced reaction steps and no need for expensive separations) and cost improvements will be the most important drivers in making a new technology attractive. The IL technology is still at an early stage of development and it will be only after many years of development and experience that it would potentially become a standard choice for industry.

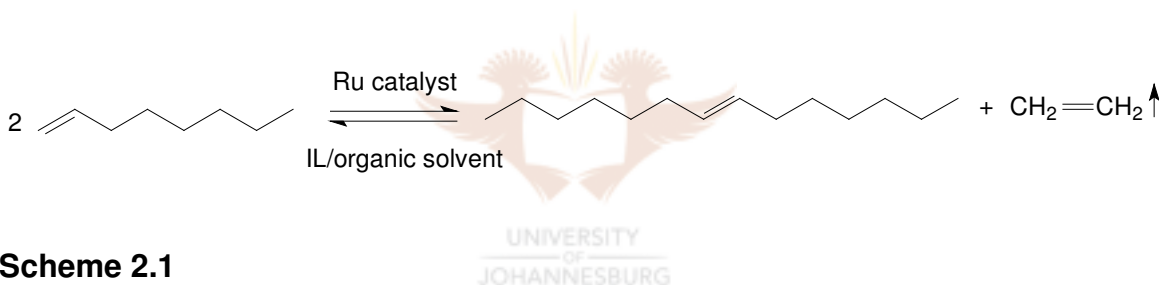


Chapter 2

Results and Discussion

2.1 Introduction

The metathesis of 1-octene (Scheme 2.1) in the presence of various ruthenium-based catalysts was investigated. The chapter is divided into three sections, dealing with the results obtained with first generation Grubbs catalyst and PHOBCAT catalyst, followed by the results with second-generation Grubbs catalyst and lastly the results obtained with the cationic ruthenium allenylidene catalyst.



Scheme 2.1

1-Octene was chosen as a suitable substrate for the present study, since it is non-volatile, inexpensive and widely available. The self-metathesis of 1-octene is a model reaction and could possibly be replaced with any other low-value olefin. A potential application for metathesis is the conversion of low value C₇ α-olefins to internal C₁₂ and similar olefins which can then be utilised as detergent alcohol (DA) feedstocks, linear alkyl benzene sulfonates (LABS), secondary alkylethoxylates (SAE), modified linear alkyl benzenes (MLAB's) or methyl branched detergent alcohols (MDA).

In this study, the use of ILs as alternative solvent systems was investigated for each catalyst system and the effect the IL has on the metathesis activity and

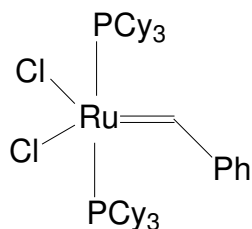
selectivity towards 1-octene and compared to conventional organic solvents. The effect of various additives on catalyst system was also investigated.

2.2 Studies on First Generation Grubbs Catalyst

2.2.1 Grubbs catalyst

In the mid 1990's Robert Grubbs at Caltech, USA developed Grubbs catalyst **1**, which proved to be a major breakthrough in homogeneous catalysis.¹⁵⁸ This ruthenium-based catalyst produced higher selectivities as well as high reaction rates and also had a good tolerance to oxygenates in feeds compared to other homogeneous catalysts based on molybdenum and tungsten.¹⁵⁹ In the literature, little work has been dedicated to metathesis of simple olefins such as those found in a typical Fischer-Tropsch-derived olefin stream. Most of the work is on the metathesis of functionalised olefins or polymerization metathesis.¹⁶⁰ Also, most of the work is carried out at relatively high catalyst concentrations (*e.g.* 0.1 – 5 mol %) which makes this catalyst system disadvantageous when using the catalyst in large-scale reactions.¹⁶¹ However, the Grubbs catalyst has been studied in the metathesis of 1-octene by various research groups.¹⁶²

In the present study, a kinetic investigation was carried out on the Grubbs catalyst, looking at the variables of temperature, influence of IL and organic solvent as well as the addition of additives such as phenol.



1

a) Influence of organic solvent

The influence of the presence of an organic solvent on the activity and selectivity of the Grubbs catalyst was investigated. Reactions were carried out at an olefin:Ru ratio of 4992:1, and a Ru concentration of 0.02 mol % with respect to the olefin. In each reaction, 2 mL of a particular solvent was added to 16 mL of 1-octene followed by the addition of 16.4 mg of the Grubbs catalyst at 40 °C. In the neat reaction, the olefin:Ru ratio was kept constant at 4992:1. Reactions were performed at 40 °C to slow down the metathesis reaction and enhance the stability of the catalyst. All reactions were homogeneous by visual inspection. The results are shown in Table 2.1.

Table 2.1: The influence of organic solvent on the formation of 7-tetradecene after 3h reaction time

Organic solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	37	99.7
Toluene	35	99.8
1,1,1-trichloroethane	35	99.8

^aas determined by GC analysis

From the results, it seems that the solvent used (toluene and 1,1,1-trichloroethane) had no effect on the formation of 7-tetradecene when compared to the neat reaction (no solvent) where the reaction was performed in bulk on the neat substrate. The selectivity was quite good at 40 °C for all solvents used.

b) Influence of feed preparation

The influence of feed preparation on metathesis activity was investigated. Although oxygenates may be tolerated by ruthenium-based catalysts, oxidants are very detrimental. Olefins readily form peroxides in the presence of trace amounts of oxygen. This build-up of peroxide in the olefin starting material is problematic and could lead to catalyst deactivation especially at the low catalyst

concentrations used here. Passing the olefin through an alumina column prior to use has proven to be successful in removing contaminants from the feed.^{162a}

Therefore, the commercially available 1-octene (Aldrich, 99%) was purified by passing it through a column of neutral alumina while bubbling argon through it for 4 hours. The 1-octene was then stored over neutral alumina under an argon atmosphere. Metathesis of these feeds to form 7-tetradecene using the Grubbs catalyst was then performed using the purified feed and was compared to the 1-octene used straight from the Aldrich bottle. Reactions were carried out with 0.02 mol % catalyst (4992:1 molar ratio of olefin:Ru) at 40 °C. Metathesis activity and selectivity are shown in Table 2.2.

Table 2.2: The influence of feed preparation on the formation of 7-tetradecene after 3h reaction time

	Conversion of 1-octene (%)	Selectivity (%) ^a
Purified 1-octene	37	99.7
Unpurified 1-octene	38	99.8

^aas determined by GC analysis

Metathesis yields of 37% and 38% were obtained for the purified and unpurified feed, respectively. This shows either that 1) the Grubbs catalyst is quite resistant to peroxide and that feed preparation is not really necessary with this catalyst or 2) that there were no peroxides present in the substrate. Whatever the case, this aspect was not central to the work and was thus not further investigated. Throughout the rest of the study, reactions were performed using purified 1-octene.

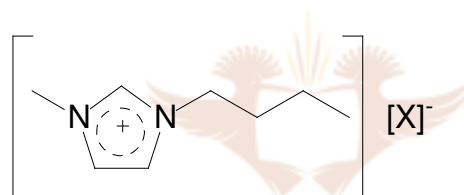
c) Influence of IL

The use of an IL for the metathesis reaction has to show distinct advantages since the metathesis reaction can take place with no organic solvent present. The use of IL can be justified if such use brings about an increased reaction rate,

enhanced selectivity and facilitates catalyst recycling. The influence of IL on the Grubbs catalyst was investigated for the metathesis of 1-octene. In each reaction, 2 mL of a particular IL was added to 16 mL of 1-octene followed by addition of 16.4 mg of the Grubbs catalyst at 40 °C. It was speculated that 2 mL of IL would be sufficient to dissolve the catalyst amount and this is why the particular substrate:IL ratio was employed. Reactions were performed at 40 °C to slow down the metathesis reaction and enhance the stability of the catalyst. 1-Octene formed a biphasic system with all of the ILs used.

i) Influence of the anion of the IL

A common cation, [1-butyl-3-methylimidazolium], in conjunction with various anions (Figure 2.1) was tested for the self-metathesis of 1-octene. The results are shown in Figure 2.2.



where X = $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$
and $[\text{O}_3\text{SO}_4]^-$

Figure 2.1: [bmim][X] ILs used for 1-octene metathesis

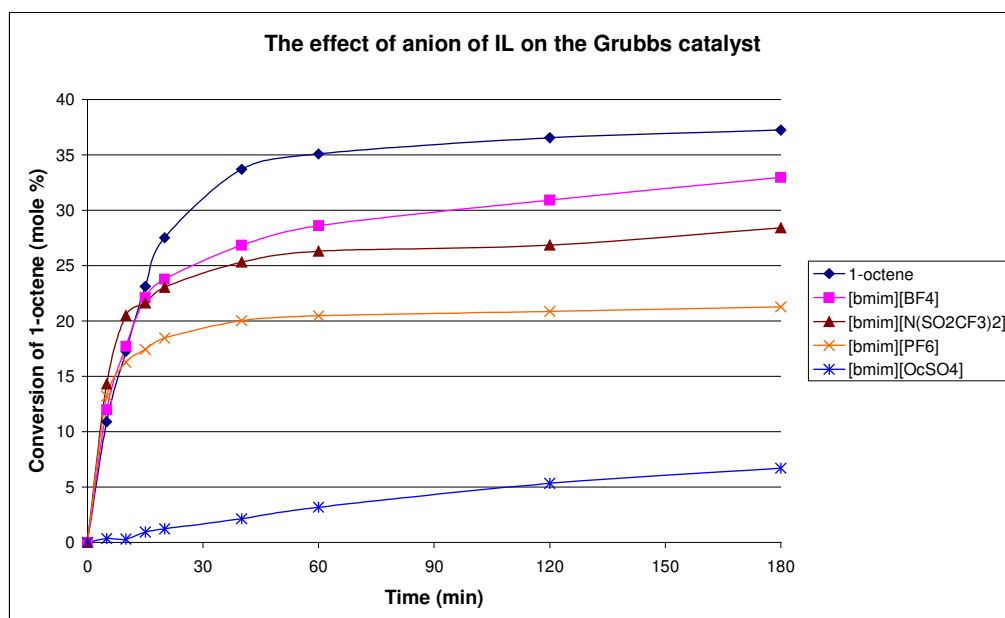


Figure 2.2: The effect of [bmim][X] type ILs on the conversion of 1-octene

From Figure 2.2, the neat reaction (1-octene as bulk substrate) outperformed all ILs with regards to activity. The activity and selectivity for the IL reactions and neat reaction are shown in Table 2.3.

Table 2.3: The effect of anion of IL on the conversion of 1-octene after 3h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	37	99.7
[bmim][BF ₄]	33	99.2
[bmim][N(SO ₂ CF ₃) ₂]	28	99.8
[bmim][PF ₆]	21	99.2
[bmim][OcSO ₄]	7	100

^aas determined by GC analysis

The selectivity remained quite high for both IL and the neat reaction. The formation of secondary metathesis products (SMPs) was, consequently, very low.

The reasons for the poor activity in [bmim][OcSO₄] are not known but are possibly due to its low polarity and to the anion also being a bit more coordinating than the other anions used. The Grubbs catalyst works well in highly polar solvents⁵ and this is seen with ILs too, since [bmim][BF₄] is the most polar of the ILs used in the study and afforded the highest activity. The same tendency was not seen with the [N(SO₂CF₃)₂]⁻ and [PF₆]⁻ anions, but this could be due to impurities present in the IL, which can be difficult to control. The polarity trend is as follows for the anions used, which give rise to a similar series of ionic liquids containing them: [BF₄]⁻ > [PF₆]⁻ > [N(SO₂CF₃)₂]⁻ >> [OcSO₄]⁻.¹⁶³ The metathesis activity trend were: [BF₄]⁻ > [N(SO₂CF₃)₂]⁻ > [PF₆]⁻ >> [OcSO₄]⁻. The activity could be largely influenced by the different coordination ability of the anion of the particular IL to the catalyst as well as the varying polarity of the ILs employed.

Significant leaching of the Grubbs catalyst was noted during the IL reactions. The leaching ability of the Grubbs catalyst from the [edmim][N(SO₂CF₃)₂] IL was investigated and XRF analyses showed that there were 101 ppm Ru present in the organic phase (7-tetradecene/1-octene mixture) after a typical 5-hour reaction time. These results show that 72% of Ru catalyst leaches into the organic phase. This indicated clearly that, with the Grubbs catalyst, there is a strong possibility that the metathesis reaction took place in the organic phase and not the ionic liquid phase.

d) Influence of temperature

The influence of temperature was studied at constant ruthenium concentration (0.02 mol %, 4992:1 olefin:Ru molar ratio) for both a [edmim][N(SO₂CF₃)₂] IL reaction and the neat reaction. It can be seen that temperature had a significant effect on catalyst behaviour. Rapid catalyst deactivation was noted at high temperatures and this is observed by the higher isomerisation activity. However, no trace of secondary metathesis products was observed in any of these reactions.

These results suggest that either the metathesis-active catalyst is converted, at higher temperatures, to a species which is metathesis-inactive and that supports isomerisation, or that the isomerisation was energetically favoured at the high temperatures from both an activation energy point of view as well as a thermodynamic stability point of view.¹⁶⁴ At the lower temperature, isomerisation was negligible. The results are shown in Table 2.4.

Table 2.4: The effect of temperature on the conversion of 1-octene in neat reaction and [edmim][N(SO₂CF₃)₂] after 3h reaction time

IL/solvent	Temperature (°C)	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	40	37	99.7
[edmim][N(SO ₂ CF ₃) ₂]	40	30	99.7
No solvent	90	62	58.4
[edmim][N(SO ₂ CF ₃) ₂]	90	68	73.4

^aas determined by GC analysis

e) Influence of phenol

The influence of phenol on the activity of the Grubbs catalyst was investigated. It has been noted by the Sasol Homogeneous Metathesis Research group that phenol has a beneficial effect on Grubbs catalyst.¹⁶⁵

The phenol was added to the 1-octene and the mixture was stirred at 40 °C, followed by addition of the catalyst (16.4 mg Grubbs catalyst) to the reaction mixture. The results are shown in Figure 2.3 and Table 2.5.

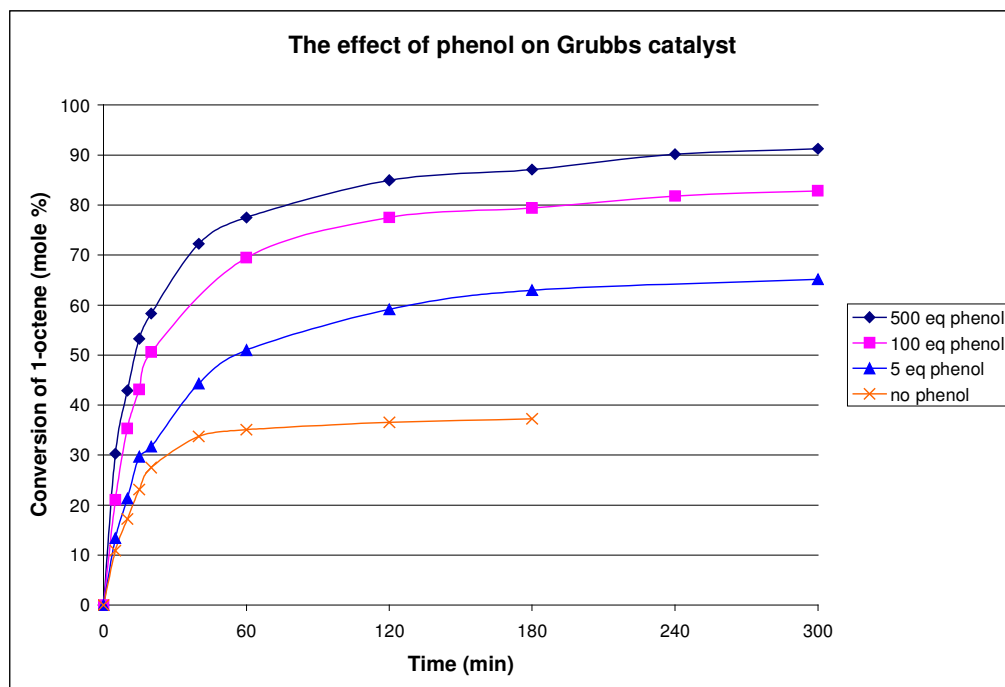


Figure 2.3: The influence of phenol on the conversion of 1-octene in a neat reaction

Table 2.5: Conversion and selectivity for self-metathesis of 1-octene with the effect of phenol after 3h reaction time

Equivalents of phenol added	Conversion of 1-octene (%)	Selectivity (%) ^a
0	37	99.7
5	63	99.7
100	79	99.2
500	87	97.4

^aas determined by GC analysis

A dramatic rate enhancement was observed for the metathesis of 1-octene when phenol was added to the reaction mixture. Furthermore, the catalyst was active even after 3 hours, in marked contrast to the neat experiment. The reaction mixture maintained a clear orange colour throughout the duration of the experiment. Optimum rates were obtained using 500 equivalents of phenol,

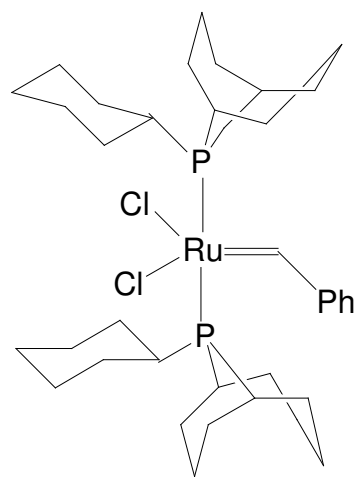
although higher equivalents of phenol need to be further evaluated. It was noted that with increasing phenol concentration the selectivity drops a little, but was still quite high. It is believed that phenol influences the relative rates of phosphine loss and rebinding, activates the carbene carbon to allow reaction with olefin and also plays a role in stabilising the active metathesis catalyst.¹⁶⁵

In conclusion, the Grubbs catalyst performed relatively poorly in comparison to second-generation Grubbs metathesis catalysts and PHOBCAT (*vide infra*), in the neat reaction (with no solvent), in conventional organic solvents as well as in the presence of ionic liquids. The use of ILs brought about no advantages when compared to a conventional organic solvent. When using ILs, lower activity was achieved compared to the neat reaction although high selectivities were maintained. Additionally, significant leaching out of the IL layer was observed with the catalyst. The Grubbs catalyst was therefore less robust, showing poor thermal stability and underwent rapid deactivation in both IL and organic solvent. The addition of phenol, however, resulted in a considerable rate enhancement as well as increased catalyst lifetime, and therefore represented a significant find.

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2.2.2 PHOBCAT

PHOBCAT $[\text{Cl}_2(\text{Phoban-Cy})_2\text{Ru}=\text{CHPh}]$ **2** is a catalyst developed at Sasol Technology, R&D in South Africa.¹⁶⁶ This catalyst resembles the Grubbs catalyst except that it has bulky, rigid phosphabicyclononane (Phoban)-containing phosphine ligands instead of tricyclohexylphosphine ligands. Studies with PHOBCAT at Sasol Technology showed that catalyst lifetime is significantly increased, that it exhibits high selectivities for metathesis reactions, is potentially recyclable and shows excellent stability to air and water.⁷ PHOBCAT is an efficient catalyst for applications where high selectivity is required, *e.g.* self-metathesis, ethenolysis, RCM and ROMP.⁷



2

a) Influence of IL

The usefulness of the IL was evaluated for the metathesis of 1-octene using PHOBCAT. Reactions were carried out at an olefin:Ru ratio of 4967:1, and a Ru concentration of 0.02 mol %. In each reaction, 2 mL of a particular IL was added to 16 mL of 1-octene and 14.2 mg of PHOBCAT catalyst at 40 °C. All ILs used were biphasic with 1-octene. The metathesis reactions in IL were compared to the base case, where only 1-octene was used with no IL present (neat reaction) and where toluene was used as an organic solvent. The results are shown in Figure 2.4 and Table 2.6.

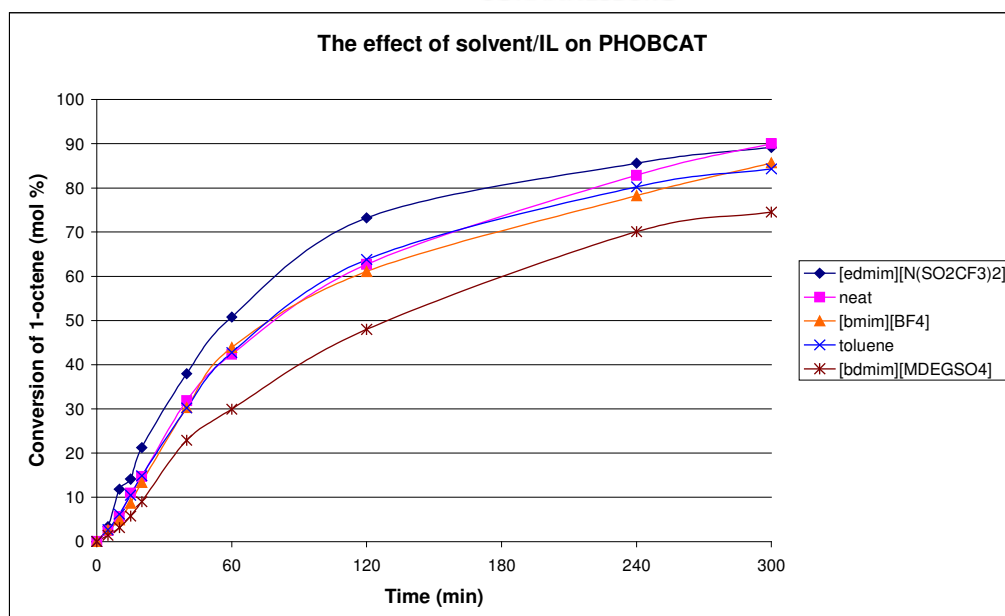


Figure 2.4: The effect of ILs on the conversion of 1-octene

Table 2.6: The effect of ILs on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	90	99.5
Toluene	84	99.4
[edmim][N(SO ₂ CF ₃) ₂]	89	99.5
[bdmim][MDEGSO ₄] ^b	75	99.2
[bmim][BF ₄]	86	99.3

^aas determined by GC analysis

^b[bdmim][MDEGSO₄] = [1-butyl-3-methylimidazolium][2-(2-methoxyethoxy)ethylsulfate]

From the results, it is evident that the use of IL had no beneficial effect. The [edmim][N(SO₂CF₃)₂] IL was only slightly faster than the “neat” reaction but reached similar conversions to the neat reaction after five hour reaction time. The other ILs, [bmim][BF₄] and [bdmim][MDEGSO₄], typically showed minor inhibitory effects. It was noted during the IL experiments, as expected from previous results, that the catalyst leached out significantly from the IL phase into the top 1-octene layer (colour visually seen in the top layer) and this is probably due to the non-polar character of the catalyst. The selectivity remained quite high for both IL and organic solvent reactions.

a) Influence of tin

The use of tin (II) chloride (in the form of the dihydrate, SnCl₂.2H₂O) as an *in situ* catalyst promoter was investigated in 1-octene, toluene and [edmim][N(SO₂CF₃)₂]. The use of tin is known in literature to act as a promoter to the metathesis reactions.¹⁶⁷ It was attempted to investigate the effect that tin has on the metathesis reaction in a neat reaction and in the presence of an organic solvent. The influence of tin (20 equivalents with respect to the catalyst) on PHOBCAT in 1-octene and toluene are shown in Figure 2.5 and 2.6, respectively. The tin (SnCl₂.2H₂O) was added to the 1-octene or 1-octene with 2

mL of toluene added and stirred at 40 °C, followed by addition of the catalyst (14.2 mg PHOBCAT) to the reaction mixture.

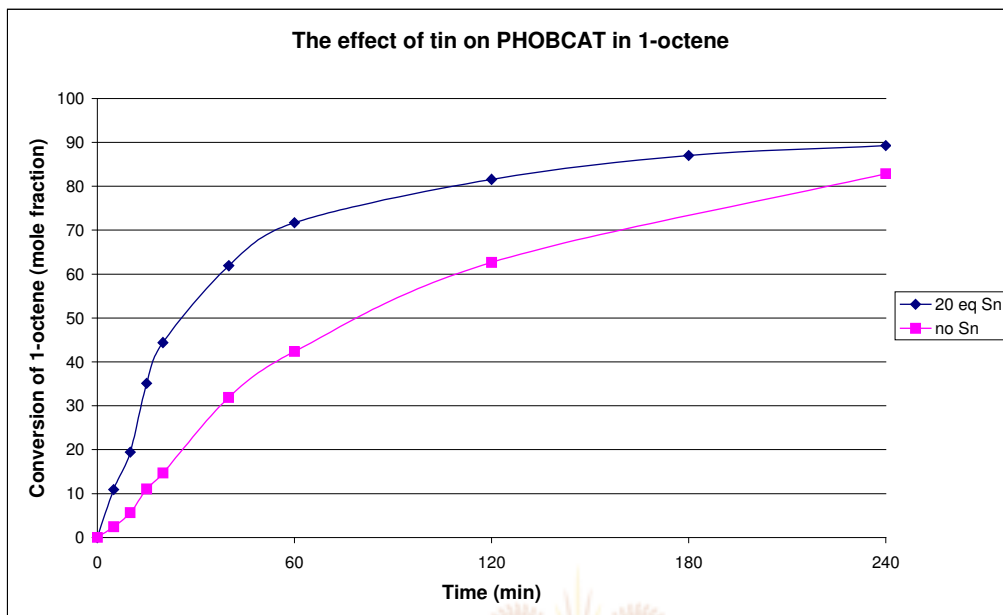


Figure 2.5: The effect of tin on the conversion of 1-octene in neat reaction

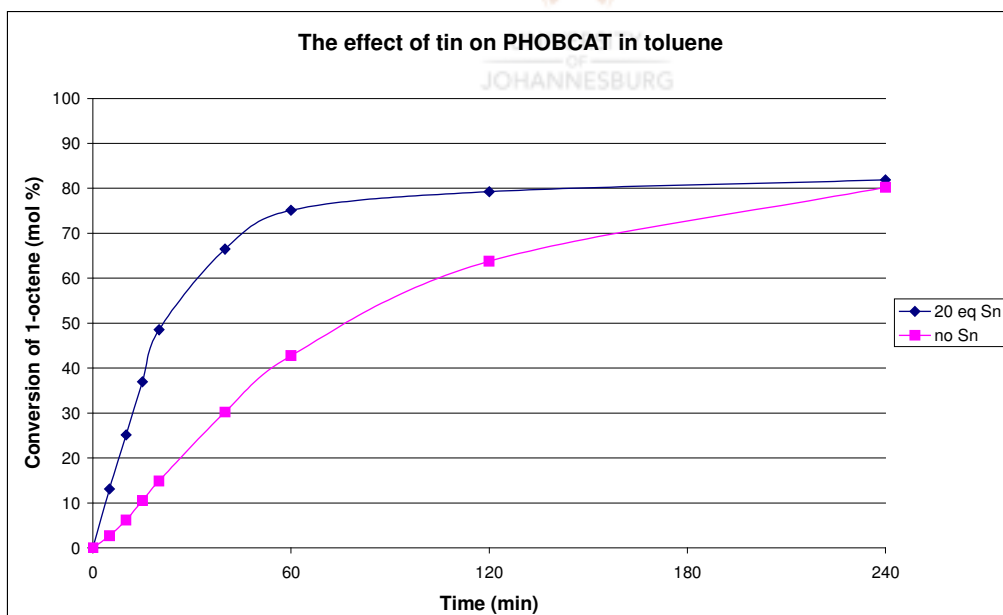


Figure 2.6: The effect of tin on the conversion of 1-octene in toluene

From the Figures, it is evident that the addition of tin significantly promoted the formation of 7-tetradecene in both 1-octene and toluene, the reaction with tin being significantly faster (Table 2.7). The selectivity remained high for all reactions.

Table 2.7: The effect of tin on the formation of 7-tetradecene after 4h reaction time

Solvent/additive	Conversion of 1-octene (%)	Selectivity (%) ^a
1-Octene	83	99.5
1-Octene + 20 eq. Sn	89	99.6
Toluene	80	99.4
Toluene + 20 eq. Sn	82	99.3

^aas determined by GC analysis

The effect of varying amounts of tin (II) chloride dihydrate was investigated for self-metathesis of 1-octene in [edmim][N(SO₂CF₃)₂] with PHOBCAT at a olefin:Ru ratio of 4967:1, and a Ru concentration of 0.02 mol % at 40 °C. A summary of the results is shown in Figure 2.7 and Table 2.8.

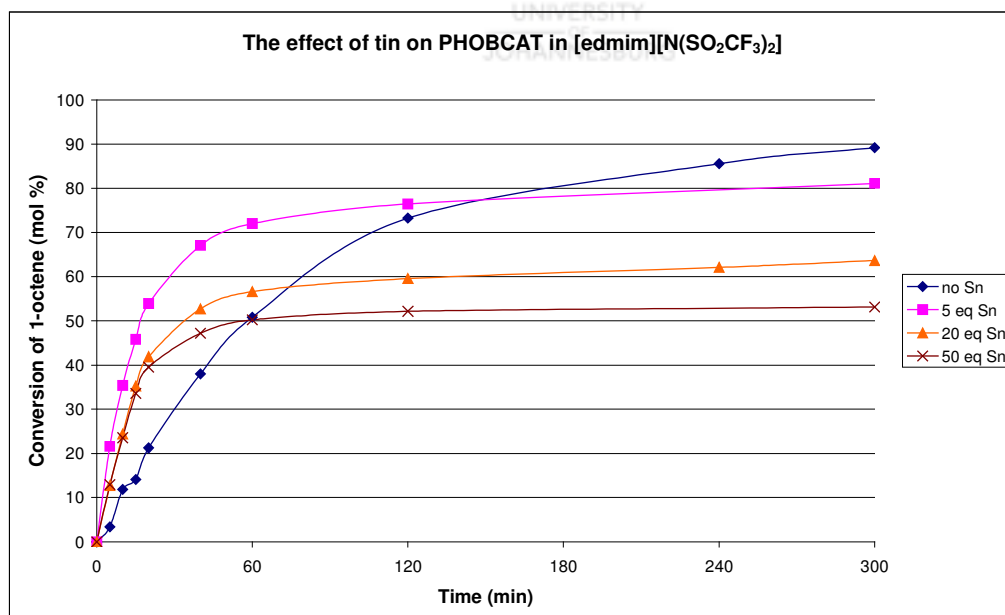


Figure 2.7: The effect of tin on the conversion of 1-octene in [edmim][N(SO₂CF₃)₂]

Table 2.8: The effect of tin on the conversion of 1-octene after 5h reaction time

IL/additive	Conversion of 1-octene (%)	Selectivity (%) ^a
[edmim][N(SO ₂ CF ₃) ₂]	89	99.5
IL + 5 eq. Sn	81	98.8
IL + 20 eq. Sn	64	98.1
IL + 50 eq. Sn	53	97.0

^aas determined by GC analysis

The addition of tin increased the initial rates of metathesis considerably, although increasing amounts of tin led to lower conversions to 7-tetradecene. Selectivity towards 7-tetradecene, also dropped with more equivalents of tin added. Interestingly, the *in-situ* catalyst formed by the addition of tin was more soluble in the IL (visually there was no colour in the top 1-octene layer), thereby resulting in less leaching of PHOBCAT out of the IL phase. Reduced catalyst activity could therefore possibly be due to mass transfer problems, especially towards the end of the reaction. The addition of tin to an IL reaction with PHOBCAT showed no major advantages over the organic reaction since the reaction appeared to be initially faster but reached lower conversions compared to the reaction where the IL was used in the absence of added SnCl₂.

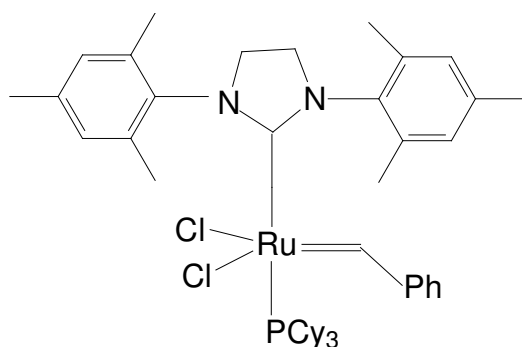
In conclusion, the reaction with PHOBCAT was slower than with other metathesis catalysts used for 1-octene metathesis, although the catalyst does tend to be very selective with little to no SMP formation. PHOBCAT is very similar to the Grubbs catalyst, but it outperformed the Grubbs catalyst in certain aspects such as activity and catalyst stability. The ILs used with PHOBCAT typically showed a minor inhibitory effect and provided no beneficial effect to the metathesis reaction. The addition of tin to PHOBCAT afforded rate enhancements with toluene and 1-octene, but this beneficial effect, although also seen in the [edmim][N(SO₂CF₃)₂] IL, there was, however, a decrease in the 7-tetradecene formation.

2.3 Studies on Second-Generation Grubbs Catalyst

The second-generation Grubbs catalysts are catalysts where one or both of the phosphine ligands have been replaced by sterically bulky and nucleophilic carbene ligands. It has been demonstrated that nucleophilic carbenes mimic phosphine ligands.¹⁶⁸ The carbene ligands are normally based on nitrogen-containing heterocycles such as substituted imidazoles.¹⁶⁹ These second-generation Grubbs catalysts were mainly developed to replace the Grubbs catalyst which have limited thermal stability and readily decompose at elevated temperatures. Dramatic improvements in activity were observed with these catalysts containing a five-membered N-heterocyclic carbene (NHC) ligand, due to the better σ -donor ability of this ligand compared to phosphines.¹⁷⁰ The discovery of these catalysts is most significant, since they compete well with regards to the activity of early transition metal catalysts (e.g. Schrock's Mo catalyst) while still retaining the functional group tolerance of Grubbs catalyst. It has been noted, however, that these second-generation catalysts initiate more slowly than the Grubbs catalyst, and this is probably due to slower phosphine dissociation.¹⁷¹ Self-metathesis of 1-octene using second-generation Grubbs catalyst has been reported in literature.^{162a} In the present study, three different second generation Grubbs catalyst were investigated for the self-metathesis of 1-octene.

2.3.1 Second-generation (H_2IMes ligand) Grubbs catalyst

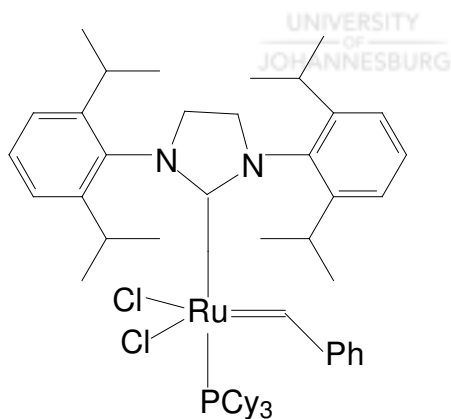
The second generation Grubbs catalyst **3** contains a carbene ligand consisting of a saturated imidazolium ring substituted with two mesityl groups on the nitrogens.



This catalyst has been widely reported in the literature and is commercially available.¹⁷² Catalyst **3** has been used in several acyclic cross metathesis reactions and produced the first example of the preparation of a trisubstituted olefin using cross-metathesis, but little has been reported on its use for the self-metathesis of linear olefins.¹⁷³ This catalyst affords much faster reaction rates and has a greatly improved catalyst lifetime compared to Grubbs catalyst **1**.¹⁶⁹

2.3.2 Second-generation ($H_2IPh^iPr_2$ ligand) Grubbs catalyst

In an attempt to further increase the reactivity and longevity of the second-generation Grubbs catalyst, Mol's group in Amsterdam^{162a}, increased the steric bulk around the NHC ligand. It was noted previously that steric effects around the ruthenium metal play a major role in catalyst performance.¹⁷⁴ They therefore prepared the 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazoline ($H_2IPh^iPr_2$) ligand and subsequently catalyst **4**. They reasoned that an increase in steric bulk of the $H_2IPh^iPr_2$ ligand as well as its superior electron-donating properties relative to the H_2IMes ligand might arise to give a highly active catalyst system. Fürstner and co-workers also prepared and characterised the same catalyst.¹⁷⁵



4

2.3.3 Metathesis of 1-octene

During the present study on the self-metathesis of 1-octene, the following parameters were investigated and will be dealt with in turn.

- a) advantage of organic solvent or IL over the neat reaction
- b) mixed solvent systems

a) Advantage of organic solvent or IL over the neat reaction

The need for IL was evaluated for the metathesis of 1-octene using catalyst **3**. Reactions were carried out at a olefin:Ru ratio of 8446:1, and a Ru concentration of 0.01 mol %. In each reaction, 6 mL of a particular IL was added to 16 mL of 1-octene and 10 mg of catalyst **3** at 60 °C. All ILs used were biphasic with 1-octene. The metathesis reactions in IL was compared to the base case, where only 1-octene was used with no IL present (neat reaction) and where toluene was used as an organic solvent. The results are shown in Figure 2.8 and Table 2.9.

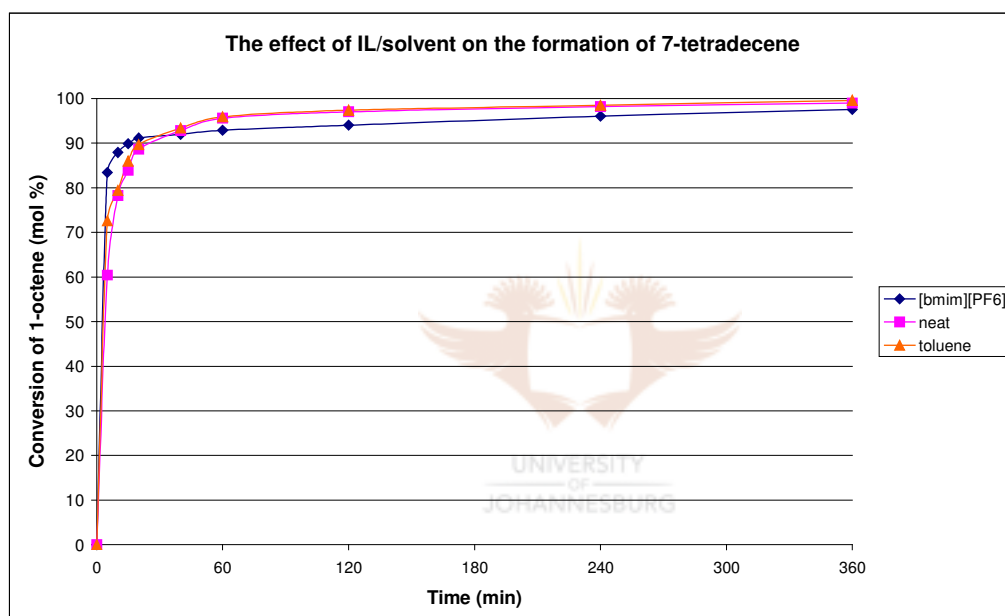


Figure 2.8: The effect of IL or organic solvent on the conversion of 1-octene using catalyst 3

Table 2.9: The effect of ILs or organic solvents on the conversion of 1-octene after 6h reaction time using catalyst 3

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	99	69.9
Toluene	99.6	53.7
[bmim][PF ₆]	98	94.6

^aas determined by GC analysis.

It is evident from the results that this catalyst was very active in both IL and organic solvent. However, selectivity for product varied. The reaction in the [bmim][PF₆] IL showed a relatively better selectivity when compared to 1-octene and toluene as solvent.

The need for IL was evaluated for the metathesis of 1-octene using catalyst **4**. Reactions were carried out at an olefin:Ru ratio of 8446:1. In each reaction, 6 mL of a particular IL was added to 16 mL of 1-octene and 10 mg of catalyst **4** at 60 °C. All ILs used were biphasic with 1-octene. The metathesis reactions in IL was compared to the base case, where only 1-octene was used with no IL present (neat reaction) and where toluene was used as an organic solvent. The results are shown in Figure 2.9 and Table 2.10.

Table 2.10: The effect of ILs or organic solvents on the formation of 7-tetradecene after 6h reaction time using catalyst 4

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	99.7	67.0
Toluene	98.5	73.1
[edmim][N(SO ₂ CF ₃) ₂]	99.1	94.3
[bmim][PF ₆]	99.3	89.2

^aas determined by GC analysis

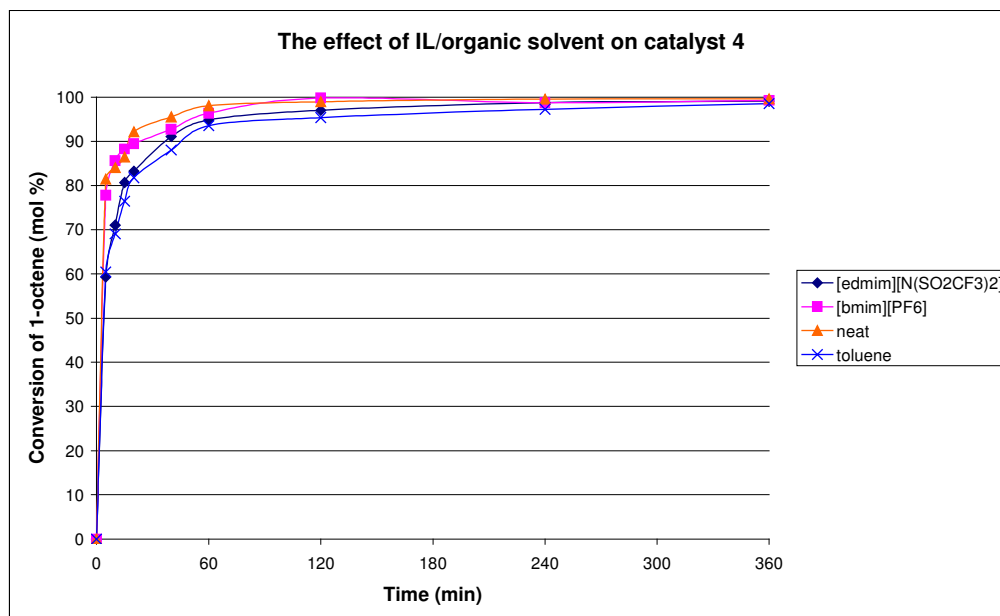


Figure 2.9: The effect of IL or organic solvent on the conversion of 1-octene using catalyst 4

It is evident from the results that this catalyst was very active in both IL and organic solvent. However, selectivity for product varied. The reactions in the IL showed a relatively better selectivity when compared to 1-octene and toluene as solvent. The [edmim][N(SO₂CF₃)₂] IL, in particular, showed a good reaction with high catalyst activity and reasonable selectivity for product, which shows that this IL stabilises the catalyst in some way.

b) Mixed solvent systems

The addition of co-solvents was investigated to allow for better catalyst solubility in the IL. In the reaction with IL and co-solvent, 5 mL of the [bmim][PF₆] IL was added to 16 mL of 1-octene, followed by the addition of 10 mg of catalyst **3** dissolved in 1 mL of dichloromethane (co-solvent) at 60 °C. The results are shown in Figure 2.10 and Table 2.11.

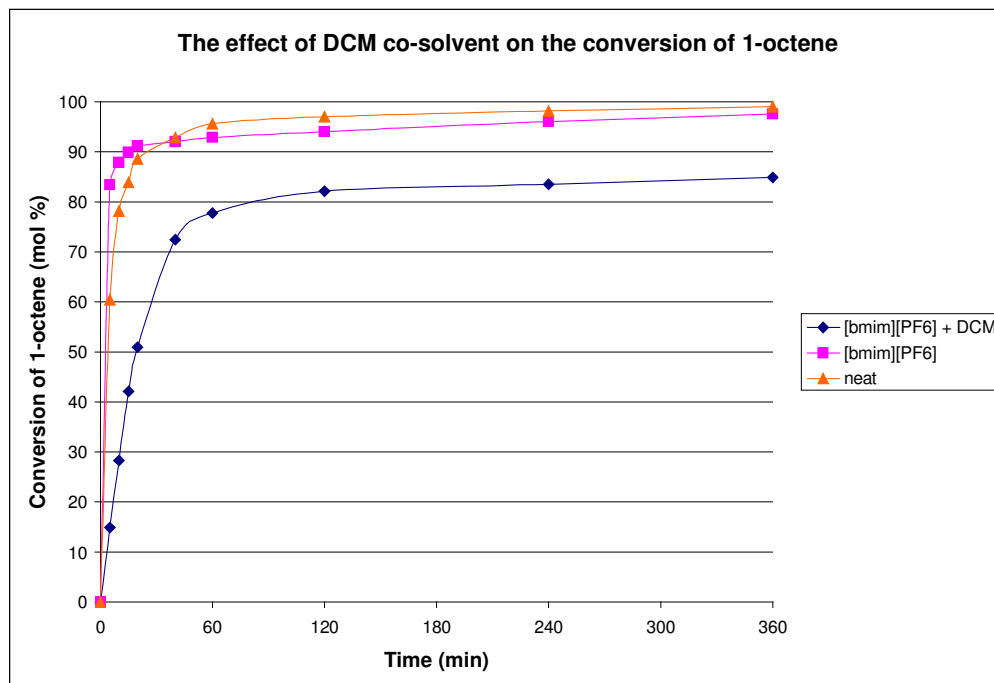


Figure 2.10: The effect of dichloromethane as co-solvent with [bmim][PF₆] on the conversion of 1-octene

Table 2.11: The effect of dichloromethane as co-solvent with [bmim][PF₆] on the conversion of 1-octene after 6h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	99	69.9
[bmim][PF ₆]	98	94.6
[bmim][PF ₆] + DCM	85	92.7

^aas determined by GC analysis

Chloroform was also investigated as a co-solvent with the [bmim][PF₆] IL. This reaction was compared with the neat reaction (1-octene as bulk substrate) and where chloroform was used as organic solvent. In the reaction with IL and co-solvent, 5 mL of the [bmim][PF₆] IL was added to 16 mL of 1-octene, followed by the addition of 10 mg of catalyst **3** dissolved in 1 mL of chloroform at 60 °C. In the case where the IL or chloroform was used as solvent, 6 ml of solvent was added to 16 ml of 1-octene. The results are shown in Figure 2.11 and Table 2.12.

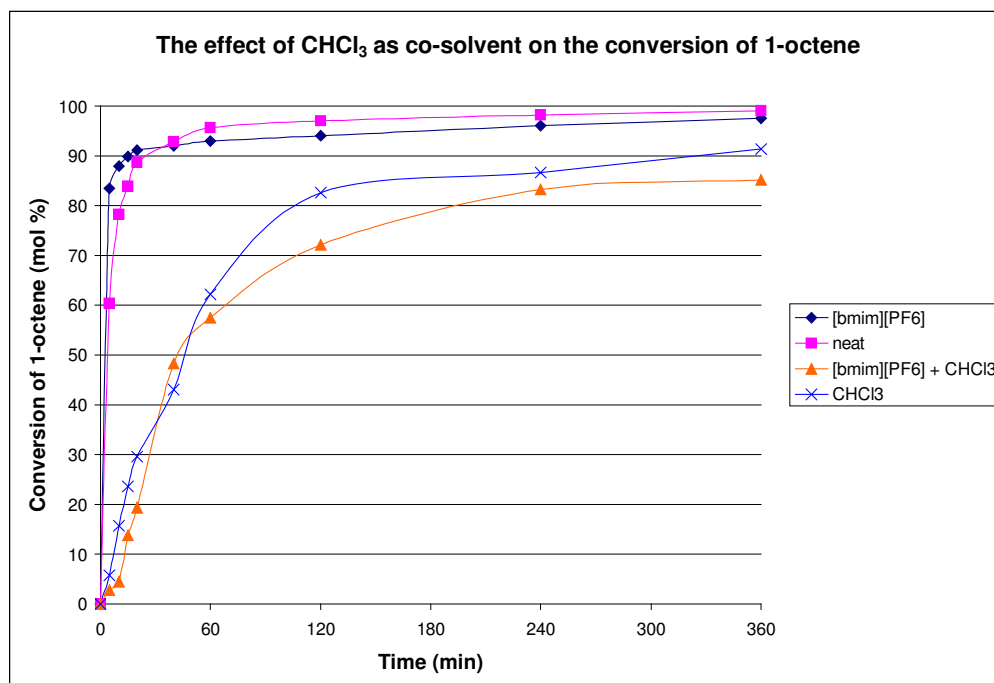


Figure 2.11: The effect of chloroform as co-solvent with [bmim][PF₆] on the conversion of 1-octene using catalyst 4

Table 2.12: The effect of dichloromethane as co-solvent with [bmim][PF₆] on the conversion of 1-octene after 6h reaction time using catalyst 4

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	99	69.9
[bmim][PF ₆]	98	94.6
[bmim][PF ₆] + CHCl ₃	85	95.5
CHCl ₃	91	52.9

^aas determined by GC analysis

The results show a detrimental effect due to the presence of the chloroform co-solvent in the mixed solvent reaction, the increased selectivity over the 1-octene only reaction is probably ascribable to the presence of the IL.

The addition of co-solvents was investigated to allow for better catalyst solubility in the IL. In the reaction with IL and co-solvent, 5 mL of the [bmim][PF₆] IL was added to 16 mL of 1-octene, followed by the addition of 10 mg of catalyst 4

dissolved in 1 mL of toluene (co-solvent) at 60 °C. The results are shown in Figure 2.12 and Table 2.13.

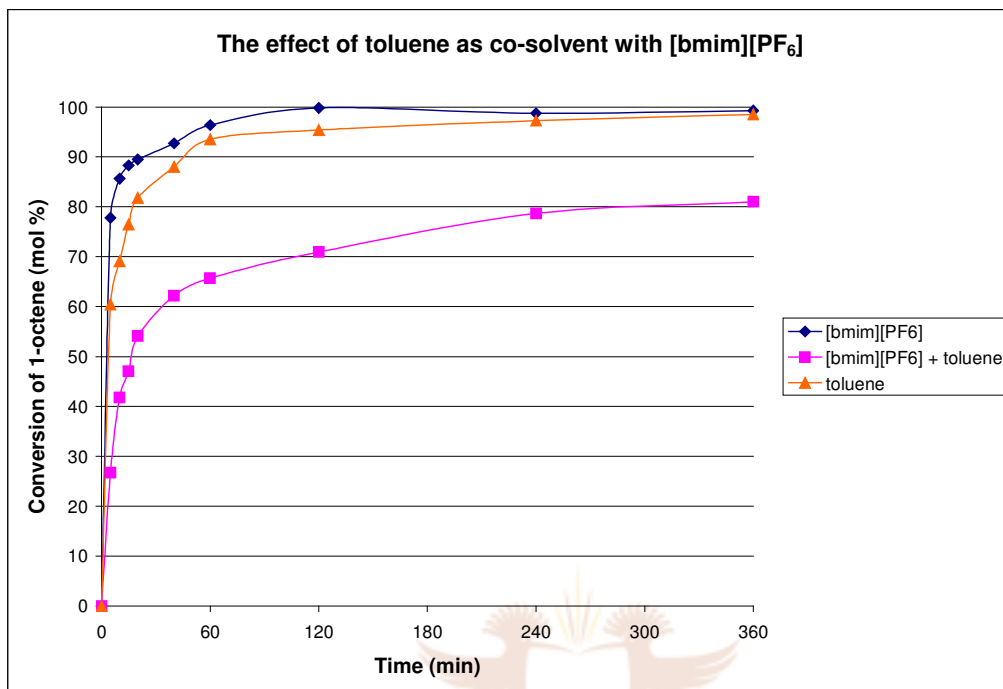


Figure 2.12: The effect of toluene as co-solvent with [bmim][PF₆] on the conversion of 1-octene

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Table 2.13: The effect of toluene as co-solvent with [bmim][PF₆] on the conversion of 1-octene after 6h reaction time

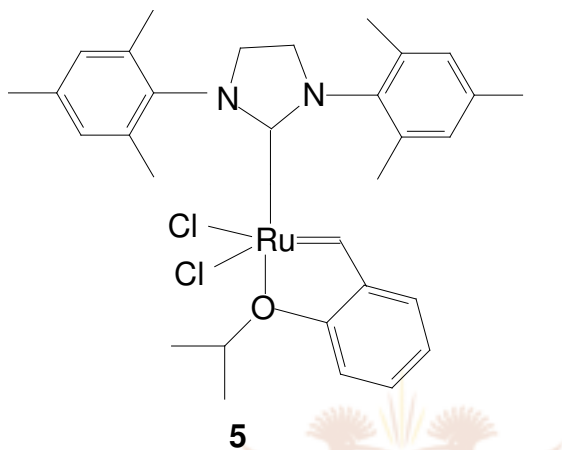
IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
Toluene	99	73.1
[bmim][PF ₆]	99	89.2
[bmim][PF ₆] + toluene	81	88.1

^aas determined by GC analysis

The results show a detrimental effect due to the presence of the toluene co-solvent in the mixed solvent reaction, the increased selectivity over the toluene only reaction is probably ascribable to the presence of the IL.

2.3.3 Second-generation Hoveyda-Grubbs catalyst

The Hoveyda-Grubbs catalyst **5** contains a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand and a styrenyl ether ligand. The styrenyl ether ligand was chosen since it could possibly allow for the easy recovery of the Ru complex while the heterocyclic ligand significantly enhances the catalytic activity.¹⁷⁶ The catalyst has been shown to be efficient for RCM, ROM and cross-metathesis.¹⁷³



a) Influence of organic solvent

The influence of organic solvent on the activity and selectivity of Hoveyda-Grubbs catalyst was investigated. Reactions were carried out at an olefin:Ru ratio of 4987:1, and a Ru concentration of 0.02 mol %. In each reaction, 2 mL of a particular solvent was added to 16 mL of 1-octene and 12.5 mg of the Hoveyda-Grubbs catalyst at 40 °C, forming a homogeneous mixture. The results are given in Figure 2.13 and Table 2.14.

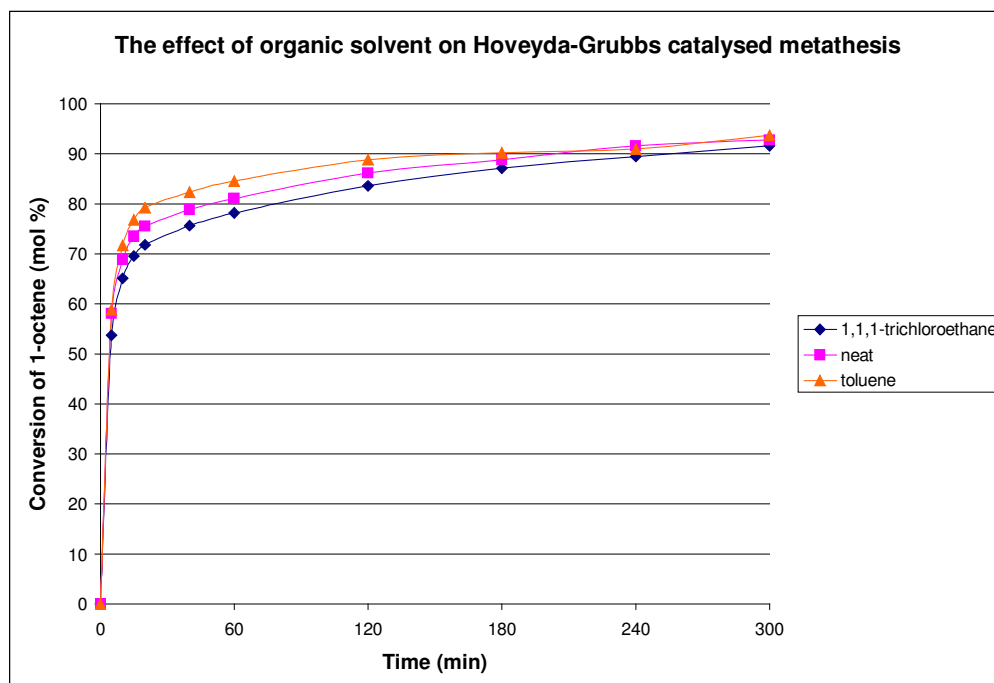


Figure 2.13: The influence of organic solvent on the conversion of 1-octene

Table 2.14: The influence of organic solvent on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
Toluene	94	87.2
1,1,1-trichloroethane	92	96.0

^aas determined by GC analysis

The results show a fairly good baseline reaction in neat 1-octene, an inhibitory effect from added toluene (confirming the influence of this solvent previously observed) and an enhanced reaction in the presence of 1,1,1-trichloroethane.

b) Influence of IL

The influence of IL on the Hoveyda-Grubbs catalyst was investigated for the metathesis of 1-octene. The Hoveyda-Grubbs catalyst was found to be quite soluble in all ILs tested and no visible leaching of the catalyst could be seen into

the organic layer. This is contrary to the other catalyst systems tested, which all showed significant leaching out of the IL.

i) Influence of the anion of the IL

A common cation, [1-butyl-3-methylimidazolium], in conjunction with various anions was tested for the self-metathesis of 1-octene. The results are shown in Figure 2.14 and Table 2.15.

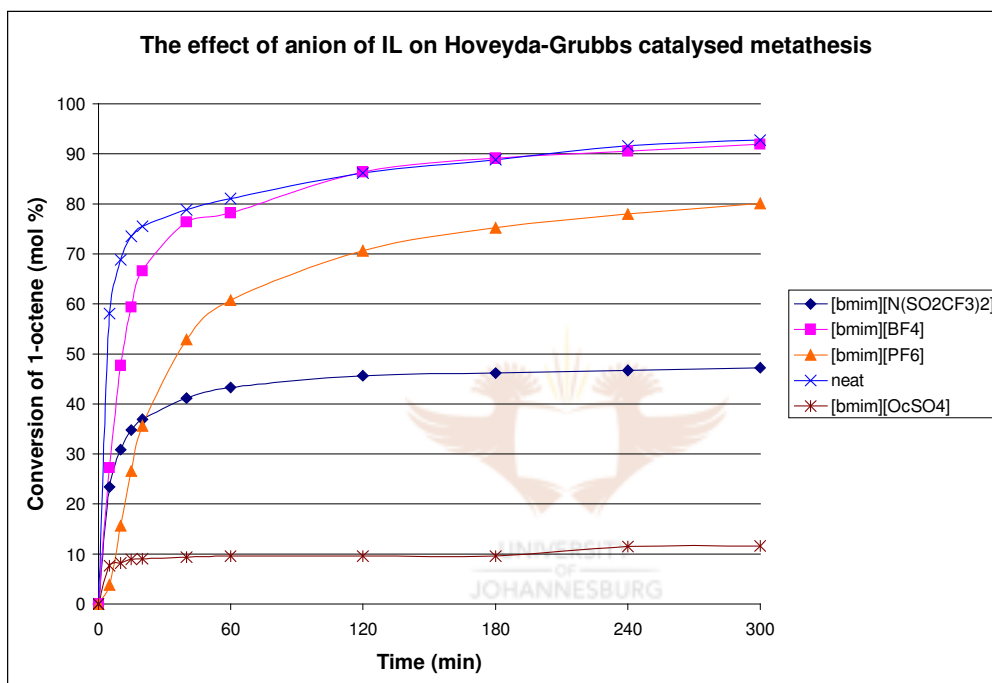


Figure 2.14: The influence of [bmim]X type ILs on the conversion of 1-octene

Table 2.15: The effect of anion of [bmim][X] type IL on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[bmim][OcSO ₄]	12	99.6
[bmim][N(SO ₂ CF ₃) ₂]	47	97.6
[bmim][PF ₆]	80	98.6
[bmim][BF ₄]	92	94.9

^aas determined by GC analysis

The Hoveyda-Grubbs catalyst worked well in polar solvents and this trend was also seen with ILs: [bmim][BF₄] is the most polar of the ILs used in the study and afforded the highest activity. The polarity trend of the anions is as follows: [BF₄]⁻ > [PF₆]⁻ > [N(SO₂CF₃)₂]⁻ >> [OcSO₄]⁻ which results in the same trend with activity (Figure 2.14 and Table 2.15). The activity could be largely influenced by the different coordination ability of the anion of the particular IL to the catalyst as well as the varying polarity of the ILs employed. All the ILs tested resulted in a higher selectivity compared with the neat reaction (with no solvent). From the reaction profile, it is quite evident that the presence of the IL had a stabilisation effect, and resulted in a trend of increasing rates and conversions that mirrored the polarity trend of the anions.

ii) Influence of the cation of the IL

The influence of varying alkyl chain length on the cation of bistriflimide- and tetrafluoroborate-based ILs was investigated to see the effect it would have on the conversion of 1-octene (Figure 2.15 - 2.17 and Table 2.16 - 2.18).

Table 2.16: The effect of cation of IL on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[emim][N(SO ₂ CF ₃) ₂]	90	97.6
[bmim][N(SO ₂ CF ₃) ₂]	47	97.6
[hmim][N(SO ₂ CF ₃) ₂]	13	98.9

^aas determined by GC analysis

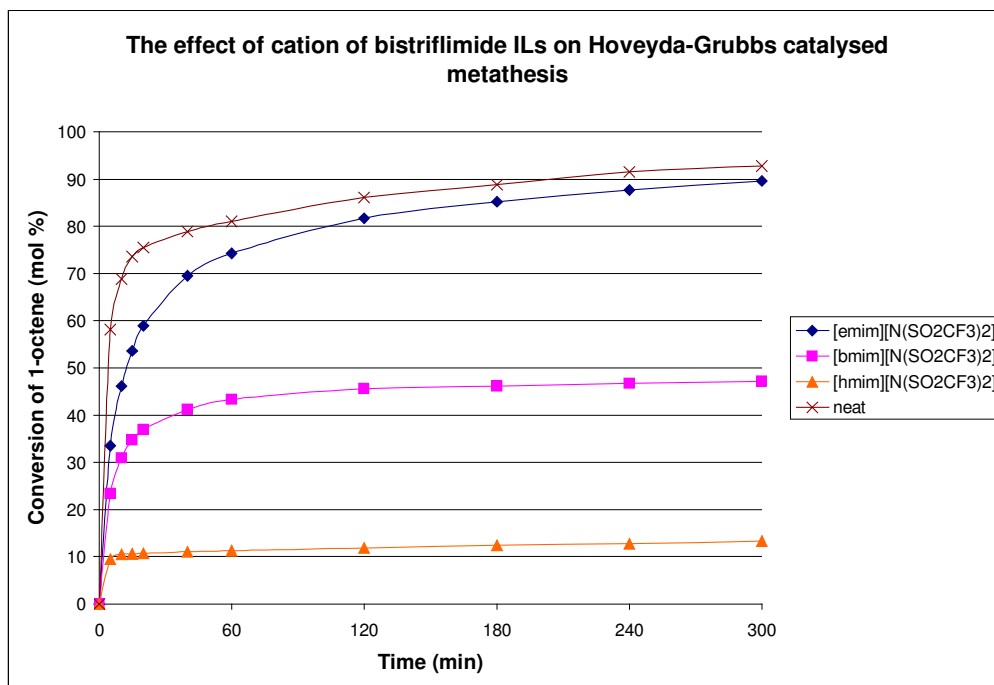


Figure 2.15: The effect of [Rmim][N(SO₂CF₃)₂] type ILs on the conversion of 1-octene

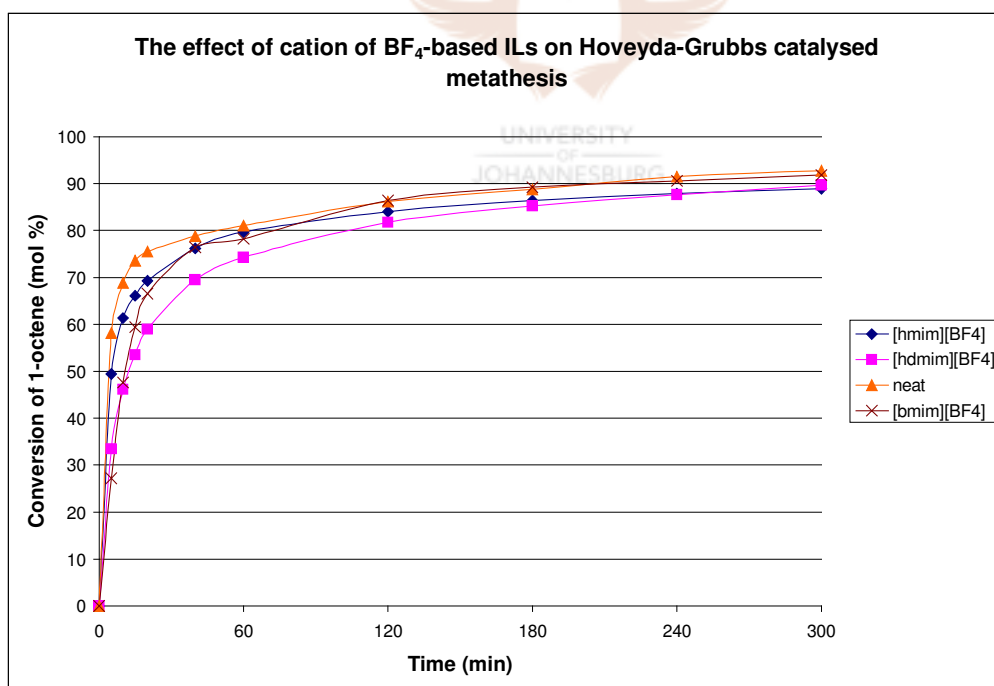


Figure 2.16: The effect of [Rmim][BF₄] type ILs on the conversion of 1-octene

Table 2.17: The effect of cation of tetrafluoroborate ILs on conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[bmim][BF ₄]	92	94.9
[hmim][BF ₄]	89	97.0
[hdmim][BF ₄]	90	97.6

^aas determined by GC analysis

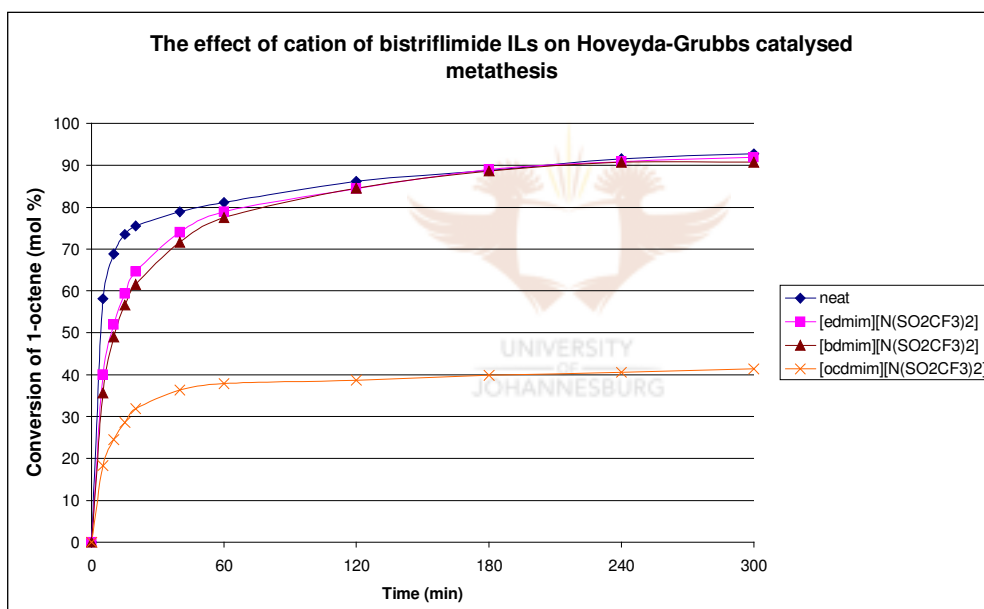


Figure 2.17: The effect of [Rdmim][N(SO₂CF₃)₂] type ILs on the conversion of 1-octene

Table 2.18: The effect of [Rdmim][N(SO₂CF₃)₂] type ILs on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[edmim][N(SO ₂ CF ₃) ₂]	92	96.8
[bdmim][N(SO ₂ CF ₃) ₂]	91	98.1
[odmim][N(SO ₂ CF ₃) ₂]	41	98.9

^aas determined by GC analysis

The bistriflimide-based ILs showed a strong dependence on the length of the alkyl group on the outcome of the reaction. Here the ILs with shorter alkyl groups are more polar, and, at least with bistriflimide as the anion, polarity had a dramatic influence on the reaction. In the case of the tetrafluoroborate-based ILs, the polarity influence of the alkyl side chains was less prominent, indicating a less sensitive, more robust reaction.

Interestingly, the [Rdmim] type of IL also played less of a role on the outcome of the reaction. Here, only the longer chain octyl derivative inhibited the reaction.

iii) Other cations in ILs

Other IL cations were investigated. For example, pyridinium, phosphonium and ammonium-type ILs were used in this work.

a) Pyridinium cations

The influence of pyridinium-based ILs on activity and selectivity of Hoveyda-Grubbs catalyst was investigated. In each reaction, 2 mL of IL was added to 16 mL of 1-octene and 12.5 mg of the Hoveyda-Grubbs catalyst at 40 °C. The results are given in Figure 2.18 and Table 2.19.

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
$[(\text{CH}_3)(\text{C}_4\text{Py})][\text{N}(\text{SO}_2\text{CF}_3)_2]^b$	75	97.0
$[\text{C}_8\text{Py}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	46	85.2

^aas determined by GC analysis

^b $[(\text{CH}_3)(\text{C}_4\text{Py})][\text{N}(\text{SO}_2\text{CF}_3)_2] = [4\text{-methyl-N-butylpyridinium}][\text{bistriflimide}]$

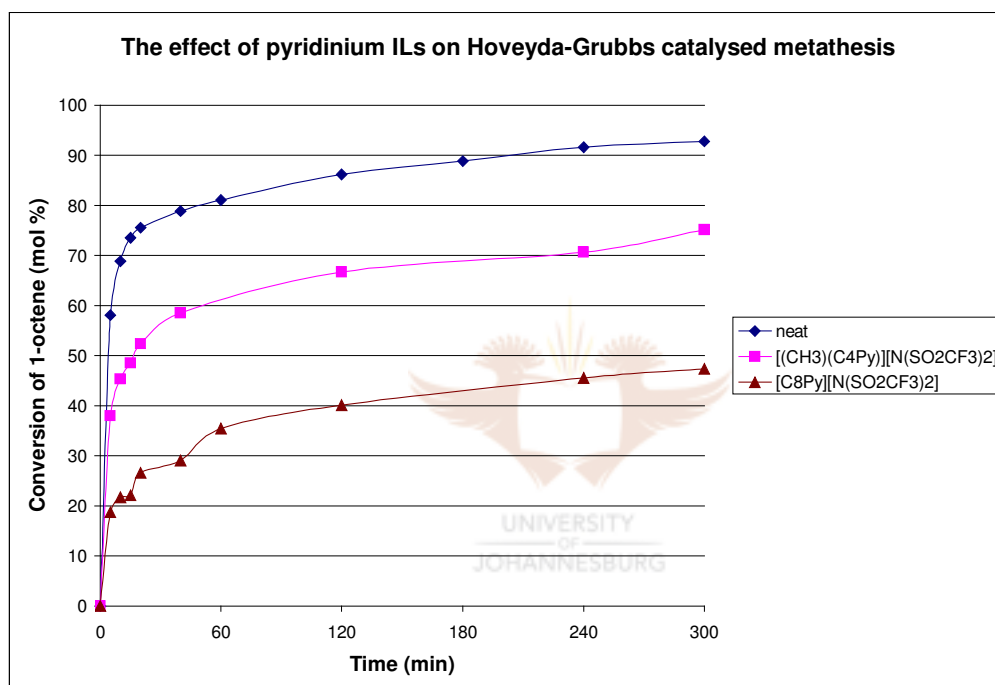


Figure 2.18: The effect of pyridinium-type ILs on the conversion of 1-octene

The results of the reactions in pyridinium-based ILs show a clear inhibitory effect of these solvents, when compared to the benchmark reaction. The origin of this inhibitory effect is unknown, but may arise from the fact that these cations are relatively non polar.

b) Phosphonium cations

The influence of phosphonium-based ILs on activity and selectivity of Hoveyda-Grubbs catalyst was investigated. In each reaction, 2 mL of IL was added to 16

mL of 1-octene and 12.5 mg of the Hoveyda-Grubbs catalyst at 40 °C. The results are given in Figure 2.19 and Table 2.20.

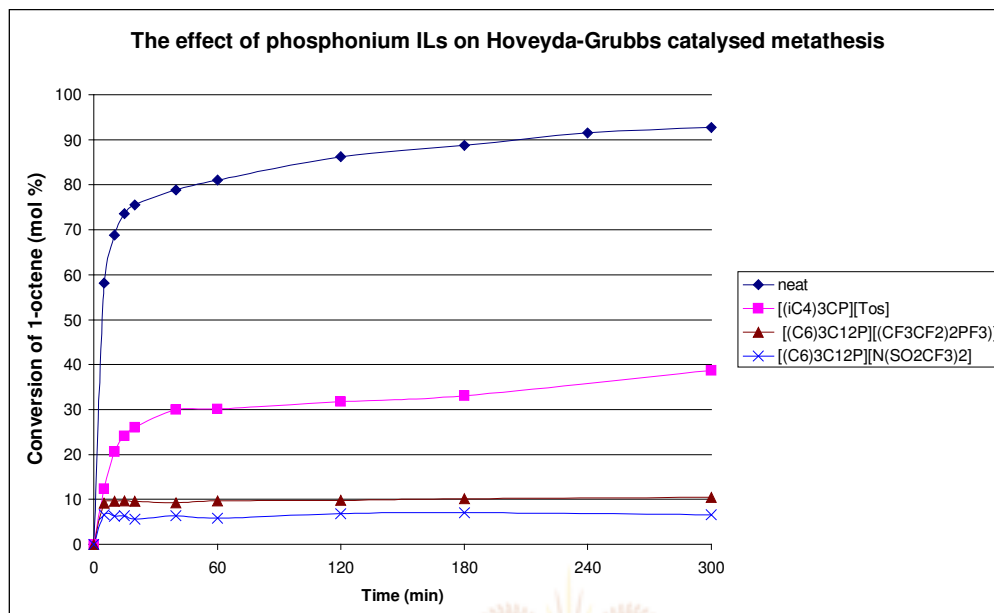


Figure 2.19: The effect of phosphonium cations on the conversion of 1-octene

Table 2.20: The effect of phosphonium type ILs on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[(C ₄) ₃ CP][Tosylate]	39	97.9
[(C ₆) ₃ C ₁₄ P][(CF ₃ CF ₂) ₃ PF ₃]	10	100
[(C ₆) ₃ C ₁₄ P][N(SO ₂ CF ₃) ₂]	7	97.4

^aas determined by GC analysis

When using phosphonium-containing ILs, as with the pyridinium cases, a strong inhibitory effect was observed, which may also be linked with the polarity of the solvent.

c) Ammonium cations

The influence of ammonium-based ILs on activity and selectivity of Hoveyda-Grubbs catalyst was investigated. In each reaction, 2 mL of IL was added to 16 mL of 1-octene and 12.5 mg of the Hoveyda-Grubbs catalyst at 40 °C. The results are given in Figure 2.20 and Table 2.21.

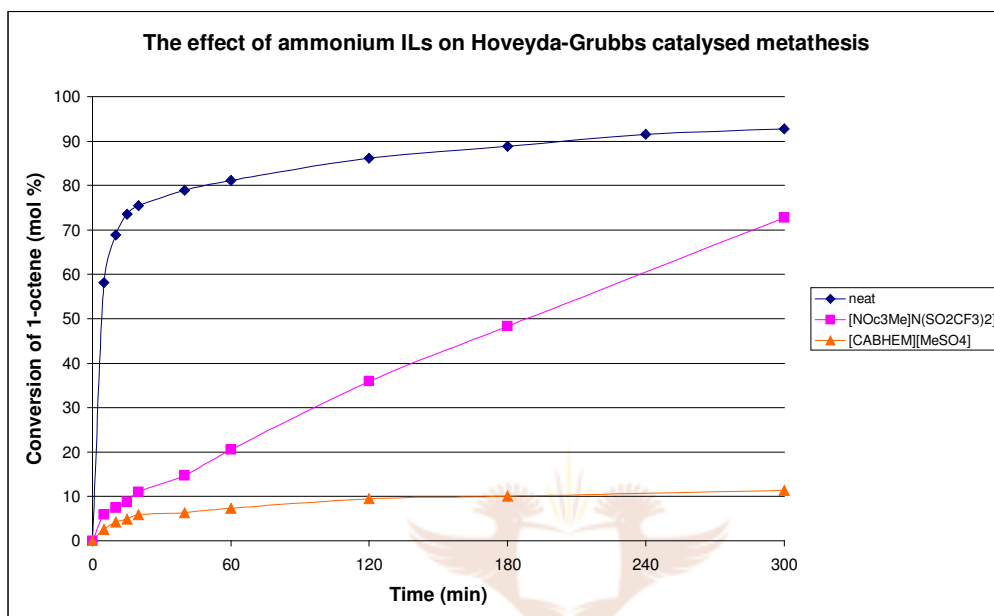


Figure 2.19: The effect of ammonium cations on the conversion of 1-octene

Table 2.21: The effect of phosphonium type ILs on the conversion of 1-octene after 5h reaction time

IL/solvent	Conversion of 1-octene (%)	Selectivity (%) ^a
No solvent	93	91.1
[NOc ₃ Me][N(SO ₂ CF ₃) ₂]	73	35.8
[CABHEM][MeSO ₄] ^b	10	78.4

^aas determined by GC analysis

^b[CABHEM][MeSO₄] = [Cocosalkylpentaethoxymethylammonium][methylsulfate]

It is evident from the results that imidazolium-type ILs performed much better as solvents when compared to phosphonium, pyridinium and ammonium-type ILs.

The results also clearly showed that conversion and selectivity also depended significantly on the anion.

iv) Studies on [edmim][N(SO₂CF₃)₂]

It was decided to investigate the influence of several other parameters on the outcome of the metathesis reaction, and [edmim][N(SO₂CF₃)₂] was selected for this purpose. The baseline reaction in this IL afforded good results (Table 2.18) and was perfectly disposed to test if reaction tweaking could lead to even better reaction.

a) Influence of reaction parameters

The effect of reaction parameters was investigated to see whether these conditions were necessary in order to carry out a metathesis reaction in ionic liquids.

i) Influence of feed pre-treatment

The effect of feed pre-treatment on Hoveyda-Grubbs catalyst was investigated in [edmim][N(SO₂CF₃)₂] as the ionic solvent. Olefins readily form peroxides in the presence of trace amounts of oxygen, olefins are therefore normally passed through an alumina column prior to its use. A batch of commercially available 1-octene (Aldrich, 98 %) was treated by passing through a column of neutral and storing over alumina followed by degassing with argon. The self-metathesis reaction was performed with this feed to form 7-tetradecene and compared to the feed used from the bottle where there was no feed pre-treatment. Reactions were carried out with 0.02 mol % Ru catalyst at 40 °C. The results are shown in Figure 2.21.

There was very little difference between the reactions using the treated and untreated olefin feed. This implies that oxygenate impurities, if indeed these are present in trace amounts, are tolerated in the IL. The rate of the reaction in the

untreated case was slightly lower than in the case of the treated olefin, but, ultimately, there was very little difference between the two reactions.

ii) Influence of nitrogen purge

The effect of nitrogen purge on the reaction outcome for the self-metathesis of 1-octene was investigated using the Hoveyda-Grubbs catalyst in [edmim][N(SO₂CF₃)₂]. It was believed that the nitrogen purge was necessary to drive the metathesis reaction to afford higher yields of the desired 7-tetradecene by driving off the ethylene formed as a by-product. This is important because the reaction is an equilibrium reaction and ethylene is a product of the metathesis reaction. Therefore, removing the ethylene would, according to Le Chatelier's principle, drive the reaction to the right hand side.

These results show that, with the IL/catalyst system, 1-octene metathesis is possible in the absence of a nitrogen purge although the equilibrium position is reached quicker. That the equilibrium product yield is a respectable 73% is ascribable in part to the volatility of the ethylene by-product removing some of this material from the liquid phase into the gas phase.

No effect in the selectivity towards 7-tetradecene was observed with no nitrogen purge.

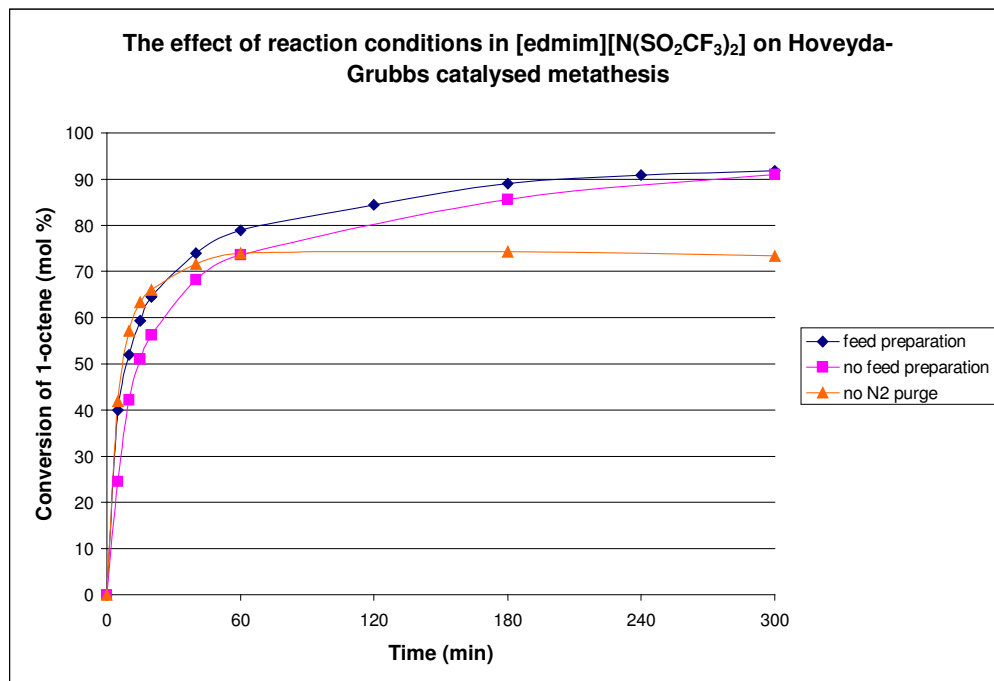


Figure 2.21: The effect of reaction conditions on Hoveyda-Grubbs catalyst

b) Influence of IL impurities

During the synthesis of ionic liquids, certain impurities are always present in minute quantities after synthesis. The effect of water, bromide and 1-methylimidazole was investigated to see the effect each of these has on the Hoveyda-Grubbs catalyst.

i) Addition of water

Self-metathesis of 1-octene was carried out under standard conditions (40 °C; 0.02 mol % Ru catalyst; 2 mL [edmim][N(SO₂CF₃)₂] with added water (100 eq). The results are shown in Figure 2.22.

It is evident from Table 2.22 that the reaction with water as additive slows the reaction initially but the same conversion is reached after 5 hours. Water therefore does not have a detrimental effect on the catalyst activity, but selectivity was slightly lower (Figure 2.22).

ii) Addition of [edmim][Br]

Self-metathesis of 1-octene was carried out under standard conditions (40 °C; 0.02 mol % Ru catalyst; 2 mL [edmim][N(SO₂CF₃)₂]) with added [edmim][Br] (100 eq.) as the source of bromide to investigate the effect of excess bromide on the catalyst system. The results are shown in Figure 2.22.

From the reaction profile it is evident that the addition of [edmim][Br] retards the rate of the metathesis reaction to a slight extent, and also results in earlier termination of the reaction.

The addition of [edmim][Br] had little to no effect on the selectivity of the reaction and yields a selectivity of 97.9%.

iii) Addition of 1-methylimidazole

The effect of 1-methylimidazole (100 eq.) on the self-metathesis of 1-octene in the presence of the Hoveyda-Grubbs catalyst was investigated. In the presence of 1-methylimidazole, the catalyst/IL phase became a bright yellow-green colour and remained that colour throughout the metathesis run. Normally the catalyst/ionic liquid phase becomes reddish-brown in colour indicating the presence of the active catalyst. No ethylene bubbles were observed. 1-Methylimidazole is detrimental to the catalyst since it is a co-ordinating base and probably tied up the catalyst in a metathesis inactive state, resulting in no catalytic activity at all (Table 2.22).

Table 2.22: The effect of IL impurities (100 eq.) on conversion and selectivity towards the formation of 7-tetradecene after 5h reaction time

IL impurity	Conversion of 1-octene (%)	Selectivity (%) ^a
IL alone	92	96.8
Water	93	89.7
Bromide ion	73	97.9
1-methylimidazole	0	0

^aas determined by GC analysis

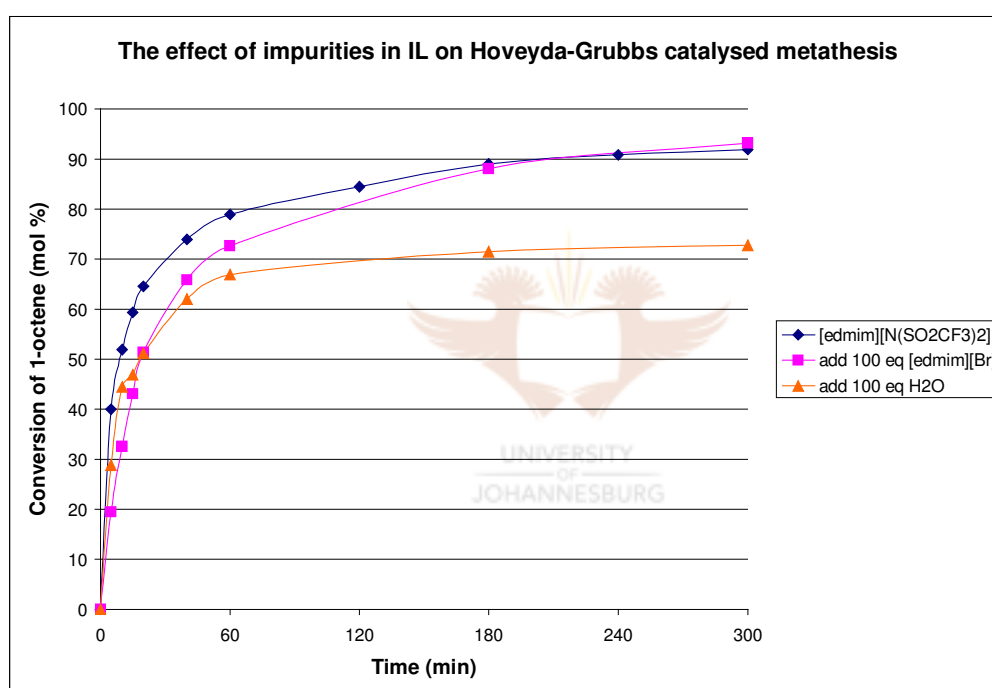


Figure 2.22: The effect of IL impurities on the Hoveyda-Grubbs catalyst

c) Influence of temperature

The influence of temperature on the outcome of the metathesis reaction in the presence of various amounts of Ru catalyst was investigated.

i) 12.5 mg Ru catalyst

The influence of temperature on the self-metathesis of 1-octene to form 7-tetradecene with the Hoveyda-Grubbs catalyst in the [edmim][N(SO₂CF₃)₂] IL

was investigated. The ruthenium concentration was kept constant at 0.02 mol % and the temperature was varied. A summary of the results is shown in Figure 2.23.

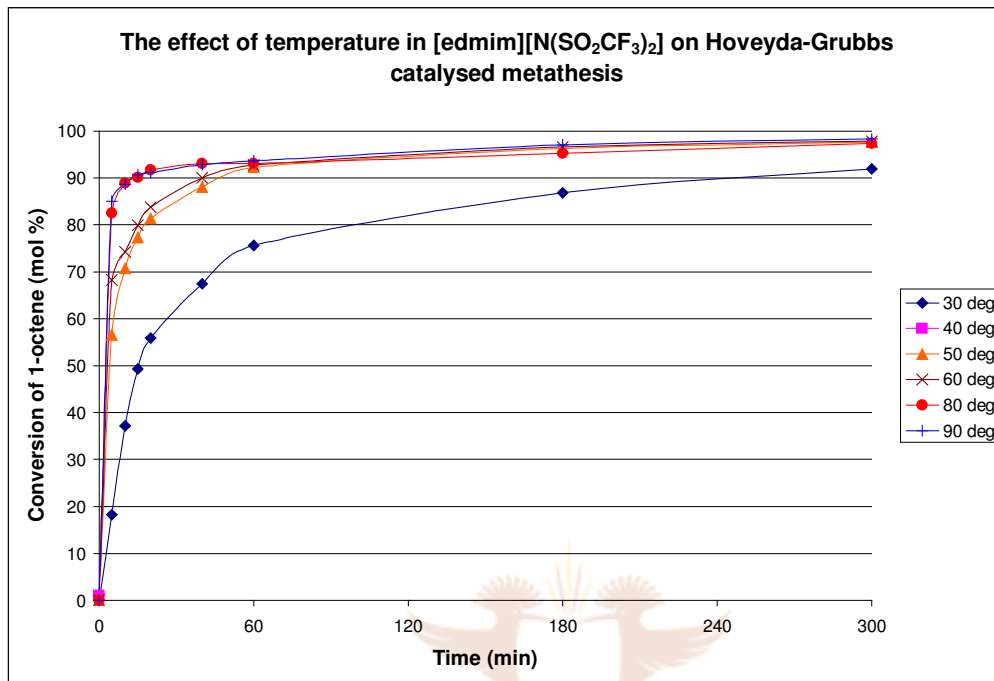


Figure 2.23: Effect of temperature on the conversion of 1-octene in [edmim][N(SO₂CF₃)₂]

It is evident from the graph that an increase in temperature resulted in an increase in initial reaction rate as would be expected. However, at temperatures 80 and 90 °C, the reaction rates were similar. The reaction rates at 50 and 60 °C were much slower than the higher temperature reactions but catalyst activity was essentially the same for these two runs. The end of run conversion (97%) was the same after five hours, which appears to be the equilibrium conversions for these systems. The reactions at the lower temperatures (30 and 40 °C) were much slower and reached a lower end conversion of 90%.

When considering the reaction selectivities to 7-tetradecene (Table 2.23), it is evident that an increase in temperature resulted in a decrease in selectivity

indicating an increase in secondary metathesis products (SMPs) (Figure 2.24). At higher temperatures, the catalyst decomposed to a significant extent to form an isomerisation active catalyst. It was also evident that, at higher temperature, more of the catalyst leached into the organic phase as evidenced by the colour in the organic phase.

Table 2.23: Effect of temperature on conversion and selectivity towards formation of 7-tetradecene after 5h reaction time

Temperature (° C)	Conversion of 1-octene (%)	Selectivity (%) ^a
30	92	98.5
40	90	97.9
50	98	96.6
60	98	96.4
80	97	92.9
90	98	91.4

^aas determined by GC analysis

At 90 °C, around 8% of by-products (SMPs) were formed corresponding to an end of run selectivity of 91% compared to a run performed at 40 °C with 2% of SMPs corresponding to an end of run selectivity of 98%.

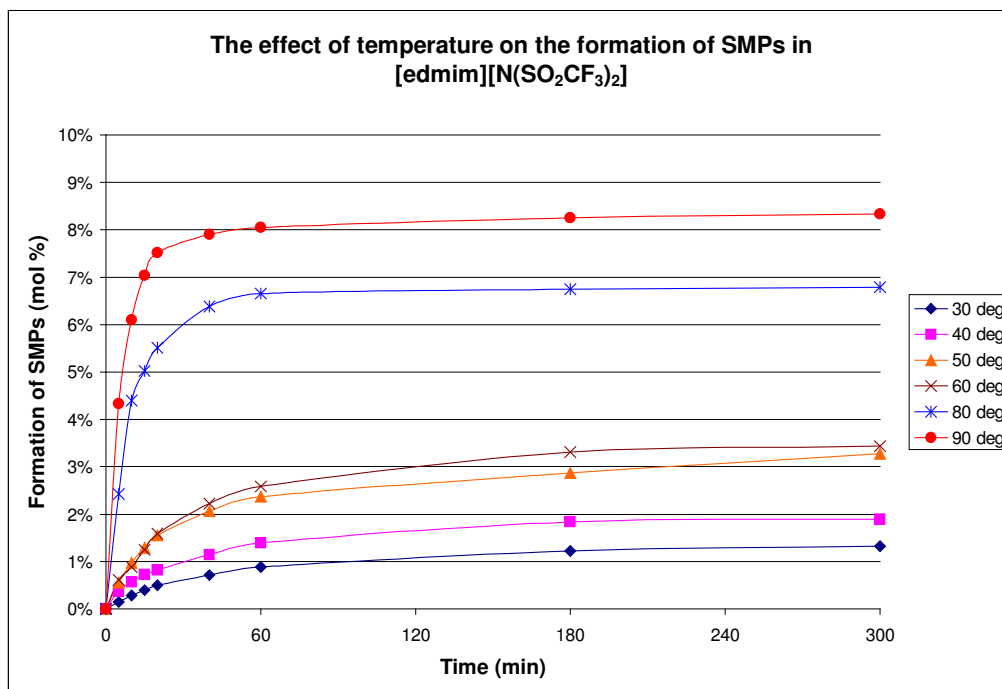


Figure 2.24: Effect of temperature on the formation of SMPs in [edmim][N(SO₂CF₃)₂]

ii) 7.5 mg Ru catalyst

A series of reactions was run at increasing temperature, at a ruthenium concentration of (7.5 mg) using [edmim][N(SO₂CF₃)₂] IL as the solvent. A summary of the results is shown in Figure 2.25 and Table 2.24.

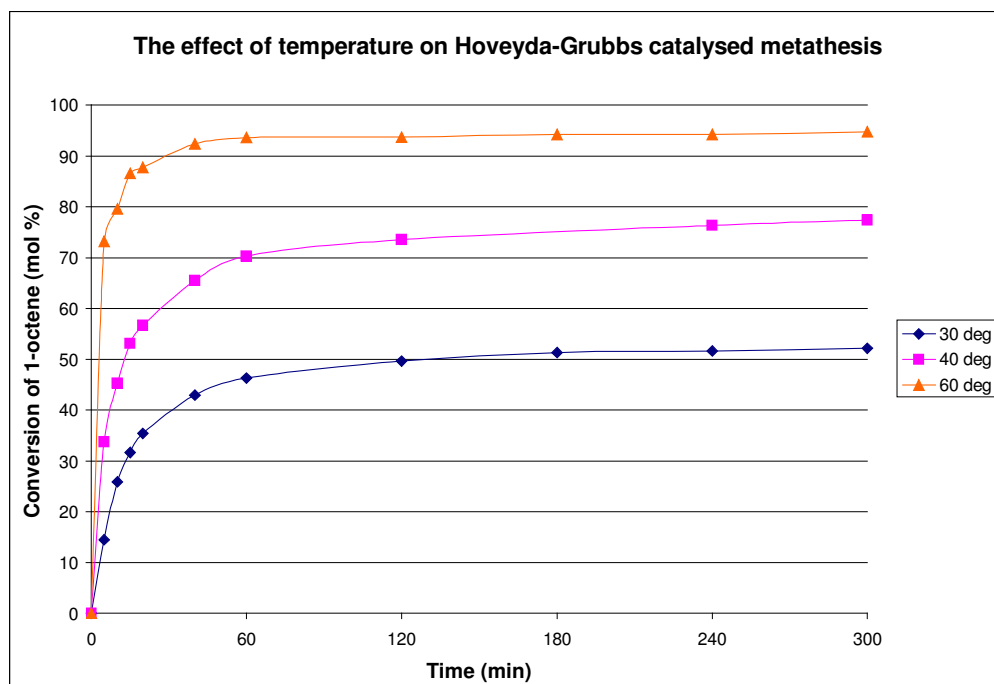


Figure 2.25: The effect of temperature on the conversion of 1-octene at lower [Ru] concentration in [edmim][N(SO₂CF₃)₂]

From the graph, it is evident that an increase in temperature results in an increase in the conversion of 1-octene with the run at 60 °C showing significant conversion of 95% after six hours. The selectivity towards the desired product, however, slightly decreased with increasing temperature.

Table 2.24: The effect of temperature at lower [Ru] concentration after 5h reaction time

Temperature (° C)	Conversion of 1-octene (%)	Selectivity (%) ^a
30	52	99.3
40	77	98.4
60	95	96.4

^aas determined by GC analysis

d) Influence of ruthenium concentration

Self-metathesis of 1-octene was carried out at 40 °C and the ruthenium concentration was varied in using the Hoveyda-Grubbs catalyst in [edmim][N(SO₂CF₃)₂] as the ionic solvent. The results are shown in Figure 2.26 and Table 2.25.

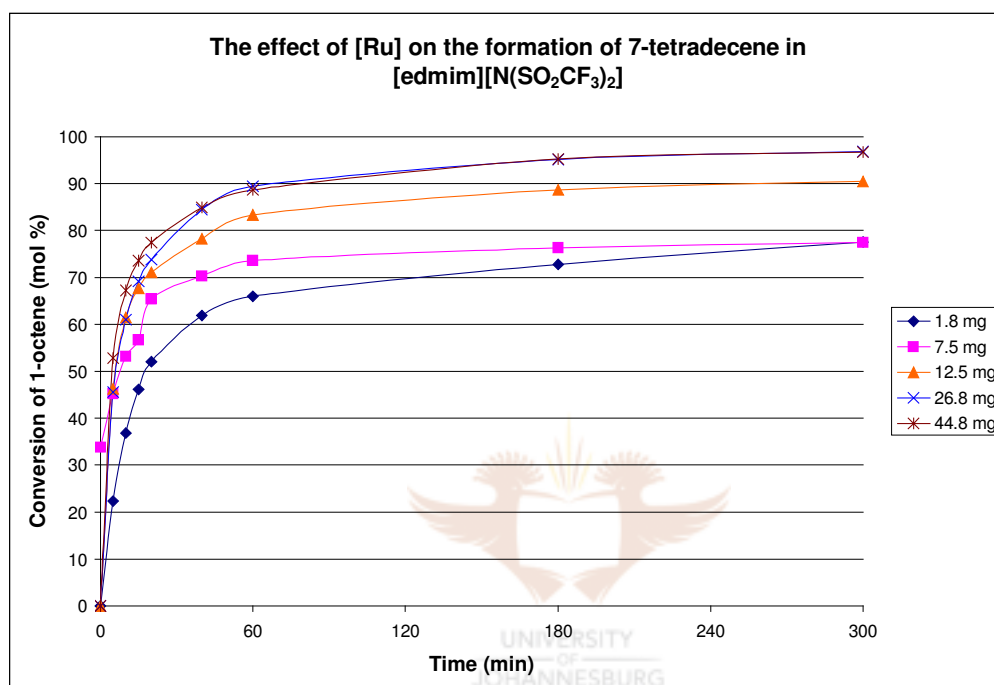


Figure 2.26: The effect of [Ru] on the conversion of 1-octene

Table 2.25: Effect of [Ru] concentration on conversion and selectivity towards formation of 7-tetradecene after 5h reaction time

[Ru] concentration (mg)	Conversion of 1-octene (%)	Selectivity (%) ^a
1.8	78	99.0
7.5	77	98.4
12.5	90	97.9
26.8	97	96.9
44.8	97	95.7

^aas determined by GC analysis

An increase in ruthenium concentration resulted in an increase in initial reaction rate, up to approximately 12.5 mg of Ru. Thereafter only marginal increases were observed that were not in line with the amount of additional catalyst added.

As the ruthenium concentration increased, conversion also increased and the selectivity towards 7-tetradecene formation decreased, which can be explained by a greater extent of leaching of the catalyst into the organic phase.

e) Hoveyda-Grubbs catalyst in 1-octene: Influence of a salt/IL

It has been noted that the addition of some salts has a positive effect on the self-metathesis of 1-octene by inhibiting the formation of SMPs.

ILs need not be used as a solvent only, but also an additive. The next aspect of the study investigated the addition of the number of equivalents of the [edmim][N(SO₂CF₃)₂] IL on the formation of 7-tetradecene, (Figure 2.27 and Table 2.26).

Table 2.26: The influence of added equivalents of [edmim][N(SO₂CF₃)₂] on the conversion and selectivity towards 7-tetradecene after 5h reaction time

Added [edmim][N(SO ₂ CF ₃) ₂]	Conversion of 1-octene (%)	Selectivity (%) ^a
5 eq. IL	96	98.3
10 eq. IL	93	97.1
50 eq. IL	97	95.1
IL (solvent, 2 mL)	92	96.8
No IL (1-octene)	93	91.1

^aas determined by GC analysis

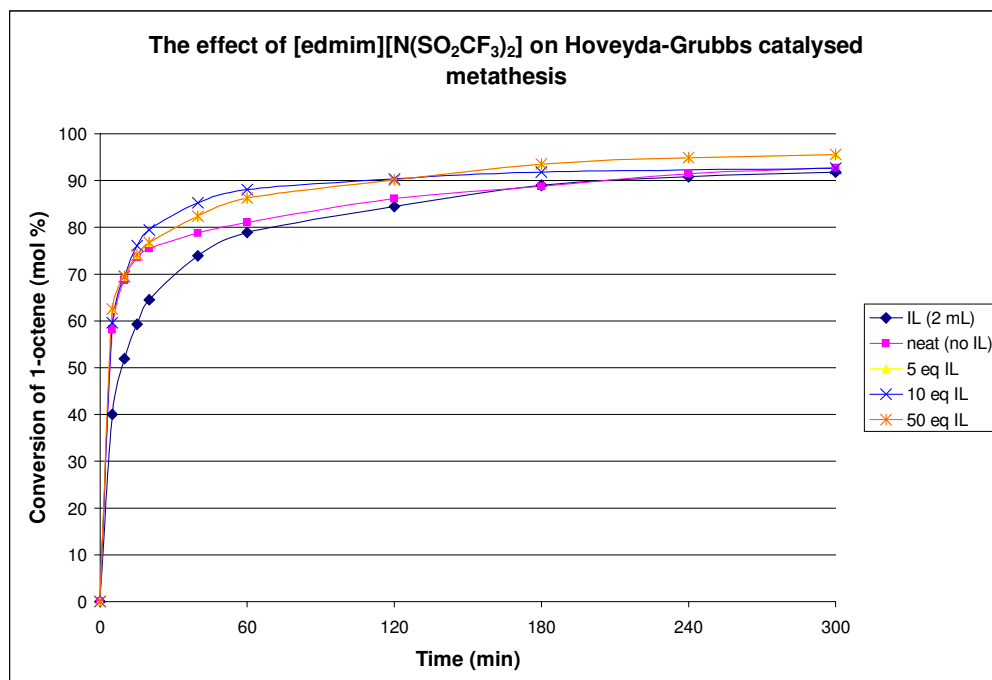


Figure 2.27: The addition of different equivalents of [edmim][N(SO₂CF₃)₂] on the conversion of 1-octene

The data in Figure 2.27 show that the addition of the IL to the reaction mixture makes a difference to the outcome of the reaction at amounts as low as five equivalents of the IL. At these low levels both conversion and selectivity were extremely high, and slightly improved upon the reaction where the IL was added as co-solvent.

Some halogenated ILs (solid form of an IL) (100 eq.) were added to 1-octene and the effect on the Hoveyda-Grubbs catalyst was investigated at 40 °C. Three different types of ionic solids were added, namely [emim][Cl], [emim][Br] and [edmim][Br] and their effects on the metathesis activity are presented in Figure 2.28 and Table 2.27.

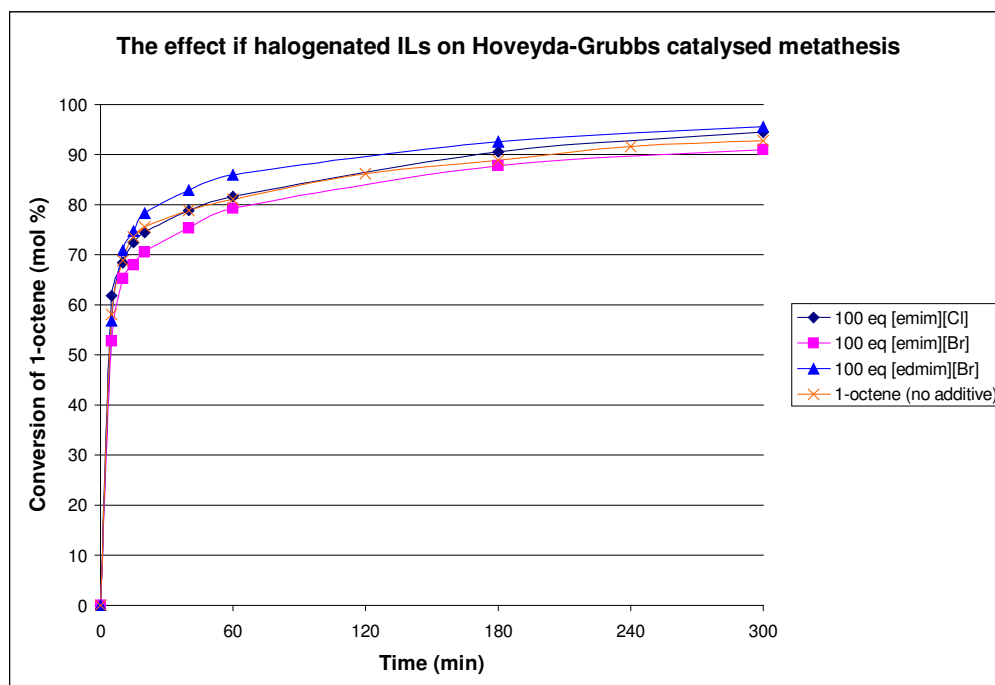


Figure 2.28: The effect of ionic solids on the conversion of 1-octene

Table 2.27: The influence of added ionic solid to the metathesis reaction on the conversion and selectivity towards 7-tetradecene after 5h reaction time

Additive	Conversion of 1-octene (%)	Selectivity (%) ^a
100 eq. [emim][Cl]	95	97.5
100 eq. [emim][Br]	91	97.7
100 eq. [edmim][Br]	95	91.1
No additive (1-octene)	93	91.1

^aas determined by GC analysis

The added ionic solid definitely enhances the outcome of these reactions over those in which no IL was added. The reactions with added solid IL show enhanced activities when compared to the “neat” reaction (1-octene employed as solvent). The selectivity with [emim][Cl] and [emim][Br] are higher than that of the “neat” reaction, signifying inhibition of SMP formation. The selectivity with [edmim][Br] showed similar selectivity to the “neat” reactions for unknown

reasons. The influence of different equivalents of [edmim][Br] on the Hoveyda-Grubbs catalyst was investigated at 40 °C. The results are shown in Figure 2.29 and Table 2.28.

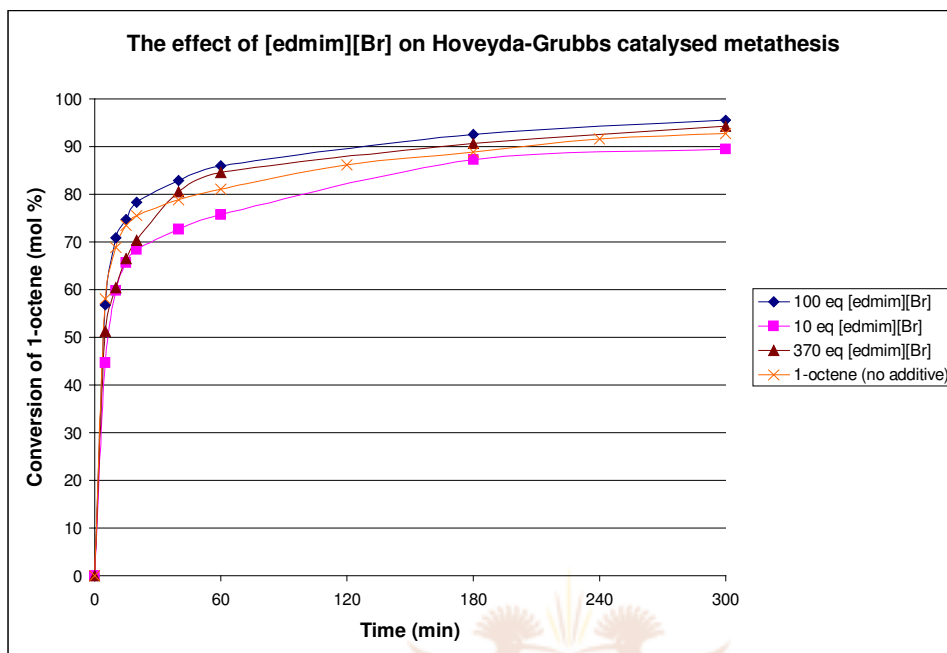


Figure 2.29: The effect of [edmim][Br] on the conversion of 1-octene

Table 2.28: The influence of [edmim][Br] to the metathesis reaction on the conversion and selectivity towards 7-tetradecene after 5h reaction time

Additive	Conversion of 1-octene (%)	Selectivity (%) ^a
10 eq. [edmim][Br]	89	97.2
100 eq. [edmim][Br]	95	91.1
370 eq. [edmim][Br]	94	92.0
No additive (1-octene)	89	91.1

^aas determined by GC analysis

The reaction with 10 equivalents of [edmim][Br] showed better selectivity compared to the reactions having more [edmim][Br] present, where SMP formation was quite significant. The activity with 10 equivalents of [edmim][Br] was similar to the “neat” reaction although the selectivity was better. In contrast,

a larger amount of added [edmim][Br] resulted in higher conversions but at the expense of selectivity.

It was decided to investigate the addition of a salt, LiBTA which closely resembles the ionic liquid [edmim][N(SO₂CF₃)₂] normally used in a metathesis run at 40 °C. The results are shown in Figure 2.30 and Table 2.29.

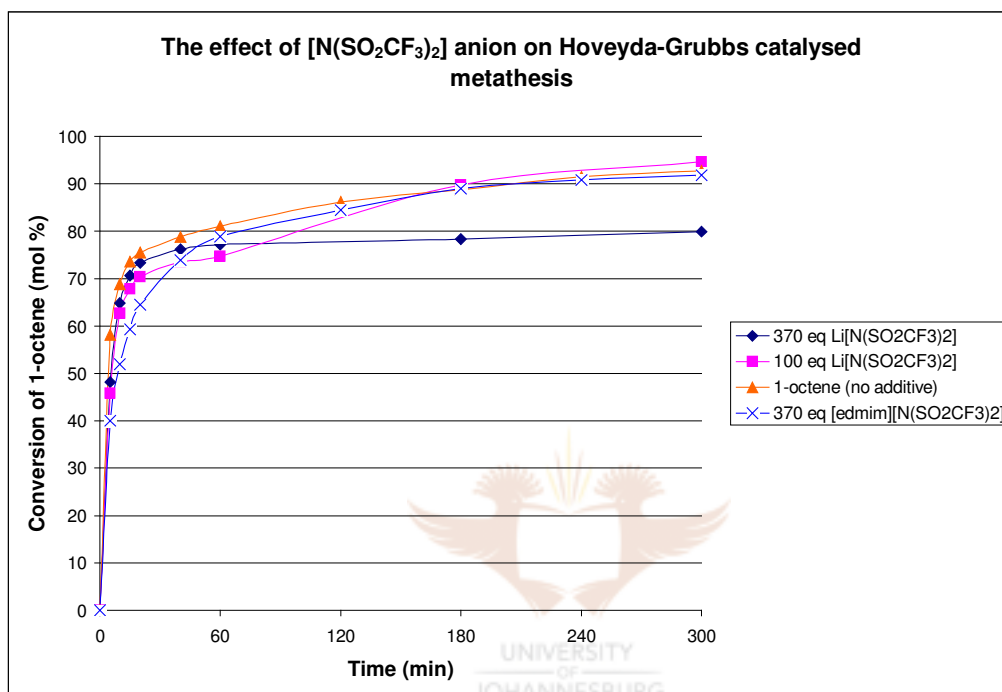


Figure 2.30: The effect of the [N(SO₂CF₃)₂] anion salt on the conversion of 1-octene

Table 2.29: The effect of added [N(SO₂CF₃)₂] anion to the metathesis reaction on the conversion and selectivity towards 7-tetradecene after 5h reaction time

Additive	Conversion of 1-octene (%)	Selectivity (%) ^a
100 eq. LiN(SO ₂ CF ₃) ₂	95	96.6
370 eq. LiN(SO ₂ CF ₃) ₂	80	97.6
370eq. [edmim][N(SO ₂ CF ₃) ₂]	92	97.9
No additive (1-octene)	93	91.1

^aas determined by GC analysis

The reactions with added $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt reached equilibrium quicker than the IL reaction using $[\text{edmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$. However, the IL had a definite stabilisation effect on the catalyst. The effect on the conversion and selectivity towards the formation of 7-tetradecene are shown in Table 2.29.

There are significant differences observed in the selectivity towards 7-tetradecene with added $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt when compared to the neat reaction (no solvent employed). The selectivity was improved when the $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ salt was added reaching a selectivity of approximately 98%. The added salt therefore inhibited the formation of SMPs, as was the case when an IL was added.

f) Influence of phenol

The influence of phenol (500 eq.) on the self-metathesis of 1-octene was investigated in $[\text{edmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ as well as in toluene as the solvent in order to make comparisons at 40 °C. The results are shown in Figure 2.31 and Table 2.30.

Table 2.30: The influence of added phenol to the metathesis reaction on the conversion and selectivity towards 7-tetradecene after 5h reaction time

Additive	Conversion of 1-octene (%)	Selectivity (%) ^a
Toluene	93	87.2
Toluene + 500 eq. Phenol	7	97.1
$[\text{edmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	92	97.9
$[\text{edmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ + 500 eq. Phenol	28	93.9

^aas determined by GC analysis

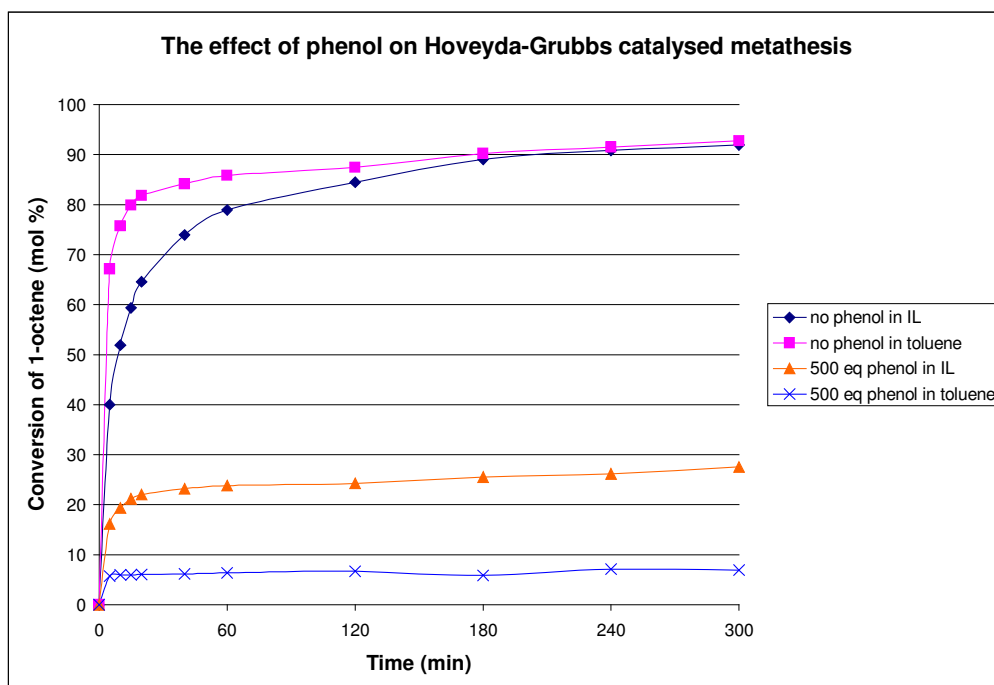


Figure 2.31: The effect of phenol in [edmim][N(SO₂CF₃)₂] and toluene on the conversion of 1-octene

From Figure 2.31, it can be seen that for both toluene and the IL reaction, phenol has a strong inhibitory effect on the conversion of 1-octene. This is contrary to the effect that phenol had on the Grubbs catalyst (see Figure 2.3 for comparison), where a marked enhancement of the rate and conversion was observed.

g) Influence of tin

The influence of tin (in the form of SnCl₂·2H₂O) (20 eq.) on the self-metathesis of 1-octene was investigated in [edmim][N(SO₂CF₃)₂] IL and toluene as the solvents in order to make comparisons at 40 °C. The results are shown in Figure 2.32 and Table 2.31.

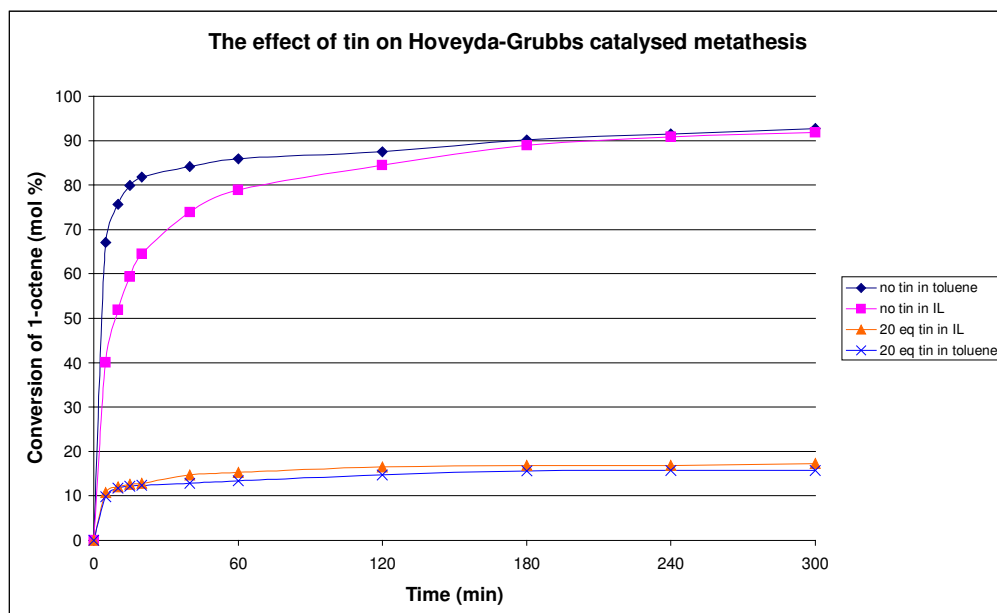


Figure 2.32: The effect of tin on the conversion of 1-octene

Table 2.31: The influence of added tin ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) to the metathesis reaction on the conversion and selectivity towards 7-tetradecene after 5h reaction time

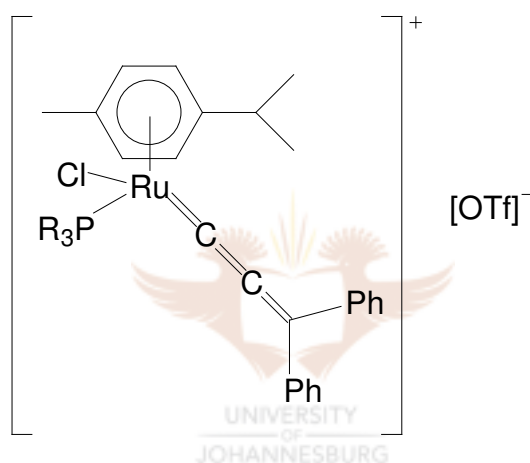
Additive	Conversion of 1-octene (%)	Selectivity (%) ^a
Toluene	93	87.2
Toluene + 20 eq. Sn	16	98.9
[edmim][N(SO ₂ CF ₃) ₂]	92	97.9
[edmim][N(SO ₂ CF ₃) ₂] + 20 eq. Sn	17	98.9

^aas determined by GC analysis

From Figure 2.32, it is apparent that the addition of tin had a negative effect on the metathesis activity resulting in rapid catalyst deactivation. This is contrary to the enhancing effect it had on first generation catalyst, PHOBCAT (see Figure 2.7 for comparisons).

2.4 Studies on Ionic Ruthenium Allenylidene Salt

Dixneuf and Fürstner's groups first reported a variety of ionic 18-electron ruthenium-allenylidene complexes of the type $[\text{RuCl}(=\text{C}=\text{C}=\text{CR}_2)(\text{arene})(\text{PR}_3)]\text{[X]}$ in 1998.¹⁷⁷ These catalysts are efficient for the RCM of dienes and enynes, although they show low activities for ROMP.¹⁷⁸ The ionic ruthenium allenylidene catalyst $[\text{RuCl}(=\text{C}=\text{C}=\text{CPh}_2)(\text{PCy}_3)(p\text{-cymene})]\text{[OTf]}$ **6** is known to transform into an active metathesis catalyst after loss of the arene ligand, thereby forming a coordinatively unsaturated species.¹⁷⁹ Ruthenium allenylidene complexes have been reported as versatile catalysts for olefin metathesis reactions.¹⁸⁰



The ruthenium allenylidene salt was evaluated for the self-metathesis of 1-octene at 80 °C in an imidazolium IL containing a triflate anion, $[\text{CF}_3\text{SO}_3]$. Reactions were carried out with Ru concentration of 0.02 mol %. In the reaction, 2 ml of the IL was added to 16 ml 1-octene and 17.76 mg of the ruthenium allenylidene catalyst at 80 °C. Results are shown in Figure 2.33.

At 80 °C, no formation of 7-tetradecene is seen and a considerable amount of isomerisation products are observed. It was wondered whether the high temperature was responsible for isomerisation, the same reaction was therefore repeated at a lower temperature of 40 °C. Results are shown in Table 2.32.

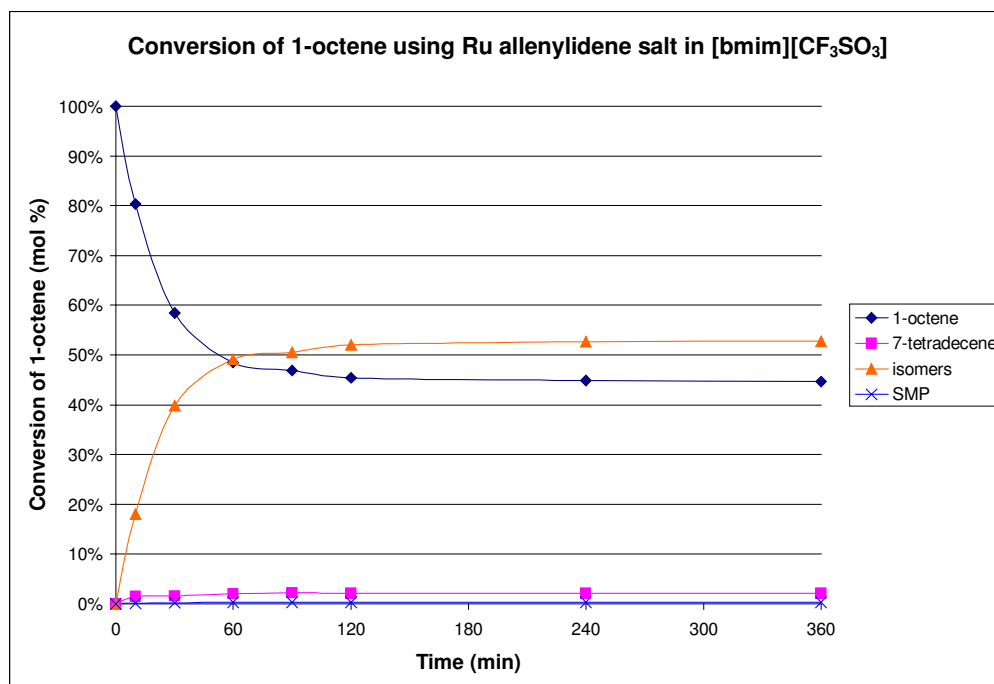


Figure 2.33: The effect of [bmim][CF₃SO₃] on the conversion of 1-octene at 80 °C

Table 2.32: The influence of temperature on the conversion and selectivity towards 7-tetradecene using Ru allenylidene salt in [bmim][CF₃SO₃]

IL/solvent	Temperature (°C)	Conversion of 1-octene (%) (reaction time)	Selectivity (%) ^a
[bmim][CF ₃ SO ₃]	40	7.50 (2h)	100
[bmim][CF ₃ SO ₃]	80	55.30 (6h)	3.9

^aas determined by GC analysis

From the results, it seems that the ruthenium allenylidene was not a good metathesis catalyst for linear olefins. At higher temperatures, the ruthenium allenylidene catalyst was an isomerisation catalyst. Contrary to literature reports, it was noted that the ruthenium allenylidene catalyst was not quite soluble in the [bmim][CF₃SO₃] IL and leaches out of the IL phase into the top organic layer.¹⁷

2.5 Conclusion

Overall, the second-generation Grubbs catalyst afforded reactions that were far superior to those performed with the first-generation Grubbs catalyst. Some interesting observations were made relating to the specific sensitivities of the metathesis reactions in question. It can be said that the presence of an imidazolium-based IL is beneficial to the reaction in amounts as low as five equivalents based on the catalyst concentration, that the IL should be relatively polar as regards the cation (shorter alkyl chains are preferred), that a nitrogen purge enhances conversions, that the catalyst is sensitive to certain impurities in the IL, that the reaction can be run at a range of temperatures but is most successful at 50-60 °C and that certain salt additives also enhance the rate and selectivity of the reaction.



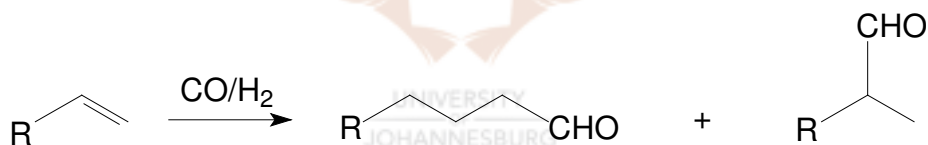
Chapter 3

Hydroformylation of Vinyl Acetate in Ionic Liquids

3.1 Introduction

3.1.1 Hydroformylation

In 1938, Otto Roelen serendipitously discovered a new chemical reaction when he passed ethylene and synthesis gas (a mixture of CO and H₂) over a supported cobalt catalyst at 150 °C and 100 atmospheres of pressure.¹⁸¹ Roelen's aim at the time was to increase the alkyl length of Fischer-Tropsch (FT) hydrocarbons. He instead formed propanal as the reaction product. This reaction would prove to be one of the key turning points of homogeneous organometallic catalysis. This new reaction is a reaction between olefins and synthesis gas to yield linear and branched (*iso*-) aldehydes (Scheme 3.1).



Scheme 3.1

The reaction was called “oxo synthesis” or oxonation during the early times and the term hydroformylation was only later introduced by Adkins.¹⁸² Today, hydroformylation is one of the most important industrial chemical homogeneous reactions using transition metals. Approximately 8.8 million tons/year of aldehydes and alcohols are produced worldwide using this important reaction.¹⁸³ These hydroformylation products have important applications in the production of detergents, plasticisers and solvents.

3.1.2 Metals used in hydroformylation

Most hydroformylation reactions today are performed using mainly four transition metals: cobalt, rhodium, platinum and ruthenium.¹⁸⁴ However, industrial processes mainly focus on cobalt- and rhodium-based catalyst systems.¹⁸⁵ Differences between cobalt and rhodium catalysts for hydroformylation are shown in Table 3.1. Academic institutions mainly focus on the rhodium metal as hydroformylation catalysts.¹⁸⁵

Table 3.1: Differences between cobalt and rhodium as hydroformylation catalysts

Cobalt	Rhodium
Relatively inexpensive	Expensive
Harsh reaction conditions are required e.g. high temperatures and pressures	Mild reaction conditions
Lower reaction rates	High reaction rates
More robust towards feed impurities	Sensitive to feed impurities
Higher catalyst concentrations required	Low catalyst concentrations required
More suitable for higher chain olefins	More suitable for lower chain olefins (< C ₁₀ carbon number)

Other metals that have been used for hydroformylation include iridium, osmium, palladium and iron, but the activities and lifetimes of these catalysts are much lower than rhodium and cobalt.¹⁸⁵

With hydroformylation catalysts, “modified” or “unmodified” catalysts can be used. In modified catalysts, a ligand is introduced and this has been shown to have a marked effect on catalyst activity and lifetime. First generation hydroformylation processes were based on cobalt catalyst systems better known as the unmodified cobalt catalyst [Co₂(CO)₈]. This was followed by the introduction of the unmodified rhodium catalyst [Rh₄(CO)₁₂]. The need for milder reaction conditions, increased selectivity to linear aldehydes and reduced by-product formation led to the introduction of second generation hydroformylation

processes based on rhodium as catalyst metal modified with a ligand. The addition of a ligand leads to lower reactivity in some instances of these second generation hydroformylation catalysts.

3.1.3 Ligands used in hydroformylation

Apart from the metal chosen for hydroformylation, the ligand is also of high importance. Ligands that have been used for hydroformylation were mainly phosphine-containing ligands. Nitrogen-containing ligands such as amines, amides or isonitriles have also been used as ligands for hydroformylation, although they show lower reaction rates. Also, ligands based on arsenic (e.g. AsPh_3) have also been used in hydroformylation.¹⁸⁶ Most industrial hydroformylation plants use phosphine (PR_3) type ligands and a few use phosphites (P(OR)_3) (Figure 3.1). In general, using ligands with low basic character and less σ -donor ability leads to faster hydroformylation rates.

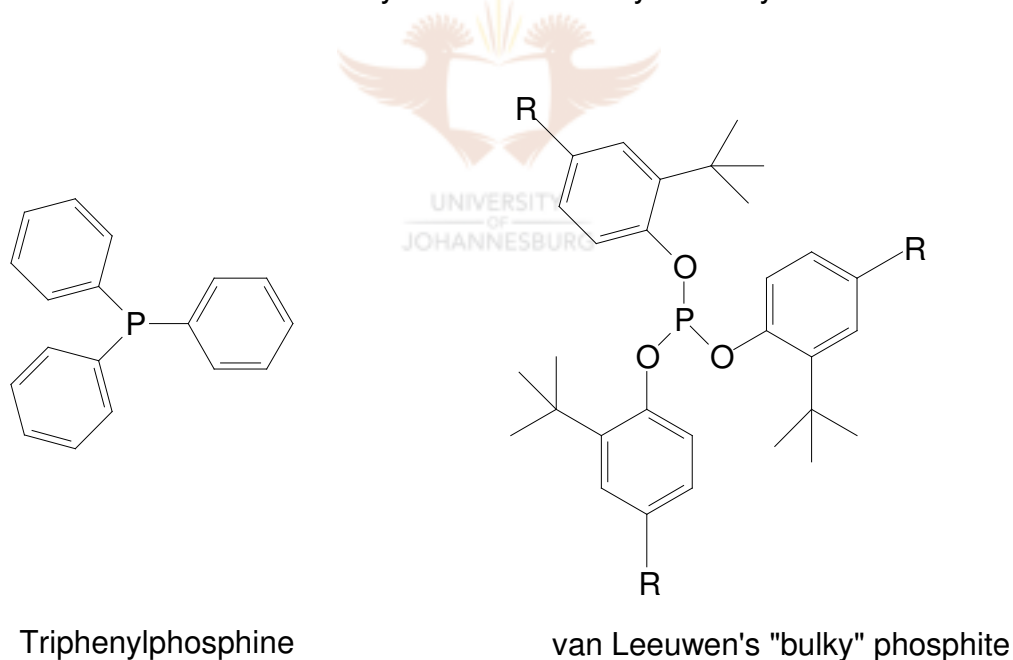


Figure 3.1: Phosphine and phosphite ligands

Milder reaction conditions are also another advantage in using modifying ligands with metal catalysts. The most widely used phosphorus-containing ligand in

hydroformylation applications has been phosphines (e.g. PPh_3).¹⁸⁷ Phosphites have also shown great potential in hydroformylation catalysts because they are stronger π -acceptors and weaker σ -donor ligands than phosphines. Higher selectivity (*n:iso*) is therefore obtained with phosphite-modified catalyst systems. Phosphites are less sensitive to oxidation than phosphines due to their electron-deficient nature but they are more sensitive to hydrolysis, alcoholysis, reaction with aldehydes, and the Arbuzov reaction.¹⁸⁸ Phosphite hydrolysis can be limited by using bulky phosphites such as tris(2,4-di-*tert*-butylphenyl)phosphite and cyclic phosphites. Phosphorus ligands are susceptible to oxidation by water, carbon dioxide, oxygen and oxidising agents.¹⁸⁹ Therefore, oxygen and hydroperoxides must be removed from the reagents and solvents before starting the catalysis. Small changes in the phosphite ligand can significantly influence the stability of the phosphite ligand and of the rhodium-phosphite complexes. Bulkier phosphite ligands are known to enhance hydroformylation rate to a significant extent and often higher selectivity is obtained.¹⁹⁰

3.1.4 Ionic liquids as solvents for hydroformylation

An increasing awareness of cleaning up manufacturing chemistry for the sake of the environment in the last two decades has led groups to seek ways to improve current processes using “greener” techniques in hydroformylation. Also, the common challenging problem in homogeneous catalysis of catalyst separation has led to many ingenious approaches. The use of water, ILs and scCO_2 are some of these “green” techniques and represents means of overcoming catalyst recovery issues.¹⁹¹

Olefin hydroformylation has been performed in ILs.¹⁹² The first hydroformylation reaction in ILs was performed by Parshall in 1972 using tetraethylammonium trichlorostannate as solvent.¹⁹³ Using ILs in olefin hydroformylation gives a biphasic system which aids in catalyst recovery and product separation. Notwithstanding the two phase system, workers frequently do experience loss of the catalyst due to leaching out of the IL phase. For example, Chauvin and co-

workers used $\text{Rh}(\text{acac})(\text{CO})_2$ with PPh_3 in a range of ILs based on anions such as $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{AsF}_6]^-$, and $[\text{BF}_4]^-$.¹⁹⁴ Although high catalytic activity was obtained, significant leaching of Rh into the organic phase was observed. Using sulfonated triphenylphosphine derivatives (ligand 3.1, Figure 3.2) reduced the leaching of Rh but at the expense of the reaction rates.

These potential problems have been alleviated by using ligands that are more soluble in ILs. Phosphorus ligands that are soluble in ILs are shown in Figure 2. These ligands have been used to immobilise rhodium complexes in ILs.¹⁹⁵

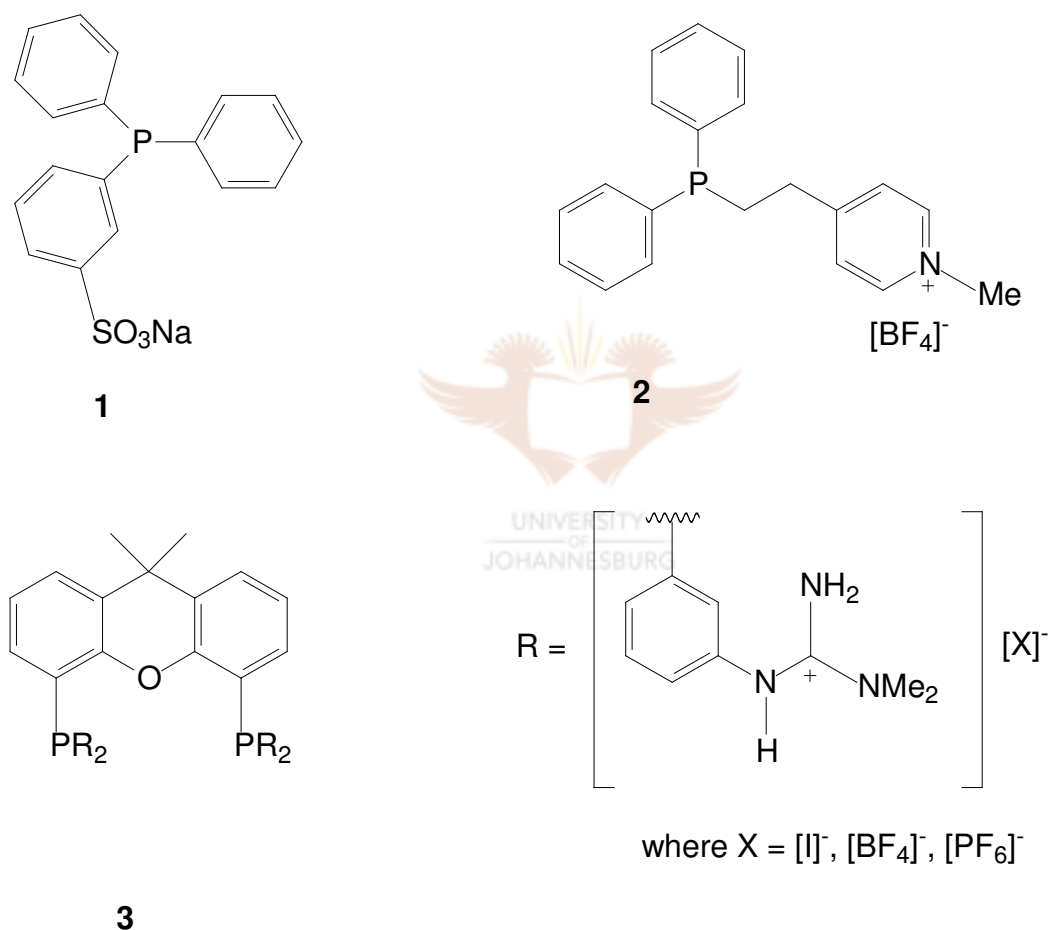
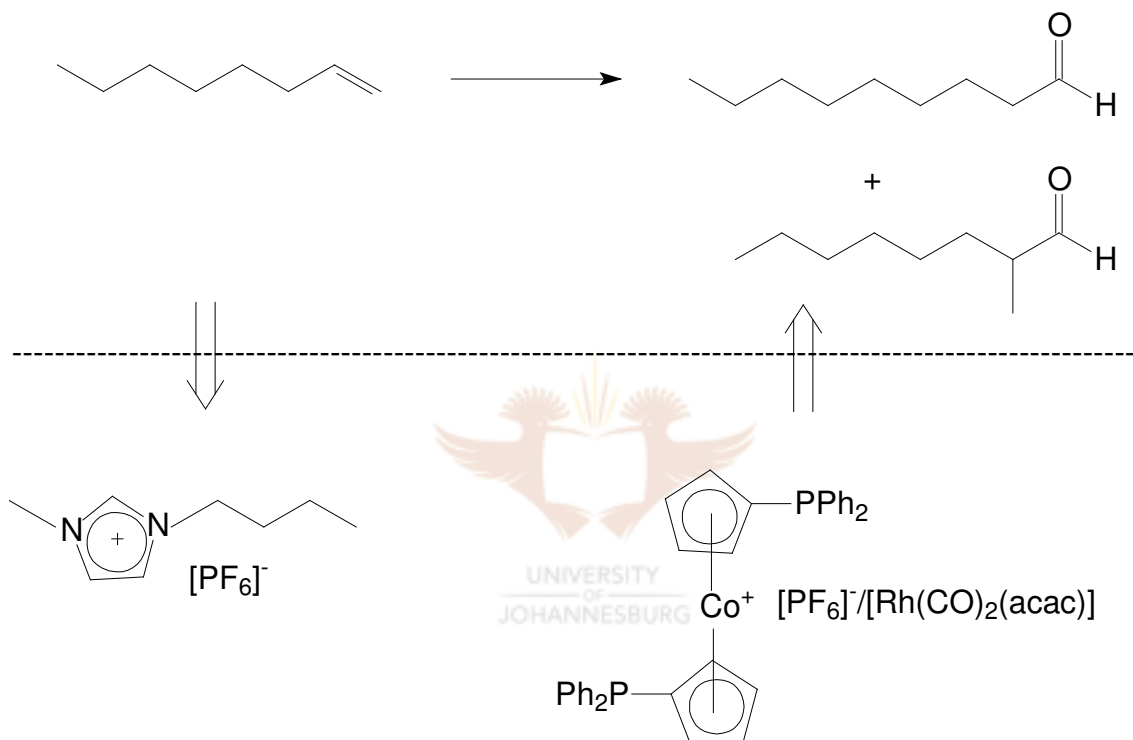


Figure 3.2: Examples of ligands used in ILs for hydroformylation

Much research has gone into the hydroformylation of linear olefins in ILs. Waffenschmidt and Wasserscheid reported the hydroformylation of 1-octene in [bmim][SnCl₃] using a platinum catalyst.¹⁹⁶ They reported high activities (TOF = 126 h⁻¹) with high regioselectivity (*n/iso* = 19). The hydroformylation of 1-octene using cobaltocenium diphosphine ligands in [bmim][PF₆] in the presence of Rh also yielded high activities (TOF = 810 h⁻¹) and high regioselectivity (*n/iso* = 16).¹⁹⁷



Scheme 3.2: Hydroformylation of 1-octene using cobaltocenium diphosphine ligands

Some novel cationic guanidinium-modified diphosphine ligands containing a xanthene backbone (ligand 3.3, Figure 3.2) have been investigated together with rhodium for the hydroformylation of 1-octene in [bmim][PF₆].¹⁹⁸ High regioselectivity was achieved (*n/iso* = 20) in that case.

Rhodium-catalysed hydroformylation of 1-hexene using high melting phosphonium salts (m.p. > 70 °C) has been reported.¹⁹⁹ The authors reported

that cooling the IL salt to room temperature would cause the phosphonium salt to solidify allowing the organic product to simply be decanted and the IL salt/catalyst system to be re-used.

A monophasic hydroformylation system of methylpent-3-enoate in [bmim][PF₆] was also reported.²⁰⁰ The report mentions that the IL could be recycled ten times without significant loss of activity.

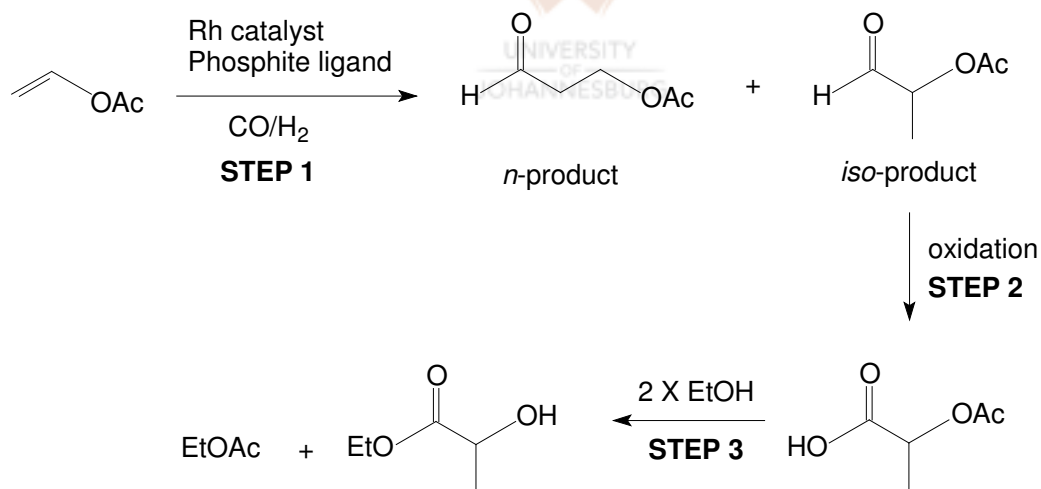
3.2 Aim of this work

Over the past number of years, ethyl lactate has received increasing attention as a high performance, environmentally friendly, “green” solvent.²⁰¹ It is anticipated that ethyl lactate could possibly replace the ozone depleting CFCs, dichloromethane, and ethylene glycol esters as the solvent of choice in the near future. The major driver to replace toxic industrial solvents with environmentally-friendly solvents such as ethyl lactate is due to the increasing pressure from environmental groups. Ethyl lactate has a low toxicity, is biodegradable and forms fewer volatile organic compounds (VOCs) than conventional solvents.²⁰² Ethyl lactate is currently used in the manufacture of pharmaceuticals, in the cosmetics industry, food industry and in the manufacture of semiconductors.

Ethyl lactate is mainly produced using fermentation technology with agricultural feedstocks. A synthetic route to ethyl lactate that we focused on was based on using vinyl acetate as primary feedstock. The fermentation route that is widely used has been calculated to be more expensive than the following proposed synthetic route. The proposed 3-step route to ethyl lactate (Scheme 3.3) is based on the hydroformylation of vinyl acetate to afford an iso/normal product mixture of α -acetoxypropionaldehyde and 3-acetoxypropionaldehyde. The selective oxidation of α -acetoxypropionaldehyde will produce α -acetoxy-lactic acid. The final step involves trans-esterification with ethanol to produce ethyl

lactate and ethyl acetate. The idea to produce lactic acid and lactates using vinyl acetate hydroformylation was first patented by Monsanto in 1975.²⁰³ They described the use of a triphenylphosphine-modified rhodium catalyst system.

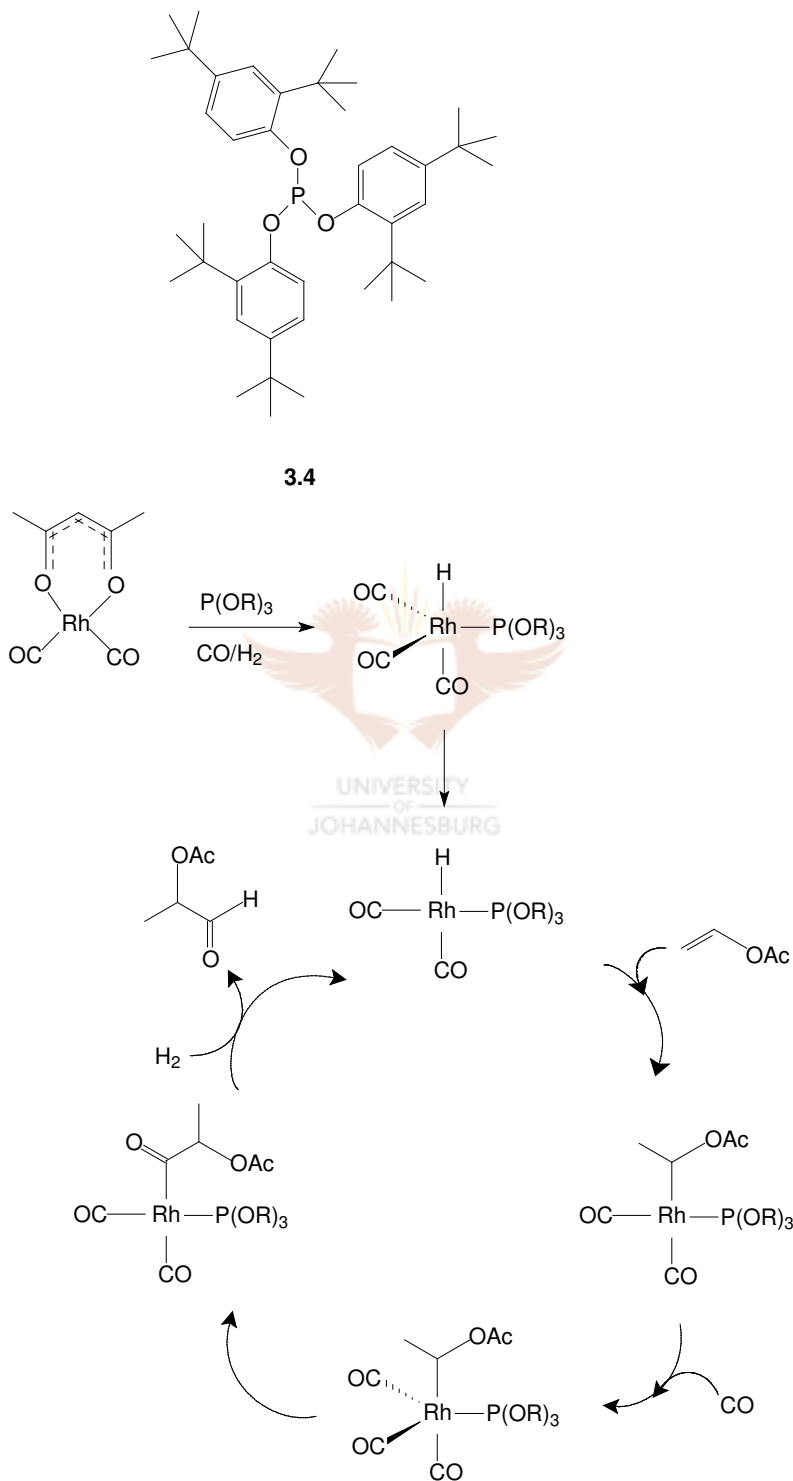
The first step in the production of ethyl lactate, namely the hydroformylation of vinyl acetate, was considered as the reaction to test for the potential of ionic liquids as solvents for the reaction using tris(2,4-di-*tert*-butylphenyl)phosphite ligand **3.4** with rhodium catalyst. As shown in Scheme 3.3, both *i*- and *n*-isomers are formed during the hydroformylation step, and this is undesirable. Optimising the formation of the *i*-product (being the preferred product) is therefore important. Suitable ionic liquid systems has been identified and reaction conditions optimised to deliver maximum rates and favourable selectivities for the hydroformylation of vinyl acetate. Cost and stability of the catalyst system, catalyst selectivity towards the *iso* product as well as easy product isolation are all important factors which could be affected by the use of ionic liquids as solvent system.



Scheme 3.3

A modified rhodium catalysed hydroformylation reaction of vinyl acetate was considered due to the thermal instability of the desired product α -acetoxypropionaldehyde (cobalt-catalysed hydroformylation would require higher reaction temperatures). The catalytic system of choice was based on a phosphite

modified rhodium complex, and the best results were obtained using tris(2,4-di-*tert*-butylphenyl)phosphite (**3.4**) as ligand. The mechanism for the hydroformylation of vinyl acetate is shown in Scheme 3.4.



Scheme 3.4

As will become clear during the discussion, and surprisingly, when results using ILs were compared to the standard homogeneous system, significantly higher *i:n* ratios with regard to the aldehyde product were observed – in some cases the *iso*-product was overwhelmingly the major product that was formed. In addition, it was shown that significantly less ligand (1:3 metal to ligand ratio) was required in the IL for the formation of a stable catalyst system (modified rhodium catalyst), compared to the homogeneous process (typically 1:100 metal to ligand ratio is required). The IL used as a reaction solvent will facilitate the easy separation of the aldehyde (α -acetoxypropionaldehyde) product *via* distillation the IL is essentially non-volatile.

3.3 Results and Discussion

ILs were investigated as solvents for the hydroformylation of vinyl acetate using the ligand [tris(2,4-di-*tert*-butylphenyl)phosphite] and the catalyst precursor [Rh(CO)₂(acac)]. This discussion is separated into the different classes of ILs used and the results are reported for each class of ILs. Most of the ILs used formed homogeneous mixtures with vinyl acetate. Therefore the advantage of easier product separation by simple decantation could not be achieved in this system. The base case conditions for the hydroformylation of vinyl acetate using the [tris(2,4-di-*tert*-butylphenyl)phosphite] ligand are shown in Table 3.2.

Table 3.2: Base case conditions for hydroformylation of vinyl acetate in ILs using phosphite ligands

Reaction parameter	Base case values
[Rh]	1 mmol L ⁻¹
Rh:P(OR) ₃	1:3
[VA]	7 mol L ⁻¹
Pressure	20 atmospheres
Temperature	85 °C

mM – millimolar (mmol/liter reaction volume)

M – molar (mol/liter reaction volume)

[VA] – concentration of vinyl acetate. This concentration was calculated from the total volume of the mixture and the known amount of VA added, since the mixture is homogeneous.

Low syngas pressure reduces capital and process costs to a great extent, if a process is to be applied industrially. A low pressure of 20 atmospheres of syngas was therefore used as the base case. Temperature and pressure are reaction parameters that have a pronounced effect on the hydroformylation reaction and their effects were investigated in ILs in this study. In the present instance, when using ILs, a ratio of 1:3 rhodium to ligand excess was used, although in the literature a high concentration of the bulky ligand (1:100 rhodium to ligand ratio) has been reported as a requirement to ensure complete formation of the very active monoligated rhodium complex. The high ligand ratio also prevents the formation of unsubstituted rhodium carbonyl complexes that could be detrimental to the reaction rate and selectivity. Catalysis therefore takes place only *via* the modified catalyst. The minimum amount required to form this complex is not stipulated in the literature and is understood to depend on the reaction conditions and rhodium concentration employed.

The rhodium-based hydroformylation of vinyl acetate gives rise to reaction mixtures containing a number of by-products in varying proportions. Products/by-products formed are α -acetoxypropionaldehyde (major product), β -acetoxypropionaldehyde (minor product) and trace amounts of acrolein, propanal and acetic acid as by-products. The presence of acrolein (which is unstable and decomposes to propanal) and acetic acid in these reactions is known in the literature²⁰⁴ and is thought to be an indication of β -acetoxypropionaldehyde decomposition. The other source of propanal is understood to be from ethylene hydroformylation. This ethylene is said²⁰⁵ to be formed *via* direct reaction of vinyl acetate and a rhodium hydride complex. Vinyl acetate is known to be thermally unstable, and one of the decomposition products is acetic acid, which could

cause degradation of the phosphite ligands. Rhodium is known to catalyse the decomposition of vinyl acetate into acetic acid and ethylene.

3.3.1 Phosphite ligands

3.3.1.1 Imidazolium-based ILs

ILs based on imidazolium cations were used to determine the effect they have on hydroformylation activity and selectivity. The effect of increasing alkyl chain length on the imidazolium cation of bistriflimide ILs (Figure 3.3) using the base case conditions are shown in Table 3.3.

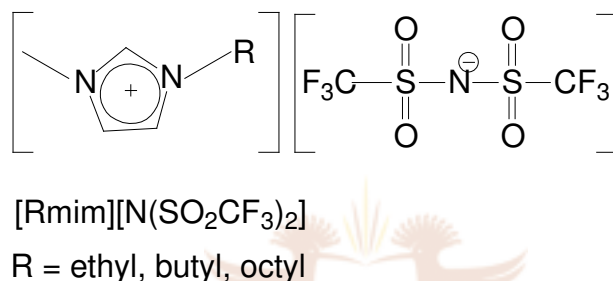


Figure 3.3: [Rmim][N(SO₂CF₃)₂]

Table 3.3: The effect of increasing alkyl chain length on imidazolium cations of bistriflimide ILs on hydroformylation activity and selectivity

IL/solvent	TOF ^a (h ⁻¹)	S.T.Y. ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
[emim][N(SO ₂ CF ₃) ₂]	3 000	3	23:1	96	94
[bmim][N(SO ₂ CF ₃) ₂]	4 500	4.5	26:1	96	94
[omim][N(SO ₂ CF ₃) ₂]	5 072	5	23:1	97	94

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

The results shown demonstrate a fairly strong dependence by the rate of the reaction on the alkyl chain length: the longer the alkyl chain, the higher the rate for this series of ILs. This implies that the less polar the IL, the higher the rate of the reaction.

The imidazolium cation should be an inert component of the IL. The C-2 proton of the imidazolium cation is, however, acidic and can be deprotonated to generate carbenes. Protection at the C-2 position on the imidazolium cation (Figure 3.4) normally prevents the carbene from forming and therefore prevents possible coordination of the ionic liquid to the catalyst. The ease of formation of carbene also depends on the nucleophilicity of the anion combined with the imidazolium cation. In this study, the effect of varying alkyl chain on the C-2 alkylated imidazolium cation of bistriflimide ILs was investigated and the results are shown in Table 3.4.

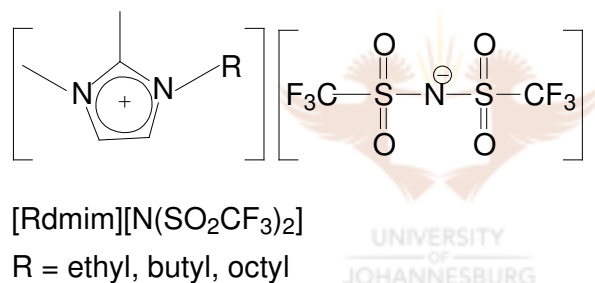


Figure 3.4: [Rdmim][N(SO₂CF₃)₂]

Table 3.4: The effect of increasing alkyl chain length on imidazolium cations of bistriflimide ILs on hydroformylation activity and selectivity

IL/solvent	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
[edmim][N(SO ₂ CF ₃) ₂]	3 379	3	> 100:1	100	90
[bdmim][N(SO ₂ CF ₃) ₂]	3 158	3	90:1	99	91
[odmim][N(SO ₂ CF ₃) ₂]	3 821	4	20:1	95	93

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Catalyst activity was somewhat higher for the ionic liquids that did not contain C-2 alkyl groups compared to their C-2 alkylated counterparts. The selectivity to the *iso*-product was higher for the C-2 alkylated ILs. Increasing the alkyl chain on the imidazolium ring resulted in an increase in hydroformylation activity for both reaction sets.

3.3.1.2 Optimisation of reaction variables in [bmim][N(SO₂CF₃)₂]

Reaction parameters were varied for the [bmim][N(SO₂CF₃)₂] IL as the solvent. This IL afforded middle of the range activities and would therefore be sensitive to changes that would reflect in the outcome of the reaction. The ligand to metal ratio, vinyl acetate concentration, rhodium concentration and temperature were varied as individual parameters to investigate the effect they have on hydroformylation activity and selectivity.

a) Ligand concentration

The metal to ligand ratio was varied from 1:3 to 1:25 to investigate the effect that ligand concentration has on the hydroformylation activity and selectivity using base case conditions. The effect of ligand excess was investigated to determine the optimum ligand ratio that can be used to ensure solubility of the ligand in the reaction mixture at 20 atmospheres of syngas pressure with 7 M vinyl acetate concentration. This particular ligand showed a relatively poor solubility in the [bmim][N(SO₂CF₃)₂] IL. Results are shown in Table 3.5.

An increase in ligand excess resulted in an increase in TOF but a decrease in *i:n* ratio. The 1:15 ligand excess seemed to be the optimum ligand ratio where good solubility was still maintained. At 1:25 ligand excess, activity dropped and a higher *i:n* ratio was obtained. No *overall* improvement was observed, and the reaction of choice would have to be selected depending on whether rate or *i:n* is important.

Table 3.5: The effect of ligand excess in [bmim][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

Ligand excess	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
1:25	3 600	4	22:1	96	91
1:15	6 300	6	17:1	94.5	95
1:7	5 800	6	17:1	94	96
1:3	4 500	4.5	26:1	96	94

1 mM Rh catalyst, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Subsequently, the vinyl acetate concentration was reduced from 7 M to 5 M and the ligand ratio varied from 1:3 to 1:100. A similar reaction was performed in toluene for the 1:3 ligand to metal ratio to see how the results (Table 3.6) compared to the IL run.

Table 3.6: The effect of ligand excess in [bmim][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

Ligand excess	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
1:100	4 600	5	36:1	97	92
1:15	3 210	3	30:1	97	91.5
1:3	2 000	2	39:1	97.5	89
1:3 (toluene)	5 700	6	21:1	95	93

1 mM Rh catalyst, 5 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

At the lower vinyl acetate concentration, the rates in the IL are lower and the regioselectivity for the branched product is higher. An increase in ligand excess

led to an increase in TOF, but no distinct trend in the *i:n* ratios was observed. Interestingly, in the reactions where ILs were used as solvents, much higher selectivity is obtained compared to the faster reaction in toluene (e.g. toluene vs IL, 21:1 vs 39:1).

b) Vinyl acetate concentration

The vinyl acetate concentration was varied using the standard conditions to investigate the effect this would have on hydroformylation activity and selectivity and the results are shown in Table 3.7.

Table 3.7: The influence of vinyl acetate concentration with constant ligand excess values in [bmim][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

[VA] (M)	TOF ^a (h ⁻¹)	S.T.Y. ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
3 M	2 300	2	49:1	98	92
5 M	2 700	3	35:1	97	92
7 M	4 500	4.5	26:1	96	94
9 M	6 000	6	19:1	95	88
10.8 M (neat)	6 400	6	20:1	95	93

1 mM Rh catalyst, 1:3 ligand excess, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

The results show that the vinyl acetate concentration had a significant effect on the catalytic activity in this system. At 20 atmospheres of syngas pressure, higher activities were observed in the case of the higher vinyl acetate concentration but lower *i:n* ratios were obtained. At low vinyl acetate concentration, activity was lower but high *i:n* values were obtained. A higher vinyl acetate concentration aided in solubilising the ligand in the ionic liquid much more effectively. The ligand showed relatively poor solubility in this particular IL.

c) Rhodium concentration

The rhodium concentration was varied from 0.5 mM to 1.25 mM relative to the total reaction volume with the Rh:ligand ratio kept constant at 1:3. The effect of rhodium concentration was investigated at 20 atmospheres of syngas pressure, and the results are shown in Table 3.8.

Table 3.8: The influence of rhodium catalyst concentration with constant ligand excess values in [bmim][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

[Rh] (mM)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	i:n	%-iso	%-CHO
0.50	6 400	3	16: 1	94	91
0.75	5 100	4	18: 1	95	91
1.0	4 500	4.5	26:1	96	94
1.25	6 600	8	30:1	97	92

1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Higher rhodium concentrations led to higher *i:n* ratios. The TOF values decreased as the rhodium concentration increased up to 1.0 mM, after which the value increased. Not surprisingly, the STY values were found to increase with increasing rhodium concentration. It seemed that, of the Rh concentrations tested, the optimum rhodium concentration is 1.25 mM.

d) Temperature

The effect of temperature in the [bmim][N(SO₂CF₃)₂] IL was investigated at 20 atmospheres of syngas pressure, and the results are summarised in Table 3.9.

Table 3.9: The influence of temperature with constant ligand excess values in [bmim][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

Temperature (°C)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
75	4 200	4	35:1	97	96
85	4 200	4	32:1	97	93
95	5 800	6	65:1	98.5	88
95 (new batch of IL)	5 800	6	62:1	98	87
95 *	8 900	9	41:1	98	88

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 20 atmospheres of pressure

** 1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 30 atmospheres of pressure*

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

An increase in temperature resulted in an increase in TOF as well as an increase in *i:n* ratio, but at the expense of selectivity for aldehyde. Earlier, mention was made of the thermal instability of vinyl acetate, and this is probably reflected in these reactions. The reaction performed at 95 °C gave the best results so far with a high *i:n* ratio (65:1). A new batch of [bmim][N(SO₂CF₃)₂] IL was synthesised and also tested to see if similar results could be obtained, and there was no significant difference. An increase in syngas pressure (30 atmospheres of syngas pressure) was investigated at 95 °C and a higher TOF was obtained compared to the 20 atmospheres of syngas pressure reaction (8 900 vs 5 800); however, this was at the expense of the *i:n* ratio at the higher pressure (41:1 vs 65:1).

3.3.1.3 Ammonium-based ILs

ILs based on ammonium cations and bistriflimide anions were used to determine the effect they have on hydroformylation activity and selectivity under base case conditions. The results are shown in Table 3.10.

Table 3.10: The effect of ammonium-type ionic liquids on hydroformylation activity and selectivity

IL/solvent	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
[NPhMe ₃][N(SO ₂ CF ₃) ₂]	5 648	6	30:1	97	91
[NBzEt ₃][N(SO ₂ CF ₃) ₂]	7 327	7	23:1	96	96
[NOc ₃ Me][N(SO ₂ CF ₃) ₂]	1 200	1	>100:1	100	89
[NBu ₄][N(SO ₂ CF ₃) ₂]	4 149	4	76:1	99	87

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

The aromatic-containing ammonium-based ILs gave quite excellent activity and reasonable selectivity although these were lower than those obtained with other ILs. The activity for [NOc₃Me][N(SO₂CF₃)₂] was low but excellent selectivity was obtained. The [NBu₄][N(SO₂CF₃)₂] IL gave higher activity and also quite high selectivity. This particular IL, however, is a solid at room temperature and melts at 94 °C. In this case, the vinyl acetate dissolved the IL, and no solidifying of the IL was observed at room temperature after cooling the reaction mixture.

3.3.1.4 Optimisation of reaction variables in [NBzEt₃][N(SO₂CF₃)₂]

Various parameters were investigated using the [NBzEt₃][N(SO₂CF₃)₂] IL, including vinyl acetate concentration, temperature and syngas pressure on the activity and selectivity of the hydroformylation reaction. This particular IL gave quite high activity under base case conditions and it was envisioned that certain parameters could be varied to enhance selectivity but still maintain the high activity.

a) Vinyl acetate concentration

The effect of vinyl acetate concentration was investigated using the base case conditions to investigate the effect this would have on the hydroformylation activity and selectivity and results are shown in Table 3.11.

Table 3.11: The influence of vinyl acetate concentration in [NBzEt₃][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

[VA] (M)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
2 M	2 961	3	35:1	97	94
3 M	3 705	4	42:1	98	95
5 M	4 037	4	26:1	96	94
7 M	7 438	7	23:1	96	93
9 M	6 443	6	22:1	96	92
10.8 M (neat)	6 400	6	20:1	95	93

1 mM Rh catalyst, 1:3 ligand excess, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Increasing vinyl acetate concentration resulted in an increase in hydroformylation activity in the ionic liquid but a drop in selectivity. An optimum activity was obtained at 7 M vinyl acetate concentration (TOF = 7 438 h⁻¹), while an optimum selectivity was obtained at 3 M vinyl acetate concentration (*i:n* = 42:1).

b) Temperature

The effect of temperature in the [NBzEt₃][N(SO₂CF₃)₂] IL was investigated at 20 atmospheres of syngas pressure, and the results are shown in Table 3.12.

Table 3.12: The influence of temperature in [NBzEt₃][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

Temperature (° C)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
65	2 348	2	13:1	93	98
75	6 875	7	15:1	94	94
85	7 438	7	23:1	96	93
90	6 969	7	29:1	97	92

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

An optimum TOF was reached at 85 °C and selectivity increased with higher temperature. An increase in temperature also causes a decrease in the percentage yield of the CHO type product yielded by the reaction.

c) Syngas pressure

The effect of syngas pressure in the [NBzEt₃][N(SO₂CF₃)₂] IL was investigated at 5 M vinyl acetate concentration, and results are shown in Table 3.13.

Table 3.13: The influence of syngas pressure in [NBzEt₃][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

Pressure (bar)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
10	1 959	2	>100:1	99	89
15	5 278	5	22:1	96	86
20	6 973	7	24:1	96	96
25	6 948	7	17:1	94.5	95

1 mM Rh catalyst, 1:3 ligand excess, 5 M vinyl acetate, 85 °C

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Increasing the syngas pressure resulted in an increase in TOF but a decrease in selectivity. The reaction at a low syngas pressure of 10 atmospheres gave excellent selectivity, although the rate at this pressure was too low.

3.3.1.5 Optimisation of reaction variables in [NOc₃Me][N(SO₂CF₃)₂]

Optimisations with the [NOc₃Me][N(SO₂CF₃)₂] IL were studied to investigate the effect of vinyl acetate concentration on the activity and selectivity of the hydroformylation reaction.

a) Vinyl acetate concentration

Preliminary optimisations, made by varying the vinyl acetate concentration with the [NOc₃Me][N(SO₂CF₃)₂] IL as the solvent, were investigated. The results are provided in Table 3.14. This IL gave the best selectivity so far using the base case conditions.

Table 3.14: The influence of vinyl acetate concentration in [NOc₃Me][N(SO₂CF₃)₂] on hydroformylation activity and selectivity

[VA] (M)	TOF ^a (h ⁻¹)	S.T.Y. ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
3 M	1 723	2	>100:1	99	88
5 M	2 307	2	>100:1	99.5	88
7 M	2 266	2	>100:1	99	90
9 M	3 732	4	>100:1	99	87
10.8 M (neat)	6 400	6	20:1	95	93

1 mM Rh catalyst, 1:3 ligand excess, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

From the results, it can be shown that with increasing vinyl acetate concentration, the TOF increased without affecting the selectivity of the reaction for the

branched product. This is an interesting observation, notwithstanding the relatively low reaction rates.

3.3.1.6 Pyridinium-based ILs

Pyridinium-based cations are also considered (like the ammonium-based cations) to be much cheaper than the imidazolium-based cations and would provide an added advantage to the cost of the ionic liquid. A few pyridinium ionic liquids were investigated for vinyl acetate hydroformylation activity and selectivity. The results are summarised in Table 3.15.

Table 3.15: The effect of pyridinium-based ionic liquids on hydroformylation activity and selectivity

IL/solvent	TOF ^a (h ⁻¹)	S.T.Y. ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
[C ₄ Py][N(SO ₂ CF ₃) ₂]	7 381	7	19:1	95	94.5
[C ₈ Py][BF ₄]	1 326	1	22:1	96	94

1 mM Rh catalyst, 1:3 ligand excess, 7 M VA, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Interestingly, it has been observed that [C₄Py][N(SO₂CF₃)₂] gave excellent activity (TOF = 7 381 h⁻¹), although the selectivity was quite poor. It was expected, based on previous observations with the imidazolium ligands, that the longer chain [C₈-pyridinium] cation would give better results.

3.3.1.7 Phosphonium-based ILs

Phosphonium ionic liquids sourced from Cytec were tested for hydroformylation activity and selectivity under the standard conditions, and the results are shown in Table 3.16.

Table 3.16: The influence of Cytec phosphonium-based ILs on hydroformylation activity and selectivity

Ionic Liquids	Water content (ppm)	TOF^a (h⁻¹)
[(C ₆) ₃ C ₁₄ P][N(SO ₂ CF ₃) ₂]	1 070	0
[(C ₆) ₃ C ₁₄ P][N(CN) ₂]	11 200	0
[(C ₆) ₃ C ₁₄ P][diisobutylphosphinate]	*	0
[(C ₄) ₃ CP][tosylate]	12 300	0

1 mM Rh catalyst, 7 M vinyl acetate, 85 °C, 20 bar pressure

** Water content could not be measured due to a side reaction in KF titration*

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

No activity was observed in any of the phosphonium ionic liquids. Possible reasons for this could be the high water content present in the ionic liquids as well as impurities present or due to thermal and chemical decomposition. Analysis of the pure ionic liquids showed substantial amounts of impurities, which may include free phosphines. The presence of such phosphines is anticipated to poison the catalyst. In the GC traces of the hydroformylation reaction products, up to 20 % ionic liquid-derived compounds were observed, which are thought to be phosphine (unreacted starting material of IL manufacture or derived from Hoffmann decomposition of the long chain phosphonium cations), haloalkanes (starting materials or alkenes formed by Hoffmann decomposition. The presence of phosphine may lead to the absence of catalytic activity by competitive binding to the vacant catalytic site. More purer phosphonium ILs need to be synthesised and tested for hydroformylation.

3.3.1.8 Sulfate-based anion IL systems

It was decided to investigate cheaper anions in the ionic liquids such as tosylate, methyl sulfate and octyl sulfate anions since the bistriflimide anions are very expensive. ILs based on sulfate anions were purchased from Solvent Innovation (purity > 98 %, Solvent Innovation, GmbH, Cologne, Germany) and tested for hydroformylation activity and selectivity. The results are taken up Table 3.17.

During the study of sulfate-anion based ILs, two ILs ([dmim][MeSO₄] and [bmim][MeSO₄]) were discovered to be biphasic with both vinyl acetate and the aldehyde product. (It has also been previously observed that the [omim][Cl] IL also formed a biphasic mixture with vinyl acetate but chloride-based ILs showed no hydroformylation activity probably due to free chloride anions that could bind the catalyst into an inactive state thereby deactivating the catalyst.) All ILs studied so far formed a monophasic mixture with vinyl acetate and the aldehyde.

A biphasic system would be advantageous for easy product separation and catalyst / ligand recovery although potential catalyst and ligand leaching out of the IL phase could be problematic. Another possibility would be to use an IL that is solid at room temperature but liquid at reaction temperature. Upon cooling the reaction mixture, the unreacted vinyl acetate and aldehyde product should ideally separate from the solid IL. In this case, it would be important for the catalyst system to be completely soluble in the IL, and the amount of product / unreacted vinyl acetate that could be trapped during the solidifying of the IL would ideally be minimal.

Table 3.17: The influence of Solvent Innovation's sulphate-based ILs on hydroformylation activity and selectivity

Ionic Liquids	Phase?	TOF ^a (h ⁻¹)
[dmim][MeSO ₄]	Biphasic	0
[bmim][MeSO ₄]	Biphasic	0
[bmim][OcSO ₄]	Monophasic	0
[bdmim][OcSO ₄] *	Solid at rt	766
[bdmim][MDEGSO ₄]	Monophasic	0
[CABHEM][MeSO ₄]	Monophasic	0

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

** i:n ratio could not be obtained because a solid reaction mixture was obtained.*

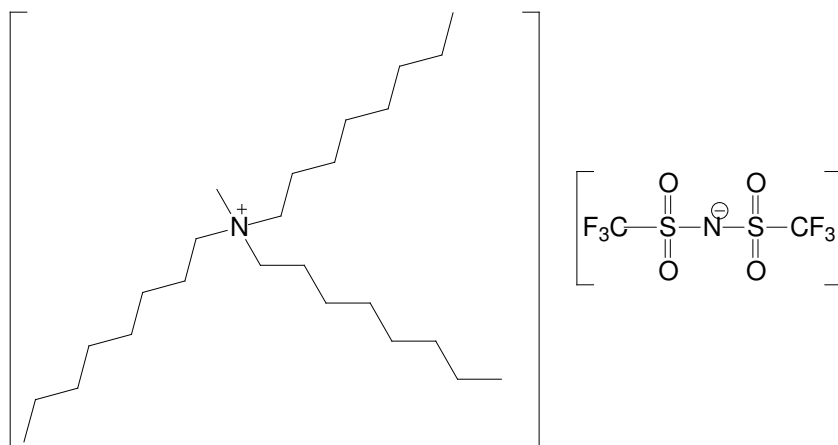
^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

No activity was observed for the sulfate-based ILs except for the [bdmim][OcSO₄] IL, where the reaction rate was slow. This particular IL is a solid at room temperature and has a melting point of 85 °C. The *i:n* ratio of this successful reaction with the [bdmim][OcSO₄] IL could not be calculated since the IL solidified at room temperature.

The reason why no activity was observed for the sulfate-based ILs is not known although it could be due to the co-ordinating sulfate anions or due to the impurities present in the IL. The stability of the MeSO₄ anion-based ILs is known to be very poor.²⁰⁶ They readily decompose in the presence of trace amounts of water to form methanol and [HSO₄]⁻. The OcSO₄ anion-based ionic ILs are however much more stable. No chloride or water impurities are present in these ILs since they have been synthesised by direct alkylation

3.3.1.9 IL combinations

Further investigations were performed into using combinations of ionic liquids to enhance ligand solubility and selectivity towards the *iso*-product. Due to the good solubility of the ligand in [NOc₃Me][N(SO₂CF₃)₂] (**3.5**) as well as the excellent selectivity achieved with this IL (compared to [bmim][N(SO₂CF₃)₂] and [NPhMe₃][N(SO₂CF₃)₂]), it was decided to use [NOc₃Me][N(SO₂CF₃)₂] in combination with the ILs that produced high rates in order to aid in the solubilisation of the ligand as well as to produce high *iso* : *normal* ratios. The solubility of the ligand in the [NBzEt₃][N(SO₂CF₃)₂] IL was good but selectivity need to be enhanced.



The $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL was therefore added to three ILs namely $[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$, $[\text{NPhMe}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ and $[\text{bmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ in 50/50 mixtures to observe the effect that the mixture would have on selectivity and activity (Table 3.18).

Table 3.18: The influence of combinations of ionic liquids (50/50 mixtures) on hydroformylation activity and selectivity

IL combinations	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	i:n	%-iso	%-CHO
3.5	1 200	1	>100:1	100	89
$[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$	7 327	7	23:1	96	96
3.5/ $[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$	2 925	3	>100:1	100	89
$[\text{NPhMe}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$	5 648	6	30:1	97	91
3.5/ $[\text{NPhMe}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$	2 935	3	>100:1	100	90
$[\text{bmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	4 500	4.5	26:1	96	94
3.5 / $[\text{bmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	2 812	3	82:1	99	86.5

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

The activity was found to be lower when using the combination of ionic liquids, compared to the single “high TOF” ionic liquid only. High selectivities to *iso*-product (up to 100:1) were observed in most cases. The activity was found to be lower in the mixtures, although the TOF was much higher than the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL on its own (TOF = 1 200 h⁻¹).

Further optimisation with the $[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL and **3.5** was undertaken to observe what the effect of adding **3.5** to the $[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL would be on hydroformylation activity and selectivity at varying vinyl acetate concentrations (2

M and 5 M vinyl acetate concentration was investigated). The results are shown in Table 3.19.

Table 3.19: The influence of combinations of ionic liquids (50/50 mixtures) on hydroformylation activity and selectivity

IL combinations, [VA]	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	i:n	%-iso	%-CHO
[NBzEt ₃][N(SO ₂ CF ₃) ₂], 5 M [VA]	4 037	4	26:1	96	94
3.5/ [NBzEt ₃][N(SO ₂ CF ₃) ₂], 5 M [VA]	2 281	2	76:1	99	91
[NBzEt ₃][N(SO ₂ CF ₃) ₂], 2 M [VA]	2 961	3	35:1	97	94
3.5/ [NBzEt ₃][N(SO ₂ CF ₃) ₂], 2 M [VA]	1 139	1	>100:1	100	89

1 mM Rh catalyst, 1:3 ligand excess, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

From the results, it was observed that the addition of the [NOc₃Me][N(SO₂CF₃)₂] IL results in a drop in activity and a concomitant increase in selectivity. The presence of 3.5, therefore, enhances the selectivity to a significant extent using both 2 M and 5 M vinyl acetate concentrations.

3.3.1.10 [NOc₃Me][N(SO₂CF₃)₂] IL as a co-solvent to an organic solvent

The [NOc₃Me][N(SO₂CF₃)₂] IL is known to be give high *iso* : *normal* ratios. Consequently, it was added as a co-solvent to a bulk solvent such as diphenyl ether to see the effect it has on the rate and selectivity. A 2 M vinyl acetate concentration was used which amounts to a volume of 7 mL. The solvent and co-solvent therefore has a volume of 33 mL. The results are reported in Table 3.20.

Table 3.20: The influence of [NOc₃Me][N(SO₂CF₃)₂] as a co-solvent in diphenyl ether as solvent on hydroformylation activity and selectivity

Diphenyl ether/ 3.5 (volumes added)	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	i:n	%-iso	%-CHO
Diphenyl ether	4 095	4	28:1	96.5	90
Diphenyl ether/ 3.5 (30/ 3 mL)	1 185	1	>100:1	99	89
Diphenyl ether/ 3.5 (31/ 2 mL)	1 931	2	39:1	97.5	89
Diphenyl ether/ 3.5 (31.5/1. 5 mL)	1 965	2	25:1	96	93
Diphenyl ether/ 3.5 (32/ 1 mL)	2 391	2	25:1	96	93

1 mM Rh catalyst, 1:3 ligand excess, 2 M vinyl acetate, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Adding [NOc₃Me][N(SO₂CF₃)₂] definitely enhanced the selectivity, although the rate was much lower. Reasons for this could be due to the differences in solubility of the CO/H₂ gases in the ionic liquid resulting in higher *i:n* ratios. It can be seen from the results that a specific amount of the [NOc₃Me][N(SO₂CF₃)₂] IL is needed to boost the *i:n* ratios. By decreasing the amounts of the [NOc₃Me][N(SO₂CF₃)₂] IL, the rates increased and this is accompanied by a concomitant decrease in the *i:n* ratios. Using 1.5 mL and less of **3.5**, the selectivity dropped significantly and the results corresponded more strongly with the reaction where no IL is present, although the rates are much lower than the reaction with only diphenyl ether.

3.3.1.11 Influence of IL impurities on hydroformylation

Impurities, and the amount thereof, in the ionic liquid can potentially influence the properties of the ionic liquid to a significant extent. The main impurities that could

be present in the ionic liquid are unreacted starting materials, halide impurities and water. Halide impurities can act as catalyst poisons, stabilising ligands, or nucleophiles depending on the nature of the reaction. Water also has a detrimental effect on the reactivity of the catalyst. Water is a co-ordinating protic solvent and is reactive with organometallic catalysts leading to catalyst poisoning.

The effect of different amounts of impurities in ILs on the hydroformylation activity and selectivity was tested by synthesising different batches of the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL and testing them in hydroformylation. The outcomes are reported in Table 3.21.

Table 3.21: The influence of different synthesis batches of $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ on the rate and selectivity of hydroformylation

Batch of $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	Method of purification	TOF ^a (h^{-1})
Batch 1	Not dried or washed	0
Batch 2	Washed 4X, not dried	0
Batch 3	Washed 4X and dried under vacuum for 20 hrs	0
Batch 4	Not washed, dried 20 hrs	0

1 mM Rh catalyst, 1:3 ligand excess, 5 M vinyl acetate, 85 °C, 20 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst. h^{-1}

The amount of impurity present in the different batches of ILs synthesised significantly affected the rate and selectivity of the hydroformylation reactions, as will become clear. The batches of the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL have a significant amount of water and chloride anions present; this had a detrimental effect on the rhodium catalyst since no activity was seen with any of the batches of ILs synthesised in which impurities were specifically not removed (Batches 1-4).

Four different additional batches of the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL were carefully synthesised separately and washed and dried to remove chloride and water impurities. The four different batches of the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL were tested for water and chloride analysis. Water present in the ILs was tested by Karl-Fischer titration and the amount of halide impurities was tested using a chemical method, namely the Volhard procedure for chloride anions. The quantities of water and chloride present in the different batches are shown in Table 3.22.

Table 3.22: Water and chloride content in different batches of $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$

Batch of $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	Water content (ppm)	Chloride content (wt %)
Batch 5	732	0.4254
Batch 6	450	0.4115
Batch 7	124	0.3855
Batch 8	177	0.5432

These four different batches of IL were then used as solvents in the hydroformylation of vinyl acetate. The influence of the different amounts of chloride and water present in the different batches of IL on hydroformylation activity and selectivity is shown Table 3.23.

Table 3.23: The influence of different “clean” batches of [NOc₃Me][N(SO₂CF₃)₂] on the hydroformylation activity and selectivity

Batch of [Noc ₃ Me][N(SO ₂ CF ₃) ₂]	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
Batch 5	1 200	1	>100:1	100	89
Batch 6	2 431	2	76:1	99	88
Batch 7	2 581	3	>100:1	99	90
Batch 8	2 266	2	>100:1	99	90

1 mM Rh catalyst, 1:3 ligand excess, 7 M vinyl acetate, 20 atmospheres of pressure, 85 °C

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

The amount of water and chloride impurities present in these four batches of IL seems to affect the rate and selectivity of the hydroformylation reaction, and the results indicate that water is an important factor. The results for the batch 5 IL show a much lower activity, highlighting the influence of the higher water content present in this IL.

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3.3.1.12 Inhibitor studies in [bmim][N(SO₂CF₃)₂]

Using the base case reaction conditions in [bmim][N(SO₂CF₃)₂], spiking experiments was performed to evaluate the influence of by-products formed during normal batch reactions. Substances tested were acetic acid, tripropylamine, and acrolein. The influence of additives on the rate of the reaction and the *i:n* ratio were subsequently investigated to determine whether the additives had an inhibiting / poisoning effect at 20 atmospheres of syngas pressure with 7 M vinyl acetate concentration. The results are shown in Table 3.24.

Table 3.24: The influence of additives in [bmim][N(SO₂CF₃)₂] on the hydroformylation activity and selectivity

Additives	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
None	4 500	4.5	26:1	96	94
Acetic acid	5 700	6	22:1	96	93
Tripropylamine	2 500	2	23:1	96	90
Acrolein	3 100	3	23:1	96	94
Acrolein (approx.1 mL)	No reaction				

1 mM Rh catalyst, 7 M vinyl acetate, 85 °C, 20 atmospheres of pressure, 0.04g (1000 ppm) additive

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

Acetic acid produced a higher TOF than the base case (5 700 *versus* 4 500). The initial induction time was about the same time as that for the base case, namely 15 minutes. It is known that acetylacetonate can be removed from rhodium-acac complexes in the presence of an acid. The present observation suggests that the acetylacetonate ligand ties up the rhodium in one or more dormant states under the current process conditions. This finding implies that pre-catalysts other than the one being investigated might further improve upon the findings of this study.

The presence of [Rh(acac)(CO)(P)] in solution under reaction conditions is unfavourable as this rhodium source is not being utilised in the reaction and therefore has negative implications. The presence of acetic acid has a positive effect on the rate of hydroformylation. It is thought that acetic acid protonates the acac anion of the [Rh(acac)(CO)(P)] species in the reaction mixture to form a *trans*-[Rh(CO)(OAc)(P)₂] complex, which is then converted into the active rhodium-hydride, [HRh(CO)₃(P)].

Tripropylamine gave a lower TOF and inhibited the hydroformylation reaction. This reaction had no induction period and started as soon as syngas was introduced, but in the greater scheme of things a rapid/slow induction period has little to no influence on the outcome of the reaction.

Acrolein (0.04 g, 1000 ppm) also produced a lower TOF with an induction period of one hour (compared to 15 minutes for the benchmark case). When acrolein was added in a larger quantity 1 mL), no reaction was observed at all. Acrolein therefore has some poisoning effect on the hydroformylation reaction.

3.3.2 Phosphine ligands

Other types of ligands, specifically phosphines, were investigated for the rhodium-catalysed hydroformylation of vinyl acetate in ILs (Figure 3.5). Ligands **3.6** and **3.7** were specifically synthesised, while the other phosphine ligands were purchased from Sigma-Aldrich.

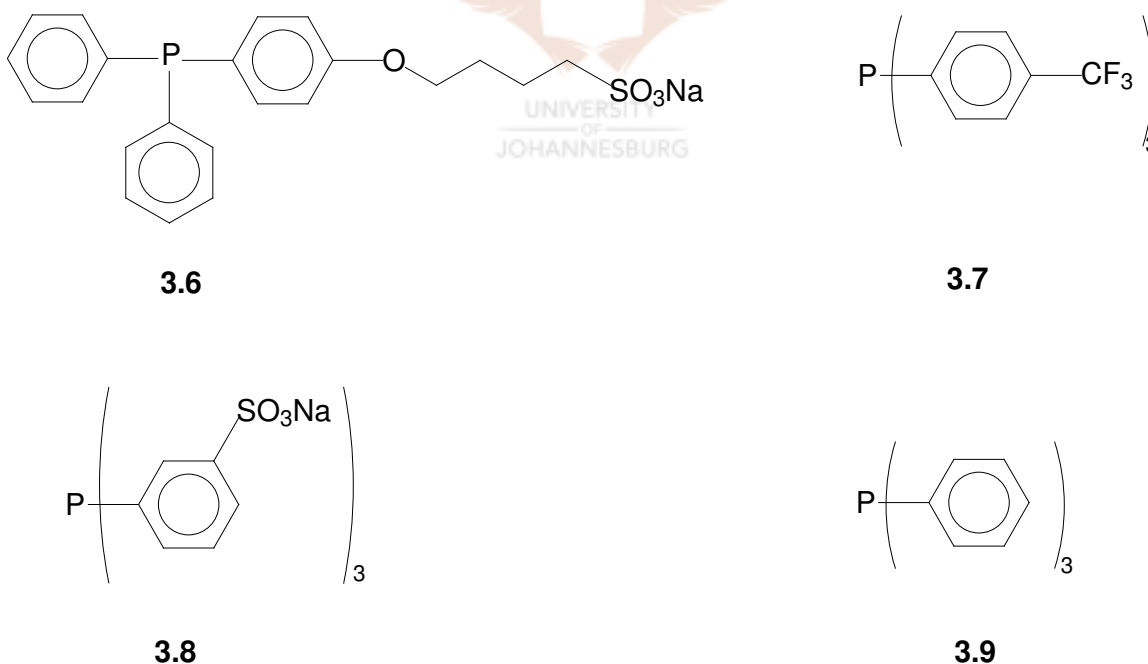


Figure 3.5: Phosphine-based ligands tested for hydrofomylation of vinyl acetate

The base case conditions for the hydroformylation of vinyl acetate using these phosphine ligands are shown in Table 3.25. It was noted that the reaction conditions were much harsher (higher temperature and pressure) for the phosphine ligand when compared to the phosphite ligands.

Table 3.25: Base case conditions for hydroformylation of vinyl acetate in ILs using phosphine ligands

Reaction parameter	Base case values
[Rh]	0.25 mmol L ⁻¹
Rh:PR ₃	1:15
[VA]	3 mol L ⁻¹
Pressure	70 atmospheres
Temperature	100 °C

mM – millimolar (mmol/liter reaction volume)

M – molar (mol/liter reaction volume)

[VA] – concentration of vinyl acetate. This concentration was calculated from the total volume of the mixture and the known amount of VA added, since the mixture is homogeneous.

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The different phosphine ligands were tested for the hydroformylation of vinyl acetate in the [bmim][N(SO₂CF₃)₂] IL and compared with the organic solvent, toluene. Hydroformylation results are shown in Table 3.26.

Table 3.26: The influence of different phosphine ligands on hydroformylation activity and selectivity in [bmim][N(SO₂CF₃)₂] and toluene

IL/solvent, Ligand used	TOF ^a (h ⁻¹)	S.T.Y ^b (mol L ⁻¹ h ⁻¹)	<i>i:n</i>	%-iso	%-CHO
[bmim][N(SO ₂ CF ₃) ₂] 3.6	496	0.1	>100:1	100	63
Toluene, 3.6	644	0.2	90:1	99	62
[bmim][N(SO ₂ CF ₃) ₂] 3.7	13 600	3	17:1	94.5	89
Toluene, 3.7	15 200	4	6:1	86	89
[bmim][N(SO ₂ CF ₃) ₂] 3.8	1 600	0.4	41:1	98	79
Toluene, 3.8	2 900	0.7	55:1	98	86.5
[bmim][N(SO ₂ CF ₃) ₂] 3.9	0	0	-	-	-
Toluene, 3.9	6 465	2	4:1	62	77

0.25 mM Rh catalyst, 3 M vinyl acetate, 1:15 ligand excess, 100 °C, 70 atmospheres of pressure

^aTOF – turn over frequency - moles product formed per mole of catalyst.h⁻¹

^bS.T.Y. – space time yield - moles product formed per L reactor content.h⁻¹

With ligand **3.6**, activity was very low for both the IL and toluene run but high *i:n* ratios were obtained for both solvents. The IL reaction produced only *iso*-product with no trace of the *n* - product being formed.

Ligand **3.7** gave very high activities in both the IL and toluene case (13 600 vs 15 200) respectively. The *i:n* ratio obtained in the IL was much higher compared to the toluene reaction (17:1 vs 6:1) but still lower than many of the better reactions.

Ligand **3.8** resulted in moderate activities and good *i:n* ratios for both the IL and toluene reactions although the toluene outperformed the IL reaction on all fronts.

Ligand **3.9** was tested in two ILs namely $[\text{NBnEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ and $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$. In both cases ligand **3.9** dissolved quite well in the ionic liquid due to its ionic character. There was activity in the $[\text{NBnEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL, although both the rates and selectivity were not spectacular. The GC trace for the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL showed no product formation. The reason for this is unclear. Interestingly, the colour of the reaction mixture was reddish-brown for the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL reaction and bright yellow for the $[\text{NBzEt}_3][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL reaction, indicating changes to the ligand sphere of the Rh complex.

Ligand **3.10** showed no activity in the IL although the rates in toluene were quite high. The reasons for the lack of activity in the IL are not known. The selectivity for the toluene reaction was, however, very poor.

3.3.3 Extraction of α -acetoxypionaldehyde from the $[\text{bmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL

A preliminary attempt was made at separating the aldehyde product from ionic liquids using supercritical carbon dioxide (scCO_2) since a monophasic system was observed. A first experiment was performed to see how feasible the use of scCO_2 would be to extract the product from the ionic liquid. The supercritical fluid system consists of two high pressure fluid delivery pumps connected to a 100 mL stainless steel autoclave. The autoclave outlet is connected to a variable flow heated restrictor system where atmospheric conditions are restored after the extraction.

The hydroformylation reaction was performed as usual in the 100 mL Parr autoclave using $[\text{bmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ as the IL. The reaction was allowed to run to completion observed by the consumption of syngas. The 100 mL Parr autoclave was then transferred to the supercritical fluid set-up and the scCO_2 lines connected to the inlet and outlet of the autoclave. The autoclave was heated to 40 °C and then pressurised with scCO_2 to 100 atmospheres. Within one hour, a yellow liquid was collected at the receiving end. When no further in the level of

the liquid being collected increase was observed, the procedure was stopped. The yellow liquid was analysed by ^1H and ^{31}P NMR spectroscopy to check for traces of ligand and / or IL. The NMR results showed traces of both the ligand and ionic liquid. The most probable explanation for the presence of the ionic liquid is that it was carried over by the scCO_2 due to high stirring / flow rates.

Re-use of the IL/catalyst system (after the extraction of the product by scCO_2) showed catalytic activity although this was not quantified. The CO_2 used was not of good quality (water was present), and in order to quantify TOF's and selectivities after extraction, high-grade CO_2 will have to be employed. This experiment was performed to prove the concept that scCO_2 can be used to extract the product from the IL.

3.4 Conclusions

In general, specific ionic liquid systems displayed the following advantages when compared to homogeneous systems:

- High $i : n$ ratios of aldehyde products are formed
- Low ligand : catalyst ratios are necessary for good selectivities

The percentage aldehyde product formed during hydroformylation is generally slightly lower in the IL case than in cases where an organic solvent was used, and catalyst stability in the presence of the low ligand ratios still has to be determined. It is possible that, if low excess ligand ratios are used, this could result in the formation of inactive dimeric/oligomeric rhodium clusters. In this scenario, there would be less of the active catalyst available, which would lead to a loss in activity. Also, dimer formation is known to occur at low pressures of hydrogen, low ligand concentrations and high rhodium concentrations. High pressure-IR would provide answers to whether the IL prevents the formation of these cluster rhodium species at the low ligand ratios.

An interesting observation was that the IL need not be used as solvent but could simply be used as an additive or co-solvent to an organic solvent. Lower activity was observed when the IL was added as an additive although very high regioselectivity was seen.

Impurities present in the IL have been shown to be of utmost importance on hydroformylation activity and selectivity. The presence of large quantities of water and chloride anions definitely deactivates the rhodium catalyst and prevents hydroformylation activity. Therefore very pure ILs need to be used when testing them for hydroformylation.

Depending on whether fast reaction rates or high regioselectivity is required, the IL can be tailored to fit the needs of the reaction. For example, with phosphite ligands, the aromatic-containing ammonium-based ILs tends to produce high reaction rates whereas the selectivity is low. The bulkier ammonium cations tend to give low rates although selectivity is very high. If the rate of the reaction could be compromised then the $[\text{NOc}_3\text{Me}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ IL would be an ideal candidate. This IL has shown to significantly enhance the selectivity of the hydroformylation reaction by merely adding the IL as an additive. Phosphonium-based ILs are not good at all for hydroformylation reactions if they are not purified sufficiently to be free of all unreacted phosphine. It has been noted that the unreacted phosphine inhibit the hydroformylation reaction significantly. Also, sulfate-based anions are detrimental to the hydroformylation catalyst and result in no activity. These anions are probably too coordinating. The imidazolium bistriflimide ILs produce moderate rates and selectivity and would essentially be a good candidate to choose as a solvent for the hydroformylation of vinyl acetate, although they are relatively expensive ILs.

Phosphine ligands in combination with ILs normally do not perform that well as hydroformylation solvent medium except for ligand **3.7**. Although high rates are also achieved when toluene was used as solvent with ligand **3.7**. Low rates or

none at all are achieved when using phosphine ligands in ILs. Therefore the phosphite ligands are the preferred ligands in ILs for the hydroformylation of vinyl acetate.

Due to the poor solubility of the [tris(2,4-di-*tert*-butylphenyl)phosphite] ligand in ILs, a ligand excess of 1:3 is preferred. Further studies need to be performed in order to investigate the optimum ligand excess required to aid in catalyst stability. Increasing the vinyl acetate concentration results in an increase in rate but a drop in selectivity. A 7 M vinyl acetate concentration is preferred since it aids in solubilising the ligand in the IL while still maintaining high rates and selectivity. An increase in rhodium concentration results in an increase in reaction rates and an increase in selectivity. The rhodium catalyst is, however, relatively expensive and a 1 mM catalyst concentration is therefore preferred. Lower syngas pressure results in a better selectivity although at the expense of the reaction rate. A pressure of 20 atmospheres of syngas seems to be the optimum with good rates and selectivity. Increasing the temperature results in an increase in reaction rates but a decrease in selectivity. A temperature of 85 °C was found to be the optimum temperature although higher temperatures such as 95 °C with [bmim][N(SO₂CF₃)₂] produced good rates and high selectivity. At such high temperatures, the vinyl acetate stability however poses a problem.

Overall, this study has been successful in determining many of the optimum reaction parameters under which vinyl acetate can be hydroformylated, affording reactions providing product in which the vast majority of the material is the desired *iso*-product in reactions that afford very high rates and selectivities for aldehydes. It is anticipated that these conditions would be applicable to a range of vinyl ethers, and this will form the basis of future studies in this group.

Chapter 4

Experimental Protocols

Standard Experimental Techniques

4.1 Gas Chromatography (GC)

4.1.1 GC method for analyses of metathesis reactions of 1-octene

GC analyses were performed on an Agilent 6890 gas chromatograph linked to a PC equipped with Class-VP software for recording and integration of chromatograms. A 50 m PONA column of 0.2 mm internal diameter and 0.5 μm film thickness with a temperature limit of 320 $^{\circ}\text{C}$ was utilised. A flame ionization detector (FID) was used for detection of reaction components with helium as the carrier gas. The GC method run time was approximately 16 min. Operating conditions for the GC are shown in Table 4.1.

Table 4.1: GC operating conditions for the metathesis of 1-octene

Operational parameter	Conditions
Carrier gas	Helium
Initial temperature	100 $^{\circ}\text{C}$
Initial wait	1 min
Temperature ramp	15 $^{\circ}\text{C}/\text{min}$
Final temperature	300 $^{\circ}\text{C}$
Final time	5 min
Injector temperature	280 $^{\circ}\text{C}$
Detector temperature	300 $^{\circ}\text{C}$

4.1.2 GC method for analyses of hydroformylation of vinyl acetate

GC analyses were performed on a Hewlett-Packard 5890 gas chromatograph linked to a PC equipped with a Class-VP software for recording and integration of chromatograms. A 50 m PONA column of 0.2 mm internal diameter and 0.5 μm film thickness was utilised. A flame ionization detector (FID) was used for detection of reaction components with nitrogen as the carrier gas. Operating conditions for the GC is shown in Table 4.2.

Table 4.2: GC operating conditions for hydroformylation of vinyl acetate

Operational parameter	Conditions
Carrier gas	Nitrogen
Initial temperature	50 °C
Initial wait	5 min
Temperature ramp	10 °C/min
Final temperature	180 °C
Final time	5 min
Injector temperature	280 °C
Detector temperature	300 °C

4.2 Ionic liquids, Solvents and Reagents

4.2.1 Ionic liquids

The following ILs were purchased from Solvent Innovation and used as received:

- [1-ethyl-3-methylimidazolium][bromide], [emim][Br]
- [1-ethyl-2,3-dimethyl-imidazolium][bromide], [edmim][Br]
- [*N*-butylpyridinium][chloride], [C₄Py][Cl]
- [4-methyl-*N*-butylpyridinium][chloride], [(CH₃)(C₄Py)][Cl]
- [1-butyl-3-methylimidazolium][octylsulfate], [bmim][OcSO₄]
- [1-butyl-2,3-dimethylimidazolium][2-(2-methoxyethoxy)ethylsulfate], [bdmim][MDEGSO₄]
- [Cocosalkylpentaethoxymethylammonium][methylsulfate], [CABHEM][MeSO₄]

The following phosphonium ILs were received from Cytec and used as received:

- [Triisobutylmethylphosphonium][tosylate], [(ⁱC₄)(C)P][Tos]
- [Trihexyltetradecylphosphonium][bistriflimide], [(C₆)₃C₁₄P][N(SO₂CF₃)₂]
- [Trihexyltetradecylphosphonium][hexafluorophosphate], [(C₆)₃C₁₄P][PF₆]
- [Trihexyltetradecylphosphonium][dicyanamide], [(C₆)₃C₁₄P][N(CN)₂]
- [Trihexyltetradecylphosphonium][diisobutylphosphinate], [(C₆)₃C₁₄P][diisobutylphosphinate]

The following phosphonium IL was purchased from Merck and used as received:

- [Trihexyltetradecylphosphonium][tris(pentafluoroethyl)trifluorophosphate], [(C₆)₃C₁₄P][(CF₃CF₂)₃PF₃]

4.2.1.1 Water and halide content in ionic liquids

The water content of the ILs were determined by Karl-Fischer titration and were normally in the range of < 1000 ppm. Halide impurities can be qualitatively determined by addition of silver nitrate to an aqueous solution. Halides were quantitatively determined by the wet-chemical Volhard method, and were generally in the region of < 1000 ppm.



4.2.2 Solvents

Toluene was dried over sodium-benzophenone under an argon atmosphere until the solution turned a deep blue colour. The solvent was freshly distilled before use.

Dichloromethane, chloroform and 1,1,1-trichloroethane were respectively heated over CaH₂ under argon followed by distillation.

4.2.3 Reagents

1-Octene (99%, Aldrich) was percolated with neutral alumina before use.

Vinyl acetate (99+%, Aldrich) was used as received.

Diphenyl ether (99+%, Aldrich) was degassed with argon prior to use.

Acrolein (99+%, Aldrich) was used as received.

Tripropylamine (99+%, Aldrich) was used as received.
Acetic acid (99.7%, Aldrich) was used as received.
Rh(CO)₂(acac) (98%, Aldrich) was used as received.
Tris(2,4-di-*tert*-butylphenyl)phosphite (99+%, Aldrich) was used as received.
Tris(trifluoromethyl)phenylphosphine (99+%, Aldrich) was used as received.
Triphenylphosphine (99+%, Aldrich) was used as received.
Monosulfonated triphenylphosphine (99+%, Aldrich) was used as received.
Phosphine ligand **3.6** was obtained from the University of Johannesburg and used as received.

4.3 Spectroscopic Methods

4.3.1 Nuclear magnetic resonance (NMR)

NMR spectra were recorded on a Varian Inova 400 instrument. All NMR spectra were recorded in CDCl₃ at room temperature with TMS as an internal standard. Chemical shift are reported as parts –per million (ppm) and coupling constants (*J*) in Hertz. The ¹H and ¹³C spectra of certain ILs were recorded to confirm the nature of the cations. It has been found that the ¹H spectra of ILs containing the same cation, *e.g.* [bmim]⁺, but different anions, *e.g.* [Cl]⁻ and [BF₄]⁻, resemble each other closely.

4.4 Chemical methods

4.4.1 Metathesis of 1-octene in ILs

a) General experimental protocol for metathesis of 1-octene

Reactions were carried out in a 100 mL three-necked flask equipped with a reflux condenser, thermometer and septum (Figure 4.1). The reflux condenser was connected to a cooling bath (8 - 10 °C) to prevent loss of olefin. The top of the condenser was connected to a cold trap, followed by a bubbler in order to monitor liquid losses and gas emissions. The thermometer was positioned in the reaction solution to monitor the temperature. A needle inserted through the septum and connected to an argon supply was used to ensure a slow and steady

stream of argon bubbles so as to eliminate evolved ethylene from the reaction mixture. Gas flow through the solution was controlled by means of needle valves and a bubbler to ensure a constant gas flow. The reaction mixture was stirred by means of a magnetic stirrer bar. Samples (1 mL) were taken at regular intervals via a syringe through the septum, and transferred to a 3 mL sample vial. The reaction was terminated by quenching by addition of one drop of a hydroperoxide such as *tert*-butyl hydroperoxide (TBHP). The quenched sample was diluted with toluene and analysed by GC. Conversions are reported as the mole fraction of 1-octene that has been converted to products (either the desired cross metathesis product, secondary metathesis products (SMPs) or internal isomers of 1-octene).

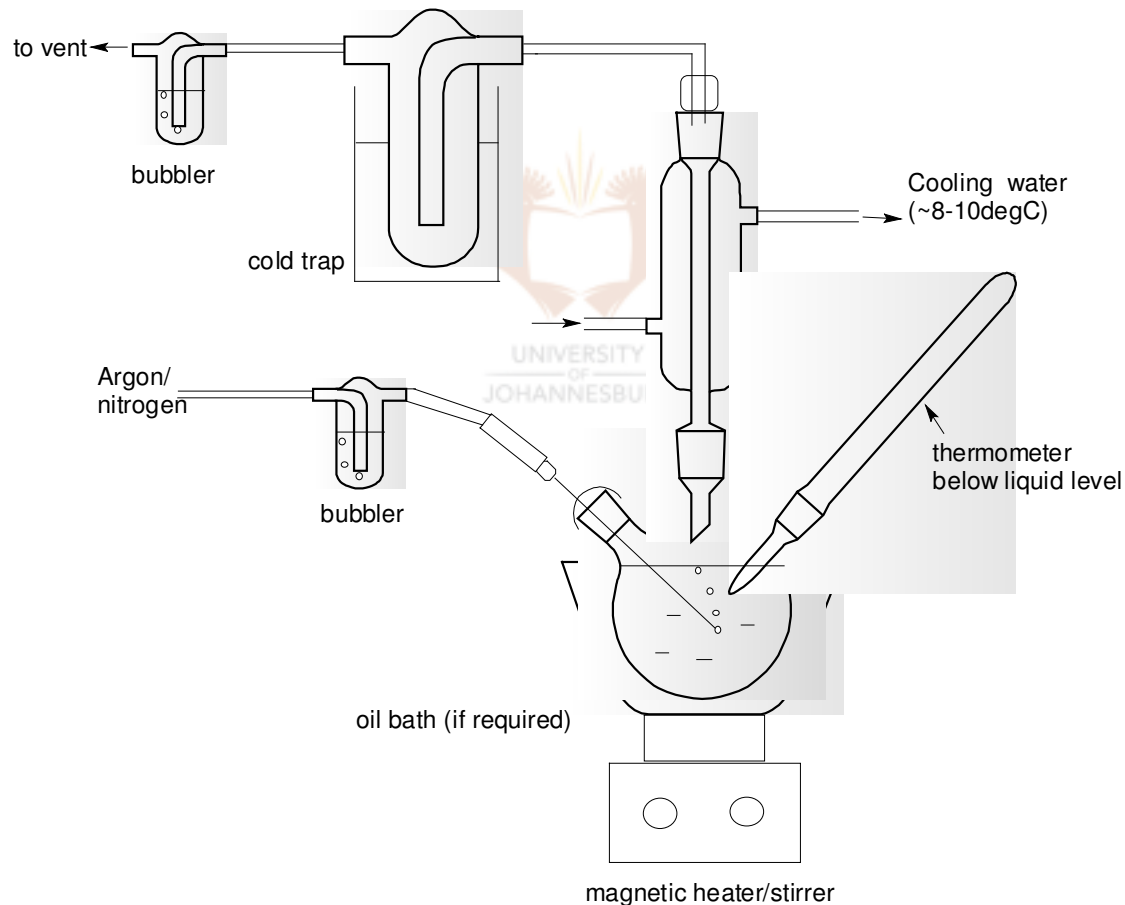


Figure 4.1: Experimental set-up for metathesis of 1-octene

i) Metathesis reaction in organic solvent

1-Octene (16 mL) in the presence of organic solvent (2 mL) was stirred at reaction temperature and catalyst was then added to the mixture. The reactions were all homogeneous. Samples were taken in minute (5, 10, 15, 20, 40, 60, 120, 240, 300 time) interval and quenched with peroxide.

For example, 1-octene (16 mL, 101.5 mmol) was stirred at 40 °C until the reaction mixture reached the reaction temperature. The Hoveyda-Grubbs catalyst (12.5 mg, 0.0199 mmol, 0.02 mol%) was added to the solvent mixture. Samples were taken at regular time intervals over a five-hour reaction. Samples were quenched by addition of one drop of TBHP to the sample vial that was then diluted with toluene.

ii) Metathesis reaction in IL

In the case of the IL reaction, 1-Octene (16 mL) was stirred in the presence of the selected IL (2 mL) at the desired reaction temperature and the catalyst was then added to the mixture. The reaction mixtures were all biphasic. Samples were taken in minute (5, 10, 15, 20, 40, 60, 120, 240, 300 time) intervals from the top organic layer and quenched with peroxide.

For example, 1-octene (16 mL, 101.5 mmol) and [edmim][N(SO₂CF₃)₂] (2 mL, 7.403 mmol) were stirred at 40 °C until the reaction mixture had reached the correct reaction temperature. The Hoveyda-Grubbs catalyst (12.5 mg, 0.0199 mmol, 0.02 mol%) was added to the mixture. Samples were taken at regular time intervals over a five-hour period. Samples were quenched by addition of one drop of TBHP to the sample vial that was then diluted with toluene.

iii) Metathesis reaction in the presence of additives

1-Octene (16 mL) was mixed with the organic solvent or IL (2 mL), the additive was stirred in at the reaction temperature, and the catalyst was then added to the mixture. Samples were taken in minute (5, 10, 15, 20, 40, 60, 120, 240, 300 time) intervals and quenched with peroxide.

For example, 1-octene (16 mL, 101.5 mmol), the [edmim][N(SO₂CF₃)₂] IL (2 mL, 7.403 mmol) and phenol additive (0.94 g, 9.974 mmol, 500 eq.) were stirred at 40 °C until the reaction mixture had reached the reaction temperature. The Hoveyda-Grubbs catalyst (12.5 mg, 0.0199 mmol, 0.02 mol%) was added to the mixture. Samples were taken at regular time intervals over a five-hour period. Samples were quenched by addition of one drop of TBHP to the sample vial that was then diluted with toluene.

b) Feed preparation

1-Octene (Aldrich, 99 %) was employed as the olefin since it is relatively non-volatile, inexpensive and freely available. Olefins are known to readily form peroxides in the presence of trace amounts of oxygen. Feed preparation was therefore required due to the fact that the build-up of peroxide in the olefinic starting material can lead to a dramatic effect on catalyst activity and lifetime. Experimental results however suggest that feed preparation was not necessary. This study was however performed using purified feed throughout. The olefin was therefore passed through a column of neutral alumina (Aluminium oxide, activated, neutral, Brockmann I, standard grade, ~150 mesh, Aldrich) and stored over alumina (15 g per 100 mL olefin) in the absence of light for at least 24 hours and further handled under argon. The olefin was degassed by bubbling argon through it for approximately 30 minutes, prior to its use.

c) Calculations

Conversion of 1-octene = $100 - (\text{moles of 1-octene} / \text{moles of all products} \times 100)$

Selectivity towards 7-tetradecene = $(\text{moles of 7-tetradecene} / (\text{moles of 7-tetradecene} + \text{moles of isomers} + \text{moles of SMPs})) \times 100$

4.4.2 Hydroformylation of vinyl acetate in ILs

a) General experimental protocol for hydroformylation of vinyl acetate

A 100 mL stainless steel Parr reactor was employed for evaluation of hydroformylation activity and selectivity. The requisite amount of the rhodium pre-catalyst $[\text{Rh}(\text{CO})_2(\text{acac})]$ and ligand [tris(2,4-di-*tert*-butylphenyl)phosphite] were weighed out and dissolved in vinyl acetate. The mixture was transferred to the Parr reactor, and the ionic liquid to be used was transferred by syringe into the reactor (to give a reaction mixture that was no more than 40% of the total reactor volume). The reaction mixture was degassed with nitrogen and subsequently pressure tested for leaks by pressurising the reactor to 40 atmospheres with nitrogen and then releasing the pressure. The ballast vessel was pressurised to the required pressure with syngas (1:1 CO/H_2 mixture) and allowed to stabilise at that pressure. The regulator connected to the syngas line was adjusted to the required reaction pressure, and the temperature was allowed to increase to the required reaction temperature while stirring at about 1250 rpm. At the reaction temperature, the reactor was pressurised with syngas to the required pressure. The supply was then immediately changed to the ballast vessel set up. The drop in pressure in the ballast vessel was used as an indication of the consumption of syngas and was used to quantify the number of moles of vinyl acetate reacted assuming that there were no detectable by-products which means that the assumption was that every mole of syngas reacted with vinyl acetate to produce the anticipated aldehyde mixture. A spreadsheet was drawn up to quantify the results by converting the observed pressure drop to the number of moles using an ideal gas equation.

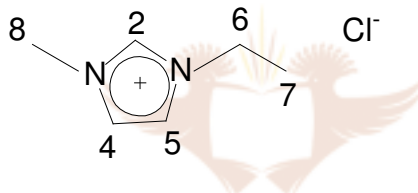
4.5 IL preparation

Generally, literature methods were used to prepare the ILs of this study.²⁰⁷

4.5.1 Synthesis of chloride-based ILs

a) Preparation of [1-ethyl-3-methylimidazolium][chloride], [emim][Cl]²⁰⁸

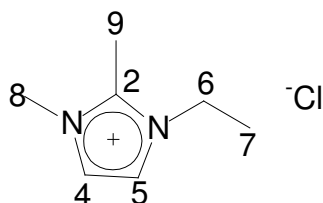
Chloroethane gas (647.3 g, 10.032 mol, 4 eq.) was condensed into a Parr reactor containing 1-methylimidazole (206.0 g, 2.508 mol, distilled from CaH₂) using a mixture of acetone and dry ice for cooling. The mixture was then stirred at 70 °C for two days. The excess chloroethane was allowed to boil off through a drying tube, resulting in a slightly off-white hygroscopic solid product. The solid IL was recrystallised from a mixture of acetonitrile and ethyl acetate, to provide the product as an off-white solid.



¹H NMR (400 MHz, CDCl₃): δ = 1.38 (t, 3H, J = 7.0 Hz, H-7); 3.88 (s, 3H, H-8); 4.18 (q, 2H, J = 7.3 Hz, H-6); 7.45 (s, 1H, H-4); 7.50 (s, 1H, H-5); 10.21 (s, 1H, H-2).

b) Preparation of [1-ethyl-2,3-dimethylimidazolium][chloride], [edmim][Cl]²⁰⁸

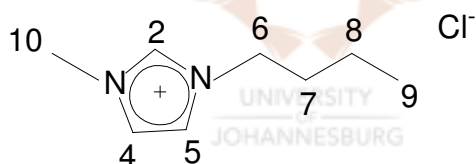
The same procedure as described for [emim][Cl] was followed except that the 1,2-dimethylimidazole was employed in the synthesis.



^1H NMR (400 MHz, CDCl_3): δ = 1.31 (t, 3H, J = 7.4 Hz, H-7); 2.65 (s, 3H, H-9); 3.83 (s, 3H, H-8); 4.18 (q, 2H, J = 7.3 Hz, H-6); 7.58 (d, 1H, J = 1.7 Hz, H-5); 7.67 (d, 1H, J = 1.8 Hz, H-4).

c) Preparation of [1-butyl-3-methylimidazolium][chloride], [bmim][Cl]²⁰⁹

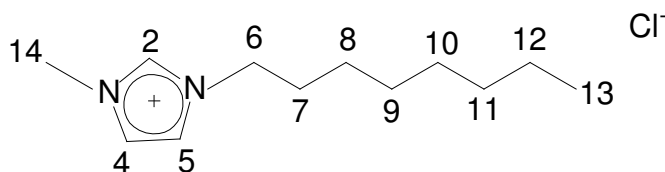
Freshly distilled 1-methylimidazole (206.0 g, 2.508 mol, distilled from CaH_2) and excess chlorobutane (928.7 g, 10.032 mol, 4 eq.) was heated at 75 °C under reflux for 48 hours under an inert atmosphere. After 2 hours, the mixture turned cloudy. After 24 hours, two layers were observed, with the IL as the bottom phase and the top layer the reactants. After 48 hours, the top layer could not be detected and a yellow bottom layer has formed. The excess chlorobutane was removed under vacuum at 75 °C. The yellow IL product was poured into an aluminium tray in the glove box and allowed to cool. The yellow IL product solidified on cooling as an off-white solid and broken into pieces and stored under argon.



^1H NMR (400 MHz, CDCl_3): δ = 0.96 (t, 3H, J = 7.3 Hz, H-9); 1.34-1.44 (m, 2H, H-8); 1.87-1.96 (m, 2H, H-7); 4.14 (s, 3H, H-10); 4.34 (t, 2H, J = 7.3 Hz, H-6); 7.78 (t, 1H, J = 1.8 Hz, H-5); 7.89 (t, 1H, J = 1.8 Hz, H-4); 10.60 (br s, 1H, H-2).

d) Preparation of [1-octyl-3-methylimidazolium][chloride], [omim][Cl]²⁰⁹

The same procedure as described for [bmim][Cl] was followed except that the chlorooctane was employed as alkylating agent in the synthesis.

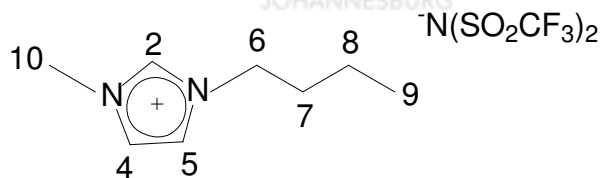


^1H NMR (400 MHz, CDCl_3): δ = 0.68 (t, 3H, J = 7.0 Hz, H-13); 1.00-1.20 (m, 10H, H-8, H-9, H-10, H-11 and H-12); 1.69-1.79 (m, 2H, H-7); 3.95 (s, 3H, H-14); 4.15 (t, 2H, J = 7.5 Hz, H-6); 7.40 (t, 1H, J = 1.7 Hz, H-5); 7.70 (t, 1H, J = 1.7 Hz, H-4); 10.39 (br s, 1H, H-2).

4.5.2 Synthesis of bistriflimide-based ILs

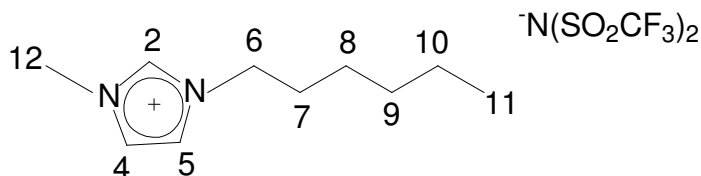
a) Preparation of [1-alkyl-3-methylimidazolium][bistriflimide], [Rmim][N(SO₂CF₃)₂] where R = ethyl, butyl, hexyl and octyl²¹⁰

To an aqueous solution of [Rmim][Cl] (0.441 mol) was added an aqueous solution of lithium bistriflimide (LiBTA) (0.485 mol, 1.1 eq. In 100 mL water) and the mixture was stirred overnight at ambient temperature. The IL produced formed a separate phase from the aqueous layer. The IL layer was separated and washed with distilled water (10 x 100 mL) to remove unreacted chloride salt and LiBTA. The aqueous layer used for washing the IL was tested for chloride using AgNO_3 until no AgCl precipitation was observed. The IL was subsequently heated under vacuum at 120 °C overnight to remove residual water.



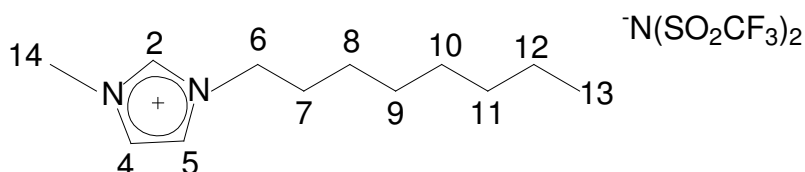
^1H NMR (400 MHz, CDCl_3): δ = 0.96 (t, 3H, J = 7.5 Hz, H-9); 1.32-1.42 (m, 2H, H-8); 1.80-1.89 (m, 2H, H-7); 3.91 (s, 3H, H-10); 4.17 (t, 2H, J = 7.5 Hz, H-6); 7.26 (d, 1H, J = 1.7 Hz, H-5); 7.31 (d, 1H, J = 1.9 Hz, H-4); 8.74 (s, 1H, H-2).

^{13}C NMR (75.4 MHz, CDCl_3): δ = 13.3 (C-9); 19.5 (C-8); 31.6 (C-7); 35.2 (C-10), 48.7 (C-6); 120.8 and 121.4 (C-4 and C-5); 122.5 (C-2).



^1H NMR (400 MHz, CDCl_3): δ = 0.87 (t, 3H, J = 7.1 Hz, H-11); 1.27-1.36 (m, 6H, H-10, H-9 and H-8); 1.80-1.91 (m, 2H, H-7); 3.92 (s, 3H, H-12); 4.15 (t, 2H, J = 7.6 Hz, H-6); 7.33-7.35 (m, 2H, H-4 and H-5); 8.67 (br s, 1H, H-2).

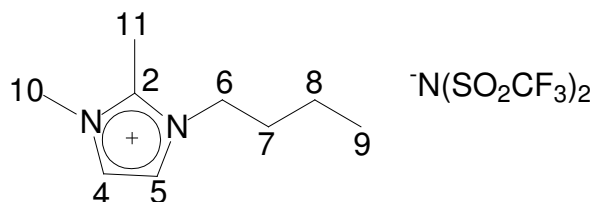
^{13}C NMR (75.4 MHz, CDCl_3): δ = 13.8 (C-11); 22.2 (C-10); 25.6 (C-9); 29.9 (C-8); 30.9 (C-7); 50.1 (C-6); 118.2 (C-12); 121.4 (C-4 and C-5); 135.8 (C-2).



^1H NMR (400 MHz, CDCl_3): δ = 0.70-0.75 (m, 3H, H-13); 0.90-1.15 (m, 10H, H-8, H-9, H-10, H-11 and H-12); 1.30-1.40 (m, 2H, H-7); 3.16 (s, 3H, H-14); 3.50 (t, 2H, J = 7.5 Hz, H-6); 6.60 (d, 1H, J = 1.3 Hz, H-4); 6.82 (d, 1H, J = 1.3 Hz, H-5); 7.82 (s, 1H, H-2).

b) Preparation of [1-alkyl-2,3-dimethylimidazolium][bistriflimide], [Rdmim][N(SO₂CF₃)₂] where R = ethyl, butyl and octyl²¹⁰

The same procedure as described for [Rmim][bistriflimide] was followed except that the [Rdmim][Cl] salt was employed in the synthesis.

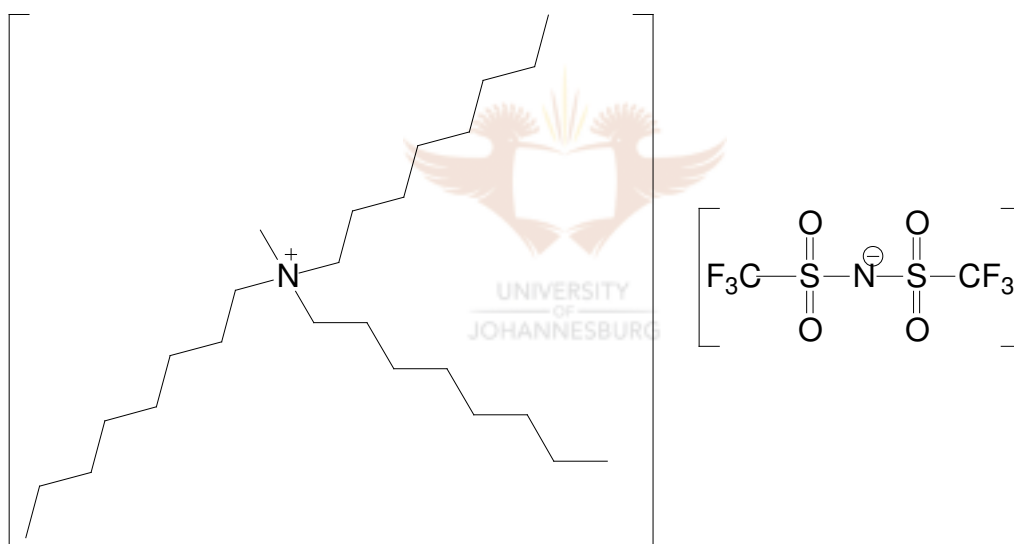


^1H NMR (400 MHz, CDCl_3): δ = 0.98 (t, 3H, J = 7.3 Hz, H-9); 1.34-1.44 (m, 2H, H-8); 1.75-1.84 (m, 2H, H-7); 2.61 (s, 3H, H-11); 3.81 (s, 3H, H-10); 4.06 (t, 2H, J = 7.6, H-6); 7.19 (d, 1H, J = 2.2 Hz, H-5); 7.22 (d, 1H, J = 2.2 Hz, H-4).

^{13}C NMR (75.4 MHz, CDCl_3): δ = 9.4 (C-9); 13.4 (C-2-CH₃); 19.5 (C-8); 31.5 (C-7); 35.3 (C-6); 48.5 (C-10); 120.8 and 121.4 (C-4 and C-5); 122.5 (C-2).

**c) Preparation of [trioctylmethylammonium][bistriflimide],
[NOc₃Me][N(SO₂CF₃)₂]²¹¹**

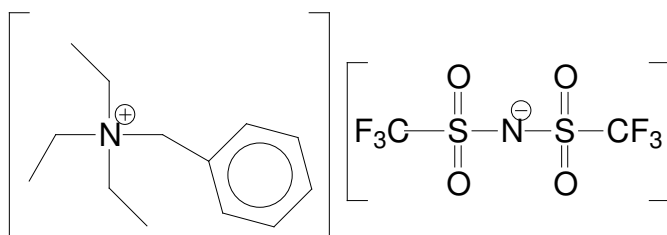
Lithium trifluoromethanesulfonimide (LiBTA) (117.2 g, 0.408 mol, 1.1 eq.) in distilled water (150 mL) was added to a solution of [trioctylmethylammonium][chloride] (150.0 g, 0.371 mol) in distilled water (300 mL) at room temperature. The reaction mixture was allowed to stir for 24 hours and the bottom ionic liquid layer was collected and washed with water (10 x 200 mL) to remove LiCl that was formed as a by-product. The IL could be washed with water to a point where no traces of halide ions were detectable in the washing water by simple titration with AgNO₃. The ionic liquid was then dried on the rotary evaporator at 120 °C under maximum vacuum for 24 hours to give a the bright yellow [NOc₃Me][N(SO₂CF₃)₂] IL.



**d) Preparation of [triethylbenzylammonium][bistriflimide],
[NBzEt₃][N(SO₂CF₃)₂]²¹²**

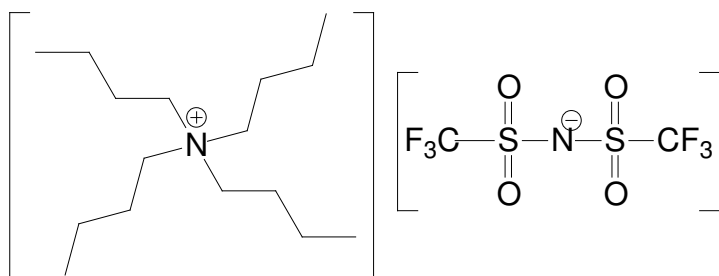
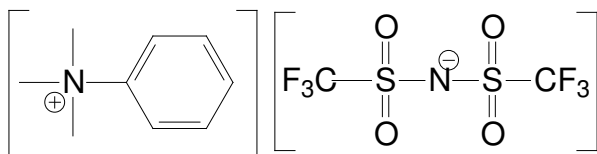
Lithium trifluoromethanesulfonimide (LiBTA) (139.0 g, 0.483 mol, 1.1 eq.) in distilled water (50 mL) was added to a solution of [triethylbenzylammonium]chloride (100.0 g, 0.439 mol) in distilled water (100 mL) at room temperature. A pure white solid formed immediately upon addition of the LiBTA/water solution hindering stirring of the reaction mixture. Chloroform (100

mL) was added to dissolve the solid ionic liquid and the reaction mixture was stirred overnight. The ionic liquid was a solid at room temperature but liquid at temperatures greater than 30 °C. The aqueous layer was extracted with chloroform (3 x 50 mL) and the organic layers subsequently washed with water (10 x 150 mL) to remove LiCl that had formed as a by-product. The chloroform was removed *in vacuo* to give [triethylbenzylammonium][N(SO₂CF₃)₂] as a room temperature white solid.



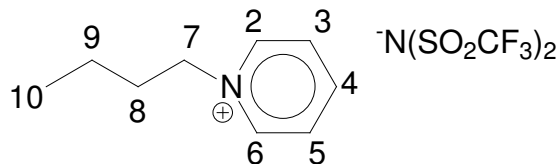
e) Preparation of [trimethylphenylammonium][bistriflimide], [NPhMe₃][N(SO₂CF₃)₂] and [tetrabutylammonium][bistriflimide], [NBu₄][N(SO₂CF₃)₂]²¹²

The same procedure as described for [triethylbenzylammonium][N(SO₂CF₃)₂] was followed except the [trimethylphenylammonium][chloride] and [tetrabutylammonium][chloride] salts were employed, respectively, in the syntheses.

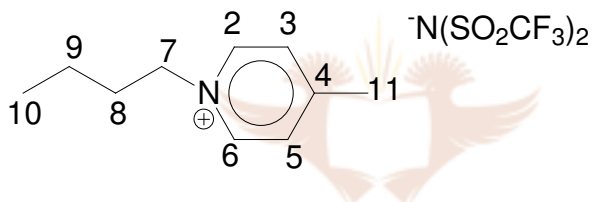


f) Preparation of [*N*-alkylpyridinium][bistriflimide], [C_n Py][N(SO₂CF₃)₂]²¹⁰

The same procedure as described for [Rmim][bistriflimide] was followed except the [C_n Py][Cl] or [(CH₃)(C₄Py)][Cl] salt was employed in the synthesis.

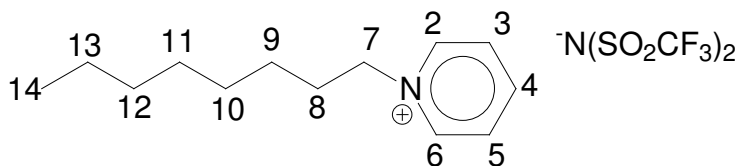


¹H NMR (400 MHz, CDCl₃): δ = 0.98 (t, 3H, *J* = 7.3 Hz, H-10); 1.34-1.46 (m, 2H, H-9); 1.93-2.04 (m, 2H, H-8); 4.54-4.64 (m, 2H, H-7); 7.99-8.10 (m, 2H, H-3 and H-5); 8.45-8.53 (m, 1H, H-4); 8.81 (d, 2H, *J* = 5.1 Hz, H-2 and H-6).



¹H NMR (400 MHz, CDCl₃): δ = 0.96 (t, 3H, *J* = 7.1 Hz, H-10); 1.32-1.43 (m, 2H, H-9); 1.90-1.99 (m, 2H, H-8); 2.66 (s, 3H, H-11); 4.50 (t, 2H, *J* = 7.6 Hz, H-7); 7.81 (d, 2H, *J* = 6.4 Hz, H-3 and H-5); 8.61 (d, 2H, *J* = 6.6 Hz, H-2 and H-6).

¹³C NMR (75.4 MHz, CDCl₃): δ = 13.2 (C-10); 18.9 (C-11); 21.7 (C-9); 33.0 (C-8); 61.3 (C-7); 118.2 and 121.6 (C-3 and C-5); 129.2 (C-4); 143.3 and 159.9 (C-2 and C-6).



¹H NMR (400 MHz, CDCl₃): δ = 0.86 (t, 3H, *J* = 6.8 Hz, H-14); 1.18-1.40 (m, 10H, H-13, H-12, H-11, H-10, and H-9); 1.94-2.05 (m, 2H, H-8); 4.59 (t, 2H, *J* =

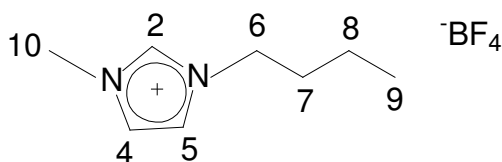
7.6 Hz, H-7); 8.05 (t, 2H, $J = 6.8$ Hz, H-3 and H-5); 8.48 (t, 1H, $J = 7.8$ Hz, H-4); 8.83 (d, 2H, $J = 5.4$ Hz, H-2 and H-6).

^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 13.9$ (C-14); 22.5 (C-13); 25.9 (C-12); 28.8 (C-11); 28.8 (C-10); 31.5 (C-9); 31.5 (C-8); 62.2 (C-7); 128.7 (C-3 and C-5); 144.4 (C-4); 145.5 (C-2 and C-6).

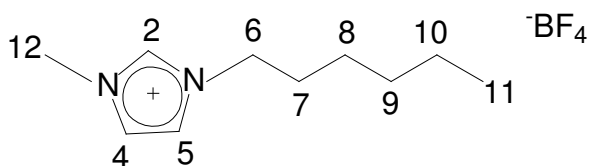
4.5.3 Synthesis of tetrafluoroborate-based ILs

a) Preparation of [1-alkyl-3-methylimidazolium][tetrafluoroborate], [Rmim][BF₄] where R = butyl and hexyl²¹³

An aqueous solution of tetrafluoroboric acid (120 mL of a 48% aqueous solution, 2 eq.) was added dropwise to a cooled aqueous solution of [Rmim][Cl] (0.459 mol in 100 mL of water). After the addition of tetrafluoroboric acid, the mixture was stirred at ambient temperature for 24 hours. The IL was extracted from the aqueous phase using dichloromethane (5 x 50 mL). The dichloromethane phase was then washed with distilled water (10 x 100 mL) to remove unreacted chloride salt and acid. The aqueous layer used for washing the organic phase was tested for residual acid using litmus paper and AgNO_3 was used to test for residual chloride. The organic phase was subsequently heated under vacuum at 120 °C overnight to remove residual water and dichloromethane, to produce a light yellow product.



^1H NMR (400 MHz, CDCl_3): $\delta = 0.96$ (t, 3H, $J = 6.7$ Hz, H-9); 1.23-1.43 (m, 2H, H-8); 1.74-1.92 (m, 2H, H-7); 3.96 (s, 3H, H-10); 4.09-4.23 (m, 2H, H-6); 7.23-7.45 (m, 2H, H-4 and H-5); 8.83 (s, 1H, H-2).



^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.3 Hz, H-11); 1.22-1.36 (m, 6H, H-10, H-9 and H-8); 1.80-1.92 (m, 2H, H-7); 3.94 (s, 3H, H-12); 4.17 (t, 2H, J = 7.3 Hz, H-6); 7.39 (t, 1H, J = 1.8 Hz, H-4); 7.42 (t, 1H, J = 1.8 Hz, H-5); 8.73 (s, 1H, H-2).

^{13}C NMR (75.4 MHz, CDCl_3): δ = 13.8 (C-11); 22.3 (C-10); 25.7 (C-9); 29.9 (C-8); 30.9 (C-7); 36.1 (C-6); 49.9 (C-12); 122.3 and 123.7 (C-4 and C-5); 136.1 (C-2).

b) Preparation of [1-hexyl-2,3-dimethylimidazolium][tetrafluoroborate], [hdmim][BF₄]²¹⁴

The same procedure as described for [Rmim][tetrafluoroborate] was followed except that the [C_nPy][Cl] salt was employed in the synthesis.

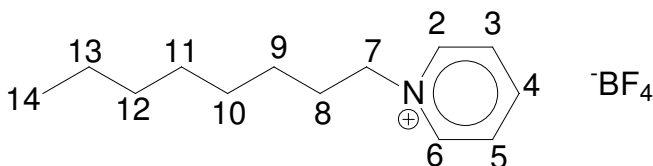


^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.3 Hz, H-11); 1.24-1.36 (m, 6H, H-10, H-9 and H-8); 1.71-1.81 (m, 2H, H-7); 2.58 (s, 3H, H-13); 3.78 (s, 3H, H-12); 4.04 (t, 2H, J = 7.6 Hz, H-6); 7.25 (d, 1H, J = 2.2 Hz, H-5); 7.31 (d, 1H, J = 2.2 Hz, H-4).

^{13}C NMR (75.4 MHz, CDCl_3): δ = 9.2 (C-11); 13.8 (C-13); 22.6 (C-10); 25.5 (C-9); 29.9 (C-8); 31.1 (C-7); 34.9 (C-6); 48.4 (C-12); 120.7 and 122.6 (C-4 and C-5); 144.2 (C-2).

c) Preparation of [*N*-octylpyridinium][tetrafluoroborate], [C₈Py][BF₄]²¹⁴

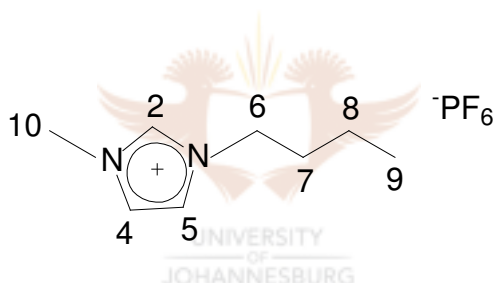
The same procedure as described for [Rmim][tetrafluoroborate] was followed except that the [C_nPy][Cl] salt was employed in the synthesis.



4.5.4 Synthesis of hexafluorophosphate-based ILs

a) Preparation of [1-butyl-3-methylimidazolium][hexafluorophosphate], [bmim][PF₆]²⁰⁹

An aqueous solution of hexafluorophosphoric acid (200 mL of a 60% aqueous solution) was added dropwise to a cooled aqueous solution of [bmim][Cl] (118.2 g, 0.677 mol in 150 mL of water). After the addition of hexafluorophosphoric acid, the mixture was stirred at room temperature for 6 hours. The IL formed a separate layer from the aqueous layer. The IL layer was separated and washed with distilled water (10 x 100 mL) to remove chloride salts and residual acid. The aqueous layer used for washing the organic phase was tested for residual acid using litmus paper and AgNO₃ was used to test for residual chloride. The IL was subsequently heated under vacuum at 120 °C overnight to remove residual water, affording the product as a light yellow liquid.



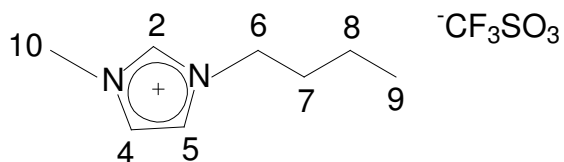
¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 3H, *J* = 7.0 Hz, H-9); 1.25-1.35 (m, 2H, H-8); 1.77-1.86 (m, 2H, H-7); 3.86 (s, 3H, H-10); 4.12 (t, 2H, *J* = 7.0 Hz, H-6); 7.30 (br s, 1H, H-5); 7.34 (br s, 1H, H-4); 8.37 (br s, 1H, H-2).

4.5.5 Synthesis of trifluoromethanesulfonate-based ILs

a) Preparation of [1-butyl-3-methylimidazolium][trifluoromethanesulfonate], [bmim][CF₃SO₃]²¹⁴

Trifluoromethanesulfonic acid (55 mL, 0.630 mol, 1.1 eq.) was added dropwise to a cooled aqueous solution of [bmim][Cl] (100.0 g, 0.543 mol in 150 mL of water). After the addition of the acid, the mixture was stirred at ambient temperature for 24 hours. The IL was extracted from the aqueous phase using dichloromethane (5 x 50 mL). The dichloromethane phase was then washed with distilled water (10 x 100 mL) to remove chloride salts and acid. The

aqueous layer used for washing the organic phase was tested for residual acid using litmus paper and AgNO₃ was used to test for residual chloride. The organic phase was subsequently heated under vacuum at 120 °C overnight to remove residual water and dichloromethane, to produce a yellowish IL.



¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, 3H, *J* = 7.3 Hz, H-9); 1.36 (sx, 2H, *J* = 7.8 Hz, H-8); 1.81-1.90 (m, 2H, H-7); 3.97 (s, 3H, H-10); 4.19 (t, 2H, *J* = 7.6 Hz, H-6); 7.40 (t, 1H, *J* = 1.7 Hz, H-4); 7.43 (t, 1H, *J* = 1.8 Hz, H-5); 9.05 (br s, 1H, H-2).

¹³C NMR (75.4 MHz, CDCl₃): δ = 13.2 (C-9); 19.3 (C-8); 31.9 (C-7); 36.3 (C-10); 49.8 (C-6); 119.0 (C-4 and C-5); 125.4 (C-2).



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