DOCTOR OF PHILOSOPHY

Recovery of Precious Metals from Secondary Sources

McAtamney, Darren Leigh Phillip

Award date: 2018

Awarding institution: Queen's University Belfast

Terms of use
All those accessing thesis content in Queen’s University Belfast Research Portal are subject to the following terms and conditions of use

• Copyright is subject to the Copyright, Designs and Patent Act 1988, or as modified by any successor legislation
• Copyright and moral rights for thesis content are retained by the author and/or other copyright owners
• A copy of a thesis may be downloaded for personal non-commercial research/study without the need for permission or charge
• Distribution or reproduction of thesis content in any format is not permitted without the permission of the copyright holder
• When citing this work, full bibliographic details should be supplied, including the author, title, awarding institution and date of thesis

Take down policy
A thesis can be removed from the Research Portal if there has been a breach of copyright, or a similarly robust reason. If you believe this document breaches copyright, or there is sufficient cause to take down, please contact us, citing details. Email: openaccess@qub.ac.uk

Supplementary materials
Where possible, we endeavour to provide supplementary materials to theses. This may include video, audio and other types of files. We endeavour to capture all content and upload as part of the Pure record for each thesis. Note, it may not be possible in all instances to convert analogue formats to usable digital formats for some supplementary materials. We exercise best efforts on our behalf and, in such instances, encourage the individual to consult the physical thesis for further information.

Download date: 17. Mar. 2022
Recovery of Precious Metals from Secondary Sources

By

Darren Leigh Phillip McAtamney, MSci (Hons)

A Thesis presented for the degree of

Doctor of Philosophy

To the School of Chemistry and Chemical Engineering

Queen’s University Belfast

February 2018
Declaration

I declare that the work presented within this thesis, except where otherwise stated, is based on my own research carried out in The School of Chemistry and Chemical Engineering, Queen’s University Belfast, between October 2013 and October 2016.

Signed

Date
Abstract

The aim of the project is to develop environmentally friendly methods for the recovery of Pd and Pt from catalytic converters, and of Au from electronics using non-toxic reagents. Currently the recovery of Pd and Pt is achieved using strong acids such as aqua regia, while CN\(^{-}\) is used to recover Au. In this work, the use of recyclable systems based on ionic liquids (ILs) or deep eutectic solvents (DESs) in combination with ligands and/or oxidants was explored. For all the new recovery methods, attempts at understanding the processes occurring were made.

The synthesis of dione and dithione ligands [1,4-dimethyl-2,3-piperazinedione (Me\(_2\)pipd), 1,4-dimethyl-2,3-perhydrodiazepinedione (Me\(_2\)dazd), 1,4-dimethyl-2,3-piperazinedithione (Me\(_2\)pipdt), and 1,4-dimethyl-2,3-perhydrodiazepinedithione (Me\(_2\)dazdt)] and their iodine adducts ([Me\(_2\)pipdtH]I\(_3\), Me\(_2\)dazdt/2I\(_2\)), which could be used for the dissolution of Pd and Pt was investigated. Me\(_2\)pipd was successfully synthesised using the conventional method reported in literature (2 hours, reflux). A novel mechanochemical method was also been developed which proceeded within 1 minute at 5 Hz. Me\(_2\)dazd can also be synthesised conventionally (50%, 24 hours, reflux) or mechanochemically (53%, 30 minutes). Me\(_2\)pipdt can be synthesised conventionally with a yield of 31% after 4 hours at reflux. An alternative sonochemical reaction has been developed with a comparable yield (35%) within the same reaction time. The adduct [Me\(_2\)pipdtH]I\(_3\) was also successfully synthesised.

The mild conditions which would lead to the dissolution of Pd, Pt, and Au were examined. Ligands Me\(_2\)pipd, Me\(_2\)dazd, Me\(_2\)pipdt, as well as a range of commercially available ligands (e.g. 2, 2′-bipyridine and 1, 10-phenanthroline) were used in combination with various oxidants (e.g. I\(_2\) and HNO\(_3\)). Only small amounts of Pd could be dissolved in several halide containing ILs but the best results were achieved in DESs, where metal solutions up to 200 mM (Reline 200) and 300 mM (Ethaline 200) were obtained, using a Pd:I\(_2\) ratio of 1:4. Au powder was dissolved in several non-halide ILs using Ph\(_3\)P:I\(_2\) (1:1). The highest Au concentration (57.1 mM) was obtained in [BMIM]OTf after 72 hours.
NMR and cyclic voltammetry (CV) studies were used to characterise the metal compounds formed in the solutions. Mixed chloride/iodide square-planar Pd(II) complexes are believed to form in the DESs. Solutions of Pd (50 mM) and I$_2$ (200 mM) in either DES produce CVs that are similar not only to each other, but also those of PdI$_2$. Peaks related to the I$^-$/I$_2$/I$_3^-$ system can be seen, as well as the reduction of Pd(II) and stripping of the metal. Dissolved Pd was recovered by electrodeposition from Reline 200 containing I$_2$ and the mixture could be recycled at least twice. Pd was also successfully recovered from a used catalytic converter as proven by cyclic voltammetry, SEM, and EDX spectroscopy.

A Ph$_3$P:I$_2$ mixture in [BMIM]OTf was able to dissolve Au at room temperature without the need of anhydrous/anaerobic conditions, unlike in conventional solvents. The Au complex formed has not been confirmed but appears to be a unique, stable product, possibly [Au(PPh$_3$)$_2$]OTf, [AuI$_3$(PPh$_3$)$_2$] or [(Ph$_3$PO)$_2$H][AuI$_2$]. The electrochemical behaviour of Ph$_3$P:I$_2$ (1:1) in [BMIM]OTf is dominated by that of I$_2$. Approximately 53% of Au was successfully recovered via electrodeposition and the remaining solution successfully re-used for further Au dissolution. Using Ph$_3$P:I$_2$ in [BMIM]OTf, metals could be dissolved from electronics and subsequently electrodeposited. EDX data showed that the main component of the deposit was Sn, but results indicated that some Au had also been deposited.
I would like to thank many people for their help and support throughout this research.

Firstly I would like to thank my supervisor Dr Cristina Lagunas for her patience, advice and guidance when carrying out this research and while writing up the results presented.

I would also like to thank my secondary supervisor Dr Geoff McCullough, whose knowledge on catalytic converters was extremely helpful, and the QUB Strategic Priority Studentships Programme which provided the funding that allowed the research to be performed.

Besides my advisors I wish to thank my colleagues in Lab 01.430 for all of their help and assistance.

Also the technicians of Queen's University Belfast from ASEP and QUILL have been extremely helpful with carrying out my characterisations.

A special thanks must be made for my family. They have supported me from childhood through to adulthood, and have always been there when I needed them. Their continued presence and motivation has made the PhD journey possible.
# Table of Contents

**List of Abbreviations**

**Chapter 1. General Introduction**

1.1 An Introduction to the Precious Metals used in this work

1.1.1 Discovery and Occurrence

1.1.2 Recovery and purification

1.1.2.1 Pd and Pt

1.1.2.2 Au

1.1.3 Properties

1.1.3.1 Pd

1.1.3.2 Pt

1.1.3.3 Au

1.1.4 Oxidation States

1.1.4.1 Pd and Pt

1.1.4.2 Au

1.1.5 Uses

1.1.5.1 Pd

1.1.5.2 Pt

1.1.5.3 Au

1.2 Catalytic Converters

1.2.1 Composition

1.2.2 Deactivation

1.2.3 Current recovery methods

1.2.3.1 Hydrometallurgical processes

1.2.3.2 Pyrometallurgical processes

1.3 Adducts for the dissolution of Pd and Pt

1.3.1 1,4-dimethyl-2,3-piperazinedione (Me_2pipd) (1) and 1,4-dimethyl-2,3-perhydrodiazepinedione (Me_2dazd) (2)

1.3.2 1,4-dimethyl-2,3-piperazinedithione (Me_2pipdt) (6) and 1,4-dimethyl-2,3-perhydrodiazepinedithione (Me_2dazdt) (7)

1.3.3 Dithione/iodine adducts and their application in the dissolution of PGMs
1.4 Adducts for the dissolution of Au
1.5 Alternative methods of Synthesis
   1.5.1 Mechanochemical Synthesis
   1.5.2 Microwave Synthesis
   1.5.3 Sonochemical Synthesis
1.6 Ionic Liquids (ILs)
   1.6.1 History
   1.6.2 Structure
   1.6.3 Properties
      1.6.3.1 Melting Point
      1.6.3.2 Viscosity
      1.6.3.3 Density
      1.6.3.4 Polarity
      1.6.3.5 Hydrophobicity/Hydrophilicity
      1.6.3.6 Electrochemical Window
      1.6.3.7 Ionic Conductivity
      1.6.3.8 Stability
   1.6.4 Synthesis
   1.6.5 Purification
   1.6.6 Dissolution of I₂ in ILs
      1.6.6.1 Ionic Conductivity
      1.6.6.2 ¹H-NMR spectroscopy
      1.6.6.3 Raman spectroscopy
   1.6.7 Applications in the extraction of Precious Metals
1.7 Deep Eutectic Solvents (DESs)
   1.7.1 History
   1.7.2 Structure
   1.7.3 Properties
      1.7.3.1 Melting Point
      1.7.3.2 Viscosity
      1.7.3.3 Density
1.7.3.4 Stability
1.7.3.5 Electrochemical Window (ECW)
1.7.3.6 Ionic Conductivity
1.7.4 Synthesis
1.7.5 Dissolution of I₂ in DESs
1.7.6 Applications in the extraction of Precious Metals
1.8 Electrochemistry
1.8.1 Basic Theory
1.8.2 Different types of electrochemical procedures
1.8.2.1 Voltammetry
1.8.2.2 Electrodeposition
1.8.3 Applications in the deposition of Precious Metals
1.8.3.1 Pd
1.8.3.2 Pt
1.8.3.3 Au
1.9 The Aim of the Project

Chapter 2. A comparison of methodologies for the synthesis of Dithiooxamides
2.1 Aims
2.2 Results and Discussion
2.2.1 Synthesis
2.2.1.1 Me₂pipd (1)
2.2.1.1a Conventional Synthesis
2.2.1.1b Mechanochemical Synthesis
2.2.1.1c Comparison of methods
2.2.1.2 Me₂pipdt (6)
2.2.1.2a Conventional Synthesis
2.2.1.2b Mechanochemical Synthesis
2.2.1.2c Microwave Synthesis
2.2.1.2d Sonochemical Synthesis
2.2.1.2e Comparison of methods
2.2.1.3 Me₂dazd (2)
2.2.1.3a Conventional Synthesis  
2.2.1.3b Mechanochemical Synthesis  
2.2.1.3c Comparison of methods  
2.2.1.4 Me$_2$Pdzdt (7)  
2.2.1.4a Conventional Synthesis  
2.2.1.4b Sonochemical Synthesis  
2.2.1.4c Comparison of methods  
2.2.1.5 [Me$_2$pipdtH]$_3$ (12)  
2.2.2 Dissolution of Pd(0) and Pt(0) using [Me$_2$pipdtH]$_3$ (12)  
2.2.2.1 Pd  
2.2.2.2 Pt  
2.3 Characterization of compounds  
2.3.1 Me$_2$pipd (1)  
2.3.1.1 $^1$H-NMR  
2.3.1.2 $^{13}$C-NMR  
2.3.1.3 IR  
2.3.2 Me$_2$pipdt (6)  
2.3.2.1 $^1$H-NMR  
2.3.2.2 $^{13}$C-NMR  
2.3.2.3 UV/Vis  
2.3.2.4 IR  
2.3.2.5 PXRD  
2.3.3 Me$_2$Pdzd (2)  
2.3.3.1 $^1$H-NMR  
2.3.3.2 $^{13}$C-NMR  
2.3.3.3 IR  
2.3.3.4 PXRD  
2.3.4 Me$_2$Pdzdt (7)  
2.3.4.1 $^1$H-NMR  
2.3.4.2 $^{13}$C-NMR  
2.3.5 [Me$_2$pipdtH]$_3$ (12)
2.3.5.1 $^1$H-NMR
2.3.5.2 Raman
2.3.5.3 PXRD
2.3.5.4 CHNS
2.4 Conclusions
2.5 Future Work

Chapter 3. Dissolution of Pd, Pt, and Au in Ionic Liquids and Deep Eutectic Solvents

3.1 Aims
3.2 Pd
3.2.1 Imidazolium ILs
3.2.1.1 Use of adduct [Me$_2$pipdtH]I$_3$ (12)
3.2.1.2 Use of I$_2$ (no added ligand)
3.2.1.3 Use of other oxidants (no added ligand)
3.2.1.4 Addition of both a ligand and an oxidant
3.2.1.5 Summary of results in imidazolium ILs and further studies in [BMIM]Br
3.2.2 [P$_{66614}$]Cl
3.2.3 DESs
3.2.4 Comparison of IL and DES results
3.3 Pt
3.4 Au
3.5 Conclusions
3.6 Future Work

Chapter 4. Raman and electrochemical investigation of dissolved Pd in Reline 200 and Ethaline 200 with subsequent removal from a catalytic converter

4.1 Aims and Introduction
4.2 Reline 200
4.2.1 Raman Spectroscopy
4.2.2 Cyclic Voltammetry
4.2.2.1 Electrochemical Window (ECW) of Reline 200
4.2.2.2 Pd(0)
Chapter 5. Dissolution of Au in [BMIM]OTf: $^{31}$P-NMR spectroscopic and electrochemical investigation, and removal of Au from electronic components

5.1 Aims and Introduction

5.2 Monitoring Experiments using NMR spectroscopy

5.2.1 Initial experiments in [BMIM]OTf

5.2.2 NMR spectra of Ph$_3$P:I$_2$ (1:1) in other ILs ([BMIM]NTf$_2$, [HMIM]NTf$_2$, and [C$_{10}$MPyr]NTf$_2$)

5.2.3 Further monitoring experiments in [BMIM]OTf

5.2.4 NMR spectra of Au dissolved in [BMIM]OTf

5.3 Cyclic Voltammetry

5.3.1 Electrochemical Window (ECW) of [BMIM]OTf

5.3.2 Addition of Ph$_3$P:I$_2$ (1:1)

5.3.3 Dissolution of Au

5.4 Electrodeposition

5.5 Recovery of Au metal from an electronic device
5.6 Conclusions

5.7 Future Work

6.1 Synthesis of Me₂pipd (1)
   6.1.1 Conventional Synthesis
   6.1.2 Mechanochemical Synthesis

6.2 Synthesis of Me₂pipdt (6)
   6.2.1 Conventional Synthesis
   6.2.2 Attempts to prepare (6) mechanochemically
   6.2.3 Microwave Synthesis
   6.2.4 Sonochemical Synthesis

6.3 Synthesis of Me₂dazd (2)
   6.3.1 Conventional Synthesis
   6.3.2 Mechanochemical Synthesis

6.4 Synthesis of Me₂dazdt (7)
   6.4.1 Conventional Synthesis
   6.4.2 Attempts to prepare (7) via sonochemical synthesis

6.5 Synthesis of [Me₂pipdtH]₃ (12)

6.6 Synthesis of Ph₃P=O.H₂O₂ and Ph₃P=O
   6.6.1 Synthesis of Ph₃P=O.H₂O₂
   6.6.2 Synthesis of Ph₃P=O

6.7 Synthesis of Ionic Liquids
   6.7.1 Synthesis of [BMIM]Cl
   6.7.2 Synthesis of [OMIM]Cl
   6.7.3 Synthesis of [BMIM]NTf₂
   6.7.4 Synthesis of [BMIM]OTf

6.8 Synthesis of DESs
   6.8.1 Reline 200
   6.8.2 Ethaline 200
   6.8.3 Imiline 700

6.9 Dissolution Studies
6.9.1 Pd and Pt

6.9.2 Au

6.10 Monitoring Experiments

6.10.1 Ph₃P:I₂ (1:1) (17) monitoring experiments

6.10.2 Ph₃P, Ph₃P=O, and Ph₃P=O.H₂O₂ monitoring experiments in [BMIM]OTf

6.10.3 Ph₃P monitoring experiments in [BMIM]OTf with known amounts of H₂O

6.11 Cyclic Voltammetry

6.12 Electrodeposition

References
List of Abbreviations

Acronyms and Abbreviations

anti = antisymmetric
asym = asymmetric
[BMIM]$^+ = 1$-butyl-3-methylimidazolium
[BMPy]$^+ = 1$-butyl-1-methylpyrrolidinium
Bu = Butyl
[C$_{10}$MIM]$^+ = 1$-decyl-3-methylimidazolium
[C$_{10}$MPy]$^+ = N$-decyl-N$-methylpyrrolidinium
Cat$^+ = Cation
[CyMPy]$^+ = 1$-cyanomethylpyridinium
CV = Cyclic Voltammogram / Voltammetry
DCA$^- = $ dicyanamide
DCM = dichloromethane
DCE = dichloroethane
[DEME]$^+ = N, N$-diethyl-N$-methyl-N$-(2$-methoxyethyl)$ammonium
DES = Deep Eutectic Solvents
DMF = dimethylformamide
DMSO = dimethyl sulfoxide
ECW = Electrochemical Window
EDX = Energy-Dispersive X-ray
[EMIM]$^+ = 1$-ethyl-3-methylimidazolium
eq = equation(s)/equivalent(s)
Et = Ethyl
EU = European Union
FAP$^- = $ tris(perfluoroalkyl)trifluorophosphate
GC = Glassy Carbon
HBA = Hydrogen Bond Acceptor
HBD = Hydrogen Bond Donor
[HMIM]$^+$ = 1-hexyl-3-methylimidazolium
HOMO = Highest Occupied Molecular Orbital
[HPy]$^+$ = 1-hexylpyridinium
IL = Ionic Liquid
INC = International Nickel Company
IR = Infra-Red
LAG = Liquid Assisted Grinding
LR = Lawesson’s Reagent, $p$-methoxyphenylthioxophosphate
LUMO = Lowest Unoccupied Molecular Orbital
LV = Linear Voltammogram / Voltammetry
max = maximum
m = medium
MEK = Methyl Ethyl Ketone
Me$_2$dazd = 1,4-dimethyl-2,3-perhydrodiazepinedione
Me$_2$dazdt = 1,4-dimethyl-2,3-perhydrodiazepinedithione
Me$_2$pipd = 1,4-dimethyl-2,3-piperazinedione
Me$_2$pipdt = 1,4-dimethyl-2,3-piperazinedithione
NMR = Nuclear Magnetic Resonance
NTf$_2^-$ = bis(trifluoromethylsulfonyl)amide
Oct = Octyl
[OMIM]$^+$ = 1-octyl-3-methylimidazolium
OSC = Oxygen Storage Component
OTf$^-$ = trifluoromethanesulfonate
[P$_{66614}$]$^+$ = trihexyl(tetradecyl)phosphonium
PGM = Platinum Group Metal
[PMIM]$^+$ = 1-propyl-3-methylimidazolium
PXRD = Powder X-Ray Diffraction
RPM = Revolutions per minute
r.t. = room temperature
RTIL = Room Temperature Ionic Liquid
s = strong
SEM = Scanning Electron Microscopy
sh = shoulder
sym = symmetric
TBANO₃ = tetrabutylammonium nitrate
[TBMA]⁺ = tributylmethylammonium
THF = Tetrahydrofuran
TLC = Thin-Layer Chromatography
TWC = Three Way Catalysts
UV/Vis = Ultraviolet/Visible Spectroscopy
vol = volume

Abbrevations and Recommended Values of Some Fundamental Constants

F = Faraday constant (96485 C mol⁻¹)

Units

°C = degrees Celsius
μm = micrometre
Å = Ångström
C = Coulombs
cm = centimetre
eV = electron Volt
g = gram
h = hour
Hz = Hertz
K = Kelvin
kcal = kilocalorie
kHz = kilohertz
km = kilometre
m = metre
M = Molar
mg = milligram
MHz = Megahertz
mins = minutes
mL = millilitre
mm = millimetre
mM = millimolar
mmol = millimole
mol = mole
mS = millisiemen
mV = millivolt
nm = nanometre
oz = ounce
p = para
Pa = Pascal
ppm = parts per million
s = second
V = Volt
W = Watts

Symbols
$ = dollar
e^- = electron
m = number of moles
n = required/lost electrons
Q = Charge
t = time
T = Temperature

Greek symbols
δ = chemical shift
ν = frequency
γ = gamma
π = pi
λ = wavelength
Chapter 1. General Introduction

Precious metals are naturally occurring metals with high economic value. The metals are less reactive than most elements and usually possess a lustre while also exhibiting a ductile property. The best known of these metals are Au and Ag, but also include the Platinum Group Metals (PGMs). The PGMs include Ru, Rh, Pd, Os, Ir, and Pt.

The recovery of precious metals is quite a significant issue, because of their increased use in technical applications and the fact that they usually have no equal to replace them. As a result, the recovery and re-use of these metals from technical devices which have reached the end of their lifetimes is an important area of research. One area in which increasing amounts of some of these metals are used is in automotive catalysts, i.e. catalytic converters, which use metals such as Pd, Pt and Rh. Other applications include electronic devices, such as mobile phones, laptops, and computers, which utilise multiple metals, e.g. Au, Ag, Pd and Pt, and fuel cells which use mainly Pt but also Ru.\textsuperscript{1,2}

The reason for more precious metals being used in catalytic converters is due to the fact that emission limits are becoming tighter. Taking the EU as an example, in 1993 the fitting of catalytic converters became mandatory for all new cars.\textsuperscript{3} Then, in 2009, legislation was passed that outlined the mandatory emission reduction targets for new cars. Under the cars regulation the fleet average to be achieved by all new cars was 130 g of CO\textsubscript{2} per kilometre (g km\textsuperscript{-1}) by 2015. This target began being phased in in 2012 and will subsequently be reduced to 95 g km\textsuperscript{-1} in 2020.\textsuperscript{4} Reaching these targets will therefore require a combination of new engine technology and the use of more precious metals. This demand in PGM is evident from the data shown in Table 1.1 (gathered by Johnson Matthey) where there is typically a greater demand for Pt and Pd than there is a supply.\textsuperscript{5,6} Pt was found to have a deficit of 652000 oz in 2015 and a deficit of 422000 oz in 2016. For Pd the deficits were 427000 and 651000 oz in 2015 and 2016 respectively.\textsuperscript{7,8}
Table 1.1 Supply and demand (in ‘000 oz) of Pt (black) and Pd (red) from 2010-14 with those associated with catalytic converters in brackets

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Supply</th>
<th>From Recycling</th>
<th>Total Gross Demand</th>
<th>Total net Demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>6050</td>
<td>7355</td>
<td>1830 (1085)</td>
<td>1850 (1310)</td>
</tr>
<tr>
<td>2011</td>
<td>6485</td>
<td>7360</td>
<td>2060 (1240)</td>
<td>2385 (1695)</td>
</tr>
<tr>
<td>2012</td>
<td>5650</td>
<td>6530</td>
<td>2040 (1130)</td>
<td>2290 (1670)</td>
</tr>
<tr>
<td>2013</td>
<td>5740</td>
<td>6430</td>
<td>2075 (1275)</td>
<td>2460 (1860)</td>
</tr>
<tr>
<td>2014</td>
<td>5100</td>
<td>6204</td>
<td>2284 (1421)</td>
<td>2690 (2106)</td>
</tr>
</tbody>
</table>

Catalytic converters, although a major user of the metals, can also prove to be a significant recovery resource if spent catalysts are properly recycled. Within these converters are the noble metals Pt, Pd, and Rh, three of the six Platinum Group Metals (PGMs). As of 31 Jan 2018 the prices of these metals were 1006.05, 1033.55, and 1780.00 $ oz\(^{-1}\) for Pt, Pd, and Rh, respectively.\(^9\) On the same date, the price of Au was 1340.60 $ oz\(^{-1}\). Considering the current difficulty in obtaining pure amounts of these metals, such as decreasing frequency in finding new deposits and the typically impure alloys they are found as, it is inevitable that the cost will increase due to the general difficulty itself increasing.

1.1 An Introduction to the Precious Metals used in this work

1.1.1 Discovery and Occurrence

Pt was discovered as far back as the 16\(^{th}\) century in Columbia and before 1914 came mainly from there and Russia. Today Pt is virtually all obtained from Canada, South Africa, and Russia, with these ores containing less than an ounce ton\(^{-1}\) (just over 28 g) of Pt.\(^{10}\) Pd was discovered in the early 19\(^{th}\) century in 1803 during the refinement of Pt of which it occurs in association.\(^{10}\) Until 1930 it was relatively rare. At this point in time the International Nickel Company (INC) began to produce the metal in significant
amounts via the electrolytic refining of Cu-Ni ores.\textsuperscript{11} It is possible to find Au in one of two forms. The first is alluvial Au which can be extracted as nuggets or grains and it is this form that lead to the Au rushes of the mid to late 19\textsuperscript{th} century. The second way to find Au is as ore in quartz and albite rocks.\textsuperscript{12}

\textit{1.1.2 Recovery and purification}

\textit{1.1.2.1 Pd and Pt}

All precious metals can be recovered from anode slimes produced during the electrolytic recovery of Cu or Ni or the Ni refining Mond carbonyl process.\textsuperscript{10} Aqua regia is first used to treat the Pt metal concentrates to dissolve Pt, Pd, and any Au present. Pd is oxidised to +2 while Pt, which is easier to oxidise, finishes in the +4 oxidation state. By treating the solution with FeSO\textsubscript{4} or chloride, H\textsubscript{2}AuCl\textsubscript{4} is reduced to Au (eq. 1.1). Addition of NH\textsubscript{4}Cl to the solution causes (NH\textsubscript{4})\textsubscript{2}[PtCl\textsubscript{6}] to precipitate and this is filtered and ignited giving impure Pt sponge. The sponge is converted to a Na\textsubscript{2}PtCl\textsubscript{6} solution which is treated with NaBrO\textsubscript{3} to oxidise the Ir, Pb, and Pd impurities. Adding NaHCO\textsubscript{3} causes these to precipitate. The filtrate is boiled with HCl, treated with NH\textsubscript{4}Cl, to form a precipitate of (NH\textsubscript{4})\textsubscript{2}[PtCl\textsubscript{6}] which is treated to give pure Pt sponge. Impure H\textsubscript{2}PdCl\textsubscript{4} is treated with dilute NH\textsubscript{3} followed by HCl, leading to [Pd(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}] precipitating (eq. 1.2 and 1.3). This is repeated until the pure salt is obtained. Further treatment gives pure Pd sponge.\textsuperscript{10} Following this procedure leads to Pt and Pd with purity >99.9%.

\[
\begin{align*}
2\text{HAuCl}_4 + 3\text{FeSO}_4 & \rightarrow 2\text{Au} + \text{Fe(SO}_4)_3 + 2\text{FeCl}_3 + 2\text{HCl} & \text{(eq. 1.1)} \\
\text{H}_2\text{PdCl}_4 + 4\text{NH}_4\text{OH} & \rightarrow [\text{Pd(NH}_3)_4]\text{Cl}_2 + 4\text{H}_2\text{O} + 2\text{HCl} & \text{(eq. 1.2)} \\
[\text{Pd(NH}_3)_4]\text{Cl}_2 + 2\text{HCl} & \rightarrow [\text{Pd(NH}_3)_2\text{Cl}_2] + 2\text{NH}_4\text{Cl} & \text{(eq. 1.3)}
\end{align*}
\]
1.1.2.2 Au

The gravity concentration of alluvial Au dates back to at least 6000 years and involves a sluice with transverse riffles. Using Hg improves the process by causing the Au to amalgamate. The Hg is then distilled of and the Au smelted. Ore is first crushed and milled, giving fine particles. This allows efficient extraction and initial treatment is like that of alluvial Au. Tail end particles are treated with alkali cyanide and compressed air (eq. 1.4), before filtering the solution and re-precipitating Au using Zn (eq. 1.5). This recovery method has an efficiency of approximately 98%. The previous smelting stage has an efficiency of 88-90%. The chlorination process is used to purify Au. For this, Cl₂ gas is bubbled through the molten Au, so that any impurities present form their chloride salts and float to the top. A 99.5% purity is achieved and, if desired, the metal can be further refined by electrolysis.¹²

\[
4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au(CN)}_2]^- + 4\text{OH}^- \quad \text{(eq. 1.4)}
\]

\[
2[\text{Au(CN)}_2]^- + \text{Zn} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2\text{Au} \quad \text{(eq. 1.5)}
\]

1.1.3 Properties

1.1.3.1 Pd

Pd is a lustrous grey-white metal which is ductile and malleable. The ductility of the metal allows it to form ductile alloys with a greater range of elements than any other metal. These include H, the PGMs, Au, Ag, Te, Pb, and Bi. It is possible to shape the metal into wires, sheets, or form it by spinning or stamping. Pd has a high melting point of 1554 °C, reasonable electrical conductivity, and at 25 °C a sublimation energy of 92.26 kcal mol⁻¹, consistent with its lower melting point compared to Pt. It is resistant to corrosion and is only possible to dissolve Pd using hot, concentrated nitric and sulphuric acids, or aqua regia. Also, in powder form, Pd is slowly attacked by HCl when in the presence of O₂.¹⁰,¹¹,¹³
1.1.3.2 Pt

As with Pd, Pt is a grey-white metal that is lustrous, ductile, and malleable, that can be shaped similarly. The melting point of Pt is 1773.5 °C and at 25 °C it has a sublimation energy of 121.6 kcal mol\(^{-1}\). Like Pd it is resistant to corrosion. Pt is slightly less reactive than Pd; it cannot be attacked by any single mineral acid but will readily dissolve in aqua regia.\(^{10,14}\)

1.1.3.3 Au

Bulk Au is a soft yellow metal, possessing the highest ductility and malleability of any element. The metal possesses a high thermal and electrical conductivity leading to use in electronics, and has a melting point of 1063 °C.\(^{12}\) As Au does not react with either O\(_2\) or S at any temperature it is considered the most ‘noble’ of metals, possessing the lowest electrochemical potential of any metal.\(^{12,15}\) It does however react with all of the halogens, Br\(_2\) being the most reactive. Using a solution of only an oxidising agent or a ligand will not dissolve Au, but the metal will dissolve if both are used together, \(e.g.\) Au will not dissolve using HCl or HNO\(_3\) on their own, but will in aqua regia.\(^{12}\)

1.1.4 Oxidation States

1.1.4.1 Pd and Pt

Pd and Pt can take on several oxidation states. When in the 0 state they have coordination numbers between 2 and 4 but can also exist as +1, +3 (PdF\(_3\)^-, PdF\(_6\)^3-), +5 (PtF\(_5\), PtOF\(_3\), and a series of hexafluoroplatinates(V)), and +6 (PtF\(_6\)). The most common for both metals is +2 and in this oxidation state, square planar is the most common geometry. +4 is possible for both but more common for Pt and in this form almost all compounds are octahedral. Pt has also been shown to possess negative oxidation states (Cs\(_2\)Pt).\(^{10,16-21}\)

1.1.4.2 Au

Au can exist in oxidation states from -1 to +5. The electron affinity of Au (2.3 eV) is high enough so that it can behave as a pseudohalogen. Consequently there are some metal
aurides known to exist, \textit{e.g.} NaAu, KAu. Au(I) complexes are commonly linear with a coordination number of typically 2, and favoured with soft ligands. Higher coordination numbers are also known that lead to trigonal planar and tetrahedral geometries, but tend to revert to the favoured linear structure, \textit{e.g.} Au(I) disproportionates in solution (eq. 1.6).\textsuperscript{12,15,22} Au(III) compounds are favoured with hard ligands with the vast majority square planar. Five and six coordinate compounds are known but rare. The only Au(V) compounds known are fluorides. The +2 oxidation state is rare and paramagnetic while Au(IV) compounds are also rare but diamagnetic.\textsuperscript{12,15}

\[
3\text{Au}^+ \rightleftharpoons 2\text{Au} + \text{Au}^{3+} \quad \text{(eq. 1.6)}
\]

\textit{1.1.5 Uses}

\textit{1.1.5.1 Pd}

Prior to the INC method for Pd production (see above, Section \textit{1.1.1}), the metal was only used in dental alloys or jewellery. Currently it is also used in electrical contacts, resistors, and thermocouples.\textsuperscript{11} Pd is an excellent and versatile catalyst which can be used in a variety of reactions, including hydrogenation, isomerisation, or oxidation. It is also used in gas purification, catalytic ignition, and in the petroleum industry for their cracking and reforming reactions.\textsuperscript{10,11,23,24}

\textit{1.1.5.2 Pt}

Pt is used in laboratory ware when high temperatures or corrosive materials are being used. Within industry, it is used to line crucibles when melting special glasses, in NH$_3$ oxidation as a surface catalyst, as a heterogeneous catalyst for hydrogenation reactions, octane fuel production, in circuit breakers, and in electrical furnaces. The metal is also used in both laboratory apparatus and industry as electrodes. Commercially, Pt is used in jewellery.\textsuperscript{10,23,24}
1.1.5.3 Au

The most common uses of Au are in jewellery and electronics. In terms of its catalytic properties, bulk Au is typically regarded as the least useful noble metal, a consequence of the filled d band inhibiting the ability of Au to chemisorb small molecules. However when Au nanoparticles are used the catalytic performance improves. Types of reactions in which Au has been employed as the catalyst include nucleophilic additions, activation of carbonyl groups and alcohols, oxidations, and hydrogenations.

1.2 Catalytic Converters

Catalytic converters are catalysts which are used to convert harmful CO, hydrocarbon, and NOx gases into more benign and environmentally friendly alternatives, as shown by equations 1.7 to 1.10. Pd and Pt catalyse the oxidation of CO and hydrocarbons (eq. 1.7 and 1.8), while Rh catalyses the reduction of NOx gases (eq. 1.9 and 1.10). Due to these reactions being carried out virtually simultaneously, they are known as three way catalysts (TWC). The exact composition of exhaust gases depends on a variety of things. The type of engine (two-stroke, four-stroke, diesel/petrol, etc.), driving conditions (rural, urban), speed, and acceleration/deceleration are all factors that can affect the resultant gas composition. Sulfur oxides can also be present but the only effective way to remove these is to reduce them to elemental S. This would cause it to collect in the system. As such the preferred method is to reduce the amount of S in the fuel.

\[
\begin{align*}
\text{CO + } \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2 \\
C_nH_m + (n + \frac{1}{4}m)\text{O}_2 & \rightarrow n\text{CO}_2 + \frac{1}{2}m\text{H}_2\text{O} \\
(8n+2m)\text{NO} + 4\text{H}_m\text{C}_n & \rightarrow (4n+m)\text{N}_2 + 2m\text{H}_2\text{O} + 4n\text{CO}_2 \\
2\text{NO} + 2\text{CO} & \rightarrow \text{N}_2 + 2\text{CO}_2
\end{align*}
\]
1.2.1 Composition

There are three main components of a catalytic converter. These are the honeycomb ceramic, the protective outer steel shell, and the fibre blanket buffer. The major part is the ceramic, a silicon-aluminium-magnesium oxide called cordierite with the chemical formula 2MgO.2Al2O3.5SiO2. A washcoat, consisting of alumina with oxide additives of Ce, Zr, La, Ni, Fe, etc., is then coated onto the ceramic in order to increase the surface area. These additives act as support stabilizers, activity promoters, and selectivity improvers. Most converters include one, usually more, of these elements, but all include PGM, alumina and ceria, with different proportions in different catalysts.3,27,29 In essence, catalytic converters must have some standard features. These are:

- High activity and selectivity
- Very fast light off (<10-20 s) – i.e. activity must be high at low temperatures

In the case of TWC, there are two other requirements:

- High thermal stability
- High oxygen storage capacity

Several compounds have been used over the years to support the metals. Metal foil has been used because it can be welded into the exhaust line, possesses high surface area and low back pressure (for efficient engine performance), and does not suffer thermal cracking experienced by ceramic material. Initial work by Johnson Matthey showed that the durability of most iron based alloys was low when exposed to exhaust gas. Eventually it was shown that the desired resistance could be achieved with iron-chromium-aluminium ferritic steels. When extruded and fired at high temperature these form aligned cordierite.3 Typically this skeleton has a density of 60-120 cells cm\(^{-2}\). The walls between cells usually have a thickness of about 150 μm.29 It should be noted that the choice of support and its geometrical characteristics are key aspects in determining converter efficiency.28

The washcoat contains alumina which helps provide a high surface area for the dispersion of the metals.3 The washcoat is between 50-200 μm thick, consisting of approximately 90% γ-Al2O3 and base metal additives. These additives are mainly the oxides of Ce, Zr,
La, Ni, Fe, and alkaline earth metals. Due to the high surface area of the washcoat, the concentration of metals can be kept low, and their high temperature sintering is inhibited. Alumina also absorbs poisons while helping bind the catalyst layer to the support. It is also chosen for its relatively good thermal stability when under the high temperatures experienced by the exhaust. Ceria (CeO$_2$) also has multiple roles, such as:

- Promotion of precious metal dispersion
- Increasing thermal stability of alumina
- Promotion of H$_2$O gas shift and steam reforming reactions
- Favouring catalytic activity at the interfacial metal-support sites
- Promotion of CO removal by oxidation through the use of lattice oxygen
- Acts as an oxygen storage component (OSC), storing and releasing O$_2$ when under lean and rich conditions respectively

Pd, Pt, and/or Rh are the key to catalytic converter functionality. Without them the catalyst will not work and today there remains no viable alternative. Within a converter there are between 1.0 g and 15.0 g of PGMs present, but typically an average of 4.0 g can be found. The amount is dependent upon the size of the converter and what it is used for. In early oxidation catalysts Pt was used. Pd or Rh was used in smaller amounts to provide durability. Eventually Pt and Rh were used together due to the need for NO$_x$ reduction as well. Pd however was not normally used in the converters during the 1980’s, despite its lower cost and broader availability. The reason for this was that Pd can be poisoned by Pb and S more easily than Pt. The HC/CO/NO$_x$ balance from a particular engine and application therefore determined the choice of either Pt/Rh or Pd/Rh. Now though, Pb content is close to zero and the amount of S in fuel is markedly reduced. As such most modern TWCs are based on Pd/Rh compositions.

1.2.2 Deactivation

Deactivation of the catalyst can occur in several ways. For example, deactivation can occur through sintering of the metal which can be caused by use of high metal loading at high temperatures. Poisoning of the catalyst, e.g. by Pd, S, Mn, or Si, can also take place.
and this is related to mileage travelled and fuel used. Sintering of the oxygen storage component (OSC) can also cause loss of the OSC and maybe even encapsulation of the precious metal. Migration of Rh\(^{3+}\) into the alumina lattice can cause deactivation of Rh.\(^{28}\)

1.2.3 Current recovery methods

Due to every new car, and essentially any engine which produces harmful gases (see eq. 1.7 to 1.10), being equipped with a converter, they are an obvious source with which to reclaim the used metal. This is especially true when considering the growth of automotive transport and the high price of the PGMs. There are two main overall methods by which this can be done; hydrometallurgical and pyrometallurgical.\(^{27}\) A combination of both is also possible.\(^{31}\) Recovery can be divided into 4 basic steps: homogenisation, compaction, dissolution, and separation of metals and their purification. A variety of methods are available for the final step, \(e.g.\) calcination, ion exchange, solvent extraction, hydrolysis, oxidation and reduction, or precipitation. The last step yields highly pure metal but is expensive.\(^{31}\)

1.2.3.1 Hydrometallurgical processes

This is a general overview of the hydrometallurgical procedure and can be altered slightly to give different methods within the overall family, \(i.e.\) segregation method, chlorination method, and the aqua regia method.\(^{31}\)

These processes are rarely applied and involve using different leaching agents. Leaching of the PGMs is the most common technique. This requires a combination of strong acids and oxidants and lead to the formation of soluble PGM complexes. Aqua regia is the most common leaching agent but not all PGMs are dissolved in it.\(^{27}\) Consequently chlorate, perchloric acid, Cl\(_2\), H\(_2\)O\(_2\), bromate, and nitrate are also used. The metals are dissolved mostly in the form of [MCl\(_6\)]\(^{2-}\) chloro-complexes.\(^{31}\) Once dissolved, the 'pregnant' solution, containing the PGMs, is separated from any residual solid. There are now various treatments of the solution possible, \(e.g.\) direct cementation with a less noble metal, solvent extraction, or adsorbing the PGMs on an ion exchange column.\(^{27}\)
Hydrometallurgical processes offer fast metal recovery with lower fixed capital costs, and low energy use. Another advantage is that it is possible to recover the ceria used in the converters via this route, i.e. ceria is lost if a pyrometallurgical process is used. The main disadvantage of hydrometallurgical processes is the large amount of liquid waste generated. Dealing with this waste is very important, as there is a need to protect the environment and the industry is moving toward ever more ‘green’ chemistry.\textsuperscript{31,32}

Jimenez de Aberasturi \textit{et al.}\textsuperscript{29} sought to develop a hydrometallurgical process which applies less aggressive and corrosive reagents allowing the recovery of at least 95\% of PGMs from real automotive catalytic converters. Two different compositions were examined with the concentrations varied. Composition A involved HCl, HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, and NH\textsubscript{4}F. It was found that the maximum PGM recovery was achieved with 65 mL of 12 M HCl, 8 mL of 15 M HNO\textsubscript{3}, and 5 mL of 18 M H\textsubscript{2}SO\textsubscript{4}. NH\textsubscript{4}F was found not to increase Rh extraction and actually decreased that of Pt. Composition B replaced HNO\textsubscript{3} with H\textsubscript{2}O\textsubscript{2}. For this composition the best results were obtained using 80 mL of 12 M HCl, 8 mL of 110 vol H\textsubscript{2}O\textsubscript{2}, and 5 mL of 18 M H\textsubscript{2}SO\textsubscript{4}. In this instance NH\textsubscript{4}F did not improve the extraction rate of any metal significantly. Ultimately their preferred composition was B. This would occur at 90 °C for 6 hours after a 22 hour thermal pre-treatment at 250 °C.

1.2.3.2 Pyrometallurgical processes

Pyrometallurgical processes are the main way in which PGMs are recovered from catalytic converters. The main process consists in forming a liquid slag of the cordierite before collecting the precious metal fraction in a metal bath. In order to melt the ceramic high temperatures are required, \textit{i.e.} between 1500 °C and 1900 °C, which can be generated via plasma, electric slag, or electric arc heating.\textsuperscript{27}

The PGMs fall through the slag and into the bath due to their high specific density. The metal bath is usually Cu but can be Fe, Pb, or Ni. An alternative method to separate the PGMs is to use collector metal drops which increase the metal-slag interface area. This leads to an increase in PGM recovery, and is particularly useful for recovering very small particles. Cu enriched with PGM, from a metal bath, is processed further via electrowinning, concentrating the precious metals in a sludge. To separate the individual
metals a number of hydrometallurgical techniques can be applied, e.g. solvent extraction, precipitation, or ion exchange. High recovery rates capable of more than 95% for Pd and Pt, and 85% for Rh are the main advantage that pyrometallurgical processes have over hydrometallurgical ones, but the former require long processing times. They also require expensive, specialised equipment that have a high energy consumption. The description above is a general overview of the pyrometallurgical procedures, i.e. rose or melting methods.

1.3 Adducts for the dissolution of Pd and Pt

Serpe et al. have used non-cytotoxic dihalogen/dithiooxamide adducts (see Scheme 1.4 below) for the recovery of Pd from spent TWC models, and also for the removal of Au from electronic devices. The adducts are prepared by reaction of either acyclic or cyclic dithiooxamides (Fig. 1.1) with dihalogens, where at least one atom is iodine, in a 1:2 ratio, in either chloroform of DCM. This type of adduct is used because they combine both complexing and oxidizing properties through the dithiooxamide and the dihalogen, respectively.

Figure 1.1 Structures of acyclic and cyclic dithiooxamides
One particular reason for looking at S based ligands, and dithiooxamides in particular, is their soft donor capability which complements the soft nature of PGMs. In addition, with two S donors in vicinal positions, the ligands are able to act as chelating ligands, thus favouring the stabilization of the metal complexes. For example, $d^8$ metal ions, such as Pt(II) or Pd(II) can form bis-chelate complexes with these ligands, in their preferred square-planar geometry. Both the donor and the dihalogen can be altered, so that the adducts can be tuned to favour the dissolution/complexation of a particular metal. The systems therefore have potential for metal selective extraction. Synthesis of the adducts involves three steps. The first is synthesis of the corresponding dione, the second is exchange of the carbonyl O atoms by S, before finally adding the dihalogen. These procedures are discussed in the next sections.

### 1.3.1 1,4-dimethyl-2,3-piperazinedione ($\text{Me}_2\text{pipd}$) (1) and 1,4-dimethyl-2,3-perhydrodiazepinedione ($\text{Me}_2\text{dazd}$) (2)

The syntheses of (1) and (2) (Scheme 1.1) were reported in 1981 by Isaksson et al.\textsuperscript{33} The authors reacted diamines with dioxalates, in a 1:1 ratio, in dry benzene, toluene, or xylene, to form the corresponding dione. Depending on the N-substituents of the diamines, the yields ranged from 20% to 75%. These yields could only be achieved if the concentration of the starting material was less than 0.1 M. It was found that at higher concentrations, open chained polymeric materials formed in large amounts. The best results were obtained when the solvent was toluene and one of the reagents was dimethyl oxalate (3) (Scheme 1.1). The use of higher boiling point solvents, e.g. xylene, caused the oxalate to thermally decompose, whereas benzene caused the amount of polymeric products to increase. For example, the reaction between dimethyl oxalate (3) and N,N′-dimethylethlenediamine (4) in dry benzene under reflux for 24 hours allowed the formation of (1). After recrystallization from toluene an analytically pure compound was obtained with 40% yield. It is unclear why the authors chose to use benzene in this particular procedure due to the issue mentioned previously. To obtain the analogous dione (2), (3) was reacted with N,N′-dimethyl-1,3-propanediamine (5) in dry toluene under reflux, for 70 hours. Recrystallization from ethanol resulted in a yield of 55%.
Scheme 1.1 Synthesis of diones (1) and (2), starting from dimethyl oxalate (3) and the relevant diamine

Deplano et al.\textsuperscript{34} showed that the synthesis of (2) can be achieved under the same conditions used by Isaksson et al.\textsuperscript{33} but the reaction time was reduced from 70 hours to only 2 hours. Compound (1) can also be prepared in dry diethyl ether or dry 2-propanol, using diethyl oxalate instead of dimethyl oxalate (3), as shown by Mueller-Westerhoff and Zhou.\textsuperscript{35} The yield obtained in this case was 90\% of purified product. The authors proposed that the reaction between (4) and diethyl oxalate proceeded via a concerted, pericyclic reaction of a charge-transfer complex between diamine and oxalate. This would pre-orientate the reactants in their cis conformation allowing nucleophilic attack on the carbonyl carbon atoms simultaneously. This mechanism was suggested as simple dialkyldiamines do not form tetraalkyloxamides under the conditions employed. However, the authors concede that the entropy change in the formation of the product could allow the stepwise reaction to occur. Experiments carried out to determine the mechanism were not conclusive. Marder et al.\textsuperscript{36} also reported the synthesis of (1), in dry diethyl ether, following a method similar to that of Mueller-Westerhoff and Zhou,\textsuperscript{35} but excluding recrystallization from toluene to purify the product. Instead, the crude product was simply dried over night at 47 °C, giving a yield of 96\%.
1.3.2 1,4-dimethyl-2,3-piperazinedithione (Me₂pipdt) (6) and 1,4-dimethyl-2,3-perhydrodiazepinedithione (Me₂dazdt) (7)

In order to convert the diones, (1) and (2), into the corresponding dithiones (6) and (7), Isaksson *et al.*[^33^] used *p*-methoxyphenylthioxophosphate (8) as the thionation reagent, which is more commonly known as Lawesson’s Reagent (LR) (Scheme 1.2). It is not known as Lawesson’s Reagent because Sven-Olov Lawesson invented it, but rather it was he who popularised the compound starting in 1978[^37^].

![Scheme 1.2 Equilibrium of LR (8) and dithiophosphineylide (9 and 10)](image)

Compound (8) was first made in 1956 and can be prepared by reacting anisole with phosphorus pentasulphide or reacting red phosphorus with elemental sulphur and anisole. In solution, the compound is unstable at temperatures above 110 °C, slowly undergoing polymerisation. However, it is a popular thionation reagent due to the high yields, convenient handling, easy work up, and availability. Regarding the mechanism of the thionation reaction involving (8), it is considered that the reagent is in equilibrium with a highly reactive dithiophosphineylide (9, 10) (Scheme 1.2).[^37^][^38^] Both (9) and (10) can then react with carbonyl groups forming thiaoxaphosphetane (11) before this decomposes, similarly to a Wittig reaction, forming the thioketone (Scheme 1.3). An important aspect in these reactions is the thermodynamic stability of the resulting product. Bonds between P and O are stronger than those between P and S. For example the P-O bond energy in POCl₃ is 110 kcal mol⁻¹ whereas the P-S bond energy is 70 kcal mol⁻¹ in the corresponding S compound. The thionation process is thus driven by the exchange of O and S atoms[^37^].
Deplano et al.\textsuperscript{34} also used (8) for the thionation step. In this case, a 1:1.2 ratio of (2):(8) was used in dry toluene, under reflux, for 1 hour. The dithione (7) was then purified by recrystallizing it from DCM and ethanol. Unfortunately no yield was given and so a comparison with other literature methods is not possible. However it is worth noting that
2 equivalents of (8) are not required. Since (8) possesses 2 S atoms which can be exchanged with O, a slight excess appears to be enough for a complete thionation process. Nemykin et al.\textsuperscript{39} followed the procedure set out by Isaksson et al.\textsuperscript{33} for the synthesis of (6), which they subsequently used to form the (Me\textsubscript{2}pipdt)Mo(CO)\textsubscript{4} complex. The authors report a yield of 82\% from the formation of (6), but as Isaksson’s procedure is followed, this may refer only to the reaction of (1) with (8), rather than to the overall synthesis.

1.3.3 Dithione/iodine adducts and their application in the dissolution of PGMs

Charge-transfer adducts can form when the lone pair from a donor atom, such as the S atom in a thione, interacts with an atom of iodine from I\textsubscript{2}. This interaction leads to an increase in the I-I bond length. In solution, the following equilibrium generally takes place: D + I\textsubscript{2} ⇌ DI\textsubscript{2} (where D is the electron donor).\textsuperscript{40}

\[
\text{Scheme 1.4 Synthesis of (12) and (13)}^{25,34,41}
\]
The reaction between (6) or (7) with I\(_2\) has been found to result in the formation of [Me\(_2\)pipdtH]I\(_3\) (12) or Me\(_2\)dazdt/2I\(_2\) (13), respectively (Scheme 1.4).\(^{25,34,41,42}\) The corresponding dithione and I\(_2\) were reacted in a 1:2 ratio in chloroform or DCM at room temperature.\(^{34,42}\) The formation of the tri-iodide salt (12) was unexpected, but this compound was still found to be effective in the oxidation/dissolution of metals. Where the H comes from has not been investigated but may originate from the solvent employed or from H\(_2\)O absorbed from the atmosphere.\(^{25,41}\) The di-iodine adduct (13) showed a strong Raman peak at 146 cm\(^{-1}\) which was assigned to \(\nu(I-I)\), suggesting a medium-strong interaction strength in the adduct.\(^{42}\) Other characterization data for (13) is given below:\(^{25}\)

\[
\text{X-ray data: } d(S\cdots I1)(\text{Å}) 2.786(2), d(I1\cdots I2)(\text{Å}) 2.818(2)
\]

\[
\text{Electronic spectroscopy: } 332 \text{ nm (CT-band), 420 nm (\(\pi^*\rightarrow\sigma^*\) dihalogen band)}
\]

In the case of (12), its X-ray crystal structure showed that it consisted of protonated Me\(_2\)pipdtH cations and I\(_3\) anions, with S\cdots I contacts formed between layers of cations and anions, \textit{i.e.} \(d(S\cdots I1): 3.932(3) \text{ Å}, d(I1\cdots I2) 2.909(1) \text{ Å}.\)^{41,43}\]

The capability, effectiveness, and selectivity of (12) and (13) for PGM dissolution has been tested.\(^{25,44,45}\) When H\(_2\)O was used as solvent, the complexes formed were insoluble, and therefore organic solvents, such as THF, acetonitrile, acetone, or methyl ethyl ketone (MEK), had to be used. The metals tested were pure samples in the form of powder, foil, or wire, and a 2:1 ratio of ligand to metal was used. There was no need for the metals to be activated and the reactions took place in relatively mild conditions. Using (12), Au and Pd could be dissolved at room temperature, while in order to dissolve Pt the mixture had to be refluxed. Compound (13) also dissolved Au and Pd at room temperature, however it could not dissolve Pt, even in refluxing acetonitrile.\(^{25}\) Unfortunately, the times needed for complete dissolution of the metals have not been reported, with the exception of the reaction between (13) and Pd which was tested on aged catalytic converters and took 168 hours. Bigoli \textit{et al.}\(^{41}\) also reported the reaction between (12) and Pt (2:1). In this case, the reaction in acetonitrile at reflux took 4 days and resulted in a 65\% yield of
[Pt(Me₂pipdt)₂][I₃]₂ (14). The X-ray crystal structure of the complex showed the metal with the expected square planar coordination. The chelation ring possesses an ‘envelope’ conformation while the ligand ring possesses a half chair conformation. Compound (12) has also been used in the dissolution of elemental Cd and Hg allowing the removal of toxic material from the environment.⁴³ A solution of (12) in THF was added at room temperature to either Cd or Hg (2:1). Within either 6 or 36 hours (Cd or Hg respectively) the metals dissolved. Adduct (13) was shown to dissolve Pd in powder form or foil; i.e. 1 hour was required to dissolve 12.3 mg of Pd powder at room temperature in THF, again with no protection from air and/or moisture, in a one-step reaction. Acetone, acetonitrile, or MEK can also be used as solvent and in all cases the yields are quantitative.⁴⁴ Spectrophotometric measurements were carried out to monitor the kinetics of the metal dissolution processes and these showed:²⁵

- First order kinetics in the dissolution of the Pd powder with (13) achieving the fastest process.
- (13)-THF solution in the dissolution of Au wires works faster for Au etching compared to the I/I₂ (H₂O) solution currently used, e.g. in microelectronic applications.

The adduct (13) was also tested on model three way catalysts (TWC).⁴⁴ The best yields were obtained using a 2.5 mM solution of (13) (i.e. in a 2:1 ratio towards Pd), and a reaction time in MEK of 168 hours. The extraction yield at either room temperature or 80 °C was ≥90%. What makes these results more remarkable are the following considerations:

- Pd content was low
- The dispersion of the metal and its strong interactions with oxides present in the washcoat
- The high level of sintering which had occurred
- PdO being present

The system, which uses a friendly reagent and solvent, shows selectivity towards Pd only, ignoring both Pt and Rh (metals also typically found in catalytic converters) even when
refluxing solvents were applied. This intrinsic selectivity appears to offset the long reaction time required. The metal could then be recovered by conventional thermal treatment, but this causes decomposition of the ligand.

1.4 Adducts for the dissolution of Au

As mentioned previously, compounds (12) and (13) can be used to dissolve Au at mild conditions. For example, Bigoli et al. used (13) in the dissolution of Au in THF, at room temperature (30 minutes) without the need for protection from air and/or moisture. The adduct solution turned from red-orange to red-brown once the metal was added, and after a short time the metal had dissolved. When the solution was allowed to stand, a solid was obtained that was recrystallized from THF-Et₂O. Well-shaped crystals of [Au(Me₂dazdtI₂)]I₃ (15) resulted. The X-ray structure of the complex showed the Au atom in a square-planar geometry with (7) acting as a S, S-chelating ligand. Its Raman spectrum shows peaks at 106(s) and 138(m) cm⁻¹ corresponding to the triiodide (symmetrical and antisymmetrical stretching respectively), which is asymmetric and essentially linear. Peaks at 153(s) and 166(sh) cm⁻¹ were believed to relate to Au-I vibrations. The analogous reaction with IBr instead of I₂ has also been described forming the adduct Me₂dazdt/2IBr (16), thus showing the versatility of these complexes. This particular adduct is able to dissolve 22 mg of Au in 30 minutes at room temperature when THF was used as solvent.

In addition, diiodophosphoranes such as Ph₃PI₂ (17), are also capable of dissolving Au. Dihalogenphosphoranes can take one of essentially three structures: The ionic species, R₃PX⁺X⁻, dominant in solution; the five coordinate solid-state compound R₃PX₂⁻; or the four coordinate solid-state ‘spoke’ structure, R₃P-X-X (Fig. 1.2). The stoichiometric reaction of Ph₃P and I₂ leads to formation of (17), which is obtained as a yellow crystalline product upon recrystallisation at 0 °C with diethyl ether. The crystal structure of (17) has been reported as the 'spoke' conformation, possessing an elongated I-I bond (3.16 Å) relative to molecular I₂ (2.67 Å). Its Raman spectrum showed a band at 160 cm⁻¹ which was assigned to the I-I stretching vibration. It was also found that (17) ionised in solution when the $^{31}$P-NMR spectrum was carried out. This showed a signal at 44.8 ppm, identical to that obtained when (17) is reacted with an additional equivalent of I₂, yielding [Ph₃PI]I₃.
The presence of $\text{I}_3^-$ was also confirmed by UV/Vis with bands at 294 nm and 366 nm. The Raman spectrum of (17), showed a peak at 160 cm$^{-1}$ which was associated with the P-I bond.$^{48,49}$

![Figure 1.2 ‘Spoke’ structure of (17)](image)

In later work, the $^{31}\text{P}$-NMR spectrum of a 1:1 mixture of $\text{Ph}_3\text{P}$ and $\text{I}_2$ in DCE has been reported to give a peak at -21.7 ppm, which was assigned to the 1:1 adduct (17).$^{50}$ Excess of $\text{Ph}_3\text{P}$ gave an averaged NMR signal rather than two separate peaks, indicating rapid exchange of the $\text{I}_2$ between the adduct and free $\text{Ph}_3\text{P}$. Increasing the $\text{I}_2$ concentration causes a downfield shift of the peak to a limiting value of 12.0 ppm. The solid-state Raman spectrum of (17) shows a band at 159 cm$^{-1}$ for the P-I bond but none for the I-I bond. The work provided proof that the adduct is in the same form in both the solution and solid states, *i.e.* that (17) exists as the ionic structure $[\text{Ph}_3\text{PI}]^+\text{I}^-$. 

\[
\text{Au} + 2 \text{Me}_3\text{PI}_2 \xrightarrow{\text{dry diethyl ether, N}_2} \begin{array}{c}
\text{(19)} \\
72 \text{h, } 25 \degree \text{C}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{Au} \\
\text{PMe}_3
\end{array} \\
\text{I} \\
\text{PMe}_3
\end{array} \xrightarrow{\text{I}} \begin{array}{c}
\text{I} \\
\text{PMe}_3
\end{array} + \frac{1}{2} \text{I}_2 \\
\text{(20)}
\end{array}
\]

**Scheme 1.5** Dissolution of Au with Me$_3$PI$_2$ (19)$^{47}$
The above shows the difficulties associated to the characterisation of iodophosphorane adducts. In addition, they are normally air and moisture sensitive and therefore the synthesis and handling must be carried out in an inert atmosphere.\textsuperscript{48,50–52}

Godfrey \textit{et al.}\textsuperscript{47} showed that an analogous adduct to (17), Me\textsubscript{3}PI\textsubscript{2} (19), could successfully dissolve Au within 72 hours at room temperature forming the Au(III) complex [AuI\textsubscript{3}(PMe\textsubscript{3})\textsubscript{2}] (20). The process required an inert atmosphere due to the sensitivity of (17). The X-ray structure of (20) showed the Au atom in the centre of a trigonal bipyramidal complex and not the expected square planar or square pyramidal structures normally associated with the d\textsuperscript{8} Au(III) ion. The UV/Vis spectrum of (20) exhibits two peaks at 379 nm and 572 nm and its \textsuperscript{31}P-NMR spectrum shows two peaks at -69.5 ppm and 30.1 ppm of near equal intensity. The former value was assigned to free Me\textsubscript{3}P and the latter to the Me\textsubscript{3}P on the four coordinate Au(III) complex. Addition of H\textsubscript{2}O to a solution of (20) causes reduction of Au(III) to Au(I) and oxidation/protonation of Me\textsubscript{3}P, forming [(Me\textsubscript{3}PO)\textsubscript{2}H][AuI\textsubscript{2}].

Due to the sensitivity to air and moisture of the reactants and products noted above, it would be beneficial if an alternative solvent could be used in the Au dissolution process. Ionic liquids have been shown to be able to stabilise phosphine compounds which are otherwise unstable in conventional solvents, and could therefore provide a convenient media for the recovery of Au.\textsuperscript{53} It should be noted that the nature of a phosphine and metal bond partly depends on the substituents of the phosphine which affect the degree of $\pi$-backbonding that occurs with the metal. P itself possess a lone pair that act as a $\sigma$-donor too the metal, but it also has empty p orbitals which can overlap with electron containing d orbitals of the metal. If the substituents of the phosphine are electron donating then the backbonding effect will be weaker than if they were electron withdrawing. For example the Me groups of Me\textsubscript{3}P are more electron donating than the Ph groups of Ph\textsubscript{3}P. This would mean a stronger $\pi$-backbonding interaction between a metal and Me\textsubscript{3}P than a metal and Ph\textsubscript{3}P.\textsuperscript{54}
1.5 Alternative methods of Synthesis

A conventional method to get reagents to react is through the application of heat. At the same time a solvent is often employed and this is typically in a large excess relative to the reactants. By carrying out reactions in this manner, a large cost input is involved, e.g. increasing the temperature and maintaining it, addition and removal of solvent; and so alternative methods of performing reactions have been developed. These include mechanochemical, microwave, and sonochemical methods.

All three methods have been applied to Diels-Alder reactions, Baylis-Hillman, coupling reactions, and oxidation reductions. Mechanochemistry has been used for Aldol and Reformatsky reactions which have, respectively, been carried out via microwave and sonochemical methods. Both microwaves and ultrasound have been used for Mannich reactions, Michael additions, and ionic liquid synthesis. Mechanochemistry has been applied to a variety of other reactions including, Luche reactions, Biginelli reaction, Knoevenagel condensation, pyrazole and disulfide synthesis, and fullerene modifications. It has also been employed for the syntheses of complex molecules such as quinoxaline derivatives, β-ketosulfones, and α-tosyloxy-β-ketosulfones by reacting substrates with hypervalent iodine reagents. When solution reactions are performed mechanochemically the resulting products are typically identical, however it is possible for alternative products to be produced. Several other reactions in which microwaves have been employed include addition reactions, cycloadditions, rearrangement reactions (pinacol–pinacolone rearrangement, Claisen rearrangement), protection/deprotection reactions (formation of acetals and dioxolanes, deprotection of the N-tert-butoxycarbonyl group, desilylation reactions, dethioacetalization reaction), anomerisation, heterocyclic compound synthesis, epoxide ring opening, nucleophilic substitutions, and click chemistry. Ultrasound has also been used for phase transfer catalysis, and Wittig reactions. A few examples of reactions carried out using these unconventional methods of synthesis are discussed in a bit more detail below.
• **Aldol reaction:**

When using ball milling for the reaction of unmodified (S)-proline with both ketone and aldehyde (1:1), excellent stereoselectivities and high yields were obtained for the anti-aldol product. In comparison, the conventional reaction, which employed magnetic stirring, gave the syn-aldol product also in high yields but the reaction proceeded much slower. Also, with reactions involving two solid reagents, a conventional method reaction time of 5-7 days was reduced to ≤1.6 days when performed mechanochemically. It was found that the Aldol reaction of acetone and p-nitrobenzaldehyde could be carried out with a lower catalyst loading and in a quicker time with a microwave method than when the reaction is performed conventionally.\(^{56}\)

• **Baylis–Hillman reaction:**

The main issue with the Baylis–Hillman reaction is the low reaction rate, taking days to weeks for completion. In one case, the typical reaction takes 3-4 days with a yield of 70-87%, however the ball milling method reduces the time to 30 minutes with a yield >98%. It has also been shown that synthesis time of allylic alcohols can be reduced from days to a matter of minutes through the application of microwaves.\(^{56}\)

• **Diels–Alder reaction:**

It has been shown that using a mechanochemical method can lead to the synthesis of products not typically accessed conventionally. For example, using sonochemistry when reacting 1-dimethylamino-1-azadienes and electron deficient dienophiles reduced the reaction time and increased the yield.\(^{55,57}\)

• **Knoevenagel condensation:**

\(\alpha, \beta\)-Unsaturated carbonyl compounds have been successfully synthesised, giving quantitative yields in a solvent-free process using a ball mill and avoiding any work up.\(^{61}\)

• **Amide synthesis:**

Amides are typically made via acid or base catalysed hydration of nitriles but the conditions employed can lead to by-products. To avoid these, the direct amidation of aryl aldehydes has been carried out with anilines in a ball mill with no solvent. Yields obtained
were up to 78%, but were much lower when the reaction was performed in acetonitrile or toluene. Microwave methods have also been applied for amide synthesis helping to avoid any by-products, e.g. quantitative conversion of nitriles in H$_2$O at neutral conditions was achieved using a Ru catalyst, at 150 °C, for 45 minutes, and hydration of nitriles to amides was carried out with a Au catalyst in a H$_2$O-THF mixture at 140 °C.\textsuperscript{61}

- C–N bond formation:

Ball milling has allowed the isolation of N-(thiocarbamoyl)benzotriazoles which in solution, form corresponding isothiocyanates and benzotriazole.\textsuperscript{57}

- Synthesis of heterocyclic compounds:

Synthesis of heterocyclic compounds by conventional methods is typically too slow but microwaves have been used to synthesise nitrogen, oxygen, and sulfur containing heterocyclic compounds. Several types of nitrogen heterocycles have been made, including pyrrolidines, piperidines, and azepanes. Using microwave irradiation, the double N-alkylation of primary amines/hydrazine derivatives was found to readily occur with alkyl dihalides/ditosylates causing the reaction time to shorten significantly, while avoiding any multistep reactions and any need for protecting groups. Cyclic ureas have also been synthesised whereby the use of microwaves not only shortens the reaction time but also eliminates formation of any by-products. Oxygen heterocycles have been synthesised using ketones to generate 1,3-dioxanes, while thioamides have been used to synthesise 1,3-thiazoles. For example, the synthesis substituted bridgehead thiazoles could be achieved in 3 minutes using microwave irradiation.\textsuperscript{55,58,59}

- Mannich reaction:

Microwave irradiation was applied to the reaction of cyclohexanone, formaldehyde, and aniline. It was found to shorten the reaction time from 30 hours to between 2 and 3 hours, and that the catalyst loading of (S)-proline could be significantly reduced. Ultrasound has also been applied to the Mannich reaction. Reacting acetone and an imine (4:1), a 50% yield of the product was achieved within 1 hour versus the 24 hours needed without the application of ultrasound.\textsuperscript{56}
Microwave-assisted cycloaddition reactions:

The [3+2] cycloaddition reaction is typically a reaction between a 1,3-dipole and a suitable alkene/alkyne. Hydantoin-, piperazinedione-, and benzodiazepinedione-fused tricyclic and tetracyclic ring systems have been synthesised using a sequence of microwave assisted, fluorous multicomponent reactions and fluorous solid-phase extractions. Polycyclic pyrrolidines have also been synthesised via a microwave process using [3+2] cycloaddition of azomethine ylides with secondary R-amino esters in solution (xylene, 130 °C, 20 minutes). A microwave assisted [4+2] cycloaddition reaction has been used to make unsymmetrically substituted 1,4-dihydropyridines. The reaction was performed at 100 °C for 5–17 minutes generating cycloadducts in excellent yields (83–96%). When performed conventionally, the time reaction took between 33 and 76 hours with yields between 73 and 86%.

1.5.1 Mechanochemical Synthesis

In many chemical productions and research the use of large amounts of solvent are required. These solvents can result in emissions that harm health and the environment. Therefore the end of solvent use in these processes is a desirable goal. In this context, it is of interest to consider the use of mechanochemistry; a branch of chemistry interested in the processes which occur in solids as a result of applying mechanical energy. This can come from the application of compression/impact, shear, or frictional forces (Fig. 1.3). Mechanochemistry is traditionally associated with grinding and milling. The first and oldest method of mechanochemistry is grinding. It has been around since the stone age and at the time carried out using a mortar and pestle, tools still in use to this day. It can only be assumed that rubbing and grinding leads to chemical transformations, i.e. using friction to create fire.

The earliest surviving document related to chemistry is ‘On Stones’ from about 315 B.C. This was written by Theophrastus of Eresus, a student of Aristotle, in which he references the reduction of HgS to Hg by grinding using a Cu mortar and pestle. Since then, grinding has been used to process grains, minerals, building materials, pharmaceuticals,
gun powder, and many more. A paper by Faraday in 1820 describes AgCl reduction by grinding, and his style of writing suggests knowledge of mechanochemical effects. Johnston and Adams mentioned in 1913 that it had been long known that grinding in a mortar will occasionally induce some degree of chemical action between solids.

There are several types of ball mill available: tumbling, planetary, shaker (vibratory), stirring (attritor), pin, and rolling ball mill. The tumbling mills were developed for industry in 1870. These used balls as milling bodies and could be quite energetic. In a small tumbling mill the impact energies can be low but by introducing a centrifuge the energies can be increased. This is the concept behind the planetary ball mill invented in 1961, providing both impact and friction/shear forces. The high powered blows of the grinding balls provide the threshold energy for the chemical reactions. The grinding balls are accelerated due to the grinding bowl rotation. These are mounted on sun discs that

**Figure 1.3** Representation of forces experienced in a shaker ball mill
counter rotate and the kinetic energy is transformed into thermal energy which dissipates, allowing chemical reactions to proceed. Shaker ball mills (like those used in this work) vibrate at set frequencies. The balls inside the jar can then exert impact or shear forces upon the reactants (Fig. 1.3).

When applied to organic chemistry, the reactions can be divided into two categories. The first involves the formation of new compounds in which covalent bonds are broken and new ones form. The product may also be different to that formed in solution. The second consists of the formation of co-crystals due to the change in secondary interactions, e.g. hydrogen bonds. In some cases catalytic amounts of solvent are added and this is termed liquid assisted grinding (LAG). Via the use of this typically solvent free process, reaction temperatures can be lowered, dissolution and reaction rates can be increased, and H2O soluble compounds formed. A planetary ball mill has been used for the thionation of PbO and PbO2 to PbS, using S under an atmosphere of N2.

1.5.2 Microwave Synthesis

Microwaves have been reported as an alternative to traditional heating, and employed in many chemical reactions. As long as one species in the system possesses a permanent dipole then dielectric heating from microwave irradiation is achievable. Typically solvents that possess a dipole such as methanol, DMF, H2O, or acetonitrile, are employed. Those with no dipole, e.g. hexane, are avoided unless another reactant in the system contains a dipole which can couple with the microwave energy. Polar molecules absorb microwaves leading to an increase in rotation, and consequently, they heat via frictional effects. Generally, the more polar the solvent, the larger the increase in temperature. The shortening of reaction times often observed in microwave reactions is attributed to the increase in pressure which develops within the reaction vessel, and results in the solvent being superheated.

A microwave method of thionation has been reported in the literature by Varma et al. The authors found that the solvent-free thionation of monoketones, flavones, or isoflavones, could be achieved in high yields (>90%), with short reaction times.
minutes), using 0.5 equivalents of Lawesson’s Reagent (8). Olsson et al.\textsuperscript{72} used a microwave synthetic procedure for making thioamides. After reacting the diamine with an acyl chloride solution, the precipitated salt was filtered and mixed with (8) (1.0-1.5 equivalents). This mixture was then irradiated in a domestic 900 W microwave oven for 8 minutes before purifying through solid phase extraction. The result was a practical, rapid method for the synthesis of thioamides. The reaction of several quinolones with (8) using a microwave based reaction procedure led to the successful synthesis of the corresponding thiones.\textsuperscript{73} Lagiakos et al.\textsuperscript{74} have also used microwave irradiation for the synthesis of thioamides but this time using a solid supported P\textsubscript{2}S\textsubscript{5} reagent (P\textsubscript{2}S\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}) for thionation. With acetonitrile as the solvent the amide was reacted at 60 °C (Power = 60 W) and full conversion occurred within 5 minutes. In comparison, the published protocol, also using acetonitrile and P\textsubscript{2}S\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}, took 6-10 hours at reflux for complete conversion. Benzylamine was irradiated with S (2 eq.) under solvent free conditions at 170 °C. Compared to the conventional solvent method, the reaction time was reduced from 2 hours to 15 minutes with comparable yields.\textsuperscript{75}

1.5.3 Sonochemical Synthesis

As with microwaves, sonication has been utilised as an alternative to refluxing/heating in order to accelerate a reaction.\textsuperscript{76} This is a useful tool in synthetic chemistry because the equipment necessary, \textit{i.e.} a sonic bath, is relatively inexpensive. In order to achieve acoustic cavitation to induce the reaction, a liquid phase is necessary, whether it be a reactant or solvent.\textsuperscript{77}

The underlying principle of using sonication is that when high powered frequencies are applied (>20 kHz) acoustic cavitation occurs. This is the formation of bubbles that grow before imploding, thus providing the energy required to drive the reaction. It is interesting that it is not the direct interaction of the sonic frequencies with the reagents that leads to the chemical reaction but rather this cavitation.\textsuperscript{55,77,78}
The propagation of the sonic frequencies occurs via compression and rarefaction waves which are induced within the reaction mixture molecules. When the rarefaction exceeds the attractive forces of the liquid molecules, cavitation bubbles are formed. These grow by taking in vapour or gas from the reaction medium, reaching an equilibrium size. At this point the natural frequency of the bubble matches that applied. Some then grow and become unstable before imploding (Fig. 1.4). This implosion is due to the destabilisation caused by interference from surrounding bubbles forming and resonating. This sudden collapse then generates the energy required for the chemical reaction to occur.\textsuperscript{55,77} Within the collapsing bubbles, intense compressional heating is created thus generating extreme transient conditions. This can lead to hot spots with temperatures above 5000 K, pressures greater than 1000 atmospheres, and heating and cooling rates that exceed $10^{10}$ K s\textsuperscript{-1}.\textsuperscript{56,78}

An example of sonication in thionation reactions is that of Sureshbabu \textit{et al.}\textsuperscript{79} Using P$_2$S$_5$ (1.2 equivalents) in THF, the authors were able to convert peptide bonds into thioamides within 20-40 minutes at room temperature. Sonochemistry (50 °C, 160 W, 40 kHz, 20 minutes) was also used when reacting AgOAc with 1,3-bis(diphenylphosphanyl)propane and (8) for the synthesis of the Ag complex \{[Ag(C$_9$H$_{12}$O$_2$-PS$_2$)(C$_{27}$H$_{56}$P$_2$)]·CHCl$_3$\}_n, a novel one-dimensional chain.\textsuperscript{80}
1.6 Ionic Liquids (ILs)

1.6.1 History

Ionic Liquids are salts with a melting point below 100 °C (arbitrarily set). They often remain liquid up until their decomposition temperature, between 300-400 °C. The first IL, [EtNH\sub{3}]NO\sub{3} (ethyl ammonium nitrate), was reported in the early 20th century. Though as a consequence of its explosive nature, its applications in research were not pursued. As of 2012 there were approximately 300 ILs available commercially, with about 1000 reported in the literature. Theoretically, 10\textsuperscript{18} cation-anion combinations are possible, so potentially an IL exists for any situation or need.

1.6.2 Structure

\textbf{Figure 1.5} IL cations used in this work and their abbreviations

\begin{itemize}
  \item n = 1, 3, 5, 7
  \item 1 = [EMIM]\textsuperscript{+}
  \item 3 = [BMIM]\textsuperscript{+}
  \item 5 = [HMIM]\textsuperscript{+}
  \item 7 = [OMIM]\textsuperscript{+}
  \item [P\textsubscript{66614}]\textsuperscript{+}
  \item [BMPyr]\textsuperscript{+}
\end{itemize}
ILs typically consist of a large unsymmetrical organic cation, with a non-polar side chain, and a smaller organic or inorganic anion. The resulting asymmetry prevents the salt from crystallising and leads to a dramatic drop of the melting point. The structures of the cations and anions used in this work are shown in Figures 1.5 and 1.6.

Figure 1.6 IL anions used in this work; Br$^-$ = bromide, Cl$^-$ = chloride, DCA$^-$ = dicyanamide, FAP$^-$ = tris(perfluoroalkyl)trifluorophosphate, NO$_3^-$ = nitrate, NTf$_2^-$ = bis(trifluoromethylsulfonyl)amide, OctSO$_4^-$ = octylsulfate, OTf$^-$ = trifluoromethanesulfonate, PF$_6^-$ = hexafluorophosphate

The anions NTf$_2^-$, PF$_6^-$ and FAP$^-$ normally produce H$_2$O-immiscible ionic liquids. The strong ionic interactions within ILs are responsible for the negligible vapour pressures, non-flammability, and high stabilities (thermal, mechanical, electrochemical). Alongside the dominant coulombic interactions, there can also be hydrogen bonding, π-π stacking, and van der Waals forces present.
1.6.3 Properties

The properties of the ILs are dependent on the nature of the cation and anion. The potential to ‘tune’ the properties of the solvents through the choice of ions, has led to some authors to label them as either ‘designer’ or ‘tunable’ solvents. \(^{81–83}\)

1.6.3.1 Melting Point

It is possible to correlate the melting point of an IL to its composition and structure, *e.g.* if the cation possesses low symmetry then the melting point will be lower as a result of poor ion packing, experiencing weaker intermolecular interactions and good distribution of charge leading to decreased salt lattice energy.\(^ {85}\) The presence of impurities, such as residual halide or H\(_2\)O, lower the melting point.\(^ {82}\) ILs that are liquid at room temperature, are referred to as room temperature ionic liquids (RTILs).\(^ {84}\)

1.6.3.2 Viscosity

Ionic liquid viscosity, strongly influenced by the anion, is generally more than that of organic solvents (1 to 3 orders of magnitude greater), ranging from 0.01 to >1.0 Pa s at room temperature.\(^ {82,83,86}\) Anions with high charge density lead to stronger intermolecular interactions and thus higher viscosities. It can however be reduced by either increasing the temperature or by changing the anion to a more bulky and/or unsymmetrical one.\(^ {85}\) For example, anions which help reduce the viscosity include dicyanimide (DCA\(^ -\)), bis(trifluoromethanesulfonyl)imide (NTf\(_2^-\)), and trifluoromethanesulfonate (OTf\(^ -\)). This is due to the bulky nature of the anions and their charge delocalisation, which reduces the strength of interactions between the ions.\(^ {83}\) Increasing the length of the alkyl chain on the cation will increase the viscosity as stronger van der Waal’s forces are experienced due to the larger cation size.\(^ {86}\) For example the viscosities of [BMIM]Br and [OMIM]Cl at 25 °C are 1.486 and 0.337 Pa s respectively, while at 30 °C the viscosity of [BMIM]Cl is 11 Pa s.\(^ {85,87,88}\) The viscosities of [BMIM]NTf\(_2\) and [BMIM]OTf are 0.045 and 0.076 Pa s respectively at 25 °C.\(^ {89}\) [OMIM]Cl at 80 °C has a viscosity of 0.375 Pa s which is greater than the 0.142 Pa s of [BMIM]Cl at the same temperature.\(^ {90}\)
1.6.3.3 Density

The density of ionic liquids is usually greater than those organic solvents or H$_2$O, with densities ranging from 1.0 to 1.6 g cm$^{-3}$. A rule of thumb is that as the bulkiness of the cation increases, then the density will decrease. It is also affected by the anion. For example at 25 °C, with the anion NTf$_2^-$, density decreases from 1.52 g cm$^{-3}$ for [EMIM]$^+$ to 1.43 g cm$^{-3}$ for [BMIM]$^+$. Changing the anion to OTf$^-$ also results in a density decrease, i.e. to 1.39 g cm$^{-3}$ and 1.29 g cm$^{-3}$ for the [EMIM]$^+$ and [BMIM]$^+$ salts respectively. In the case of [BMIM]$^+$ ILs, the densities decrease with the anion in the order BF$_4^-$ (1.26) < OTf$^-$ (1.29) < PF$_6^-$ (1.35) < NTf$_2^-$ (1.43). The density of [OMIM]Cl is 1.0 g cm$^{-3}$ at 25 °C while that of [OMIM]NTf$_2$ is 1.32 g cm$^{-3}$.

1.6.3.4 Polarity

Polarity in ILs is dependent on several factors, such as the size of the anion, cation substituent, and the cation alkyl chain length. Using E$^N_T$ Reichardt’s scale Galonde et al. found a variety of ammonium, imidazolium, pyridinium, and pyrrolidinium ILs to possess polarity similar to short chain alcohols, i.e. methanol and ethanol.

1.6.3.5 Hydrophobicity/Hydrophilicity

The hydrophobicity/hydrophilicity of ILs can be affected by both ions. In particular, the alkyl chain length of the cation and the nature of the anion can have a strong influence, e.g. ILs containing hexafluorophosphate (PF$_6^-$) are more hydrophobic than those with tetrafluoroborate (BF$_4^-$). ILs with NTf$_2^-$ anions are also hydrophobic.

1.6.3.6 Electrochemical Window

A characteristic that makes ILs convenient solvents for electrochemistry is their generally wide electrochemical windows (ECW). This is the voltage range in which the IL is neither reduced nor oxidized (determined by the cation and anion respectively), and can be affected by many factors, including the electrode material, cut off current, and impurities. ECWs are typically greater than 4.0 V for ILs, even reaching 6.0 V in some cases. ILs consisting of non-coordinating ions and charges which are delocalised are fairly resistant to oxidation and reduction leading to large ECWs. The ECW of imidazolium based
ILs are typically smaller over a Pt working electrode compared to glassy carbon. This is due to the high acidity of proton at the C-2 position of the imidazolium ring which can be catalytically removed, leading to the IL breaking down earlier.\textsuperscript{92}

1.6.3.7 Ionic Conductivity

The ionic conductivity (the ability of a system to carry a current via the movement of ions) of ILs is generally of the magnitude 10.0 mS cm\textsuperscript{-1}, comparable to sea H\textsubscript{2}O, but can range from 0.1 to 20.0 mS cm\textsuperscript{-1}. There is an inverse relationship between conductivity and viscosity.\textsuperscript{82, 84} Increasing the temperature increases conductivity, and hole theory is currently the best way to describe this effect in ILs. It is assumed that the IL contains empty spaces which constantly fluctuate in size due to thermal motions.\textsuperscript{93} The movement of ions is then facilitated by these holes and with increasing temperature the presence/frequency of holes large enough for ion movement will also increase. This in turn will increase conductivity. The conductivities of [BMIM]BF\textsubscript{4}, [BMIM]NTf\textsubscript{2}, and [BMIM]OTf were reported to be 0.35, 0.40, and 0.29 mS cm\textsuperscript{-1} respectively at 25 \textdegree C.\textsuperscript{86}

1.6.3.8 Stability

Stability in ILs seems to be mostly dependent on the anion.\textsuperscript{83} For many ILs the thermal stability extends beyond 350 \textdegree C, though for long-term stability, lower values are usually found.\textsuperscript{82} Although known to be air, moisture, and temperature stable, the halogenated anions BF\textsubscript{4}\textsuperscript{-} and PF\textsubscript{6}\textsuperscript{-} can experience hydrolytic and thermal decomposition. This generates volatile and toxic compounds. It should be noted though that both NTf\textsubscript{2}\textsuperscript{-} and OTf\textsuperscript{-} based ILs are the most hydrolytically stable.\textsuperscript{83}

1.6.4 Synthesis

The synthesis of ionic liquids can be carried out via several methods (equations 1.11 to 1.14, ILs shown in red). The first method, and probably the most used, involves metathetic exchange of the anion of a halide IL, formed by reacting a base with an alkyl halide, with a metal salt (eq. 1.11). For example, reacting [BMIM]Cl with LiNTf\textsubscript{2} and producing [BMIM]NTf\textsubscript{2} and LiCl. Halide by-products (M\textsuperscript{+}X\textsuperscript{-}) are produced that can be difficult to
remove, especially for hydrophilic ILs. The second and third methods consist of the reaction of a base, e.g. imidazole, with a Brønsted acid (eq. 1.12) and direct alkylation (eq. 1.13), respectively. These methods avoid the presence of halides which increases atom efficiency. The drawback of method two however is that obtaining ILs of high purity is difficult. On the other hand, method three is limited by the reactivity and availability of the alkylating agents. In the fourth method (eq. 1.14) carbonates, e.g. dimethylcarbonate, are used instead of alkyl halides, but there is limited availability of acids (H\(^+\)X\(^-\)).

\[
\begin{align*}
A + R^+X^- & \rightarrow [AR]^+X^- + M^+Y^- \rightarrow [AR]^+Y^- + M^+X^- \quad \text{(eq. 1.11)}
\end{align*}
\]

\[
\begin{align*}
A + H^+X^- & \rightarrow [AH]^+X^- \quad \text{(eq. 1.12)}
\end{align*}
\]

\[
\begin{align*}
A + R^+X^- & \rightarrow [AR]^+X^- \quad \text{(eq. 1.13)}
\end{align*}
\]

\[
\begin{align*}
A + R_2CO_3 + H^+X^- & \rightarrow [AR]^+X^- + CO_2 + ROH \quad \text{(eq. 1.14)}
\end{align*}
\]

1.6.5 Purification

Purity of ILs is an important issue as their physical and chemical properties can be affected even by small amounts of impurities and can discolour the solvent. The most typical sources of impurities are residual starting materials from an incomplete reaction or halide by-products. Removing the impurities can be achieved by using activated charcoal or by passing the IL, sometimes with a solvent added to reduce viscosity, through silica/alumina.\(^{82}\) H\(_2\)O is another impurity but can be removed by heating under vacuum or by adding drying agents such as MgSO\(_4\), though it is difficult to achieve complete dryness.

1.6.6 Dissolution of I\(_2\) in ILs

The effect of I\(_2\) on imidazolium based ionic liquids was investigated by Fei et al.\(^{94}\) with a variety of anions. It was found that I\(_2\) was poorly soluble in NTf\(_2^-\) and PF\(_6^-\) based ILs, but would readily dissolve in BF\(_4^-\) ILs. Fei et al. attributed this to the larger charge
delocalization in NTf$_2^-$ and PF$_6^-$ compared to BF$_4^-$. This would lead to stronger F⋯I interactions in the latter. Through the addition of enough I$_2$ to a solvent, polyiodides can form. The simplest of these is I$_3^-$ (eq. 1.15) but due to the weakness of the I-I bond (dissociation energy of I$_2$ is 36 kcal mol$^{-1}$) the anion dissociates to I$^-$ and I$_2$. From this, all polyiodides (and many have been reported, e.g. eq. 1.16 and 1.17) can be thought of as adducts which consist of I$^-$ with varying amounts of I$_2$.$^{94,95}$

\[
\begin{align*}
\Gamma + I_2 & \rightleftharpoons I_3^- \quad \text{(eq. 1.15)} \\
I_3^- + I_2 & \rightleftharpoons I_5^- \quad \text{(eq. 1.16)} \\
I_5^- + I_2 & \rightleftharpoons I_7^- \quad \text{(eq. 1.17)} \\
I^- + I_3^- & \rightleftharpoons I_3^- + I^- \quad \text{(eq. 1.18)}
\end{align*}
\]

Combinations of polyiodides with ILs have been applied as iodination solvents for organic synthesis, the removal and storage of radioactive iodine, and as redox pairs in dye sensitised solar cells.$^{94}$ The high conductivity of polyiodide species has been explained by the Grotthuss mechanism, which states that in order for conduction to occur, a continuous path of mobile carriers must exist within the system, suggesting a bond-exchange reaction (eq. 1.18) similar to that proposed to explain the high mobility of protons in H$_2$O.$^{94–96}$

1.6.6.1 Ionic Conductivity

A series of polyiodides with 1-propyl-3-methylimidazolium ([PMIM]$^+$) cations were examined by Jerman et al.$^{96}$ and Thorsmolle et al.$^{95}$ As the amount of I$_2$ was increased, and thus that of I$^-$, an increase in ionic conductivity was observed that was consistent with the basic Grotthuss mechanism, explained above. Jerman et al. suggested that ‘bridges’ or ‘chains’ would form, aiding the conduction process. Thorsmolle et al. noted that, as the I$_2$ concentration increases, the higher polyiodides (I$_5^-$ and I$_7^-$) become more common, thus decreasing the amount of small, fast anions. Combined with the dilution effect, the conductivity would be expected to decrease at high I$_2$ concentration. The observed increase is attributed to an enhanced Grotthuss mechanism resulting from the increased
iodine/iiodide packing density. This then reduces the distance between the iodide and polyiodide species involved in bond exchange.

1.6.6.2 $^1$H-NMR spectroscopy

Fei et al.$^{94}$ investigated the effect I$_2$ would have on imidazolium based ionic liquids ranging from [EMIM]$^+$ (1-ethyl-3-methylimidazolium) to [OMIM]$^+$ (1-octyl-3-methylimidazolium). Their initial investigations examined the IL [PMIM]I (1-propyl-3-methylimidazolium iodide) and found that increasing the amount of I$_2$ causes an upfield shift of the acidic proton at the C-2 position of the imidazolium ring, in the $^1$H-NMR spectrum. The increase in shielding which leads to the shift is thought to be a result of hydrogen bond interactions occurring between the acidic proton and the polyiodide anion formed with the increasing addition of I$_2$. Channel inclusion features’ consist of cations in ‘channels’ encased by polyiodides. These are present in the solid state and if also present in the liquid state, then the observed chemical shift could be accounted for by the increased shielding this would generate. Similar upfield shifts were noted for both [PMIM]Br (1-propyl-3-methylimidazolium bromide) and [BMIM]I (1-butyl-3-methylimidazolium iodide). As well as the same chemical shifts observed above, for [OMIM]Cl (1-octyl-3-methylimidazolium chloride) there was a noticeable decrease in viscosity.

1.6.6.3 Raman spectroscopy

The Raman spectra of polyiodides can be interpreted in terms of I$_2$, I$^-$, and I$_3^-$ subunits which aggregate to form the higher polyiodides as stated by Jerman et al.$^{96}$ The I$_2$ molecule acts as a Lewis acid that coordinates with electron donors I$^-$ and I$_3^-$. The result is anti-bonding I-I orbitals being occupied causing an increase in the I-I bond length. Accordingly, the stretching frequency found for I$_2$ in the solid state (at 180 cm$^{-1}$) shifts to 145-165 cm$^{-1}$ in the adducts. The use of model compounds shows that linear I$_5^-$ exhibits bands at 108 and 165 cm$^{-1}$ with a third eventually appearing at 145 cm$^{-1}$.

Jerman et al.$^{96}$ did not see any evidence of I$_3^-$ present in the Raman spectrum of [PMIM]I which is to be expected. When I$_2$ was added, bands at 111 and 148 cm$^{-1}$ appeared. The first corresponds to the symmetric stretch ($v_{sym}(I_5^-)$) of the I$_5^-$ while the second was
considered too intense to ascribe to the antisymmetric stretch ($v_{\text{anti}}(I_3^-)$) of the symmetric triiodide. The spectra of discrete symmetric $I_3^-$ has a weak, shoulder like band between 130 and 142 cm$^{-1}$ corresponding to $v_{\text{sym}}(I_3^-)$. Therefore, it was their belief that the strong band at 148 cm$^{-1}$ was caused by a strongly asymmetric $I_3^-$ which changed the symmetry selection rules, enhancing the intensity of the $v_{\text{asym}}(I_3^-)$ band. Another explanation proposed was the presence of tetraiodides ($v_{\text{sym}}(2I^-\cdots I_2)$) which only exhibit a band between 145 and 155 cm$^{-1}$, existing in equilibrium with $I_3^-$ at low I$_2$ concentrations, as the tetraiodides do not show a band at 111 cm$^{-1}$. As the I$_2$ concentration increases, the band at 148 cm$^{-1}$ decreases and one at 141 cm$^{-1}$ becomes visible, with this new band being attributed to the antisymmetric stretch ($v_{\text{anti}}(I_3^-)$) of symmetric $I_3^-$, suggesting a preference for triiodide formation.$^{96}$

As the concentration of I$_2$ is continually increased, a band at 165 cm$^{-1}$ appears with weaker ones present at 111, 141, and 148 cm$^{-1}$ and all these are associated with the $I_5^-$ anion. The band at 165 cm$^{-1}$ is present in the spectrum of both discrete linear and V-shaped $I_5^-$, corresponding to the symmetric stretching of outer I-I ($v_{\text{sym}}(I-I)_{\text{outer}}$). The anion $I_5^-$ is also observed in the L-shaped ($I_3^--I_2$) adduct but at a weaker intensity. The linear ion has the symmetric stretching of inner I-I ($v_{\text{sym}}(I-I)_{\text{inner}}$) at 105-107 cm$^{-1}$ whereas the V-shaped ions have a strong band at 143-147 cm$^{-1}$ caused by the outer antisymmetric stretching ($v_{\text{anti}}(I-I)_{\text{outer}}$), a $v_{\text{sym}}(I-I)_{\text{inner}}$ at 112 cm$^{-1}$, and a $v_{\text{sym}}(I-I)_{\text{outer}}$ between 155 and 160 cm$^{-1}$. Combining the presence of these bands with the lack of the I$_2$ band Jerman et al. concluded that their [PMIM]I/I$_2$ mixtures consisted of discrete, linear $I_5^-$ ions.$^{96}$

1.6.7 Applications in the extraction of Precious Metals

Ionic liquids have been used for the extraction of PGMs. For example, trioctylammonium based protic ionic liquids have been used to selectively extract Pd and Pt from HCl solutions.$^{97}$ Mixtures of the NTf$_2^-$ and NO$_3^-$ ILs were tested and it was found that the extraction improved as the NO$_3^-$ IL content was increased. HNO$_3$ was then used to extract the metals and if this concentration was controlled then selective stripping of Pt was possible. Whitehead et al.$^{98}$ used [BMIM]HSO$_4$ alongside Fe$_2$(SO$_4$)$_3$ as oxidant and
thiourea as ligand for the extractions of metals. The system shows a high preference for Au and Ag. Au recovery from both a synthetic oxidic ore and a natural sulfidic ore was >85 % when using Fe$_2$(SO$_4$)$_3$ and thiourea. When compared to the aqueous system the yields were virtually identical. The IL system showed a slower Au extraction rate associated with the greater viscosity of ILs, but it did exhibit a greater stability towards recycling. Varying the length of the cation alkyl chain from butyl to octyl caused the Au extraction to decrease. Again this was related to the increase in viscosity caused by increasing the chain length. Variation of the anion was also examined in the series BF$_4^-$, OTf, Cl and DCA$. The use of BF$_4^-$ and OTf ILs led to a slight reduction in Au extraction while Cl and DCA resulted in minimal extraction.

1.7 Deep Eutectic Solvents (DESs)

1.7.1 History

DESs are a sub-class of ionic liquids possessing many of their characteristics and properties, however it is important to highlight that the two are in fact different types of solvents. DESs contain various species which give rise to an 'eutectic' mixture, i.e. with a melting point lower than that of either individual component. Relative to ILs, research on DESs can be considered quite recent with the first publication released in 2001.

1.7.2 Structure

As mentioned before, DESs and ILs are two different types of solvents. While ILs are comprised of discrete cations and anions, DESs are eutectic mixtures of Lewis/Brønsted acids and bases. Like ILs, they consist of large asymmetric ions with these ions possessing a low lattice energy and thus a low melting point. DESs can also be formed between non-ionic species further highlighting the difference with ILs.
DESs can be generally described using the formula $\text{Cat}^+X^-\text{Y}$. The cation can be an ammonium, phosphonium, or sulfonium ion, and $X^-$ is a Lewis base (hydrogen bond acceptor, HBA), usually a halide anion. $Y$ refers to the molecule that interacts with the anion (a hydrogen bond donor, HBD).
Most DESs are based upon quaternary ammonium or imidazolium cations. Choline chloride (21) is an ammonium salt commonly used, partly due to its nontoxicity and relatively low cost. In Europe it is classed as a provitamin and used in animal feed, being produced on the megatonne scale. It is possible to separate DESs into four types. This is dependent on the nature of the complexing agent:

- **Type I**: Solvents formed from quaternary ammonium salts and MCl$_x$; may be thought of as being analogous to metal halide/imidazolium salt systems.
- **Type II**: Hydrated metal halides are used with (21).
- **Type III**: Formed from (21) and a HBD and the type used in this work. A wide range of transition metal compounds dissolve in this type of DES, including chlorides and oxides. They are easy to prepare, fairly low cost, unreactive toward H$_2$O, and many are biodegradable. Altering the HBD will change the physical properties of the DES, making this class particularly adaptable for specific needs.
- **Type IV**: Involve a mixture of metal halides with urea (22).

### 1.7.3 Properties

The chemical properties of DESs and ILs are different. Their physical properties however are similar, as it has the potential to be ‘tuned’ to a particular need. Like ILs, DESs are non-flammable, and while their vapour pressure is low their liquid range is relatively wide. Two properties that give them an advantage over traditional ILs are their ease of synthesis and that they consist of relatively cheap, easily available components. On the other hand, they are typically less chemically inert.

#### 1.7.3.1 Melting Point

The melting point (or freezing point as it can be termed) of the DES mixture is lower than that of the individual constituent components, a result of the charge delocalization that occurs through hydrogen bonding between the HBD (halide anion) and the HBA. Most are liquid between room temperature and 70 °C but the melting point is ultimately
determined by the nature of the HBA and HBD as well as the molar ratio employed.\textsuperscript{99,101} For example, the DES Reline 200 is formed by 1 eq. of (21) and 2 eq. of (22), and its melting point is 12 °C, compared to 302 °C for (21) and 133 °C for (22). The melting point of Ethaline 200 (1 eq. (21):2 eq. ethylene glycol (23)) is -66 °C, whereas a mixture of 3 eq. of (21) and 7 eq. of imidazole (24) has a melting point of 56 °C.\textsuperscript{100,101} No name could be found for this in the literature and so will be referred to as Imiline 700 in this work.

1.7.3.2 Viscosity

Most DESs have a viscosity that is quite high compared to other ILs and conventional solvents, generally >0.1 Pa s at room temperature.\textsuperscript{99,101} The high viscosity is usually associated with the extensive hydrogen bond network present which results in less mobility of the free species. Large ion and small hole size, electrostatic, or Van der Waals forces may be contributors. The viscosity of Reline 200 and Ethaline 200 at 25 °C are 0.75 and 0.037 Pa s respectively.\textsuperscript{101}

1.7.3.3 Density

Most DESs have a density greater than that of H\textsubscript{2}O.\textsuperscript{101} It has been found that density increases with the number of hydroxyl groups and that the presence of aromatic groups decreases it. Changing the halide also has an effect, e.g. Br\textsuperscript{-} HBDs have larger densities compared to Cl\textsuperscript{-}.\textsuperscript{100} At 25 °C the density of Reline 200 is 1.25 g cm\textsuperscript{-3} and at the same temperature Ethaline 200 has a density of 1.12 g cm\textsuperscript{-3}.\textsuperscript{101}

1.7.3.4 Stability

In terms of stability, DES solvents are chemically inert to H\textsubscript{2}O and biodegradable. For the most part their stability is similar to traditional ILs.\textsuperscript{99–101}

1.7.3.5 Electrochemical Window (ECW)

The ECW of DESs is significantly lower than that of traditional ILs but usually sufficient for deposition of some metals, e.g. Zn, as they are larger than aqueous systems.\textsuperscript{99}
1.7.3.6 Ionic Conductivity

Ionic conductivity is lower for DESs compared to other ILs and conventional solvents. This is strongly related to viscosity. The higher the viscosity, the lower the conductivity. As a result, most DESs have poor conductivities (<1.0 mS cm\(^{-1}\) at room temperature). Large conductivities are shown only for those which contain (23) or (24) alongside (21). The conductivity of Reline 200 at 40 °C is 0.199 mS cm\(^{-1}\) and that of Ethaline 200 is 7.61 mS cm\(^{-1}\) at 20 °C. At a temperature of 90 °C Imiline 700 possesses a conductivity of 26 mS cm\(^{-1}\). Abbott et al. used hole theory to establish that ion mobility, and therefore conductivity, are influenced by the type and strength of interactions as well as the accessibility of suitable holes.

1.7.4 Synthesis

The synthesis of DESs typically involves the complexation of a quaternary ammonium salt with a metal salt/HBD. This is a simple mixing procedure with application of moderate heat in some cases. The cost therefore is low and the process can be considered green as the synthesis has 100% atom economy.
1.7.5 Dissolution of $I_2$ in DESs

Unlike in aqueous systems, $I_2$ is quite soluble in DESs. As with ILs this is most likely due to low charge delocalization in the halide anions, allowing the formation of strong Cl⁻–I interactions.

1.7.6 Applications in the extraction of Precious Metals

The major application of DESs today is incorporating metal ions in solution for metal deposition, dissolution, or processing. This is due to their advantages over aqueous systems with high metal salt solubility, absence of H$_2$O, and high conductivity compared to nonaqueous systems. DESs can accept or donate electrons/protons with which to form hydrogen bonds. This means that a large number of compounds can dissolve in them, including inorganic salts, aromatic acids, amino acids and metal oxides. It has been found that oxides with high ionic character are highly soluble in DESs, whereas those with a greater covalent character are poorly soluble. It should also be noted that as the anion in a DES is in concentrations around 5-10 M, even strong ligands bound to a metal ion can be displaced. The anion dominates complexations due to its significant Lewis basicity. $I_2$ has been used as an oxidant in Ethaline 200 for the safe removal of Au from fossil samples which were analysed by SEM. The coatings were completely removed using a 20.0 mM $I_2$ solution and the fossils were found to be undamaged even while submerged for 12 hours. Solutions with lower $I_2$ concentrations were tested for up to 60 hours and no damage was observed. In all cases $I_2$ was in large excess but overall this work indicates the relative gentleness of these solutions with $I_2$.

1.8 Electrochemistry

Electrochemistry is the study of chemical reactions taking place in a solution at the interface of an electron conductor and ionic conductor. In other words it examines the phenomena linked with separation of charge and its transference. Examples of electron conductors are metals or semiconductors while an electrolyte would be an ionic conductor.
Electrochemistry goes as far back as 1799 to the invention of Volta’s pile. Then ‘electricity’ referred to static electricity. This also set the basis for electrical engineering and telecommunications. Today, it is an important application for developing new areas of science as well as technology. It also plays an essential role in contributing towards a solution for global energy and environmental issues.

1.8.1 Basic Theory

The basic principle of electrochemistry is the transfer of an electron from the electrode to the electrolyte/species in solution. Should an external voltage be applied (*e.g.* in electrolysis) or if the source of the voltage is a chemical reaction (*i.e.* within a battery) then the reaction is termed electrochemical. A reaction where an electron is transferred between molecules is termed oxidation-reduction. The standard electrochemistry set-up consists of separated redox reactions connected by an external electric circuit (Fig. 1.9).

![Figure 1.9 Basic electrochemical set-up](image-url)
Figure 1.9 shows a simple two electrode set-up. One electrode acts as the working electrode and it is here where the reaction under study takes place. The material used must be a good electron conductor, *e.g.* glassy carbon, Pt, and Au. The other electrode must act as a reference, from which to measure the voltage of the working electrode, and a counter to balance the current generated. This dual function means it is difficult to maintain a constant potential while countering the current. This is solved by using the three electrode electrochemical cell. One is the working electrode and the other two are the reference and counter electrodes. The reference allows the potential of the working electrode to be compared to a stable, accurate value while the counter solely balances the current.\textsuperscript{108}

1.8.2 *Different types of electrochemical procedures*

All electrochemical techniques involve the use of an electrode. From this common point they can be divided into two groups, depending on whether they are based on electrode reactions or not. Those based on electrode reactions can be further divided (Table 1.1).\textsuperscript{106}

### Table 1.1 Classification of electrochemical techniques

<table>
<thead>
<tr>
<th>Group</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Based on electrode reactions</td>
<td>A - Methods that electrolyze the electroactive species under study completely</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B - Methods that electrolyze the electroactive species under study partially</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C - Methods that do not electrolyze the electroactive species under study</td>
</tr>
<tr>
<td>2</td>
<td>Not based on electrode reactions</td>
<td>Conductivity, High frequency method</td>
</tr>
</tbody>
</table>
1.8.2.1 Voltammetry

Voltammetry is a method by which a current is detected as a function of an applied potential. Several species which react at different potentials can be identified almost simultaneously with no need to separate into individual experiments. State of the art equipment and prior concentration of the analyte on the electrode surface means it is possible to detect concentrations as low as $10^{-12}$ M. Voltammetries can be linear or cyclic. In a linear voltammogram (LV), the potential is swept between two values, while in cyclic voltammetry (CV) the potential is also scanned in the reverse direction to complete the cycle. For a CV, a reversible reaction is one possessing fast electrode dynamics relative to the timescale of the sweep and will show oxidation and reduction peaks of equal intensity. In irreversible reactions the scan will only show oxidation or reduction peaks in the forward scan. On the return no peaks will be observed. Most redox reactions are somewhere in between, exhibiting quasi-reversible behaviour. Essentially the reverse peak appears but is smaller than the forward peak. Measuring the peak potentials allows for the deduction of standard rate constants from tables consisting of peak separation for simple electrode processes.

1.8.2.2 Electrodeposition

This is a type of electrolysis and the process carried out during electroplating, for which most of the work is in aqueous acidic/basic solutions with some specialist situations using organic solvents. The overall equation for metal (M) electrodeposition is shown in equation 1.19. This equation does not specify the phase each species is in and does not account for the solvents role. As such it can be rewritten as equation 1.20. Depending on the metal the number of solvent molecules in the solvation sphere may differ hence the non-specific value in the equation. In order for a metal to be deposited, the solvation sphere must be completely removed, requiring a lot of energy. For 100% electrolysis to occur a particular number of electrons is required and can be estimated using equation 1.21. $Q$ is the charge in Coulombs (C), $n$ is the required/lost electrons, $m$ is the number of moles, and $F$ is the Faraday constant (96485 C mol$^{-1}$). By dividing the actual charge passed by that calculated for 100% electrolysis, the extent achieved can then be calculated.
Typically, electrodeposition in non-aqueous solvents is only carried out when use of an aqueous solution is impossible. A number of technical difficulties can arise. To avoid hydrogen evolution, which is also a problem in H₂O, non-aqueous media with no active protons should be used. This would therefore exclude alcohols. Molten salts are often used to prevent hydrogen evolution, e.g. anhydrous molten MgCl₂ is used for the manufacture of metallic Mg and molten cryolite (Na₃AlF₆) is used for aluminium production from bauxite (Al₂O₃). Similarly, ionic liquids can also be used in electrodeposition, which could be then carried out at room temperature.

1.8.3 Applications in the deposition of Precious Metals

1.8.3.1 Pd

Huang and Chen reported the use of 1-butyl-1-methylpyrrolidinium dicyanamide ([BMPyr]DCA) to dissolve PdCl₂. The IL was chosen because of the strong coordination ability of the DCA anion. In order to dissolve PGM chloride salts, extra Cl⁻ is normally added to improve metal ion solubility (i.e. through the formation of MClₙ⁻-complexes). However by using DCA⁻, the addition of extra complexing agent is not needed. CVs were carried out using a Pt disc working electrode, a Pt spiral counter electrode, and a reference electrode of Pt wire in a ferrocene (Fc)/ferrocenium (Fc⁺) solution. When carrying out electrodeposition the working electrode was changed to a Fe wire. The cyclic voltammograms showed two reduction peaks due to Pd(II) being reduced to Pd(0). The two peaks were assigned to two types of Pd(II) complexing ions, similar to what had been reported in [BMIM]Cl. A small oxidation peak was also observed and this was related to anodic stripping of the Pd which had been deposited. This assignment was confirmed through electrochemical studies using a Pd electrode, which also showed a small stripping peak. The electrodeposition of Pd gave rise to deposits with different
morphologies depending on the potential applied. Using the most positive potential the deposit consisted of many fragments. Increasing the negativity of the potential changed the deposit from smooth cracks to 3D clusters of Pd grains. At the most negative potential the deposit was smooth and compact. Jayakumar et al.\textsuperscript{111,111} reported the electrochemical behaviour of fission Pd in the ionic liquid [BMIM]Cl. The CV of PdCl\textsubscript{2} in the ionic liquid at 100 °C, showed a reduction peak at -0.61 V (vs Pd), due to the reduction of Pd(II) to Pd(0). A second peak was observed at \textit{ca.} -1.13 V if the negative potential limit was extended. Two oxidation peaks were present at -0.26 V and 0.31 V. The diffusion coefficient of Pd(II) in [BMIM]Cl was determined to be of approximately 10\textsuperscript{-7} cm\textsuperscript{2} s\textsuperscript{-1}. The electrodeposition of Pd, at 100 °C for 2 hours, appeared to occur via dendrite formation after initial nucleation. The authors compared the use of [BMIM]Cl vs. HNO\textsubscript{3} as solvent for the recovery of PGMs.\textsuperscript{112} In the case of [BMIM]Cl, the recovery of Pd was >80% while in HNO\textsubscript{3}, Pd was recovered quantitatively. Both in the IL and HNO\textsubscript{3}, Pd deposition resulted in dendrites. The electrodeposition of Pd was investigated by Bando \textit{et al.}\textsuperscript{113} in [BMPyr]NTf\textsubscript{2}. PdBr\textsubscript{2} or PdCl\textsubscript{2} was dissolved in the IL using some [BMPyr]Br or Cl, \textit{e.g.} 1 eq. PdBr\textsubscript{2} and 2 eq. [BMPyr]Br. The addition of the halide ILs was necessary for the formation of the square planar Pd complexes, which was confirmed by UV/Vis analysis. The electrochemical behaviour of [PdCl\textsubscript{4}]\textsuperscript{2-} was found to be similar to that of [PdBr\textsubscript{4}]\textsuperscript{2-}. Thus, the CV of PdBr\textsubscript{2} showed a reduction peak at -1.6 V, assigned to the reduction of [PdBr\textsubscript{4}]\textsuperscript{2-} to Pd(0), while an oxidation peak at -0.4 V was assigned to the anodic stripping of deposited Pd. The process was irreversible and appeared to occur via two one electron steps, although this was not confirmed. Electrodeposition experiments and simulation curves showed that the deposition process occurred initially via progressive nucleation. Higher current densities resulted in black, powdery deposits whereas lower current densities led to bright, smooth deposits. In the case of PdCl\textsubscript{2} the reduction peak appeared at -1.8 V. The difference was attributed to the higher stability of the chloro-complex compared to [PdBr\textsubscript{4}]\textsuperscript{2-}.

Lanzinger \textit{et al.}\textsuperscript{114} investigated the electrodeposition of Pd films from ILs and DESs. For this, PdCl\textsubscript{2} was dissolved in various solvents at 30-70 °C. The solution in Reline 200 became yellow, and in Ethaline 200 orange-red. Dissolution of PdCl\textsubscript{2} in a [BMIM]Cl/BF\textsubscript{4} mix also gave an orange-red solution. It was suggested that the orange-red colour
indicates the presence of square planar \([\text{PdCl}_4]^2-\). Cyclic voltammetry was carried out on the solutions over glassy carbon at scan rates between 25 and 150 mV s\(^{-1}\) and temperatures of 50, 75, and 100 °C. In Ethaline 200, the reduction of Pd(II) to Pd(0) is observed at -0.61 V. Two oxidation peaks at -0.39 and 0.03 V are related to the anodic stripping of the bulk and surface electrodeposits. The CV in Reline 200 shows the reduction of Pd(II) at -0.5 V and the oxidative anodic stripping of bulk electrodeposits at 0.42 V. The difference in the oxidation peaks indicates that different dissolution mechanisms are occurring in the two DESs, and that the different colours of the solutions support this. The CV of the solution in [BMIM] IL is similar to that in Ethaline 200, with a reduction peak at -0.93 V and two oxidation peaks at -0.43 and -0.06 V. All CVs exhibited a nucleation loop which is typical of an electrodeposition process that requires nucleation overpotential. The large separation of the reduction and oxidation peaks suggest the reduction of Pd(II) to be a process controlled by both kinetics and diffusion. In order to carry out electrodeposition it was necessary to optimise viscosity and conductivity by using select temperatures for each solvent (Ethaline = 30 °C, Reline = 70 °C, [BMIM]Cl/\(\text{BF}_4\) = 100 °C). The deposits obtained were semi-bright grey to dull dark grey. It was found that current density used and electrolyte composition both affected the morphology of the deposit with the deposit from Ethaline 200 fine grained and dense. Increasing the current density altered this to a dense compact deposit. From Reline 200, the deposit was coarse grain, nodular, less compact, and became fine grained and compact. The IL deposit at first was nanosized, nodular and less compact but after increasing the current density the Pd particle size increased with a less compacted deposit. Related work carried out by Mehner et al.\(^{115}\) investigated hydrogen embrittlement of Pd deposits from Reline 200 and an aqueous electrolyte. It was found that the Pd layers deposited from the DES showed no significant brittleness, whereas the deposit from the aqueous electrolyte had clear indicators of hydrogen embrittlement. This illustrates a benefit of using a DES over an aqueous system, the kind used in industry today for the deposition of metals.

1.8.3.2 Pt

ILs have been used for the electrochemical dissolution of metallic Pt. Deferm et al.\(^{116}\) tested different ionic liquids containing Cl\(^-\) for the dissolution of Pt, evaluating their
dissolution rate and current efficiency. It was found that dissolution only occurred in type I DESs ZnCl$_2$-[EMIM]Cl and ZnCl$_2$-(21). For this, the maximum dissolution rate was 192.2 g m$^{-2}$ h$^{-1}$ and 9.090 g m$^{-1}$ h$^{-1}$ respectively, while the maximum current efficiency was 99% and 96%. Addition of a metal chloride salt, with a decomposition potential more than 1.5 V, was necessary and the ECW of the IL had to be 1.5 V, preferably 2 V. Zhang et al.\textsuperscript{117} investigated the electrodeposition of Pt nanoparticles in N, N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate ([DEME]BF$_4$) over a glassy carbon electrode. Either K$_2$[PtCl$_4$] or K$_2$[PtCl$_6$] was dissolved in the IL before running CV and electrodeposition. The process by which deposition of Pt occurred was found to be dependent on the potential applied. At -2.0 V, a disproportionation mechanism (eq. 1.22) was found to occur, whereas a four electron reduction occurred when held at -3.5 V through disproportionation (eq. 1.23 and 1.24). SEM of the -2.0 V deposit showed the electrode covered in fairly uniform particles between 10 and 50 nm, whereas the -3.5 V deposit irregularly covered the electrode with particles between 50 and 200 nm. This difference in the deposits’ morphology was related to the different reduction mechanisms; i.e. the four electron reduction caused Pt to deposit on the glassy carbon electrode while the disproportionation mechanism led to Pt depositing more easily onto Pt that was already on the electrode.

\begin{align*}
2\text{PtCl}_4^{2-} &\rightarrow \text{PtCl}_6^{2-} + \text{Pt} + 2\text{Cl}^- \quad \text{(eq. 1.22)} \\
\text{PtCl}_6^{2-} + 2\text{e}^- &\rightarrow \text{PtCl}_4^{2-} + 2\text{Cl}^- \quad \text{(eq. 1.23)} \\
2\text{PtCl}_4^{2-} + 2\text{e}^- &\rightarrow \text{PtCl}_6^{2-} + \text{Pt} + 4\text{Cl}^- \quad \text{(eq. 1.24)}
\end{align*}

1.8.3.3 Au

Bozzini et al.\textsuperscript{118} examined the electrodeposition of Au using KAu(CN)$_2$ in [EMIM]NTf$_2$. The working electrodes used for cyclic voltammetry was a glassy carbon and polycrystalline Au, while Pt was used for electrodeposition. The cyclic voltammetry of the Au salt showed four new peaks, both in the reduction and oxidation areas. Two peaks observed at -0.4 and 0.07 V, both small, were assigned to the reorientation or selective
adsorption of the IL ions. Electrodeposition of Au was observed between -1.3 and 1.6 V. SEMs of the electrodeposits show initial deposit formation as dendrites consisting of nanosized spherical grains. As deposition time increased continuous deposits form of needle shaped grains. The reduction of Au(III) to Au(0) has been studied in [EMIM]BF$_4$ and [BMIM]BF$_4$ by Oyama et al.$^{119,120}$ Both two and one electron reductions were observed for the [AuCl$_4$]$^-$/[AuCl$_2$]$^-$ (eq. 1.25) and [AuCl$_2$]$^-$/Au couples, respectively. The disproportionation reaction shown in equation 1.26 was also found to occur significantly in the systems.$^{119}$

\[
\text{[AuCl}_4^- + 2e^- \rightarrow [AuCl}_2^- + 2Cl^- \quad \text{(eq. 1.25)}
\]

\[
3\text{[AuCl}_2^- \rightarrow [AuCl}_4^- + 2Au + 2Cl^- \quad \text{(eq. 1.26)}
\]

\[
\text{Au + 2Cl}^- \rightarrow [\text{AuCl}_2^- + e^- \quad \text{(eq. 1.27)}
\]

\[
\text{[AuCl}_2^- + 2Cl^- \rightarrow [AuCl}_4^- + 2e^- \quad \text{(eq. 1.28)}
\]

Na[AuCl$_4$] was also dissolved in [EMIM]BF$_4$ using varying amounts of [EMIM]Cl and the CV studied over Pt and Au working electrodes.$^{120}$ The voltammetry of [EMIM]Cl in [EMIM]BF$_4$ showed a peak at 1.0 V for the reduction of either Cl$_2$ or Cl$_3^- \rightarrow$ Cl$^-$ and the corresponding reverse oxidation. Addition of Na[AuCl$_4$] and [EMIM]Cl at the same concentrations resulted in two new reduction and oxidation peaks. The peaks were assigned to the reduction of Au(III) to Au(I) and then Au(I) to Au(0) (as explained above), followed by the corresponding oxidations in the reverse scan.

\[
\text{I}_2 + 2e^- \Leftrightarrow 2\text{I}^- \quad \text{(eq. 1.29)}
\]

\[
\text{I}_2 + \text{I}^- \Leftrightarrow \text{I}_3^- \quad \text{(eq. 1.30)}
\]

\[
\text{I}_3^- + 2e^- \Leftrightarrow 3\text{I}^- \quad \text{(eq. 1.31)}
\]

Aldous et al.$^{121}$ have also studied the electrochemistry of Au(III) in [BMIM]NTf$_2$. Glassy carbon was used as the working electrode, Pt mesh as the counter electrode, and a Ag/Ag$^+$
reference of AgNO₃ (0.01 M) in [BMIM]NO₃. It was observed that Au(III) was reduced in two steps (Au(III)/Au(I)/Au), and oxidation peaks relating to the oxidation of Cl⁻ were identified. Abbott et al.¹²²,¹²³ have used the I₂/I⁻ system as an electrocatalyst in Ethaline 200 (1 eq. (21):2 eq. (23)). In the CV of the solutions over Pt working electrode, two reduction and two oxidation peaks were observed, suggesting the formation of trihalide species, e.g. I₃⁻ or I₂Cl⁻, in the diffusion layer after I₂ reduction (eqs. 1.29-1.31). The I₂/I⁻ /Ethaline solutions were used for the dissolution of Zn and Cu powder. After leaching for 24 hours at 40 °C, a Ni cathode and IrO₂ coated Ti mesh anode were used at a potential of 0.9 V to deposit the Cu within 2 hours. A solution of I₂ (0.1 M) in Ethaline 200 was used to remove Au/Ag ore grains from sulfide based gangue. After 10 minutes, the Au/Ag alloy was completely dissolved. Samples of Au/Ag (∼90.0 mg) dissolved in the I₂/Ethaline mixtures were obtained after heating at 50 °C for 48 h. These solutions were then held at a current density of 4.0 mA cm⁻² for either 2 or 20 hours and the Au deposited onto a Ni sheet. Longer deposition times caused a thicker metal deposit with no change in morphology. EDX analysis confirmed that only Au and Ag were present in the deposits and that Au appeared to be preferentially concentrated in the precipitates.

1.9 The Aim of the Project

The main aim of the project is to develop a sustainable method for the recovery of precious metals, e.g. Pd and Pt, from automotive catalysts using non-toxic reagents in ionic liquids under mild conditions. Conditions currently employed involve the use of strong acids, such as aqua regia, which are environmentally unfriendly.¹⁰ The process will consist of two stages: An oxidation/dissolution stage, followed by electrodeposition. For the oxidation / dissolution step, L---I₂ adducts will be used in the first instance, where I₂ acts as the oxidant. The ligands (L) contain ‘soft’ S donor atoms and favour the square planar geometry that ‘soft’ d⁸ noble transition metals (e.g., Pd²⁺, Pt²⁺) prefer. They also act as chelating ligands which further favours metal dissolution, by stabilising the oxidised metals in solution. Other ligand / oxidant systems will also be investigated as well as those which do not use ligands. A third, somewhat bonus stage, will be investigating the re-use of our system. Is it possible and if so how many times can we do so?
A secondary aim is the recovery of Au. Nowadays due to shortages and its usage in ever present electronics it is important to recover this metal wherever and whenever possible. As with Pd and Pt the conditions used currently are bad for the environment, *i.e.* using CN\(^{-}\).\(^{12}\) Therefore a more environmentally friendly system is desired. This leads to the Ph\(_3\)P/I\(_2\) adduct mentioned prior. The aim of this part of the project is to study the formation and stability of the adduct in ILs and explore the ability of these mixtures to dissolve Au powder. Electrodeposition from the IL mixture will be used to recover the Au before also investigating the viability of re-using this system.

An additional aim was to develop more efficient methods to synthesise dithiooxamide ligands which are used in precious metal recovery processes in the literature. For this various non-conventional synthetic methods including mechanochemical, sonochemical, and microwave reactions were tried and the results compared to the conventional synthesis in solution.
Chapter 2. A comparison of methodologies for the synthesis of Dithiooxamides

2.1 Aims

The aim of this Chapter was to successfully synthesise dithiooxamide-diiodine adducts that can be used to dissolve Pt or Pd in ionic liquids. For this, the dione ligands \(\text{Me}_2\text{pipd} \, (1)\) and \(\text{Me}_2\text{dazd} \, (2)\) have to be prepared before carrying out a thionation reaction. The resulting dithione ligands \(\text{Me}_2\text{pipdt} \, (6)\) and \(\text{Me}_2\text{dazdt} \, (7)\) are then used to obtain the dithiooxamide-diiodine adducts \([\text{Me}_2\text{pipdtH}]I_3 \, (12)\) and \(\text{Me}_2\text{dazdt/2I}_2 \, (13)\). The capability of these adducts to dissolve Pd and Pt in ionic liquids will then be tested.

Initially the ligand synthesis was carried out following literature methods, but alternative synthetic methods have also been investigated, e.g. involving mechanochemical, microwave, and sonochemical reactions, in order to achieve the synthesis of the ligands in a more environmentally friendly manner and/or better yields.

2.2 Results and Discussion

2.2.1 Synthesis

As discussed in the introduction, there are three stages towards the synthesis of \([\text{Me}_2\text{pipdtH}]I_3 \, (12)\) or \(\text{Me}_2\text{dazdt/2I}_2 \, (13)\). The first step is a cyclization reaction involving dimethyl oxalate \(3\) with either \(\text{N,N'\text{-dimethylethylenediamine} (4)}\) or \(\text{N,N'\text{-dimethyl-1,3-propanediamine (5)}}\) to form \(\text{Me}_2\text{pipd} \, (1)\) or \(\text{Me}_2\text{dazd} \, (2)\), respectively. The second step involves the thionation of \((1)\) and \((2)\) using LR \(8\). The resulting dithiones, \(\text{Me}_2\text{pipdt} \, (6)\) and \(\text{Me}_2\text{dazdt} \, (7)\), are then reacted with diiodine to give \((12)\) or \((13)\), respectively.\(^{25,33-36,39,41}\)

Part of this work was done in collaboration with Ms. Niamh Wilson, an undergraduate student who carried out her final year research project in our research group under my supervision. In particular, she focused on the microwave and sonochemical experiments as well as some of the conventional routes to synthesise \((6)\) and \((7)\). She also attempted
the preparation of the metal complexes [Pd(Me₂pipdt)₂](I₃)₂ (17) and [Pt(Me₂pipdt)₂](I₃)₂ (14).

2.2.1.1 Me₂pipd (1)

2.2.1.1a Conventional Synthesis

As mentioned in the introduction, the preparation of (1) has been previously reported by several authors. In the first instance, (1) was prepared following the general method reported by Deplano et al.,³⁴ which consisted of the 1:1 reaction between dimethyl oxalate (3) and N,N’-dimethylethylenediamine (4), in dry toluene, under a N₂ atmosphere at reflux, for 2 hours (Scheme 2.1). The ¹H-NMR spectrum of the reaction mixture was carried out after 2 hours and this showed no starting reagents present, meaning an apparent full conversion to (1), which was not isolated at this stage. A conversion close to 100% is comparable to that previously reported by Mueller-Westerhoff and Zhou³⁵ (90%) and Marder et al.³⁶ (96%), and it is a significant improvement from that of Isaksson et al.³³ (40%). In one of the attempts, the reaction was monitored using thin-layer chromatography (TLC) over 3 hours. This showed that the process was complete after 2 hours and there was no significant difference with the 3 hours reaction. Table 2.1 shows isolated yields of (1), which were consistent (96% on average) regardless of reagent concentration (0.1 M-0.2 M) and scale of the reaction (20-100 mL of solvent). This contrasts with previous reports, where open chained polymeric materials were observed.
to form in large amounts if the concentration of the starting materials was higher than 0.1 M.\textsuperscript{33}

Table 2.1 Reaction conditions and isolated yields of (1) obtained following the conventional synthetic method\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent volume/Concentration of reagents</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 mL / 0.1 M</td>
<td>93-99\textsuperscript{b}</td>
</tr>
<tr>
<td>2</td>
<td>20 mL / 0.2 M</td>
<td>94\textsuperscript{c}</td>
</tr>
<tr>
<td>3</td>
<td>50 mL / 0.1 M</td>
<td>98\textsuperscript{d}</td>
</tr>
<tr>
<td>4</td>
<td>50 mL / 0.2 M</td>
<td>99\textsuperscript{e}</td>
</tr>
<tr>
<td>5</td>
<td>100 mL / 0.1 M</td>
<td>99\textsuperscript{f}</td>
</tr>
<tr>
<td>6</td>
<td>100 mL / 0.2 M</td>
<td>96\textsuperscript{g}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: All reactions carried out in toluene at reflux, 1:1 ratio of (3):(4), 2 hours
\textsuperscript{b}: 0.2362 g, 2.0 mmol, 0.1 M (3), 0.22 mL, 2.0 mmol, 0.1 M (4)
\textsuperscript{c}: 0.4724 g, 4.0 mmol, 0.2 M (3), 0.44 mL, 4.0 mmol, 0.2 M (4)
\textsuperscript{d}: 0.5904 g, 5.0 mmol, 0.1 M (3), 0.55 mL, 5.0 mmol, 0.1 M (4)
\textsuperscript{e}: 1.1806 g, 0.01 mol, 0.2 M (3), 1.1 mL, 0.01 mol, 0.2 M (4)
\textsuperscript{f}: 1.1806 g, 0.01 mol, 0.1 M (3), 1.1 mL, 0.01 mol, 0.1 M (4)
\textsuperscript{g}: 2.3618 g, 0.02 mol, 0.2 M (3), 2.2 mL, 0.02 mol, 0.2 M (4)

2.2.1.1b Mechanochemical Synthesis

In an attempt to synthesise (1) in a shorter amount of time and to also reduce the amount of solvent used, the mechanochemical reaction between dimethyl oxalate (3), and N,N'--dimethylethlyenediamine (4) was tried using a Retsch MM 400 ball mill. Several parameters can be changed in this process, including frequency, time, or amount of reactants present in the ball mill jar. The effect of using small amounts of solvent during the process (LAG or liquid assisted grinding) was also investigated.

Initially, reactions were carried out at 15 Hz (Table 2.2, entries 1 and 2) for 5 minutes both with and without toluene (1 eq.), ensuring the reactants ratio was 1:1. Purification of the resulting product was then carried out by washing with toluene (10 mL) for 15 minutes before filtering and drying. On average, each reaction was repeated 3 times, and the range of yields of purified product obtained are included in Table 2.2. The range observed in
the yields is partly due to the difficulty to remove all the solid from the milling jars, in particular when the resulting particle size is small (see below). The reactions carried out without toluene (entry 1) gave on average a lower yield (63%) than those using the solvent (entry 2, 74%). Therefore, LAG was used in all subsequent ball mill reactions. When the reactions were carried out for a shorter reaction time (1 minute; entry 3), the average yield (60%) was lower compared to the 5 minute process (entry 2). A final set of reactions were run for 1 minute at lower frequency (5 Hz), achieving an average yield of 71% (entry 4). The increase in product yield was also observed by Štrukil et al.\(^{124}\) in the reaction of \(p\)-phenylenediamine with \(p\)-methoxyphenyl isothiocyanate when using LAG (except H\(_2\)O).

Table 2.2 Reaction conditions and isolated yields for the mechanochemical synthesis of (1)\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Liquid Assisted Grinding</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^b)</td>
<td>None</td>
<td>56-74</td>
</tr>
<tr>
<td>2(^b)</td>
<td>Toluene</td>
<td>69-81</td>
</tr>
<tr>
<td>3(^c)</td>
<td></td>
<td>54-64</td>
</tr>
<tr>
<td>4(^d)</td>
<td></td>
<td>69-72</td>
</tr>
</tbody>
</table>

\(a\): All reactions carried out using 0.2194 g (1.86 mmol) of (3), 0.2 mL (1.86 mmol) of (4)
\(b\): 15 Hz, 5 minutes
\(c\): 15 Hz, 1 minute
\(d\): 5 Hz, 1 minute

The results above suggest that at higher frequencies a longer reaction time is needed. Scanning electron microscopy (SEM) was run on the samples from entries 3 (A-C) and 4 (D-F) in Table 2.2 and are shown in Figure 2.1. Pictures A-C show that the product's particle size ranges between 0.7-4.4 \(\mu\)m for the reactions at 15 Hz, whereas D-F (1 Hz) have particles ranging in size between 1.4-7.8 \(\mu\)m. The use of higher frequency therefore results in finer particles, and also a smaller size range compared to the lower frequency.
Figure 2.1 SEM images of product (1) obtained after purification from the reactions carried out during 1 minute at 15 Hz (A-C) and 5 Hz (D-F)

To ensure that the reaction did not proceed in the NMR tube during the characterisation of the products, a sample containing the starting materials in a 1:1 ratio ((3) = 86 mM, (4) = 93 mM, in 5 mL of CDCl$_3$) was prepared and monitored over time by NMR. $^1$H-NMR spectra were run straight after mixing the starting materials, and then after 30 minutes, 1
hour, and 2 hours. Finally, spectra were taken daily for 96 hours. The spectra run right away, and after 2 and 24 hours are shown in Figure 2.2.

The signals for the starting materials are observed at 3.90 ppm for (3), and at 2.69 (CH$_2$) and 2.42 (CH$_3$) ppm for (4). Methanol is produced as a by-product and its concentration increases with time (i.e. signal at 3.46 ppm (CH$_3$) in Fig. 2.2). It can be seen that the spectrum taken just after mixing the starting materials shows the presence of (1), i.e. peaks

Figure 2.2 $^1$H-NMR spectra (CDCl$_3$, 2.4-4.0 ppm region) taken immediately after mixing (3) and (4) (top), after 2 hours (middle), and after 24 hours (bottom)
at 3.08 ppm (CH$_3$) and 3.55 ppm (CH$_2$). The conversion at this stage is ca. 4%. This increases to 39% after 120 minutes, and to 98% after one day. This experiment shows that the use of mechanochemical methods significantly speeds up the reaction from 24 hours for almost full conversion in solution, to a near instantaneous reaction.

### 2.2.1.1c Comparison of methods

A higher yield (>90%) can be achieved with the conventional synthesis, compared to the process in the ball mill (70-75%), however the solvent volume required for the reaction and the purification step is very large. For example, the number of toluene equivalents required for 1 eq. of starting materials (not including recrystallization), is between 50 and 100. In addition, the solvent must be heated in order to reach refluxing temperatures, it is necessary to use an inert atmosphere, and when using toluene to recrystallize the product it also must be heated, whereas the mechanochemical method simply uses it at room temperature. Using the mechanochemical method, yields of 74% on average were obtained after 1 minute at 15 Hz (Table 2.2., entry 2). Even if the frequency was lowered to 5 Hz, an average of 71% was still achieved (Table 2.2., entry 4). All of the reactions involving LAG only used 1 eq. of toluene, which is a significant reduction compared to the conventional method. Even the toluene used for the purification could theoretically be re-used. In addition, the ball-mill process does not require heating and can be carried out in the open air.

### 2.2.1.2 Me$_2$pipdt (6)

#### 2.2.1.2a Conventional Synthesis

The second stage in the synthesis of the ligands is the preparation of (6) (Scheme 2.2). In the literature, Lawesson’s Reagent (8) was used to thionate the dione.$^{33}$ This was achieved through the preparation of (1) in toluene, as described above, followed by the in-situ addition of (8) (1.2 eq.) while under N$_2$ due to its air and moisture sensitivity. Upon removing the toluene, the crude product was purified from DCM/ethanol (4:1). Similar procedures were carried out herein in the first instance but, as discussed below, results were inconsistent. The reason for the low, inconsistent, yields could be due to the
degradation of the LR (8) over time. It is known that (8) is air and moisture sensitive and can decompose or slowly polymerise in solution at temperatures over 110 °C.125

![Scheme 2.2 Synthesis of (6)](image)

To investigate the potential degradation of (8), its \(^1\)H-NMR spectrum in CDCl\(_3\) was monitored over the course of four consecutive days (Fig. 2.3) at room temperature. The signals corresponding to (8) appear at δ (ppm) 8.49 (dd, 4H, \(^3\)J=9, 8.1 Hz, Ph), 7.10 (m, Ph), and 3.93 (s, 6H, OCH\(_3\)), and are present in the spectrum of day 1 (Fig. 2.3). No \(^1\)H-NMR data of (8) could be found in the literature for comparison. Data could be found for the monomer \(\text{p-MeO(C}_6\text{H}_4)\text{PS}_2\) (9), and the additional peaks at δ 7.92, δ 6.98, and δ 3.87 are believed to correspond to it.126,127 This is expected as (8) dissociates and it is in equilibrium with the monomer in solution. Over time these peaks become broader, increase in intensity, and slowly shift upfield. It has been shown however, that the O-analogue of (9), \(\text{p-MeO(C}_6\text{H}_4)\text{P(S)}\text{O}\), has a very similar \(^1\)H-NMR spectrum.127 No chemical shift values or solvent data are provided for \(\text{p-MeO(C}_6\text{H}_4)\text{P(S)}\text{O}\) in the paper, but a small downfield shift for the aromatic protons of \(\text{MeO(C}_6\text{H}_4)\text{P(S)}\text{O}\) compared to (9) is reported. Another possibility is that (8) dissociates immediately on dissolution and there is a fast equilibrium between (8) and (9), with only an average signal observed on the NMR time scale. In this case, the new signals currently marked (9) in Figure 2.3 would correspond to decomposition products. These peaks then increase in intensity as time progresses.
Figure 2.3 $^1$H-NMR spectra (CDCl$_3$, 3.0-9.0 ppm region) of (8) taken over 4 days at room temperature; top NMR taken of (8) when first obtained.

With the current data, it is therefore not possible to establish if the peaks appearing at $\delta$ 7.87 (m, 4H, Ph), $\delta$ 6.94 (m, 4H, Ph), and $\delta$ 3.84 (m, 6H, OCH$_3$) at 96 hours correspond to (9), and/or decomposition products, i.e. a trimer formed of $p$-MeO(C$_6$H$_4$)P(S)O.$^{37}$ Nevertheless, since the spectrum after 24 hours does not show significant degradation of (8), the reason for the low thionation yield reported remains unclear.
Table 2.3 Reaction conditions and isolated yields of (6) following the conventional synthetic method*a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent Volume/Concentration of reagents ((1), (8))</th>
<th>Time/hours</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 mL / 0.1 M, 0.12 M</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>20 mL / 0.087 M, 0.1048 M</td>
<td>16.5</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>20 mL / 0.06 M, 0.12 M</td>
<td>24</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>20 mL / 0.087 M, 0.1048 M</td>
<td>48</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>20 mL / 0.06 M, 0.12 M</td>
<td>48</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>50 mL / 0.1 M, 0.12 M</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>100 mL / 0.1 M, 0.12 M</td>
<td>48</td>
<td>33, 75</td>
</tr>
</tbody>
</table>

*a: All reactions carried out in toluene at reflux. For entries 1-3 and 6-7: (1) was not isolated prior to the addition of (8). In these cases, the amount of (1) reported in the table has been estimated assuming full conversion in the first step of the process

b: 0.2843 g, 2.0 mmol, 0.1 M (1), 0.9707 g, 2.4 mmol, 0.12 M (8), ratio of 1:1.2
c: 0.2417 g, 1.7 mmol, 0.087 M (1), 0.8494 g, 2.1 mmol, 0.1048 M (8), ratio of 1:1.2
d: 0.1706 g, 1.2 mmol, 0.06 M (1), 0.9748 g, 2.4 mmol, 0.12 M (8), ratio of 1:2
e: 0.7108 g, 5.0 mmol, 0.1 M (1), 2.4268 g, 6.0 mmol, 0.12 M (8), ratio of 1:1.2
f: 1.4216 g, 0.01 mol, 0.1 M (1), 4.8536 g, 0.012 mol, 0.12 M (8), ratio of 1:1.2

Table 2.3 contains a summary of the reaction conditions tried and isolated yields of (6) obtained (see Scheme 2.2). In some cases, (1) was not isolated prior to the addition of (8), which is used in excess, and the yields reported are overall yields for the full process, *i.e.* entries 1-3 and 6-7. Initially the thionation step was carried out for 1 hour, in dry toluene, under a N₂ atmosphere at reflux, as stated by Deplano *et al.⁴⁴, however the resulting overall yield was only 8% (entry 1). As mentioned before, the authors do not state their yields and so a comparison to their work cannot be made based on this. For a second attempt, the thionation step was left overnight, for a total of 16.5 hours. The overall yield for this was 39% (entry 2), comparable to the overall yield of 32% reported by Isaksson *et al.³³, In further attempts, the reaction time was increased first to 24 hours and then to 48 hours. Overall yields increased again to 52% and 75% respectively (entries 3 and 7). This is a clear improvement compared with the literature data. It should be noted that in the case of entry 7 the reaction was also carried out at a larger scale which could have also had an impact on the yield, *e.g.* the larger mass of product obtained may minimise losses during the work-up of the reaction. However, when this procedure was repeated several
months later, a yield of only 33% was achieved. The reasons for this are unclear. In an attempt to improve reproducibility, the reaction was carried out after having isolated (1). As with the in-situ reaction, (1) was reacted with (8) in toluene at reflux for 48 hours. Two different (1):(8) ratios were used (1:1.2 and 1:2), but the resulting yields of isolated (6) were still low (ca. 30%, entries 4 and 5). Thus, the use of additional (8) or prior isolation of (1) have no effect on the yield. Since, at this stage, the yield could not be improved, the in-situ reaction was considered more convenient, as it uses less solvent and simplifies considerably the work-up. Upon increasing the scale of the reaction (from entry 3 to entry 6) the percentage yield increased again by 13%.

Given the above results, and in order to improve the yield and preparation method of (6), the reaction between (1) and (8) was carried out using mechanochemical, microwave and sonochemical synthetic methods.

### 2.2.1.2b Mechanochemical Synthesis

Several attempts were made at synthesising (6) mechanochemically. The first attempt involved the LAG ball-mill reaction of (1) and (8) at a 1:2 ratio, at 15 Hz for 4 hours with 1 eq. of toluene. The colour change observed during the conventional reaction in toluene (from a pale yellow suspension, to dark red/brown) was not seen during the mechanochemical procedure. It was noticed, however, that a sticky yellow coating formed around the ball. To see if the solvent was the cause of the coating, a second attempt, was carried out without adding toluene, but again the yellow coating formed (Fig. 2.4A). At this point it was thought that the stainless steel grinding ball used may be too large (13.6 g and 11 mm in diameter), and three smaller balls (4.03 g and 9 mm in diameter) were used instead (with no added solvent). This time, after 4 hours, no paste formed but there was no evidence of the reaction occurring (i.e. no colour change observed, Fig. 2.4B). The reaction was also tested on a smaller scale, but it also failed to form the product. Given these results, the mechanochemical synthesis of (6) was abandoned.
Figure 2.4 Resulting mixtures after the mechanochemical 1:2 reaction of (1) and (8) (at 15 Hz, 4h, no added solvent): A = ball used: 13.6 g and 11 mm in diameter; B = balls used: 4.03 g and 9 mm in diameter

2.2.1.2c Microwave Synthesis

A microwave method of thionation of ketones, flavones, isoflavones, lactones, amides, and esters using (8) has been reported in the literature by Varma et al.71 Based on this, the synthesis of (6) was attempted using a microwave oven. The influence on the reaction of varying the solvent, wattage, temperature, and time was studied. The results are summarised in Table 2.4. All the reactions were performed using a 1:2 ratio of Me₂pipdt (1) and LR (8). The experiments were carried out in a 10 mL test tube. During the reactions, part of the solid adhered to the test tube and was difficult to remove. Therefore, the ¹H-NMR spectra of the crude products were used to estimate the yields of (6). Most of the reactions were done using toluene as solvent, but dioxane was also tried as it is a more polar solvent. The ¹H-NMR spectra of the crude products were done without removing the solvent. However, in the case of dioxane, the signals of the solvent overlapped with those of the starting materials and products, and the yields could not be estimated (entries 8 and 9). It was because of this that dioxane was not used in further experiments. A neat reaction was also carried out (entry 10), but no conversion took place. In contrast, Varma et al.71 were capable of performing their reactions without solvent.

Initially, the reaction was tried at 150 W (entries 1 and 2), for 3 minutes at either 60 °C or 80 °C. Conversion (15%) took place only at the lower temperature. However, when the
reaction at 80 °C was left for 12.5 minutes, 87% yield was obtained (entry 3). A lower temperature of 50 °C (entry 4) gave no conversion after 15 minutes, whereas a higher wattage of 300 W led to the solid being burned (entries 5 and 6). It appears therefore, that a relatively long reaction time using low wattage and high temperature leads to better results. In the experiment described in entry 7, the temperature was set at 150 °C (i.e. above the reported decomposition temperature of (8)), but the power was set relatively low (50 W). In these conditions the yield of (6) was 92% after 90 minutes.

Table 2.4 Reaction conditions and yields (determined by ¹H-NMR) for the microwave synthesis of (6)\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time/mins</th>
<th>Temp./°C</th>
<th>Power/W</th>
<th>Yield(^b/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>3</td>
<td>60</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3</td>
<td>80</td>
<td>150</td>
<td>No conversion</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>12.5</td>
<td>80</td>
<td>150</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>15</td>
<td>50</td>
<td>150</td>
<td>No conversion</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>15</td>
<td>80</td>
<td>300</td>
<td>Solid burned</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>20</td>
<td>80</td>
<td>300</td>
<td>Solid burned</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>90</td>
<td>150</td>
<td>50</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>Dioxane</td>
<td>3</td>
<td>60</td>
<td>150</td>
<td>Signal Overlap</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>3</td>
<td>80</td>
<td>150</td>
<td>Signal Overlap</td>
</tr>
<tr>
<td>10</td>
<td>No Solvent</td>
<td>3</td>
<td>80</td>
<td>150</td>
<td>No conversion</td>
</tr>
</tbody>
</table>

\(^a\): All reactions carried out using a 1:2 ratio of (1) (0.0711 g, 0.5 mmol) and (8) (0.4043 g, 1.0 mmol), in 6 mL of solvent or no solvent

\(^b\): Yields were estimated from the ¹H-NMR spectra of the crude reaction mixtures

Using the power and temperature conditions of entry 7, three additional reactions were carried out for a total reaction time of 1 hour with different sampling times. Samples were taken at either every 10, 15 or 30 minutes and analysed by ¹H-NMR spectroscopy. This was done to better identity the time required for the reaction to occur and to see if it could
be reduced from the 1.5 hours employed in entry 7, where the reaction was run without interruptions for the 90 minutes. In each of the three additional experiments, the reaction was set to run for the required time before the sample had to be taken (i.e. 10, 15 or 30 mins). After this, the microwave oven was turned off and a sample was taken for NMR analysis, before the oven was started again.

**Figure 2.5** $^1$H-NMR spectra (CDCl$_3$, 3.0-4.0 ppm region) of microwave reactions between Me$_2$pipdt (1) and LR (8) (1:2) in toluene (150 °C, 50 W) to form (6) with different sampling times; the spectra shown were all taken after 1 hour
During the first monitored reactions, samples were taken every 10 and 15 minutes. In both cases, after 1 hour, the $^1$H-NMR spectrum still showed evidence of unreacted (1) (Fig. 2.5). As such, the sampling time was increased to every 30 minutes. The NMR spectrum after 1 hour showed no peaks associated with (1) (Fig. 2.5). It is worth pointing out that the NMR after the first 30 minutes showed only a small amount of (1). This indicates that at some point between 15 and 30 minutes the reaction completes.

2.2.1.2d Sonochemical Synthesis

As mentioned in the Introduction, thionation reactions have been reported using sonochemical methods. The synthesis of (6) was therefore attempted by reacting (1) and (8) in a sonic bath. In all the reactions carried out, the temperature and power setting on the sonic bath were kept constant at 80 °C and 9, respectively. Initially, tests were carried out in test tubes to determine the feasibility of the process but as reactions were scaled up these were done in round bottom flasks.

A summary of the results is included in Table 2.5. The 1:2 reactions between (1) and (8) in toluene or dioxane at $t \leq 90$ minutes (entries 1-3, 9) were unsuccessful. Longer reaction times (180-240 mins) in toluene led to product (6) being obtained with a moderate yield of 30-35% (entries 6-7). In these, the solvent volume and reagents concentration had also been slightly increased, compared to entries 1-3. Increasing the scale of the reaction (entry 8) did not change significantly its outcome. Interestingly, by using a reactant ratio of 1:1 ((1):(8)), a small isolated yield of 4% of (6) was obtained after 90 minutes (entry 4), but an increase of the reaction time to 240 minutes led to a yield of 45% (entry 5). It is not clear why using an excess of (8) would lead to the decrease in yield, but a similar effect was observed in the ultrasound work of Kawase and Kakurai where the weight fractions (%) of the desired block copolymers decreased with increasing polymer concentration.

In the case of this work, it may be due to there being too much additional reactant for the amount of solvent used and the increased pressure this would exert upon the bubbles (cavities) formed. As mentioned previously, the underlying principle of sonochemistry is acoustic cavitation where cavities form before imploding, thus providing the energy required for the reaction to proceed. Therefore if there is too much solid present then the
cavities may not form, not grow to a sufficient size before implosion, or simply not enough will form.

Table 2.5 Reaction conditions and isolated yields obtained for the sonochemical synthesis of (6)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent/Concentration of reagents (1) and (8)</th>
<th>Time/mins</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 mL toluene / 0.0834 M (1), 0.1666 M (8)\textsuperscript{b}</td>
<td>30</td>
<td>No conversion</td>
</tr>
<tr>
<td>2</td>
<td>6 mL toluene / 0.0834 M (1), 0.1666 M (8)\textsuperscript{b}</td>
<td>60</td>
<td>No conversion</td>
</tr>
<tr>
<td>3</td>
<td>6 mL toluene / 0.0834 M (1), 0.1666 M (8)\textsuperscript{b}</td>
<td>90</td>
<td>No conversion</td>
</tr>
<tr>
<td>4</td>
<td>10 mL toluene / 0.1 M (1), 0.1 M (8)\textsuperscript{c}</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>10 mL toluene / 0.1 M (1), 0.1 M (8)\textsuperscript{c}</td>
<td>240</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>10 mL toluene / 0.1 M (1), 0.1 M (8)\textsuperscript{c}</td>
<td>180</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>20 mL toluene / 0.1 M (1), 0.2 M (8)\textsuperscript{d}</td>
<td>240</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>20 mL toluene / 0.1 M (1), 0.2 M (8)\textsuperscript{d}</td>
<td>240</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>6 mL dioxane / 0.0834 M (1), 0.1666 M (8)\textsuperscript{f}</td>
<td>90</td>
<td>No conversion</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All reactions carried out at 80°C and a power setting of 9
\textsuperscript{b} 0.0711 g, 0.5 mmol (1), 0.4043 g, 1.0 mmol (8), ratio of 1:2
\textsuperscript{c} 0.1422 g, 1.0 mmol (1), 0.4045 g, 1.0 mmol (8), ratio of 1:1
\textsuperscript{d} 0.1422 g, 1.0 mmol (1), 0.8089 g, 2.0 mmol (8), ratio of 1:2
\textsuperscript{e} 0.2843 g, 2.0 mmol (1), 1.6179 g, 4.0 mmol (8), ratio of 1:2
\textsuperscript{f} 0.0711 g, 0.5 mmol (1), 0.4043 g, 1.0 mmol (8), ratio of 1:2

2.2.1.2e Comparison of methods

When comparing the different methods it should be taken into account that the conversions of the microwave experiments were estimated by \textsuperscript{1}H-NMR spectroscopy, whereas isolated yields are given for the conventional and sonochemical methods. Also, both the microwave and sonochemical synthesis still require further work to be fully optimised. The attempts at mechanochemically synthesising (6) proved ineffective.

A direct comparison between the conventional and sonochemical methods can be made through the reactions described in entry 5 in Table 2.3 and entry 8 in Table 2.5. Both reactions were carried out with (1) and (8) at a 1:2 ratio in 20 mL of toluene and yielded
ca. 30% of product but the conventional method required a reaction time of 48 hours whereas the sonochemical reaction was done in 4 hours. This is quite a significant reduction in reaction time. At the same time it should be noted that the conventional method proceeds in dry toluene at reflux and under N$_2$, whereas the sonochemical method is carried out in normal toluene at 80 °C while open to the air. With the current data, a direct comparison between the conventional and the microwave methods is difficult, due to the different conditions used. However, the highest yield has been achieved using a microwave reaction (Table 2.4, entry 7: 92% yield after 1.5 hours), compared to a maximum yield of 65% obtained through the conventional method in 24 hours (Table 2.3, entry 6).

2.2.1.3 Me$_2$dazd (2)

2.2.1.3a Conventional Synthesis

The synthesis of (2) was carried out initially using the method reported by Deplano et al.$^{34}$ (Scheme 2.3), which consisted of the 1:1 reaction of (3) and (5) in 20 mL of dry toluene for 2 hours while under reflux and an atmosphere of N$_2$. Results are summarised in Table 2.6.

![Scheme 2.3 Synthesis of (2)](image_url)
Table 2.6 Reaction conditions and isolated yields obtained for the conventional synthesis of (2)a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent Volume/Concentration of reagents</th>
<th>Time/hours</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 mL / 0.1 Mb</td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>20 mL / 0.2 Mc</td>
<td>24</td>
<td>39, 53</td>
</tr>
<tr>
<td>3</td>
<td>100 mL / 0.1 Md</td>
<td>48</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>100 mL / 0.2 Me</td>
<td>24</td>
<td>68, 72</td>
</tr>
<tr>
<td>5</td>
<td>100 mL / 0.2 Me</td>
<td>72</td>
<td>43</td>
</tr>
</tbody>
</table>

a: All reactions carried out in toluene at reflux, 1:1 ratio of (3):(5)
b: 0.2362 g, 2.0 mmol, 0.1 M (3), 0.25 ml, 2.0 mmol, 0.1 M (5)
c: 0.4724 g, 4.0 mmol, 0.2 M (3), 0.5 ml, 4.0 mmol, 0.2 M (5)
d: 1.1809 g, 0.01 mol, 0.1 M (3), 1.25 ml, 0.01 mol, 0.1 M (5)
e: 2.3618 g, 0.02 mol, 0.2 M (3), 2.5 ml, 0.02 mol, 0.2 M (5)

The first attempt to synthesise (2) was unsuccessful as after 2 hours, starting materials still remained in the mixture. A second attempt was then carried out where the reaction time was increased and the progress of the reaction was monitored by $^1$H-NMR spectroscopy. A sample of the reaction mixture was taken at the beginning of the process and then at 2, 3, and 4 hours with a final sample taken after 24 hours. The $^1$H-NMR spectra showed the peaks which correspond to (3) and (5) to slowly decrease over time. After 4 hours, there is still a small amount of starting materials remaining, and this is similar after 24 h. Toluene was then removed under high vacuum and the product recrystallized from toluene with the yield obtained (53%, Table 2.6, entry 2) comparable to that reported by Isaksson et al.33 after 70 hours. As there are no significant differences between the spectra at 4 hours and 24 hours, compound (2) was isolated after a 4 hour reaction (Table 2.6, entry 1) but the resulting yield was only 27%. To improve this, the reaction was then left for 24 hours, but the yield in this attempt was only slightly better at 39% (entry 2). The effect of changing the concentration of reagents and the scale of the reaction was then investigated (entries 3-5). Doubling the concentration of reagents did not lead to a better yield, even after a 48 hours reaction (entry 3). Interestingly, when entries 2 and 4 are compared, it is seen that by increasing the scale of the reaction the yield increases significantly to ca. 70%. This may be attributed, at least partly, to a reduction of mechanical loss during the
workup of the reaction. As observed above, doubling the concentration of reagents caused a decrease of yield (entry 5).

The lower yields of (2) compared to (1) is expected. As mentioned in Section 1.3.1 the synthesis of (1) is believed to occur via a concerted, pericyclic reaction and so the same process is believed to occur for (2).\textsuperscript{35} In this case an important aspect which can affect the yield obtained is ring strain. Ring strain itself is a combination of angle strain (caused by deviation from the ideal angle of 109.5° for sp\textsuperscript{3} C atoms) and torsional strain (resulting from a compound existing in the eclipsed conformer rather than the more stable staggered form). In terms of ring size, the strain experienced is less for a 6 membered ring than that of a 7 membered one. This is because the 6 membered ring can adopt the chair conformation that both allows the ideal angle 109.5° for sp\textsuperscript{3} C atoms and minimises any torsional strain. Due to the extra C atom present in the 7 membered ring there would be torsional strain present as the substituents on some C atoms would eclipse each other. To minimise this, the ring adopts a twist chair conformation, however this can cause substituents to interact with each other, increasing strain. At the same time, the extra C causes deviation from the ideal bond angle of sp\textsuperscript{3} C atoms.\textsuperscript{23} Although the formation of (1), and therefore (2), is believed to occur via a concerted, pericyclic reaction, experiments carried out to determine the mechanism could not rule out the stepwise reaction.\textsuperscript{35} In this situation, the amount of entropy/disorder associated with the amines must also be considered. The entropy associated with amine (5) is greater than that of (4) because (5) contains an extra C-C bond resulting in a greater amount of total bond rotation. Therefore, to form the heterocycle both this and the added distance must be overcome, \textit{i.e.} after the first N has bonded to (3) there is greater difficulty in getting the second N of (5) to bond to (3) as it is further away and experiencing more bond rotation.\textsuperscript{23} The free rotation of the second N atom of (5) may then increase the possibility of polymeric species forming as noted by Isaksson \textit{et al.},\textsuperscript{33} \textit{i.e.} the use of a reagent concentration above 0.1 M led to the formation of open chained polymers. However, this was not observed herein in the preparation of the analogous compound (1) (see section 2.2.1.1a) where even at double the recommended concentration, high yields were still obtained of (1). The longer reaction time needed for the synthesis of (2) (24-48 hours) compared to (1) (2 hours) may
have an influence in the different outcome, increasing the likelihood of polymeric species forming.

### 2.2.1.3b Mechanochemical Synthesis

As with (1), attempts to synthesise (2) mechanochemically for the purpose of speeding up the process and reducing solvent use were carried out. To assess the viability of the method, two reactions using LAG were performed (Table 2.7). These were carried out at 15 Hz in the presence of 1 eq. of toluene. The purification of the resulting product was performed in the same way as with (1), i.e. washing with toluene (10 mL) for 15 minutes before filtering and drying. The results show that the synthesis was successful, with the yield increasing with time from 10% (after 5 mins) to 50% (after 30 mins). Unlike in the mechanochemical synthesis of (1), where yields between 55-80% were obtained in 1-5 minutes reactions (see Table 2.2), a longer reaction time of at least 30 minutes is needed for (2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time/minutes</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

\(a: \) All reactions carried out at 15 Hz using 0.1880 g (1.59 mmol) of (3), and 0.2 mL (1.60 mmol) of (5) with 0.17 mL of toluene (LAG)

The solution reaction of (5) and (3) was monitored by \(^1\)H-NMR spectroscopy to ensure that the reaction did not simply proceed in the NMR tube during sample characterisation. For this, a 1:1 mixture of the reagents in 5 mL of CDCl\(_3\) ((3) = 78.0 mM, (5) = 80.0 mM) was prepared, and its \(^1\)H-NMR spectrum taken straight away (t = 0). Subsequent spectra were then taken after 30, 60, and 120 minutes, and then 24, 48, and 72 hours. The spectra at t = 0 and t = 2 h are included in Figure 2.6, showing that only the starting materials are
present in the solution after 2 h. Only after 24 hours it was possible to see peaks associated with (2) in the NMR spectrum.

![Figure 2.6](image)

**Figure 2.6** $^1$H-NMR spectra (CDCl$_3$, 1.6-4.0 ppm region) taken immediately after mixing (3) and (5) (top) and after waiting 2 hours (bottom)

2.2.1.3c Comparison of methods

Comparing the data in Tables 2.6 and 2.7, it can be seen that the mechanochemical synthesis is a faster alternative to the conventional method for the preparation of (2). For
example, after grinding at 15 Hz for 30 minutes (Table 2.7, entry 2) a yield of 50% is obtained. This is almost double that of entry 1 in Table 2.6 (27%) which takes 4 hours. To get a comparable yield of 53% using conventional synthesis, takes 24 hours (Table 2.6, entry 2). In addition, the mechanochemical synthesis does not require an inert atmosphere and uses less solvent.

2.2.1.4 Me$_2$dazdt (7)

2.2.1.4a Conventional Synthesis

The conventional synthesis of (7) (Scheme 2.4) was carried out in a similar way to that of (6), with some modifications in the reaction time. Several attempts were made at the synthesis of (7) (Table 2.8). After synthesising (2), its reaction with (8) was carried out for 1 hour (entry 1), as reported by Deplano et al., but isolating (7) could not be achieved, possibly due to not enough product being synthesised and the difficulty to separate it from excess starting material/by-products. Attempts to make it easier to isolate (7) by increasing the amount formed, either by increasing the reaction time (entries 2, 3) or the concentration of reagents (entry 4), proved unsuccessful.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration of reagents (2) and (8)</th>
<th>(2):(8)</th>
<th>Time/hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M (2), 0.12 M (8)$^b$</td>
<td>1:1.2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.3 M (2), 0.36 M (8)$^c$</td>
<td>1:1.2</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>0.04 M (2), 0.006 M (8)$^d$</td>
<td>1:1.5</td>
<td>168</td>
</tr>
</tbody>
</table>

Table 2.8 Reaction conditions used for the conventional synthesis of (7)$^a$

---

$a$: All reactions carried out in 20 mL of toluene at reflux using (2) and (8)

$b$: 0.3124 g, 2.0 mmol, 0.1 M (2), 0.9707 g, 2.4 mmol, 0.12 M (8)

$c$: 0.9371 g, 6.0 mmol, 0.3 M (2), 2.9122 g, 7.2 mmol, 0.36 M (8)

$d$: 0.1140 g, 0.74 mmol, 0.04 M (2), 0.4449 g, 1.1 mmol, 0.06 M (8)
Scheme 2.4 Synthesis of (7)

Figure 2.7 \(^1\)H-NMR spectra (CDCl\(_3\), 1.9-3.8 ppm region) of (2) (top) and (7) (bottom; crude product from reaction described in entry 3, Table 2.8)
As can be seen from the $^1$H-NMR spectra of the crude product from entry 3 (Fig. 2.7, bottom) there is a clear shift of the CH$_2$ signal from 2.00 ppm in the starting material (2) to 2.19 ppm in (7), and of the NCH$_3$ singlet from 3.06 ppm (2) to 3.50 ppm (7). This agrees well with the data reported by Isaksson et al.,$^{33}$ e.g. CH$_2$ = 2.05 ppm (2) to 2.20 ppm (7) and CH$_3$ = 3.10 ppm (2) to 3.44 ppm (7). There is also a shift of the NCH$_2$ signal to 3.54 ppm (7) from 3.41 ppm (2). A downfield shift from 3.45 ppm (2) to 3.58 ppm (7) for this signal has also been described in the literature.$^{33}$

**Figure 2.8** $^{13}$C-NMR spectra (CDCl$_3$, 20-200 ppm region) of (2) (top) and (7) (bottom, crude product from reaction described in entry 3, Table 2.8)
The $^{13}$C-NMR spectra of the crude product from entry 3 in Figure 2.8 shows that the peaks for compound (7) (Fig. 2.8, bottom) shift downfield compared to those for (2) (Fig. 2.8, top). The C=O/S peak shows the largest shift of ca. 30 ppm, i.e. 164.64 (C=O, (2)) to 195.50 (C=S, (7)). The shifts for the other signals are as follows, CH$_2$: from 26.62 ppm (2) to 27.69 ppm (7), NCH$_3$ from 33.61 ppm (2) to 40.83 ppm (7), and NCH$_2$: from 45.61 ppm (2) to 51.13 ppm (7). There is no $^{13}$C-NMR data for (7) in the literature, but a predicted $^{13}$C-NMR spectra [calculated using Advanced Chemistry Development, Inc. (ACD/Labs) Software V11.01 (© 1994-2017 ACD/Labs)] could be found and gave chemical shifts ca. 185.29, 52.94, 39.71, and 30.88 ppm. These match reasonably well with those found in this work, especially the signals for NCH$_2$, NCH$_3$, and CH$_2$. No further work was carried out to synthesise (7) using the conventional route.

2.2.1.4b Sonochemical Synthesis

As the sonochemical procedure proved effective in synthesising (6), it was also tried for the synthesis of (7). This was only attempted once (Table 2.9), with the $^1$H-NMR spectrum of the resulting mixture showing no peaks which could be associated with (7). No further investigations into the preparation of (7) using either the conventional or sonochemical methods were made at this stage.

<table>
<thead>
<tr>
<th>Concentration of reagents (2) and (8)</th>
<th>(2):(8)</th>
<th>Time/hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1564 M (2), 0.8098 M (8)</td>
<td>1:2</td>
<td>4</td>
</tr>
</tbody>
</table>

*a: Reaction carried out in 10 mL of toluene, at 80 °C, and a power setting of 9, 0.2443 g, 1.56 mmol, 0.16 M (2), 3.2754 g, 8.10 mmol, 0.81 M LR (8)*

2.2.1.4c Comparison of methods

With the above data it is difficult to determine which method is better as it took at least 72 hours to detect the presence of (7) using the conventional synthesis, and the sonochemical method was only performed for 4 hours. In saying this however some
thoughts can be made, *i.e.* the reaction times required to synthesise (7) conventionally when compared to (6) appear to be greater. This may also be true with regard to the sonochemical method. If it is, then the conventional process may be better to prepare (7) as the N₂ atmosphere required will prevent/limit any decomposition of (8) which might occur. In comparison the sonochemical method used herein is performed open to the air.

2.2.1.5 [Me₂pipdtH]I₃ (12)

Several attempts have been made at forming (12). Based on a literature method, the first attempt involved adding a chloroform solution of I₂ (2 eq.) to a chloroform solution of (6). The reaction vessel was then left sealed and stirred for 5 days at room temperature, after which a dark brown solid precipitated. The resulting yield was only 10.5%. Using a slightly different method, the combined chloroform solutions of (6) and I₂ were left in the reaction vessel stirring, open to the air, at room temperature. Within 2 hours the chloroform had evaporated and shiny black crystals were obtained, giving 56% yield of (12) (Table 2.10, entry 1). In an analogous procedure using DCM as the solvent, an average yield of 67% was achieved (entry 2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chloroform</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>67</td>
</tr>
</tbody>
</table>

*a: All reactions carried out in 15 mL of solvent at room temperature, in a reaction vessel open to the air 1:2 ratio of (6):I₂, 0.0131 g, 0.075 mmol, 5.0 mM (6), 0.0381 g, 0.15 mmol, 0.01 M I₂.

As detailed below, ¹H-NMR spectroscopy showed there was no significant difference between (6) and (12), but it appears to be some interaction between I₂ and the H₂O present in the NMR solvent (ref. Section 2.3.5.1). Raman analysis (Section 2.3.5.2) shows there are peaks which correspond well with some of the literature data, but the spectrum does not fully match that reported for (12). Finally, CHNS analysis (Section 2.3.5.4) indicate
the adduct has been formed but that there is still some DCM remaining. Formation of (12) is further confirmed by its PXRD data, which matches well the calculated pattern.

2.2.2 Dissolution of Pd(0) and Pt(0) using \([\text{Me}_2\text{pipdtH}]I_3\) (12)

2.2.2.1 Pd

Two methods were employed for the dissolution of Pd(0) which was used as a powder. The first involved the addition of (6) and I\(_2\) separately to the metal powder and the second consisted of using (12) directly. In the literature, it has been shown that 2 equivalents of (12) successfully dissolves Pd in acetonitrile at room temperature to form \([\text{Pd(Me}_2\text{pipdt})_2]\) (13) (25), however no reaction time is given.\(^{25}\) Another reaction from the literature involved using 2 equivalents of (13) in THF at room temperature, taking 1 hour to dissolve Pd (12.3 mg).\(^{44}\) 2 equivalents of (12) were also used to dissolve Pt in acetonitrile. This required 4 days at reflux.\(^{41}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent/mL</th>
<th>Pd concentration</th>
<th>([\text{Me}_2\text{pipdtH}]I_3) (12) concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^b)</td>
<td>Acetonitrile/20 mL</td>
<td>2.35 mM</td>
<td>4.69 mM</td>
</tr>
<tr>
<td>2(^c)</td>
<td>Acetonitrile/60 mL</td>
<td>0.78 mM</td>
<td>1.6 mM</td>
</tr>
<tr>
<td>3(^c)</td>
<td>Acetone/60 mL</td>
<td>0.78 mM</td>
<td>1.6 mM</td>
</tr>
</tbody>
</table>

*a: All reactions carried out at room temperature, with a Pd:(12) ratio of 1:2
b: 168 hours
c: 216 hours

Initially, Pd(0) (2.35 mM), (6) (4.69 mM) and I\(_2\) (18.8 mM), \(i.e.\) 1:2:8 ratio, were mixed in acetonitrile (20 mL) at room temperature for 168 hours. The reaction was monitored to see if the metal dissolved but it was not observed to either after 1 hour or throughout the remaining time period. The initial dark colour of the mixture however did lighten over time. This may be due to the loss of I\(_2\) over the reaction period. In the second method, Pd powder was mixed with compound (12) at a 1:2 ratio, and with different solvents.
In neither of the attempts was dissolution of the metal observed, although, as noted with the first attempt, the colour of the solutions became lighter.

2.2.2.2 Pt

Only one attempt was carried out for the synthesis of $[\text{Pt(Me}_2\text{pipdt)}_2](\text{I}_3)_2$ (14). As with Pd, Pt was not observed to dissolve at the conditions used, in contrast to the literature results.$^{25,41}$ Herein, Pt(0) (powder, 2.35 mM) was mixed with 2 eq. of (6) (4.69 mM) and 8 eq. of I$_2$ (18.8 mM) in acetonitrile (20 mL), and the mixture stirred at room temperature for 4 days. As there was no apparent dissolution of Pt no further investigations were carried out.

2.3 Characterization of compounds

2.3.1 Me$_2$pipd (1)

There are two sets of NMR data reported in the literature for (1):

Marder et al.$^{36}$ $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ 2.99 (s, 6H, CH$_3$), 3.50 (s, 4H, CH$_2$)

$^{13}$C-NMR (200 MHz, CDCl$_3$): $\delta$ 34.74 (CH$_3$), 45.91 (CH$_2$), 157.35 (C=O)

Isaksson et al.$^{33}$: $^1$H-NMR (CDCl$_3$): $\delta$ 3.15 (s, 6H, CH$_3$), 3.65 (s, 4H, CH$_2$)

2.3.1.1 $^1$H-NMR

The $^1$H-NMR spectrum of the final product obtained herein showed two singlets at 3.55 and 3.10 ppm, corresponding to the CH$_2$ and CH$_3$ groups respectively. These are comparable to the literature data above.
2.3.1.2 $^{13}$C-NMR

The $^{13}$C-NMR spectrum gave peaks at 157.67, 46.28, and 35.14 ppm. These correspond to the carbon atoms in the C=O, CH$_2$, and CH$_3$ groups respectively. These values are comparable to those reported by Marder et al.$^{36}$ for (1).

2.3.1.3 IR

No IR data was found in the literature and so the IR spectrum of (1) was obtained using a KBr pellet. The spectrum contains a sharp intense peak at 1676 cm$^{-1}$ which corresponds to the C=O stretching frequency. At around 2937 cm$^{-1}$ there are peaks corresponding to the CH-alkyl stretching bands.

2.3.2 Me$_2$pipdt (6)

The following characterisation data are available in the literature for (6). As in the case of the dione (1), there are two different sets of $^1$H-NMR data:

- Isaksson et al.$^{33}$: $^1$H-NMR (CDCl$_3$): $\delta$ 2.80 (s, 6H, CH$_3$), 3.60 (s, 4H, CH$_2$)
- Nemykin et al.$^{39}$: $^1$H-NMR (CDCl$_3$): $\delta$ 3.56 (s, 6H, CH$_3$), 3.74 (s, 4H, CH$_2$)
- $^{13}$C-NMR (CDCl$_3$): $\delta$ 45.2 (CH$_3$), 49.1 (CH$_2$), 189.0 (C=S)
- IR (KBr): 2919 (alkyl C-H), 1500 (C=S)
- UV/Vis [$\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$), CHCl$_3$]: 500 (200), 430 (350), 404sh, 360sh, 316 (4300)

2.3.2.1 $^1$H-NMR

The $^1$H-NMR spectrum of (6) showed peaks at 3.74 (CH$_2$) and 3.58 (CH$_3$) ppm, in good agreement with the data reported by Nemykin et al.$^{39}$ When compared to those reported by Isaksson et al.$^{33}$ there is a significant difference, in particular for the signal assigned to the CH$_3$ group, with a shift of 0.78 ppm.
2.3.2.2 $^{13}C$-NMR

The $^{13}C$ NMR spectrum of (6) has peaks at 44.48 ($\text{CH}_3$), 49.89 ($\text{CH}_2$), and 185.75 ($\text{C=S}$) ppm. These correspond well with the NMR data reported by Nemykin et al.$^{39}$

2.3.2.3 UV/Vis

The UV/Vis spectrum of (6) was run in chloroform, at a concentration of 0.05 mM. The spectrum (Fig. 2.9) shows the following bands:

$$\lambda_{\text{max}}, \text{nm (ε, } \text{M}^{-1} \text{ cm}^{-1}) : 428 (400), 408\text{sh}, 356\text{sh}, 316 (5000)$$

The spectrum (Fig. 2.9) agrees well with that reported by Nemykin et al.$^{39}$ (see above), with the exception of the band at 500 nm, which is not clearly seen in our case.

![UV-Vis spectrum of (6)](image-url)
According to the literature, the absorption at 500 nm would correspond mainly to the HOMO $\rightarrow$ LUMO $n\rightarrow \pi^*$ transition, whereas the band at 410 nm would be associated with the HOMO-1 $\rightarrow$ LUMO transition (second $n\rightarrow \pi^*$) excitation. The maximum at 316 nm, the most intense, was believed to be a superposition of several transitions (two $\pi \rightarrow \pi^*$ and two $n \rightarrow \pi^*$ transitions). As the ligand possesses $C_{2v}$ symmetry, low intensity $n \rightarrow \pi^*$ ($a_1 \leftarrow b_2$, HOMO-1 $\rightarrow$ LUMO) transitions are allowed, as well as the higher intensity $\pi \rightarrow \pi^*$ ($a_2 \leftarrow b_2$, HOMO-2 $\rightarrow$ LUMO) transitions. In contrast, the lowest energy transition, HOMO $\rightarrow$ LUMO ($b_1 \leftarrow b_2$) $n \rightarrow \pi^*$, is symmetry forbidden.

2.3.2.4 IR

The IR spectrum of (6) was obtained using a KBr pellet. The spectrum contains a sharp intense peak at 1502 cm$^{-1}$ which corresponds to the C=S stretching frequency and is in good agreement to that reported in the literature (see above). As expected, the C=S band appears at lower frequency than the C=O band in (6) (1676 cm$^{-1}$). This shift relates to the larger atomic mass of S compared with O. The C-H-alkyl stretching bands are seen around 2922 cm$^{-1}$.

2.3.2.5 PXRD

The simulated PXRD pattern for the compound was obtained, using Mercury 3.5 and Conquest 1.17, from the available X-ray crystallographic data (Fig. 2.10). The experimental PXRD pattern of (6) is also shown. As can be seen, the simulated and experimental PXRD patterns match very well.
Figure 2.10 Comparison of calculated (top) and experimental (bottom) PXRD patterns of (6)

2.3.3 Me₂dazd (2)

Only one set of ¹H-NMR data could be found in the literature for (2):
Isaksson et al.33: $^1$H-NMR (CDCl$_3$): $\delta$ 2.05 (m, 2H, CH$_2$), 3.10 (s, 6H, CH$_3$), 3.45 (m, 4H, NCH$_2$)

2.3.3.1 $^1$H-NMR

The peaks observed in the $^1$H-NMR spectrum of (2) were at 3.41, 3.05, and 1.99 ppm, corresponding to the NCH$_2$, CH$_3$, and the CH$_2$ groups respectively. These are similar to those previously reported.

2.3.3.2 $^{13}$C-NMR

The $^{13}$C-NMR spectrum of (2) gave peaks at 165.11 (C=O), 45.88 (NCH$_2$), 33.87 (CH$_3$), and 26.53 (CH$_2$) ppm. The peaks associated with CH$_3$ and NCH$_2$ are quite similar in compounds (1) and (2). The largest difference, 7.16 ppm, is seen with the C=O peak. Using the Advanced Chemistry Development, Inc. (ACD/Labs) Software V11.01 (© 1994-2017 ACD/Labs) a calculated $^{13}$C-NMR spectra could be found and gave chemical shifts ca. 166.25 (C=O), 51.25 (NCH$_2$), 36.25 (NCH$_3$), and 31.25 (CH$_2$) ppm which well with those found in this work.

2.3.3.3 IR

No IR data was found in the literature and so the IR spectrum was obtained using a KBr pellet. The spectrum contains a sharp intense peak at 1610 cm$^{-1}$ corresponding to the C=O stretching frequency. Several peaks at 2780-2945 cm$^{-1}$ relate to C-H stretching frequencies.

2.3.3.4 PXRD

Figure 2.11 contains the pattern for compound (2). No PXRD pattern was found in the literature.
2.3.4 Me₂dazdt (7)

Only one set of data could be found in the literature for (7):

Isaksson et al.\textsuperscript{33}: $^1$H-NMR (CDCl\textsubscript{3}): $\delta$ 2.20 (m, 2H, CH\textsubscript{2}), 3.44 (s, 6H, CH\textsubscript{3}), 3.58 (m, 4H, NCH\textsubscript{2})

2.3.4.1 $^1$H-NMR

Although compound (7) was not isolated pure, two peaks observed in the $^1$H-NMR spectra of some of the product mixtures agreed well with the literature.\textsuperscript{33} These peaks appeared at 2.18 ppm and 3.49 ppm and correspond to the CH\textsubscript{2} and NCH\textsubscript{3} groups respectively. The peak for NCH\textsubscript{2} is believed to appear at 3.54 ppm.
2.3.4.2 $^{13}$C-NMR

As mentioned previously a predicted $^{13}$C-NMR spectra (calculated using Advanced Chemistry Development, Inc. (ACD/Labs) Software V11.01 (© 1994-2017 ACD/Labs) could be found providing chemical shifts ca. 185.29, 52.94, 39.71, and 30.88 ppm. These match reasonably well with those of this work at 195.50 (C=S), 51.13 (NCH$_2$), 40.83 (NCH$_3$), and 27.69 ppm (CH$_2$), especially those for NCH$_2$, NCH$_3$, and CH$_2$.

2.3.5 [Me$_2$pipdtH]I$_3$ (12)

The following characterisation data are available in the literature for (12):

Mercuri et al.$^{43}$: Raman (cm$^{-1}$): 2972mw, 2909m, 2843w, 2183vw, 1900vw-br, 1562w, 1441mw, 1366mw, 1284w, 1248mw, 1142mw, 1106m, 672mw, 538m, 426w, 324w, 224m, 112vs

CHNS: C=13.19%, H=1.93%, N=5.06%, S=11.55%
[Calcd. for C$_6$H$_{11}$N$_2$S$_2$I$_3$ (555.928): C% 12.96; H% 1.99; N% 5.04; S% 11.54]

Further information of the Raman spectra associated with I$_2$ and I$_3^-$ was also found in the literature. In 1974, Loos and Jones investigated various KI-I$_2$ solutions and assigned Raman peaks at 114 cm$^{-1}$ and 155 cm$^{-1}$ to I$_3^-$ and to higher polyiodide species, respectively.$^{129}$ In 1989, Nour and Shahada investigated I$_3^-$ complexes of some polycyclic amines.$^{130}$ No bands were observed between 170 and 200 cm$^{-1}$, the indicative range of amine-I$_2$ complexes. Bands at 108 and 110 cm$^{-1}$ were assigned to the symmetric stretch ($v_{sym}(I-I)$) of I$_3^-$ and bands at 130 and 145 cm$^{-1}$ to its asymmetric stretch ($v_{asym}(I-I)$). More recently, the symmetric stretch of I$_3^-$ has been noted at 112 cm$^{-1}$, and the asymmetric at 145 cm$^{-1}$.$^{131,132}$ The Raman spectrum of the adduct Me$_2$dazdt/2I$_2$ (13) shows a $v(I-I)$ vibration at 150 cm$^{-1}$, compared to that of free I$_2$ at 180 cm$^{-1}$.$^{25}$
There is no NMR data for (12) reported in the literature. Attempts at using $^1$H-NMR spectroscopy for the analysis of (12) in DMSO-$d_6$ proved difficult (Fig. 2.12). The $^1$H-NMR spectrum obtained for the product of the reaction between (6) and I$_2$ showed peaks at 3.76, 3.46, and 3.44 ppm. The two first peaks correspond well with those of the starting
material (6) in DMSO-\textsubscript{d\(_6\)}, \textit{i.e.}, two singlets at 3.75 ppm (CH\(_2\)) and 3.45 ppm (CH\(_3\)). This is not unexpected as the structure of the ligand’s backbone is not significantly altered on formation of the adduct. In addition, the spectrum of (6) contained a peak at 3.35 ppm, corresponding to H\(_2\)O in the deuterated solvent. This H\(_2\)O peak then appears to be the peak at 3.44 ppm in the \textsuperscript{1}H-NMR spectrum of (12). In a test where 1, 1.5, and 2 equivalents of I\(_2\) were added to (6) dissolved in DMSO-\textsubscript{d\(_6\)} (Fig. 2.12), the H\(_2\)O peak, initially at 3.66 ppm, moved downfield in the NMR spectrum to 3.76 ppm (1.5 eq. of I\(_2\)), overlapping the peak associated with (6) at this chemical shift. After the addition of 2 equivalents of I\(_2\), the peak was at 3.86 ppm. It appears that, in solution, I\(_2\) interacts with the H\(_2\)O present in the solvent, most likely through hydrogen bonding and that when (12) is dissolved some of the I\(_2\) present dissociates causing the downfield shift of H\(_2\)O observed.

\subsection*{2.3.5.2 Raman}

Figure 2.14 shows the Raman spectrum of (12), with a broad, structured, peak centred at 110 cm\(^{-1}\), and a more intense peak at 160 cm\(^{-1}\) with a shoulder at \textit{ca.} 155 cm\(^{-1}\). There are also additional peaks at 220 (weak), 317, and 465 (broad) cm\(^{-1}\). From 500 cm\(^{-1}\) there is no more clearly defined peaks except for a possible peak at 1333 cm\(^{-1}\) and a broad peak at 2099 cm\(^{-1}\). The bands at 110 cm\(^{-1}\) and 155 cm\(^{-1}\) agree with the literature data for the I\(_3\)\(^-\) ion (see above; \nu\textsubscript{sym}(I-I): 108-114 cm\(^{-1}\) and \nu\textsubscript{asym}(I-I): 130-155 cm\(^{-1}\)). The peak at 160 cm\(^{-1}\) could be associated to higher polyiodides,\textsuperscript{129} and/or the presence of a C=S---I-I adduct, similar to Me\(_2\)dazdt/2I\(_2\) ((13); see above).\textsuperscript{25} The peak at 317 cm\(^{-1}\) appears to correspond to the C-C chain while that at 2099 cm\(^{-1}\) appears to relate to N-C=S, as it is present in the region associated with isothiocyanate.\textsuperscript{133} There are some discrepancies between the Raman spectrum obtained herein for (12) and that previously reported by Mercuri \textit{et al.}\textsuperscript{43} For example, the bands in the region between 100-500 cm\(^{-1}\) are compared below:

This work: 465w, 317w, 220w, 160s (155sh), 110 cm\(^{-1}\)
Reported in Literature\textsuperscript{43}: 426w, 324w, 224m, 112vs
Figure 2.13 Raman spectrum of (12) (including expansion of the 100-300 cm\(^{-1}\) region)

The most significant difference is the absence of the strong peak at 155-160 cm\(^{-1}\) in the literature data. As discussed above, this could be due to the presence of excess iodide (which would result in formation of polyiodides) and/or the presence of C=S---I-I interactions.

2.3.5.3 PXRD

The simulated PXRD pattern for compound (12) was obtained, using Mercury 3.5 and Conquest 1.17, from the available X-ray crystallographic data and compared to the experimental data (Figure 2.14). Although the experimental PXRD contained excessive background noise, the pattern agrees well with the simulated one.
Figure 2.14 Comparison of calculated (top) and experimental (bottom) PXRD patterns of (12)
2.3.5.4 CHNS

The calculated elemental analysis of (12) is C=12.96%; H=1.99%; N=5.04%; and S=11.54% (Table 2.12). For the sample of (12) prepared herein, it was found to be C=13.09%; H=1.85%; N=4.41%; and S=9.53%. This corresponds well with the calculated analysis for (12) with 1.5 equivalents of DCM (C=13.18%; H=2.06%; N=4.10%; and S=9.38%), and indicates that the sample was not sufficiently dry.

<table>
<thead>
<tr>
<th>Calculated for C₆H₁₁N₂S₂I₃/*%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>12.96</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Calculated C₆H₁₁N₂S₂I₃:DCM (2:3): C = 13.18%, H = 2.06%, N = 4.10%, S = 9.38%

2.4 Conclusions

Compound (1) has been successfully synthesised using the conventional method reported in literature. This ligand can also be prepared using a novel mechanochemical method which proceeds within 1 minute at 5 Hz, a reaction time reduced from the conventional 2 hours at reflux. There is also a significant reduction in solvent employed and no need for the inert atmosphere employed conventionally. Compound (6) has also been synthesised successfully (75% after a 48 hour reaction) using a slightly modified literature procedure. Microwave and sonochemical methods have also been used for the synthesis of (6). Although both of these alternative methods need to be optimised, the microwave method allows yields up to 92% within 1.5 hours and the sonochemical reaction gives a comparable yield (35%) to the conventional synthesis (31%) within 4 hours. Both of these methods are improvements over the conventional synthesis as there is no need to maintain an inert atmosphere and any heating is for a shorter period of time. The synthesis of (2) was carried out using the conventional method successfully. Although a long reaction time (24 hours) is needed, the ligand is obtained in good yield (72%) when carried out at a larger scale. The compound has also been made using a mechanochemical method.
which takes only 30 minutes to achieve a similar yield (50%) to the conventional (53%) smaller scale reaction. The isolation of (7) has been the more difficult, as the compound could not be separated from remaining starting materials. In addition, the reaction required a long time (168 hours). The adduct (12) has been successfully synthesised by reacting (6) and I₂ in a 1:2 ratio. An initial attempt using chloroform as solvent and leaving the reaction vessel sealed led to a yield of 10.5%. When repeated with the vessel open to the atmosphere to allow evaporation of the solvent, the yield increased to 56%. This was increased further to 67% when DCM was used as solvent. Attempts to synthesise the complexes (25) and (14) using Pd(0) and Pt(0), were unsuccessful.

2.5 Future Work

The synthesis of the diones and dithiones described herein could be improved by using different methods or further optimising some of the procedures used. For example:

- Optimise the mechanochemical synthesis of (1), e.g. by testing frequencies lower than the 5 Hz employed or by changing the solvent used for LAG. Materials other than stainless steel for the balls could also be tested. A different purification method may help to improve the yield.
- Optimise the microwave synthesis of (6), for example, by testing a wider range of temperatures and power settings, alongside different solvents and reagent ratios.
- Optimise the sonochemical synthesis of (6) by applying different temperatures and using different solvents and reagent ratios.
- Optimise the mechanochemical synthesis of (2) via either testing frequencies lower than the 15 Hz used or an extended reaction time. As in the case of (1), other solvents as LAG could be used, different materials for the balls, or even a different purification method.
- Attempt the synthesis of (7) using the microwave and sonochemical methods and try to find a superior purification method.
Chapter 3. Dissolution of Pd, Pt, and Au in Ionic Liquids and Deep Eutectic Solvents

3.1 Aims

The aim of this Chapter was to perform an initial screening study to investigate the mild conditions which would lead to the dissolution of Pd, Pt, and Au. For Pd and Pt, a variety of ILs were used. Initially, a family of imidazolium ILs was used, where the anion/cation were systematically varied. Imidazolium ILs are relatively easy to synthesise and purify and have previously been shown to be efficient for the selective extraction of precious metals, e.g. extraction of Au. As mentioned in the introduction (Section 1.6.3), the properties of the ILs, such as melting point, viscosity, or hydrophilicity, are dependent on the nature of the IL cation and anion. In order to assess how these various properties could affect the dissolution of metals, imidazolium cations with various chain lengths, and combined with a variety of anions, were chosen (Table 3.1 and Figs. 3.1-3.2). For example, the viscosity of the ILs with the same anion increases with the length of the alkyl chain, whereas for the same cation, NTf₂⁻ ILs are generally the least viscous followed by OTf⁻ and halide ILs. Since the second step of the metal recovery involves electrochemical deposition from the IL solution, the electrochemical window of the IL is also a property that should be taken into account (Table 3.1). Following these initial experiments and in view of the results with the imidazolium ILs, a phosphonium chloride, [P₆₆₆₁₄]Cl, was also tested (i.e. the best results for Pd dissolution were obtained using imidazolium halides, as discussed below). In addition, two pyridinium, and two pyrrolidinium ILs were used for the dissolution of Pt. These additional ILs were chosen to see if results could be improved, as dissolution of Pt in the imidazolium and phosphonium ILs proved difficult. Pyridinium salts are generally more viscous than the equivalent imidazolium and pyrrolidinium salts, but less viscous than phosphonium ILs.
Table 3.1 Comparison of viscosities and melting points of the ILs used in this work (the temperature the measurement was taken at is given in brackets if available)

<table>
<thead>
<tr>
<th>IL</th>
<th>Melting Point/°C</th>
<th>Viscosity/ Pa s</th>
<th>Density/g cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM]BF₄</td>
<td>-71¹³⁵</td>
<td>0.088 (25 °C)¹³⁶</td>
<td>1.2¹³⁵</td>
</tr>
<tr>
<td>[BMIM]Br</td>
<td>76¹³⁷</td>
<td>1.486 (25 °C)⁸⁷</td>
<td>—</td>
</tr>
<tr>
<td>[BMIM]Cl</td>
<td>65⁹³</td>
<td>11 (30 °C)⁸⁸</td>
<td>0.142 (80 °C)⁹⁰</td>
</tr>
<tr>
<td>[BMIM]Br</td>
<td>—</td>
<td>0.10 (20 °C)¹³⁸</td>
<td>1.62 (20 °C)¹³⁸</td>
</tr>
<tr>
<td>[BMIM]Cl</td>
<td>16⁹³</td>
<td>0.045 (25 °C)⁸⁹</td>
<td>1.29 (25 °C)⁸⁶</td>
</tr>
<tr>
<td>[BMIM]CTSO₄</td>
<td>34¹³⁹,¹⁴⁰</td>
<td>0.874 (20 °C)¹³⁹</td>
<td>1.07¹⁴⁰</td>
</tr>
<tr>
<td>[BMIM]OTf</td>
<td>12¹⁴¹</td>
<td>0.214 (25 °C)¹³⁶</td>
<td>1.38 (25 °C)¹⁴¹</td>
</tr>
<tr>
<td>[EMIM]NTf₂</td>
<td>-15¹⁴²</td>
<td>0.029 (25 °C)¹³⁶</td>
<td>1.52 (25 °C)⁸⁶</td>
</tr>
<tr>
<td>[EMIM]OTf</td>
<td>-9⁹³</td>
<td>0.041 (25 °C)¹³⁶</td>
<td>1.39 (25 °C)⁸⁶</td>
</tr>
<tr>
<td>[OMIM]Cl</td>
<td>-5⁹⁰</td>
<td>0.377 (25 °C)³⁵</td>
<td>1.0 (25 °C)⁸⁶</td>
</tr>
<tr>
<td>[OMIM]NTf₂</td>
<td>&lt; -50¹⁴³</td>
<td>0.104 (25 °C)¹⁴³</td>
<td>1.32 (25 °C)⁸⁶¹⁴³</td>
</tr>
<tr>
<td>[OMIM]PF₆</td>
<td>—</td>
<td>0.714 (25 °C)¹⁴⁴</td>
<td>1.23¹⁴⁵</td>
</tr>
<tr>
<td>[CyMPy]NTf₂</td>
<td>44¹⁴⁶</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[HPy]NTf₂</td>
<td>3¹⁴⁷</td>
<td>0.0845 (25 °C)¹⁴⁷</td>
<td>1.39¹⁴⁷</td>
</tr>
<tr>
<td>[BMPyr]DCA</td>
<td>&lt; -50¹⁴⁸</td>
<td>0.030 (25 °C)¹³⁶</td>
<td>1.02¹⁴⁸</td>
</tr>
<tr>
<td>[BMPyr]NTf₂</td>
<td>-6¹⁴⁹</td>
<td>0.063 (25 °C)¹³⁶</td>
<td>1.4¹⁴⁹</td>
</tr>
<tr>
<td>[P₆₆₆₁₄]Cl</td>
<td>-50¹⁵⁰</td>
<td>1.824 (25 °C)¹⁵⁰</td>
<td>0.88¹⁵⁰</td>
</tr>
</tbody>
</table>
Figure 3.1 IL cations used in this work and their abbreviations: [EMIM]$^+$ = 1-ethyl-3-methylimidazolium, [BMIM]$^+$ = 1-butyl-3-methylimidazolium, [HMIM]$^+$ = 1-hexyl-3-methylimidazolium, [OMIM]$^+$ = 1-octyl-3-methylimidazolium, [CyMPy]$^+$ = 1-cyanomethylpyridinium, [HPy]$^+$ = 1-hexylpyridinium, [BMPyr]$^+$ = 1-butyl-1-methylpyrrolidinium, [P$_{66614}$]$^+$ = trihexyl(tetradecyl)phosphonium
Figure 3.2 IL anions used in this work: DCA\(^-\) = dicyanamide, FAP\(^-\) = tris(perfluoroalkyl)trifluorophosphate, NTf\(_2\)\(^-\) = bis(trifluoromethylsulfonyl)amide, OctSO\(_4\)\(^-\) = octylsulfate, OTf\(^-\) = trifluoromethanesulfonate.

Several DESs (Fig. 3.3) were also tested, i.e., Reline 200, Ethaline 200, and Imiline 700, as these type of solvents have previously been used successfully in metal processing, including metal extraction and electrodeposition.\(^{99,101}\) The three solvents chosen have different compositions and physical properties (Table 3.2), which would allow a comparative study. For example, Reline 200 and Ethaline 200, have been extensively applied for metal electrodeposition and are relatively low cost and easy to prepare. Compared to Reline 200, Ethaline 200 has a lower melting point and viscosity (resulting in higher conductivity) and could lead to more efficient dissolution and electrodeposition processes. For comparison, Imiline 700 which contains imidazole (24) and possesses relatively high conductivity, was used.
Figure 3.3 Structures of some HBA and HBDs used in this work to form DESs: choline chloride (21), urea (22), ethylene glycol (23), imidazole (24). DESs: Imiline 700 = 3 eq. (21):7 eq. (24), Reline 200 = 1 eq. (21):2 eq. (22), Ethaline 200 = 1 eq. (21):2 eq. (23) ((21) and (22) also used as ligands)

Table 3.2 Comparison of physical properties of the DESs used in this work (the temperature the measurement was taken at is given in brackets if available)

<table>
<thead>
<tr>
<th>DES</th>
<th>Melting Point/°C</th>
<th>Viscosity/ Pa s</th>
<th>Density/g cm⁻³</th>
<th>Electrochemical Window/V</th>
<th>Ionic Conductivity /mS cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reline 200</td>
<td>12¹⁰⁰,¹⁰¹</td>
<td>0.75 (25 °C)¹⁰¹</td>
<td>1.25 (25 °C)¹⁰¹</td>
<td>1.7 (40 °C)¹⁵¹</td>
<td>0.199 (40 °C)¹⁰²</td>
</tr>
<tr>
<td>Ethaline 200</td>
<td>-66¹⁰⁰,¹⁰¹</td>
<td>0.037 (25 °C)¹⁰¹</td>
<td>1.12 (25 °C)¹⁰¹</td>
<td>1.9 (40 °C)¹⁵¹</td>
<td>7.61 (20 °C)¹⁰³</td>
</tr>
<tr>
<td>Imiline 700</td>
<td>56¹⁰⁰,¹⁰¹,¹⁰⁴</td>
<td>0.008 (90°C)¹⁰⁴</td>
<td>—</td>
<td>3.0 (70 °C)¹⁰⁴</td>
<td>26 (90 °C)¹⁰⁴</td>
</tr>
</tbody>
</table>

The effect of adding various ligands (Fig. 3.4) and/or oxidants (HNO₃, I₂, TBANO₃ (tetrabutylammonium nitrate), CeO₂ (ceria)), at different ratios, was also tested. Most of the ligands selected are bidentate and able to form stable chelated complexes in order to favour the dissolution of the metal. For comparison, the monodentate Ph₃P was also used. A range of different bidentate ligands were chosen in order to establish what factors would be important in the dissolution processes. For example, the nature of the donor atoms was varied in order to test soft (S, P), hard (O) or intermediate (N) Lewis bases. The flexibility, e.g. compare (30), (26) and (27), and the length, e.g. (28), (31), (32), of the connecting chain was also varied. Ligand (29) contains both N and O donor atoms and could potentially form tetra- or hexa-coordinated complexes.
Figure 3.4  Ligands used in this work: Ph₃P, Me₂pipd (1), Me₂dazd (2), dimethyl oxalate (3), Me₂pipdt (6), 2, 2′-bipyridine (26), 1, 10-phenanthroline (27), 1, 2-bis(diphenylphosphino)ethane (28), ethylenediaminetetraacetic acid (29), ethylene diamine (30), 1, 4-bis(diphenylphosphino)butane (31), 1, 6-bis(diphenylphosphino)hexane (32)
As mentioned above (see Sections 1.3.3, 2.2.1.2, 2.2.1.4), dithione ligands, such as \(6\), were previously used for the dissolution of precious metals in the presence of iodine but were difficult to synthesise.\(^{25,34,41-45}\) The precursor dioxygen ligands \((1)-(3)\) (hard Lewis bases) are more accessible and could form complexes with Pd(II) or Pt(II) (soft Lewis acids) which are less stable that those of the dithiones. This may result in an easier electrodeposition/decomposition step following dissolution of the metals.

Initially, experiments were carried out using \(I_2\) as oxidant, as it is able to form charge-transfer adducts with the ligands and induce oxidation of precious metals, as explained above.\(^{25,34,41-45}\) Following the initial results, a stronger oxidant, \(HNO_3\), was tested, as well as TBANO\(_3\), \textit{i.e.} to exploit the oxidative properties of the nitrate anion, avoiding the use of a strong acid. Finally, CeO\(_2\) was tested, as it is already present in automotive catalysts, and if successful would allow for the process to take place without having to add other oxidants. Unless otherwise stated, experiments for Pd and Pt were all carried out in 4 mL of solvent, at several temperatures (r.t., 60 °C, or 90 °C), open to the air, and normally left for a maximum of 168 hours. If a time other than 168 hours is recorded then this is the time at which full dissolution was observed, with checks performed 3 times throughout the working day. The metal and ligand/oxidant were added simultaneously, with between 0.3 to 0.7 mg of metal added (measured using a 4 figure balance). With this small amount, it was challenging to be accurate, and reproducibility was sometimes difficult. Stirring was performed in all tests. Since experiments were done open to the air, the amount of \(H_2O/O_2\) incorporated into the mixtures over long reaction times can also relate to the inconsistency of results found in occasions. However it was found that overall, the procedure was adequate for the initial large set of screening experiments.

3.2 Pd

3.2.1 Imidazolium ILs

Table 3.3 shows the results of all the tests carried out using imidazolium ILs to dissolve Pd. A range of cation and anion combinations were tested and it was found that those which resulted in the dissolution of Pd were [BMIM]Br, [BMIM]Cl, and [OMIM]Cl.
Table 3.3 Experiments carried out for the dissolution of Pd in imidazolium ILs (4 mL, unless otherwise indicated). Positive results are highlighted in red.

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL</th>
<th>Concentration (mM) of Pd, ligand (L) and oxidant (O)</th>
<th>Ratio Pd:L:O</th>
<th>Time/hours</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pd L O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>[EMIM]NTf$_2$ (60 °C)</td>
<td>0.94 (6) (4.40) I$_2$ (9.87)</td>
<td>1:5:11</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1.17 N/A N/A N/A</td>
<td></td>
<td>168</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1.88 N/A N/A</td>
<td></td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>4a</td>
<td>[BMIM]Br (90 °C)</td>
<td>1.25 (6) (4.97) N/A</td>
<td></td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>[BMIM]Cl (90 °C)</td>
<td>1.88 (26) (4.65) N/A</td>
<td></td>
<td>336</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1.17 N/A I$_2$ (1.48)</td>
<td>1:0:1</td>
<td>192</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1.17 N/A TBANO$_3$ (1.23)</td>
<td>1:0:1</td>
<td>192</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>1.65 N/A TBANO$_3$ (2.14)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>1.17 N/A Ceria (1.31)</td>
<td>1:0:1</td>
<td>192</td>
<td>Yes</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>1.65 (26) (4.15) TBANO$_3$ (2.14)</td>
<td>1:3:1</td>
<td>336</td>
<td>No</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>1.41 N/A N/A</td>
<td></td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>1.88 N/A N/A</td>
<td></td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>13</td>
<td>[BMIM]FAP (60 °C)</td>
<td>1.88 (26) (4.00) N/A</td>
<td></td>
<td>168</td>
<td>Yes</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>1.41 N/A I$_2$ (1.87)</td>
<td>1:0:1</td>
<td>192</td>
<td>No</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.94 N/A TBANO$_3$ (1.15)</td>
<td>1:0:1</td>
<td>120</td>
<td>Yes</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>1.65 N/A TBANO$_3$ (1.89)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.94 N/A Ceria (1.07)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>18</td>
<td>[BMIM]OTf (90 °C)</td>
<td>1.65 (26) (3.68) TBANO$_3$ (1.89)</td>
<td>1:2:1</td>
<td>168</td>
<td>Yes</td>
</tr>
<tr>
<td>19a</td>
<td>[BMIM]FAP (60 °C)</td>
<td>1.25 (6) (4.60) I$_2$ (6.57)</td>
<td>1:4:5</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>20</td>
<td>[BMIM]NTf$_2$ (90 °C)</td>
<td>1.17 N/A I$_2$ (1.48)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>21</td>
<td>[BMIM]OctSO$_4$ (60 °C)</td>
<td>1.41 N/A TBANO$_3$ (1.48)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>1.17 N/A Ceria (1.28)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>23a</td>
<td>[BMIM]PF$_6$ (60 °C)</td>
<td>1.57 (6) (4.40) I$_2$ (7.37)</td>
<td>1:3:5</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>24</td>
<td>[BMIM]OTf (90 °C)</td>
<td>1.17 N/A I$_2$ (1.38)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>25</td>
<td>[BMIM]PF$_6$ (60 °C)</td>
<td>1.17 N/A I$_2$ (5.42)</td>
<td>1:0:5</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>26</td>
<td>[BMIM]OTf (90 °C)</td>
<td>0.94 N/A TBANO$_3$ (1.23)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>1.17 N/A Ceria (1.16)</td>
<td>1:0:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>28a</td>
<td>[BMIM]PF$_6$ (60 °C)</td>
<td>1.25 (6) (4.60) I$_2$ (9.20)</td>
<td>1:4:7</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>No.</td>
<td>Ionic Liquid</td>
<td>Temp.</td>
<td>PV @ 298 K</td>
<td>Viscosity</td>
<td>Diffusion</td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
<td>-------</td>
<td>-------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>29</td>
<td>[BMIM]Cl: [BMIM]NO₃</td>
<td>90°C</td>
<td>50:50 vol</td>
<td>1.41</td>
<td>N/A</td>
</tr>
<tr>
<td>30a</td>
<td>[HMIM]NTf₂</td>
<td>60°C</td>
<td>1.25</td>
<td>(6) (3.25)</td>
<td>I₂ (8.40)</td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td>2.35</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td>2.35</td>
<td>N/A</td>
<td>HNO₃ (2.35)</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td>2.83</td>
<td>N/A</td>
<td>HNO₃ (11.8)</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td>0.94</td>
<td>N/A</td>
<td>HNO₃ (204)</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td>0.94</td>
<td>N/A</td>
<td>I₂ (0.99)</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td>2.35</td>
<td>N/A</td>
<td>I₂ (2.65)</td>
</tr>
<tr>
<td>37</td>
<td></td>
<td></td>
<td>1.88</td>
<td>N/A</td>
<td>I₂ (14.5)</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td></td>
<td>2.12</td>
<td>N/A</td>
<td>TBANO₃ (2.55)</td>
</tr>
<tr>
<td>39</td>
<td></td>
<td></td>
<td>1.41</td>
<td>N/A</td>
<td>TBANO₃ (1.72)</td>
</tr>
<tr>
<td>40</td>
<td>[OMIM]Cl</td>
<td>60°C</td>
<td>1.88</td>
<td>N/A</td>
<td>TBANO₃ (9.20)</td>
</tr>
<tr>
<td>41</td>
<td>[OMIM]NTf₂</td>
<td>60°C</td>
<td>0.94</td>
<td>PH₃P (3.91)</td>
<td>I₂ (1.38)</td>
</tr>
<tr>
<td>42</td>
<td>[OMIM]NTf₂</td>
<td>60°C</td>
<td>0.94</td>
<td>PH₃P (3.91)</td>
<td>I₂ (4.33)</td>
</tr>
<tr>
<td>43a</td>
<td>[OMIM]Cl</td>
<td>60°C</td>
<td>1.57</td>
<td>(6) (4.40)</td>
<td>I₂ (6.70)</td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td>0.94</td>
<td>(22) (2.91)</td>
<td>I₂ (0.99)</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td>0.94</td>
<td>(22) (2.91)</td>
<td>I₂ (3.05)</td>
</tr>
<tr>
<td>46</td>
<td></td>
<td></td>
<td>1.41</td>
<td>(22) (2.91)</td>
<td>I₂ (5.81)</td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td>1.41</td>
<td>(26) (3.52)</td>
<td>I₂ (1.87)</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
<td>1.41</td>
<td>(26) (3.52)</td>
<td>I₂ (3.55)</td>
</tr>
<tr>
<td>49</td>
<td></td>
<td></td>
<td>1.41</td>
<td>(27) (3.05)</td>
<td>I₂ (1.48)</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td>1.41</td>
<td>(27) (3.05)</td>
<td>I₂ (3.55)</td>
</tr>
<tr>
<td>51</td>
<td></td>
<td></td>
<td>0.94</td>
<td>(28) (1.88)</td>
<td>I₂ (1.08)</td>
</tr>
<tr>
<td>52</td>
<td></td>
<td></td>
<td>0.94</td>
<td>(28) (1.88)</td>
<td>I₂ (1.97)</td>
</tr>
<tr>
<td>53</td>
<td>[OMIM]NTf₂</td>
<td>90°C</td>
<td>1.18</td>
<td>N/A</td>
<td>TBANO₃ (1.23)</td>
</tr>
<tr>
<td>54</td>
<td></td>
<td></td>
<td>0.94</td>
<td>(26) (2.40)</td>
<td>TBANO₃ (1.07)</td>
</tr>
<tr>
<td>55</td>
<td></td>
<td></td>
<td>1.18</td>
<td>(27) (3.20)</td>
<td>TBANO₃ (1.48)</td>
</tr>
<tr>
<td>56b</td>
<td>[OMIM]PF₆ (_{6})</td>
<td>60°C</td>
<td>2.09</td>
<td>(6) (5.72)</td>
<td>I₂ (15.3)</td>
</tr>
</tbody>
</table>

*a: 3 mL of ionic liquid  
b: 1.8 mL of ionic liquid*
3.2.1.1 Use of adduct \([\text{Mespipdt}H]I_3\) \((12)\)

As explained in Chapter 2, 2.2.2, \((12)\) was tested for the dissolution of Pd in conventional solvents, as in the literature, but found to be unsuccessful. The adduct was also tried in ILs to see if it would work in these. This was done with the separate additions of \((6)\) and I\(_2\) and the results are shown in Table 3.3: Entries 1 ([EMIM]NTf\(_2\)), 19 ([BMIM]FAP), 23 ([BMIM]OctSO\(_4\)), 28 ([BMIM]PF\(_6\)), 30 ([HMIM]NTf\(_2\)), 43 ([OMIM]Cl), and 56 ([OMIM]PF\(_6\)). Dissolution of Pd was observed only in [OMIM]Cl (entry 43). This suggests that the IL itself and not the adduct was more influential in the dissolution of Pd. As such, any further work involving \((12)\) (or \((6)\)) did not proceed. It should be noted that using [OMIM]Cl on its own, at 60 °C (entry 31), did not lead to dissolution of Pd. However, the metal dissolved upon addition of only I\(_2\) (no ligand) in [OMIM]Cl at 60 °C (entry 36). The same process at 90 °C (entry 35) did not work, and this may be due to loss of I\(_2\) while working at a higher temperature. Surprisingly, dissolution was also not observed when the experiment was repeated at 60 °C, but increasing the number of I\(_2\) equivalents to 8 (entry 37). Given these results, further experiments were carried out in which only I\(_2\) was added to the IL.

3.2.1.2 Use of I\(_2\) (no added ligand)

Dissolution of Pd in [BMIM]Cl with added I\(_2\) (entry 14) was not observed. As in the case of [OMIM]Cl, it may be due to the high temperature used in the experiment (note that all reactions in [BMIM]Cl were done at 90 °C, as its melting point is ca. 70 °C). Other [BMIM]X ILs were also tested using I\(_2\) as oxidant at 90 °C, \textit{i.e.} X = Br\(^-\), NTf\(_2\), and OTf\(^-\) (entries 6, 20, and 24-25 respectively). Dissolution was not observed in any.

3.2.1.3 Use of other oxidants (no added ligand)

In addition to I\(_2\), other oxidants were tested: HNO\(_3\), TBANO\(_3\), and CeO\(_2\) (ceria). HNO\(_3\) was used because it is known to readily dissolve Pd, in particular in combination with HCl (aqua regia). To avoid the use of a strong acid, we decided to test TBANO\(_3\), and CeO\(_2\) was chosen as it is already present in automotive catalytic converters. HNO\(_3\) was tested in [OMIM]Cl at 60 °C (entries 32-34). Positive results were obtained using \textit{ca.} 1 eq. of acid (entry 32) after 192 hours, but metal dissolution was not observed when the number
of HNO₃ equivalents were increased to 4 (entry 33). Using a large excess of HNO₃ (entry 34), Pd dissolution was observed within 24 hours. This high concentration of acid, however, is undesirable. Neither ceria or TBANO₃ on their own were successful at dissolving Pd in non-halide ILs: [BMIM]X [X = NTf₂ (entries 21-22), OTf (entries 26-27)] or [OMIM]NTf₂ (entry 53, for TBANO₃). In halide ILs, TBANO₃ gave mixed, inconsistent results, as discussed below. Ceria was tested in [BMIM]X (X = Br, Cl; entries 9 and 17) and showed positive results only in the bromide IL (see below). Using TBANO₃ in [BMIM]Cl at 90 °C was successful in one of the attempts (entry 15), and unsuccessful in another one (entry 16). In both cases, the Pd:TBANO₃ ratio was ca. 1:1, but the second test was done with a higher amount of metal (0.7 mg vs. 0.4 mg). In [BMIM]Br (entries 7-8), dissolution of Pd was observed after 192 hours, but the metal remained undissolved after 168 hours. TBANO₃ was also used in [OMIM]Cl (entries 38-40). The reaction at 60 °C and 1:1 ratio of TBANO₃:Pd, resulted in the metal dissolving within 192 hours (entry 38). The use of higher TBANO₃:Pd ratios, entries 39 (2:1, 90 °C) and 40 (5:1, 60 °C), was however unsuccessful. A 50:50 volume mixture of [BMIM]Cl and [BMIM]NO₃ (entry 29) was used as an attempt to have the oxidant (nitrate anions) as a part of the ionic liquid media, but this did not work.

3.2.1.4 Addition of both a ligand and an oxidant

In order to increase the metal concentration in the solutions and/or reduce the dissolution times, various ligands were used in combination with the oxidant (I₂ or TBANO₃). In particular, Ph₃P together with dinitrogen and diphosphine ligands were tested (see Figs. 3.3-3.4 above). As seen previously, positive results were only obtained with halide ILs. For example, the use of (26) or (27) with TBANO₃ in [OMIM]NTf₂ (entries 54-55) was unsuccessful. TBANO₃ and (26) were used in [BMIM]Br (entry 10) and [BMIM]Cl (entry 18), but Pd only dissolved in the latter. Interestingly, metal dissolution was also observed by using ligand (26) on its own in [BMIM]Cl (entry 13), but not in [BMIM]Br (entry 5). A larger screening of ligands including Ph₃P, (22), and (26)-(28), was done in [OMIM]Cl/ I₂ systems (entries 41-52). In all cases, dissolution of Pd was observed only when the number of I₂ equivalents was at least the same as those of the ligand.
3.2.1.5 Summary of results in imidazolium ILs and further studies in [BMIM]Br

As mentioned above, Pd dissolved only in halide imidazolium ILs, which indicates that the formation of stable Pd(II) halide complexes, in particular $[\text{PdX}_4]^{2-}$, may be the main driving force for the dissolution of the metal. In [OMIM]Cl, the metal dissolved in the presence of HNO$_3$, TBANO$_3$ or I$_2$ as oxidants, as well as in a range of ligand/I$_2$ combinations. However, addition of a ligand did not significantly improve the amount of metal dissolved or shortened the reaction time. In [BMIM]Cl, dissolution of Pd was observed when either TBANO$_3$ or ligand (26) (or both) were added, but experiments were unsuccessful with other oxidants (I$_2$ or ceria). By contrast, in [BMIM]Br, the metal dissolved in mixtures containing ca. 1 eq. of ceria, TBANO$_3$ or I$_2$, but not when only ligand (26) (or (6), entry 4) were added. Interestingly, the metal also dissolved when using only [BMIM]Br (entry 2), but this result was not reproduced when the experiment was repeated with a slightly larger amount of metal (entry 3). Overall, however, [BMIM]Br appears to be more suitable for metal dissolution than [BMIM]Cl. This may be due to the higher stability of $[\text{PdBr}_4]^{2-}$ compared to $[\text{PdCl}_4]^{2-}$ but it can also be related to the viscosity of the IL or the amount of H$_2$O/O$_2$ present. This is discussed further in Section 3.2.4.\textsuperscript{54,152}

3.2.2 $[P_{66614}]Cl$

The effect of using a different IL cation, while keeping a halide anion, was investigated. In particular, a range of experiments were performed in $[P_{66614}]Cl$. As mentioned previously all experiments were carried out in 4 mL of solvent at 60 °C while open to air and left for 168 hours unless stated otherwise. Table 3.4 shows the results of all the tests carried out. The IL itself does not dissolve Pd and so the oxidants I$_2$, TBANO$_3$, and ceria were all tested initially at 90 °C (entries 3, 4, and 6, respectively) but dissolution of metal was not observed. Adding a variety of ligands alongside TBANO$_3$ or I$_2$ was also tested. It was found that a combination of TBANO$_3$ with (26) (entries 13-14) or (27) (entries 15-16) resulted in Pd dissolving after 168 hours. In particular, full dissolution was observed by using 2 eq. of ligand for every 1 eq. of Pd. Interestingly, it was found that adding the ligand on its own (entries 1 and 2) also resulted in Pd dissolution, indicating that
something else is acting as an oxidant. As with [BMIM]Br this may be H₂O or O₂ absorbed by the IL (see Section 3.2.4).

Table 3.4 Experiments carried out for the dissolution of Pd in [P₆₆₆₁₄]Cl at 60 °C unless stated otherwise, all for 168 hours

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration (mM)</th>
<th>Ratio Pd:L:O</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Ligand</td>
<td>Oxidant</td>
</tr>
<tr>
<td>1</td>
<td>1.18</td>
<td>(26) (2.73)</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>0.94</td>
<td>(27) (2.08)</td>
<td>N/A</td>
</tr>
<tr>
<td>3 (90 °C)</td>
<td>1.17</td>
<td>N/A</td>
<td>I₂ (1.48)</td>
</tr>
<tr>
<td>4 (90 °C)</td>
<td>0.94</td>
<td>N/A</td>
<td>TBANO₃ (0.99)</td>
</tr>
<tr>
<td>5</td>
<td>1.18</td>
<td>N/A</td>
<td>TBANO₃ (1.31)</td>
</tr>
<tr>
<td>6 (90 °C)</td>
<td>1.17</td>
<td>N/A</td>
<td>Ceria (1.60)</td>
</tr>
<tr>
<td>7</td>
<td>1.18</td>
<td>Ph₃P (5.35)</td>
<td>TBANO₃ (1.40)</td>
</tr>
<tr>
<td>8</td>
<td>1.18</td>
<td>(1) (3.00)</td>
<td>TBANO₃ (1.64)</td>
</tr>
<tr>
<td>9</td>
<td>0.94</td>
<td>(2) (2.08)</td>
<td>TBANO₃ (1.07)</td>
</tr>
<tr>
<td>10</td>
<td>0.94</td>
<td>(3) (1.91)</td>
<td>TBANO₃ (1.32)</td>
</tr>
<tr>
<td>11</td>
<td>1.41</td>
<td>(21) (3.22)</td>
<td>I₂ (5.82)</td>
</tr>
<tr>
<td>12</td>
<td>1.17</td>
<td>(21) (4.66)</td>
<td>I₂ (4.73)</td>
</tr>
<tr>
<td>13</td>
<td>0.94</td>
<td>(26) (0.96)</td>
<td>TBANO₃ (1.15)</td>
</tr>
<tr>
<td>14</td>
<td>0.94</td>
<td>(26) (1.92)</td>
<td>TBANO₃ (1.31)</td>
</tr>
<tr>
<td>15</td>
<td>1.41</td>
<td>(27) (1.53)</td>
<td>TBANO₃ (1.72)</td>
</tr>
<tr>
<td>16</td>
<td>1.41</td>
<td>(27) (3.20)</td>
<td>TBANO₃ (1.72)</td>
</tr>
<tr>
<td>17</td>
<td>1.41</td>
<td>(28) (2.83)</td>
<td>TBANO₃ (1.64)</td>
</tr>
<tr>
<td>18</td>
<td>1.18</td>
<td>(29) (2.48)</td>
<td>TBANO₃ (1.32)</td>
</tr>
<tr>
<td>19</td>
<td>1.18</td>
<td>(30) (1.50)</td>
<td>TBANO₃ (1.48)</td>
</tr>
<tr>
<td>20</td>
<td>0.94</td>
<td>(31) (1.94)</td>
<td>TBANO₃ (1.07)</td>
</tr>
<tr>
<td>21</td>
<td>1.18</td>
<td>(32) (2.42)</td>
<td>TBANO₃ (1.48)</td>
</tr>
</tbody>
</table>

3.2.3 DESs

Given that the amount of metal dissolved in ILs was small after long reaction times, the use of DESs was then investigated. In particular, dissolution of elemental Pd was tested in three different DESs: Imiline 700 (3 eq. (21):7 eq. (24)), Reline 200 (1 eq. (21):2 eq. (24)), and another DES (see Section 3.2.4).
and Ethaline 200 (1 eq. (21):2 eq. (23)). Table 3.5 shows the results of all the tests carried out open to the air, using 4 mL of solvent at 60 °C unless otherwise stated.

**Table 3.5** Experiments carried out for the dissolution of Pd in DESs (4 mL, open to air).

Positive results are highlighted in red

<table>
<thead>
<tr>
<th>Entry</th>
<th>DES</th>
<th>Concentration (mM)</th>
<th>O = Oxidant</th>
<th>Ratio Pd:O</th>
<th>Time/hours</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Imiline 700 (90 °C)</td>
<td>1.17</td>
<td>N/A</td>
<td>N/A</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1.17</td>
<td>I₂ (4.73)</td>
<td>1:4</td>
<td>96</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.94</td>
<td>N/A</td>
<td>N/A</td>
<td>288</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>20.2</td>
<td>I₂ (80.3)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>40.4</td>
<td>I₂ (161)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>49.8</td>
<td>I₂ (202)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>60.8</td>
<td>I₂ (244)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>79.6</td>
<td>I₂ (321)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>Reline 200 (60 °C)</td>
<td>99.8</td>
<td>I₂ (401)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>99.8</td>
<td>I₂ (403)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>150</td>
<td>I₂ (601)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>200</td>
<td>I₂ (802)</td>
<td>1:4</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>1.41</td>
<td>TBANO₃ (1.64)</td>
<td>1:1</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>1.41</td>
<td>TBANO₃ (2.96)</td>
<td>1:2</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>1.41</td>
<td>TBANO₃ (4.43)</td>
<td>1:3</td>
<td>168</td>
<td>No</td>
</tr>
<tr>
<td>16</td>
<td>Ethaline 200 (60 °C)</td>
<td>2.11</td>
<td>I₂ (6.40)</td>
<td>1:3</td>
<td>6</td>
<td>Yes</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>48.2</td>
<td>I₂ (194)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>98.2</td>
<td>I₂ (398)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>147</td>
<td>I₂ (593)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>206</td>
<td>I₂ (832)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>259</td>
<td>I₂ (1.05 M)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>300</td>
<td>I₂ (1.23 M)</td>
<td>1:4</td>
<td>3</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Pd dissolved in the three DESs tested in the presence of I$_2$. Experiments using TBANO$_3$ (entries 13-15) or no oxidant (entries 1 and 3) were unsuccessful. In most cases where dissolution was observed, 4 equivalents of I$_2$ were used as this consistently dissolved Pd within 24 hours. The use of less I$_2$ was investigated (see Table 3.6 below), and it was found that at least 3 equivalents were needed. In Imiline 700, Pd dissolved within 96 hours. This experiment was carried out at 90 °C due to the melting point of this DES being 56 °C.$^{100,101,104}$ Reline 200 and Ethaline 200, both at 60 °C, dissolved Pd in 24 and 3 hours respectively when using 4 equivalents of I$_2$. The differences may relate to the composition of the DES; *i.e.* compounds (22) and (23) (components of Reline 200 and Ethaline 200, respectively) are able to form chelating complexes with the metal ((23) in particular would result in a 5-member ring which is more favourable than the 4-member formed with (22)), whereas this is not the case for (24) (in Imiline 700). TBANO$_3$ was tested as the oxidant in Reline 200 (entries 13-15) but may be too strong an oxidant, oxidising (21).

![Figure 3.5](image-url)

**Figure 3.5** Stages of Reline 200 during Pd dissolution process; A = Reline 200 as a mixture of solids at room temperature, B = Reline 200 as a clear liquid after slight heating, C = Reline 200 after dissolving I$_2$ (200 mM) and then Pd (50 mM)

In order to find the maximum amount of metal that could be dissolved, additions of Pd in *ca.* 50 mM increments were carried out (Table 3.5). In Reline 200 the maximum concentration achieved was 200 mM (entry 12, Fig. 3.5). For Ethaline 200 it was found to be 300 mM (entry 22, Fig. 3.6).
Figure 3.6 Stages of Ethaline 200 during Pd dissolution process; A = Ethaline 200 as a clear liquid at room temperature, B = Ethaline 200 after dissolving I\(_2\) (200 mM) and then Pd (50 mM).

Table 3.6 Experiments carried out of Reline 200 system; open vs closed, at 60 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Open/Closed</th>
<th>Concentration (mM)</th>
<th>Ratio</th>
<th>Time/hours</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pd</td>
<td>I(_2)</td>
<td>Pd: I(_2)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Open</td>
<td>1.17</td>
<td>1.28</td>
<td>1:1</td>
<td>168</td>
</tr>
<tr>
<td>2</td>
<td>Open</td>
<td>1.17</td>
<td>2.56</td>
<td>1:2</td>
<td>168</td>
</tr>
<tr>
<td>3</td>
<td>Open</td>
<td>1.41</td>
<td>4.24</td>
<td>1:3</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>Open</td>
<td>1.41</td>
<td>4.53</td>
<td>1:3</td>
<td>168</td>
</tr>
<tr>
<td>5</td>
<td>Open</td>
<td>2.82</td>
<td>9.65</td>
<td>1:3</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Open</td>
<td>1.17</td>
<td>4.24</td>
<td>1:4</td>
<td>168</td>
</tr>
<tr>
<td>7</td>
<td>Open</td>
<td>1.17</td>
<td>4.93</td>
<td>1:4</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>Closed</td>
<td>1.17</td>
<td>1.58</td>
<td>1:1</td>
<td>168</td>
</tr>
<tr>
<td>9</td>
<td>Closed</td>
<td>1.41</td>
<td>2.86</td>
<td>1:2</td>
<td>168</td>
</tr>
<tr>
<td>10</td>
<td>Closed</td>
<td>1.64</td>
<td>5.02</td>
<td>1:3</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>Closed</td>
<td>1.17</td>
<td>4.14</td>
<td>1:4</td>
<td>168</td>
</tr>
<tr>
<td>12</td>
<td>Closed</td>
<td>1.41</td>
<td>6.01</td>
<td>1:4</td>
<td>24</td>
</tr>
</tbody>
</table>

With the aim of evaluating if H\(_2\)O or O\(_2\) absorbed from the atmosphere was having an effect on the dissolution of Pd, experiments were performed where some sample vials were left open and others were closed (cap added to vial; Table 3.6). Experiments 6 and 11 are inconsistent with the rest possibly due to experimental error in these particular mixtures. With the exception of 6 and 11, there is no significant difference between the
open and closed systems. The main factor is that there has to be at least 3 equivalents of I$_2$ for dissolution to occur although the dissolution times are inconsistent.

3.2.4 Comparison of IL and DES results

Serpe et al.\textsuperscript{44} managed to dissolve Pd powder (12.3 mg) within 1 hour at room temperature using 2 equivalents of (13) in THF. When (13) was employed in MEK at 80 °C for use on a model aged catalytic converter, a near quantitative extraction of Pd was achieved within 168 hours.\textsuperscript{25} It is unknown if the increase in dissolution time is a consequence of the solvent being changed or the extra material now present due to the converter. In this work while using ILs, the time required for successful dissolution of Pd powder ranges from 24-192 hours depending on the conditions employed. Compared to the dissolution time observed by Serpe et al.\textsuperscript{44} (1 hour), this is a large increase in time and in one instance requires a large amount of acid (Table 3.3, entry 34) to dissolve Pd powder. Due to the greater viscosity of ILs compared to conventional solvents, if any of these methods were carried forward for use on a catalytic converter the dissolution times would only increase further as observed by Serpe et al. using (13) in conventional solvents.\textsuperscript{25,44} This would be due to the greater difficulty of the reactants coming into contact with each other and the increased difficulty of the IL penetrating into the catalytic converter. The DESs dissolve Pd powder faster than the ILs (Imiline 700 = 96 hours, Reline 200 = 24 hours, Ethaline 200 = 3 hours), with Ethaline 200 in particular showing a dissolution time not too dissimilar to the 1 hour achieved by Serpe et al., albeit still requiring an elevated temperature. The DES systems also avoid the need to synthesise a ligand/adduct, only requiring addition of I$_2$. As with the ILs, the higher viscosity of DESs compared to the conventional solvents may lead to the dissolution time increasing when applied to catalytic converters.

In order for Pd to be oxidised and to dissolve there must be sufficient mixing between the metal and the oxidant and/or ligand. The viscosities of the halide ILs are normally higher than the non-halide analogues, and therefore, given the above results, the main factor contributing to the dissolution of the metal is the presence of halide, not the viscosity. For example, the viscosities of [BMIM]NTf$_2$ and [BMIM]OTf are 0.045 and 0.076 Pa s,
respectively at 25 °C,\textsuperscript{89} whereas [BMIM]Br has a viscosity of 1.486 Pa s (25 °C), and [BMIM]Cl of 11 Pa s (30 °C).\textsuperscript{87,88} The lower viscosity of the former two is related to the bulkier NTf\textsubscript{2} and OTf\textsuperscript{−} anions and their charge delocalisation which reduces the electrostatic interactions and hinders organisation and packing of the ions. The fact that the viscosity of [BMIM]Br is lower than that of [BMIM]Cl can also be related to the larger Br\textsuperscript{−} anions making it more difficult for structured packing of the ions to occur. At the temperatures used in the experiments herein (60-90 °C), the viscosities of the ILs will be lower than those reported above, all around room temperature, but it is expected that the bromide IL will still be less viscous than the chloride analogue, and both will be more viscous than the non-halide imidazolium ILs. The viscosity of [OMIM]Cl has been reported to be 0.375 Pa s at 80 °C, which is greater than that of [BMIM]Cl (0.142 Pa s) at the same temperature.\textsuperscript{90} This increase is due to the larger alkyl chain length of the cation which results in greater Van der Waals forces and thus a greater viscosity. Therefore, the viscosity in the three halide ILs used decreases in the order [OMIM]Cl > [BMIM]Cl > [BMIM]Br. As mentioned above, the relatively better results obtained in [BMIM]Br is mainly attributed to the higher stability of Pd-bromide complexes.

Table 3.7 Amount of H\textsubscript{2}O measured by Karl Fischer titration for the imidazolium ILs used in this work

<table>
<thead>
<tr>
<th></th>
<th>[EMIM]</th>
<th>[BMIM]</th>
<th>[HMIM]</th>
<th>[OMIM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br\textsuperscript{−}</td>
<td>N/A</td>
<td>0.266 Wt%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cl\textsuperscript{−}</td>
<td>N/A</td>
<td>N/A\textsuperscript{a}</td>
<td>N/A</td>
<td>0.598 Wt%</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{−}</td>
<td>N/A</td>
<td>0.412 Wt%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>NTf\textsubscript{2}</td>
<td>0.115 Wt%</td>
<td>0.007 Wt%</td>
<td>0.039 Wt%</td>
<td>0.100 Wt%</td>
</tr>
<tr>
<td>OTf\textsuperscript{−}</td>
<td>N/A</td>
<td>0.611 Wt%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PF\textsubscript{6}\textsuperscript{−}</td>
<td>N/A</td>
<td>0.116 Wt%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\textsuperscript{a: Due to being a solid}

All solvents were dried using Schlenk techniques prior to their use, but traces of H\textsubscript{2}O remained. The amount of H\textsubscript{2}O present in the solvent at the start of each experiment or absorbed during the procedure should be taken into account, as this has an effect on the
viscosity (e.g., small amounts of H$_2$O can significantly reduce the viscosity of ILs) and may also increase the amount of O$_2$ dissolved in the mixtures. The H$_2$O content of the imidazolium ILs used in this work, measured by Karl Fischer titration, are included in Table 3.7. In addition, the values found for [P$_{66614}$]Cl, Reline 200, and Ethaline 200 were 0.251 Wt%, 0.553 Wt%, and 0.429 Wt%, respectively. Overall, there is no correlation between the amount of H$_2$O remaining in the solvent and its capacity to dissolve Pd. The H$_2$O content of the solvents which successfully dissolve Pd was measured also after 168 hours. This was carried out by taking 4 mL of the solvents and heating at 60 °C. Table 3.8 shows the results. There appears to be no connection between the increase in H$_2$O content and the ability of each solvent to dissolve Pd. For example, the two most successful solvents for Pd dissolution (entries 5-6) show both the least and most change. However, there is a significant increase in H$_2$O content in all cases, and this may be a factor aiding metal dissolution.

### Table 3.8 Change in the amount of H$_2$O, measured by Karl Fischer, during the length of the dissolution tests for the ILs and DESs which dissolved Pd

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL</th>
<th>0 hours Wt%</th>
<th>168 hours Wt%</th>
<th>Δ Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[BMIM]Br</td>
<td>0.266</td>
<td>1.142</td>
<td>0.876</td>
</tr>
<tr>
<td>2</td>
<td>[BMIM]Cl</td>
<td>N/A</td>
<td>2.998</td>
<td>2.998</td>
</tr>
<tr>
<td>3</td>
<td>[OMIM]Cl</td>
<td>0.598</td>
<td>4.170</td>
<td>3.572</td>
</tr>
<tr>
<td>4</td>
<td>[P$_{66614}$]Cl</td>
<td>0.251</td>
<td>1.213</td>
<td>0.962</td>
</tr>
<tr>
<td>5</td>
<td>Reline 200</td>
<td>0.553</td>
<td>1.322</td>
<td>0.769</td>
</tr>
<tr>
<td>6</td>
<td>Ethaline 200</td>
<td>0.429</td>
<td>4.613</td>
<td>4.184</td>
</tr>
</tbody>
</table>

*a: Due to being a solid*

As mentioned above, the main factor influencing the dissolution of Pd is the presence of halide anions in the solvent, allowing the formation of stable Pd(II)-halide species. The soft character of Pd(II) results in the affinity order I$^-$ > Br$^-$ > Cl$^-$. The covalent character of the Pd(II)-X bond increases with the atomic weight of the halide and the size of the orbitals which would lead to better orbital overlap. This may explain why [BMIM]Br is capable of dissolving Pd without addition of an oxidant whereas [BMIM]Cl is not, even
though it has a greater H$_2$O content after 168 hours (Table 3.8). The difference in
dissolution ability of the ILs and DESs may relate to the components in the latter also
being able to coordinate Pd(II), but this point is unclear at this stage.$^{99,100}$ Of the oxidants
tested, I$_2$ appears to be the best as it is strong enough to oxidise Pd but not any parts of the
solvents, i.e. as HNO$_3$ or TBANO$_3$ seem to.

3.3 Pt

Screening dissolution tests were carried out for Pt, almost in the same way as for Pd, with
the addition of two pyridinium and two pyrrolidinium ILs. A summary of results can be
seen in Table 3.9. The only successful dissolution of Pt involved a large excess (319 eq.)
of HNO$_3$ in [OMIM]Cl (entry 18). This dissolved the metal within 48 hours. In
comparison Bigoli et al.,$^{41}$ using (12) in acetonitrile at reflux, were able to dissolve Pt
powder in 96 hours and avoided using a large amount of acid. Ultimately Pt proved
extremely difficult to dissolve. The difference observed in the oxidation/dissolution of
the two metals is related to Pt possessing an inner shell of f electrons.$^{10}$ The 5d electrons
of Pt are thus better shielded than the 4d of Pd which does not possess any f electrons.
Therefore the 1$^{\text{st}}$ ionisation potential of Pt is greater than that of Pd because the first
electron lost by Pt comes from an s orbital.
Table 3.9  Experiments carried out for the dissolution of Pt in ILs and DESs. Positive results are highlighted in red.

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL</th>
<th>Concentration (mM)</th>
<th>Ratio Pd:L:O</th>
<th>Time/ hours</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L = Ligand, O = Oxidant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>[BMIM]Br (90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[BMIM]Cl (90 °C)</td>
<td>0.64 N/A N/A I₂ (0.79)</td>
<td>1:0:1 192</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[BMIM]Br (90 °C)</td>
<td>0.64 N/A TBANO₃ (0.74)</td>
<td>1:0:1 192</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[BMIM]Cl (90 °C)</td>
<td>0.64 N/A Ceria (0.73)</td>
<td>1:0:1 192</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[BMIM]Cl (90 °C)</td>
<td>0.77 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[BMIM]NTf₂ (90 °C)</td>
<td>0.64 N/A N/A I₂ (0.89)</td>
<td>1:0:1 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>[BMIM]OTf (90 °C)</td>
<td>0.77 N/A TBANO₃ (0.82)</td>
<td>1:0:1 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>[BMIM]Cl:50:50 vol. [BMIM]NO₃ (90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>2.56 N/A HNO₃ (817)</td>
<td>1:0:319 48</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.51 N/A I₂ (1.81)</td>
<td>1:0:4 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.51 N/A TBANO₃ (3.28)</td>
<td>1:0:6 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.51 N/A TBANO₃ (3.28)</td>
<td>1:0:6 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A Ceria (0.73)</td>
<td>1:0:1 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>[OMIM]Cl (60 °C, except entries 18-21 90 °C)</td>
<td>0.64 N/A N/A N/A</td>
<td>N/A 168</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Entry</td>
<td>Ionic Liquid</td>
<td>Temperature</td>
<td>I$_2$ (mmol)</td>
<td>Ratio</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>-------------</td>
<td>--------------</td>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>25</td>
<td>[CyMPy]NTf$_2$</td>
<td>(60 °C, except entry 32-90 °C)$^b$</td>
<td>1.23</td>
<td>(6) (2.30)</td>
<td>I$_2$ (5.52)</td>
</tr>
<tr>
<td>32</td>
<td>[HPy]NTf$_2$</td>
<td>(60 °C, except entry 34-90 °C)$^a$</td>
<td>0.68</td>
<td>(6) (1.72)</td>
<td>I$_2$ (5.13)</td>
</tr>
<tr>
<td>34</td>
<td>[BMPyr]DCA</td>
<td>(60 °C, except entry 36-90 °C)$^a$</td>
<td>1.02</td>
<td>(6) (2.98)</td>
<td>I$_2$ (4.40)</td>
</tr>
<tr>
<td>37</td>
<td>[BMPyr]NTf$_2$</td>
<td>(60 °C, except entry 38-90 °C)$^a$</td>
<td>0.85</td>
<td>(6) (1.91)</td>
<td>I$_2$ (4.07)</td>
</tr>
<tr>
<td>39</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.51</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>41</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.51</td>
<td>N/A</td>
<td>I$_2$ (0.69)</td>
</tr>
<tr>
<td>42</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.64</td>
<td>N/A</td>
<td>TBANO$_3$ (0.57)</td>
</tr>
<tr>
<td>43</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.51</td>
<td>N/A</td>
<td>Ceria (0.73)</td>
</tr>
<tr>
<td>44</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.64</td>
<td>(26) (2.67)</td>
<td>TBANO$_3$ (0.90)</td>
</tr>
<tr>
<td>45</td>
<td>[P$_{66614}$]Cl</td>
<td>(60 °C, except entries 40,42, 43-90 °C)</td>
<td>0.64</td>
<td>(27) (2.67)</td>
<td>TBANO$_3$ (0.90)</td>
</tr>
<tr>
<td>46</td>
<td>Imiline 700 (90 °C)</td>
<td></td>
<td>0.77</td>
<td>N/A</td>
<td>I$_2$ (3.05)</td>
</tr>
<tr>
<td>47</td>
<td>Reline 200</td>
<td></td>
<td>0.51</td>
<td>N/A</td>
<td>I$_2$ (2.17)</td>
</tr>
<tr>
<td>48</td>
<td>Ethaline 200</td>
<td></td>
<td>0.64</td>
<td>N/A</td>
<td>I$_2$ (3.15)</td>
</tr>
</tbody>
</table>

*a: 3 mL of ionic liquid*

*b: 2.5 mL of ionic liquid*

*c: 1 mL of ionic liquid.*
3.4 Au

The work on Au dissolution was carried out in collaboration with Ms. Katherine Gregg, an undergraduate student working on her final year research project in our research group while under my supervision. The focus of this work was the dissolution of Au using a 1:1 mixture of Ph₃P and I₂ (17) in several imidazolium ILs.

Dissolution of Au was first attempted in [BMIM]NTf₂, [BMIM]OTf, and [HMIM]NTf₂ without (17), with the systems open to the air (Table 3.10; entries 1, 3 and 5). Dissolution of Au was not observed after 336 hours except for [BMIM]OTf (entry 3). The experiments were then repeated by adding Ph₃P:I₂ (1:1) (17) to see if any improvements were observed, this time ensuring the system was closed to prevent any decomposition of the adduct. Ph₃P and I₂ were added in a 1:1 ratio, allowing both reactants to dissolve first before adding Au. The Au:Ph₃P:I₂ ratio used was 1:2:2. All reactions were carried out in 4 mL of solvent at room temperature using 5 mg of Au. Entries 2 and 6 show that after 120 hours, Au dissolved in both [BMIM]NTf₂ and [HMIM]NTf₂. In [BMIM]OTf (entry 4), Au successfully dissolved after 72 hours. The 72 hours required here is quite a bit longer than the 30 minutes it took for Bigoli et al. 42 and Cau et al. 46 to dissolve Au powder using (13) and (16) respectively. In both cases THF was used as the solvent and dissolution was carried out at room temperature, as in this work.

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL</th>
<th>(17)</th>
<th>Time/hours</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[BMIM]NTf₂</td>
<td>No</td>
<td>336</td>
<td>No</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>[BMIM]NTf₂</td>
<td>Yes</td>
<td>120</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>[BMIM]OTf</td>
<td>No</td>
<td>336</td>
<td>Yes</td>
</tr>
<tr>
<td>4ᵇ</td>
<td>[BMIM]OTf</td>
<td>Yes</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>[HMIM]NTf₂</td>
<td>No</td>
<td>336</td>
<td>No</td>
</tr>
<tr>
<td>6ᵇ</td>
<td>[HMIM]NTf₂</td>
<td>Yes</td>
<td>120</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*a: All reactions carried out using 5 mg (6.34 mM) of Au in 4 mL of IL
*b: Ph₃P (13.3 mg, 12.7 mM) and I₂ (12.9 mg, 12.7 mM) were left to dissolve in the IL before adding Au.
The shorter dissolution time needed in the OTf− IL may relate to viscosity and/or H₂O content (as discussed above). However, at 25 °C, the viscosity of [BMIM]OTf (0.076 Pa s) is higher than that of [BMIM]NTf₂ (0.045 Pa s). According to the data in Table 3.7, [BMIM]OTf has the largest H₂O content of the three ILs, which may explain why Au dissolves faster in this than the other two, as the additional H₂O can lower the viscosity, aiding mixing of the reactants and at the same time may be acting as an additional oxidant.

Using 2 equivalents of Ph₃P:I₂ for every equivalent of Au, the maximum concentration of metal in the three ILs was determined. The highest concentration of dissolved Au achieved was of 11.4 mM in [BMIM]NTf₂, 57.1 mM in [BMIM]OTf, and 25.4 mM in [HMIM]NTf₂.

3.5 Conclusions

Dissolution of small amounts of Pd has been achieved in several halide containing ILs. The addition of an oxidant and/or a stabilising ligand is needed in most cases, and in some instances have contributed toward accelerating the process (e.g. in [OMIM]Cl, metal dissolution occurred after 192 hours if only I₂ was present, but needed only 48-72 hours if a ligand was also added). In the reactions where dissolution took place without an added oxidant, it is assumed that the amount of H₂O/O₂ present in the mixtures was enough to oxidise the metal, as experiments were carried out open to the air. The fact that some Pd powder could be oxidised and dissolved at relatively mild conditions is significant, but the concentrations of metal achieved in the IL mixtures (1-2 mM) are too small for the processes to be viable for scale up. The use of DESs for the oxidation/dissolution of Pd metal was more successful, as concentrations up to 300 mM of metal were obtained when adding >3 eq. of I₂. As in the ILs, the presence of halide ligands in the solvents was necessary. Overall, the best results were obtained in Reline 200 (200 mM of Pd, 24 hours) and Ethaline 200 (300 mM of Pd, 3 hours). Dissolution of Pt powder using similar conditions in ILs or DESs was not achieved. In the case of Au, oxidation/dissolution was achieved at room temperature, in several non-halide ILs in the presence of Ph₃P:I₂ (1:1). The highest concentration of Au (57.1 mM) was obtained in [BMIM]OTf after 72 hours.
3.6 Future Work

- Test iodide and polyiodide ILs for the dissolution of Pd to see if these can act as both oxidant and ligand and thus remove the need for addition of these.
- Investigate other DESs for a more complete picture of what type of HBDs/HBAs aid the dissolution of Pd.
- For Pt, a suitable oxidant needs to be found which is strong enough to oxidise the metal but does not require a large excess or oxidises the solvent. Using DESs would also be investigated as these were more successful for Pd dissolution and may be the case for Pt. A solution may be to use the DES consisting of 1 equivalent choline nitrate and 2 equivalents of (22).\textsuperscript{100,101}
- Expand the type of ILs and DESs used for Au dissolution when using Ph\textsubscript{3}P:I\textsubscript{2} (17) mixtures.
- Test different phosphine/I\textsubscript{2} adducts for the dissolution of Au, whereby the phosphine has different substituents or is polydentate.
Chapter 4. Raman and electrochemical investigation of dissolved Pd in Reline 200 and Ethaline 200 with subsequent removal from a catalytic converter

4.1 Aims and Introduction

The aim of this Chapter was to investigate solutions of Pd in both Reline 200 (1 eq. choline chloride (21):2 eq. urea (22)) and Ethaline 200 (1 eq. choline chloride (21):2 eq. ethylene glycol (23)) in order to determine which metal species formed, as well as their electrochemical behaviour. For comparison, Pd(II) salts, e.g. PdCl$_2$ and K$_2$PdCl$_4$, were dissolved in the same solvent mixtures and their electrochemical behaviour examined. Solutions of I$_2$ and Pd were also examined electrochemically and by Raman spectroscopy. The final aim of this chapter was to test the extraction of Pd from a real automotive catalytic converter and analysing the results.

There are some aspects to consider when planning to use DESs in electrochemical systems, i.e. their high viscosity (affecting laminar flow) and limited conductivity (particularly problematic when using ultramicroelectrodes). Metallocene reversible probes have been examined in DESs and show a separation of peak potentials that are higher than expected for kinetically reversible systems. This in turn creates problems in determination of kinetic parameters such as formal rate constant and charge transfer coefficient which are obtained from methods which use the separation of peak potentials.\textsuperscript{153–155} Despite these concerns, classical electrochemical approaches have been applied with some DESs, such as Reline 200 and Ethaline 200, when investigating DES properties. A particular focus was put on mass transport phenomena and the diffusion of charged species within the solvent. The CVs of ferricyanide reduction and ferrocene oxidation in Ethaline 200 displayed voltammograms which were well defined and showed the classical shape expected for a reversible redox couple. Linear variations of the peak current showed that mass transport of the redox species was controlled by diffusion from the bulk species to the electrode. Reline 200, however, was considered a less adapted solvent because of its higher viscosity and lower conductivity. Ferrocene was also found to be less soluble in Reline 200 than in Ethaline 200. The CVs of ferricyanide in Reline
200 were found to be well defined but those of ferrocene were not, and this was attributed to its low solubility and the partial blocking of the electrode as a result. As expected, diffusion in Reline 200 was found to be lower owing to its greater viscosity.\textsuperscript{156}

The electrochemical kinetics of the Fe(II)/Fe(III) redox couple and ferric ions in Reline 200 have also been investigated. The redox reaction exhibited quasi-reversible behaviour and the ferric ion transport properties were found to be comparable to those of ILs. Dissolution of FeCl\textsubscript{3} in the DES led to the formation of [FeCl\textsubscript{4}]\textsuperscript{-}. Peak current density of the CVs was 10 times lower in Reline 200 than the aqueous system showing mass transport is slower, but the reversibility of the Fe(II)/Fe(III) system in the DES is close to that in H\textsubscript{2}O. The peak currents of the DES system also increased rapidly with increasing temperature, attributed to both enhanced reaction kinetics and improved ion transport.\textsuperscript{157}

Reline 200 and Ethaline 200 were also investigated as electrolyte media for an all Fe redox flow battery. It was found that the resulting all Fe battery using DESs had a similar performance as that of the aqueous system. Using Zn alongside Fe the performance is initially excellent but ultimately fails, the reason of which is unclear.\textsuperscript{158}

Various metals have been deposited electrochemically from Reline 200 and Ethaline 200 including Cu,\textsuperscript{159–162} Ag,\textsuperscript{159} Sn,\textsuperscript{159,162–164} Ni,\textsuperscript{159,165–169} As,\textsuperscript{170} and Pd.\textsuperscript{114,115} Several alloys such as Cu-Ga,\textsuperscript{171–173} Cu-Sn,\textsuperscript{174} Zn-Sn,\textsuperscript{175} Co-Sn,\textsuperscript{176} Ni-Cu,\textsuperscript{177} and Ni-Mo\textsuperscript{178} have also been deposited.

Various metal salts (CuCl\textsubscript{2}, AgCl, NiCl\textsubscript{2}, and SnCl\textsubscript{2}) commonly used in the printed circuit board industry were dissolved in Reline 200 and Ethaline 200 and examined via CVs before the metals being electrodeposited, with both processes performed at various temperatures (40-90 °C). It was found that generally electrodeposition improved as the temperature increased, however the optimum conditions had to be found for each formulation. Variations were shown to exist between metals and even different solvents containing the same metal. Cu(II) solutions had an optimum temperature of 80 °C whereas the Reline 200 solution of Ag(I) functioned better at 60 °C. In Reline 200, Ni(II) had to be used at higher temperatures so as to form a certain complex (not identified) otherwise deposition would not occur.\textsuperscript{159} 3D hierarchical nanoporous Cu films were fabricated electrochemically in Reline 200 and Ethaline 200 containing ZnCl\textsubscript{2}. First, a
Cu-Zn alloy was formed before selectively etching the Zn. Compared to the Cu films produced from Reline 200, those from Ethaline 200 possessed a hierarchical porous architecture where the distribution of the channel/pore size could be tailored. With both solvents, nanoporosity was found to be highly dependent on both the temperature and time, indicating a surface diffusion controlled thermal activation process.\(^\text{160}\) In other work, separate solutions of CuCl\(_2\).2H\(_2\)O and SnCl\(_2\).2H\(_2\)O were made and [CuCl\(_4\)]\(^2-\) was found to be reduced through a two-step mechanism while [SnCl\(_3\)]\(^-\) was reduced via a two electron process.\(^\text{162}\) Sn was deposited onto a glassy carbon electrode from Reline 200 and Ethaline 200. The choice of HBD did not significantly affect the chemistry of Sn in solution. Chronoamperometric analysis suggested that Sn nucleation on the electrode was controlled by diffusion with growth proceeding via a 3D instantaneous process.\(^\text{163}\) Electrodeposition of Ni was performed using a solution of NiCl\(_2\).6H\(_2\)O in either Reline 200 or Ethaline 200. The deposition kinetics and thermodynamics differ from those of the aqueous processes and result in different morphologies of the deposit. Both were dark grey deposits but the Reline 200 sample was darker and a more nodular growth observed. The sample from Ethaline 200 was less rough. As the deposition process was kinetically slow, the shape of the stripping peaks were found to depend upon the sweep rate.\(^\text{165}\) Ni has been successfully deposited from Ethaline 200. Similar deposition rates were observed as those of aqueous solutions regardless of viscosity and conductivity differences. There was an observed difference of the DES deposit morphology (significant hardness increase) compared to the aqueous deposit. The DES deposit also had a lower surface roughness and was mirror bright. The differences were attributed to variation of the Ni speciation occurring from either the DES or H\(_2\)O environment.\(^\text{166}\) NiCl\(_2\).6H\(_2\)O was dissolved in Ethaline 200 and its effect on the density, surface tension, viscosity, and conductivity of the DES examined. The density, surface tension, and viscosity decreased while the conductivity increased. CVs obtained showed irreversible electrochemical behaviour of the Ni(II)/Ni system.\(^\text{168}\) As discussed in Section 1.8.3.1 Lazinger et al.\(^\text{114}\) dissolved PdCl\(_2\) in Reline 200 and Ethaline 200. Our aim is to achieve the dissolution of Pd(0) (through and oxidation-dissolution process) rather than Pd(II), so that the metal can be recycled in a one-pot two-step system which has not been described before.
4.2 Reline 200

Initially, Raman spectroscopy and cyclic voltammetry were carried out on a blank sample of Reline 200, then repeated after dissolving I$_2$. The next step was dissolving Pd and performing the analysis again before carrying out work on electrodeposition.

4.2.1 Raman Spectroscopy

On addition of I$_2$ (800 mM) to the sample of blank Reline 200 (Fig. 4.1) two broad peaks appear at 111 cm$^{-1}$ and 171 cm$^{-1}$, together with some broad absorption in the region of 130 cm$^{-1}$ to 162 cm$^{-1}$.

Jerman et al.$^{96}$ studied the Raman spectra of [PMIM]I (1-propyl-3-methylimidazolium iodide) and I$_2$ mixtures, and observed the formation of I$_5^-$ and I$_7^-$, including the three variations of the pentaiodide (see below) as the dominant species. The authors noted that a peak at 111-114 cm$^{-1}$ corresponded to the symmetric stretch ($v_{\text{sym}}$(I$_3^-$)) of the I$_3^-$ anion, whereas a shoulder-like band between 130 and 142 cm$^{-1}$ was related to discrete, asymmetric I$_5^-$.

In addition, tetraiodides which exist in equilibrium with I$_5^-$ at low concentrations of I$_2$, also exhibit a band ($v_{\text{sym}}$(2I$^-$…I$_2$)) between 145 and 155 cm$^{-1}$, but in this case the band at 111 cm$^{-1}$ is not present. The I$_5^-$ anion can either be linear, V-shaped, or L-shaped with all three structures exhibiting a band at 165 cm$^{-1}$. In the linear anion, a band at 105-107 cm$^{-1}$ is associated with the symmetric stretching of inner I-I ($v_{\text{sym}}$(I-I)$_{\text{inner}}$), whereas several bands are observed for the V-shaped ion ($v_{\text{sym}}$(I-I)$_{\text{inner}}$: 112 cm$^{-1}$, $v_{\text{anti}}$(I-I)$_{\text{outer}}$: 143-147 cm$^{-1}$, $v_{\text{sym}}$(I-I)$_{\text{outer}}$: 155-160 cm$^{-1}$).$^{96}$ The Raman spectra of I$_2$ in a range of donor solvents (e.g. thiourea derivatives, nitriles, amines), where it forms charge transfer complexes, show that I$_5^-$ is present in almost all cases, independently of the basicity of the solvent, i.e. giving the characteristic bands at 114 cm$^{-1}$ and 133-140 cm$^{-1}$. In addition, a band between 140 and 210 cm$^{-1}$ has been attributed to the I-I stretching mode of donor-I$_2$ complexes. Even in weak donor solvents, ‘free’ I$_2$ has been difficult to detect. This is expected to give a stretching band between 205 cm$^{-1}$ and that of I$_2$ gas, 213 cm$^{-1}$.$^{179}$
The band observed in Reline 200 at 111 cm\(^{-1}\) can therefore be attributed to I\(_3^+\) (symmetric stretch). The second band or shoulder expected at \textit{ca.} 130-140 cm\(^{-1}\) for I\(_3^+\) can be hidden under the broad absorption observed in that region (Fig. 4.1). The band at 171 cm\(^{-1}\) may be related to I\(_5^-\), in particular to the symmetric stretching of outer I-I (\(v_{\text{sym}}(\text{I-I})_{\text{outer}}\)). Additional bands related to I\(_5^-\) could be again within the broad absorptions, \textit{i.e.} in the 130-162 cm\(^{-1}\) region, seen in the spectrum of I\(_2\) in Reline 200 (Fig. 4.1). When Pd(0) is dissolved in the I\(_2\)/Reline 200 mixture to a concentration of 200 mM, the spectrum showed very intense, broad absorptions between \textit{ca.} 1200-1977 cm\(^{-1}\) (max. 1358 cm\(^{-1}\)), and 217-
938 cm\(^{-1}\) (max. 457 cm\(^{-1}\)). These bands are likely to be luminescence bands hiding the Raman scattering peaks. In the region 100-200 cm\(^{-1}\), however, two peaks at 111 cm\(^{-1}\) and 154 cm\(^{-1}\) can be seen. These are attributed to the presence of I\(_3^-\), as discussed above. The lack of the intense peak at \(ca.\) 170 cm\(^{-1}\) would indicate that I\(_5^-\) is not present or at least not in large amounts.

Table 4.1 Vibrational frequencies of Pd(II) and Pt(II) halide complexes (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>PdCl(_4^{2-})</th>
<th>PtCl(_4^{2-})</th>
<th>PtI(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tilde{\nu}_1)</td>
<td>303</td>
<td>330</td>
<td>155</td>
</tr>
<tr>
<td>(\tilde{\nu}_2)</td>
<td>164</td>
<td>171</td>
<td>85</td>
</tr>
<tr>
<td>(\tilde{\nu}_3)</td>
<td>150</td>
<td>147</td>
<td>105</td>
</tr>
<tr>
<td>(\tilde{\nu}_4)</td>
<td>275</td>
<td>312</td>
<td>142</td>
</tr>
<tr>
<td>(\tilde{\nu}_5)</td>
<td>321</td>
<td>313</td>
<td>180</td>
</tr>
<tr>
<td>(\tilde{\nu}_6)</td>
<td>161</td>
<td>161</td>
<td>127</td>
</tr>
</tbody>
</table>

Pd dissolved in Reline 200 is likely to form Pd/halide complexes, e.g. [PdCl\(_4^{2-}\)], [PdI\(_4^{2-}\)], or chloride/iodide mixed species. For comparison, Table 4.1 shows Raman data found in the literature for [PdCl\(_4^{2-}\)]. Bands at 150-165 cm\(^{-1}\), corresponding to [PdCl\(_4^{2-}\)] may be present in the spectrum recorded in Reline 200, under the broad absorption observed in that region (Fig. 4.1). Data on vibrational frequencies for [PdI\(_4^{2-}\)] has not been found, but it is expected that the bands would be similar to those of [PtI\(_4^{2-}\]); \(i.e.\) [PdCl\(_4^{2-}\)] and [PtCl\(_4^{2-}\)] give similar spectra (Table 4.1). Given the broadness of the bands, it is difficult to draw conclusions, but a peak around 180 cm\(^{-1}\), related to [PdI\(_4^{2-}\)], is not obviously present. As mentioned above, mixed Pd(II)-Cl/I\^- complexes could also form.

In summary, it is not possible to identify with certainty the nature of the Pd(II) complexes present, but it appears that [PdI\(_4^{2-}\)] does not form in a significant amount. Solutions of I\(_2\) (800 mM) in Reline 200 contain I\(_3^-\) and, possibly also I\(_5^-\) anions. To further clarify the species formed in the Pd/I\(_2\)/Reline 200 solutions, cyclic voltammetric studies were then carried out.
4.2.2 Cyclic Voltammetry

4.2.2.1 Electrochemical Window (ECW) of Reline 200

Figure 4.2 shows the ECW of Reline 200. At a glassy carbon working electrode and 60 °C, the ECW is 2.75 V (between -2.25 V and 0.5 V). This value is large compared to that achieved by Costa et al.\textsuperscript{151} using a hanging Hg working electrode, a glassy carbon counter electrode, and a Ag wire reference. These authors reported an ECW of \textit{ca.} 1.55 V at 60 °C, and \textit{ca.} 1.7 V at 40 °C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cv_graph}
\caption{CVs showing the ECW of Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C}
\end{figure}
In scan 1 of Figure 4.2, as the voltage moves toward negative potential, a reduction peak appears at -0.95 V which does not appear on the second scan, and has no associated oxidation peak. CVs acquired by Costa et al.\textsuperscript{151} noted an oxidation and reduction peak around 0 V which were similar to those observed in the CV of aqueous thiourea on Hg. Further work led the group to attribute the peaks to the formation of a film of urea at the Hg electrode surface. It is possible that the peak at -0.95 V has a similar origin, e.g. urea deposited on the GC electrode used herein, but it could also be related to a small amount of impurity in the solvent or the electrode surface.

Figure 4.3 CVs showing extension of Reline 200 ECW limits; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C
To further explore the ECW of Reline 200, CVs were performed with the limits extended (Fig. 4.3). The positive limit was extended to 0.75 V (black lines), and the negative limit was extended to -2.5 V (red lines). In the second scan of the -2.25 V – 0.75 V range, a small reduction peak is seen at -1.05 V, similar to that discussed above, but it is only seen after partial oxidation of the solvent. Scans were then performed with a more positive limit (Fig. 4.4). A large reduction peak appears at -1.65 V in the second scan, i.e. after significant oxidation of the solvent takes places. The most likely component of the DES to be oxidised is the Cl\(^-\) of (21), as the negative limit is related to reduction of urea (22). It would then appear that the reduction peak at -1.65 V is Cl\(_2\) being reduced to Cl\(^-\).\(^{151}\)

**Figure 4.4** CVs of Reline 200 showing reduction peak of Cl\(_2\) to Cl\(^-\); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\(^+\) (0.1 M AgNO\(_3\) in [BMIM]NO\(_3\)), Scan rate = 50 mV s\(^{-1}\), Temperature = 60 °C
4.2.2.2 Pd(0)

In Reline 200, Pd was dissolved to a concentration of 50 mM, using I\textsubscript{2} (200 mM). CVs were then performed with a working electrode of glassy carbon, a Pt wire counter electrode, and a Ag/Ag\textsuperscript{+} reference consisting. The CVs, shown in Figure 4.5, were carried out at 60 °C with potential limits between -2.0 V and 1.25 V.

**Figure 4.5** CVs of I\textsubscript{2} (200 mM) and Pd (50 mM) in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C

In the first scan (toward negative potential) there are four reduction peaks at -0.40 V (I), -0.84 V (II), -1.35 (III) and -1.57 V (IV). In the return scan there are two oxidation peaks.
at -0.12 V (V) and 0.24 V (VI). In the second (consecutive) scan, the reduction peaks are more intense, with a new peak (or shoulder) at -0.32 V (VII). On return, the first oxidation peak (V) remains unchanged at -0.12 V, whereas VI is slightly shifted. A new small oxidation wave is observed at 0.09 V (peak VIII). In order to assign the peaks, the scans in Figure 4.5 were compared to those of I₂, PdI₂, PdCl₂, and K₂[PdCl₄] dissolved in Reline 200.

4.2.2.3 I₂

I₂ was dissolved in Reline 200 to a concentration of 200 mM. CVs were recorded on GC, at 60 °C with potential limits between -3.0 V and 1.25 V and are shown in Figure 4.6.

Figure 4.6 CVs of I₂ (200 mM) in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C
In the first scan, a reduction peak is present at -0.57 V (peak I). In the reverse scan there is a broad oxidation wave, where three oxidation peaks can be distinguished at 0.29 (peak VI), 0.66 (peak IX), and 0.95 V (peak X). In the second scan a reduction peak then appears at -0.27 V (peak VII) followed by a second at -0.53 V. The oxidation peaks still appear at 0.29, 0.66, and 0.97 V.

Abbott et al.\textsuperscript{122,123} investigated the I\textsubscript{2}/I\textsuperscript{−} system as an electrocatalyst in Ethaline 200 (1 eq. (21):2 eq. (23)), and observed two reduction and two oxidation peaks in the CV, using a Pt disc working electrode, a Pt foil counter electrode, and Ag/Ag\textsuperscript{+} reference. They suggested the formation of a trihalide species, e.g. I\textsubscript{3}− or I\textsubscript{2}Cl\textsuperscript{−}, in the diffusion layer after I\textsubscript{2} reduction (eqs 4.1-4.3). The oxidation processes are correspondingly assigned to eqs. 4.4-4.6. The I/I\textsubscript{2}/I\textsubscript{3}− redox system has also been studied in traditional ILs. For example, using a Pt macrodisk working electrode Bentley et al.\textsuperscript{181,182} studied the system in various imidazolium ILs, a pyrrolidinium IL, and two ammonium ILs. The reduction/oxidation of I\textsubscript{2} in the ILs also occurred in two steps, via a I\textsubscript{3}− intermediate, i.e. an initial two electron reduction reaction of I\textsubscript{2} to I\textsubscript{3}− followed by formation of I\textsuperscript{−}, as shown in equation 4.3.

\[
\begin{align*}
I_2 + 2e^- &\rightarrow 2I^- \\
I_2 + I^- &\rightarrow I_3^- \\
I_3^- + 2e^- &\rightarrow 3I^- \\
3I^- &\rightarrow I_3^- + 2e^- \\
I_3^- &\rightarrow I_2 + I^- \\
2I^- &\rightarrow I_2 + 2e^- 
\end{align*}
\]  

(eq. 4.1)  
(eq. 4.2)  
(eq. 4.3)  
(eq. 4.4)  
(eq. 4.5)  
(eq. 4.6)

According to the literature data above, peak I in Figure 4.6 would be the reduction of I\textsubscript{3}− to I\textsuperscript{−} (eq. 4.3). The reverse process would correspond to peak VI (eq. 4.4, followed by 4.5). Peak IX or X can be then be attributed to the oxidation of I\textsuperscript{−} to I\textsubscript{2}, i.e. equation 4.6, with the reverse (eqs. 4.1 and 4.2) occurring at peak VII. The additional oxidation peak that appears in the scans could be related to the formation of other trihalides, for example, to the oxidation reaction 2I\textsuperscript{−} + Cl\textsuperscript{−} $\rightarrow$ I\textsubscript{2}Cl\textsuperscript{−} + 2e\textsuperscript{−} (i.e. similar to equation 4.4). The fact that
the first scan shows mainly only one broad reduction peak (I) indicates that the main species present at that stage is I$_3^-$ with I$_2$ forming during the oxidation scan. This is in agreement with the Raman data discussed above, and which showed that I$_3^-$ appeared to be one of the main species present in the solution of I$_2$ in Reline 200.

Figure 4.7 CVs of I$_2$ (800 mM) in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

The CVs of I$_2$ in Reline 200 at a higher concentration (800 mM, Fig. 4.7) are slightly different, i.e. there is a shift in the peaks. The first scan of Figure 4.7 shows the two reduction peaks at -0.25 and -0.80 V. When the scan direction is reversed, two oxidation peaks are observed at 0.80 and 1.36 V. In the second scan, the two reduction peaks appear
slightly shifted to -0.42 and -0.90 V, and they are more intense, whereas the oxidation peaks remain similar. A similar effect has been observed in ionic liquids, where the potential gap between the two redox processes becomes larger with concentration.\textsuperscript{181} Formation of different polyiodides at higher concentrations is also possible.

It was observed that the ECW of Reline 200 (-2.25 – 0.5 V) increased by 1.5 V when I\textsubscript{2} was added at a concentration of 200 mM (-3.0 – 1.25 V) and by 2.0 V when the concentration was 800 mM (-3.25 – 1.5 V). As discussed in \textit{1.6.6.1}, the Grotthuss mechanism has been used to explain the high conductivity of polyiodide species, specifically by Jerman \textit{et al.}\textsuperscript{96} and Thorsmolle \textit{et al.}\textsuperscript{95} The Grotthuss mechanism states that in order for conduction to occur, there must be a continuous path of mobile carriers which exist within the system. Therefore a bond-exchange reaction is proposed, similar to that used to explain the high mobility of protons in H\textsubscript{2}O.\textsuperscript{94–96} For Jerman \textit{et al.}\textsuperscript{96} the increase in conductivity suggested the presence of ‘bridges’ or ‘chains’ that aid the conduction process. Thorsmolle \textit{et al.}\textsuperscript{95} proposed that an enhanced Grotthuss mechanism resulted from an increase in the iodine/iodide packing density. This then reduces the distance between the iodide and polyiodide species involved in bond exchange. Fei \textit{et al.}\textsuperscript{94} investigated the effect of I\textsubscript{2} on imidazolium based ionic liquids and believed channel inclusion features (cations in ‘channels’ encased by polyiodides) formed.

It may be that the increased packing density/formation of channel inclusion features, or both, cause the ECW to increase through closer proximity of the polyiodides leading to an increase in interactions. If (22) or Cl\textsuperscript{-} were included as either a part of these structures or within the channel then, by making it harder to reduce/oxidise them, their stability may have been enhanced leading to the enlarged ECW. An added factor would be the growth in polyiodide size aiding the non-coordinating nature of the anion and allowing delocalisation of the charge over a larger area.

\textbf{4.2.2.4 PdI\textsubscript{2}}

The CVs of PdI\textsubscript{2} (50 mM) in Reline 200 are shown in Figure 4.8. Scan 1 has reduction peaks at -0.88 V (peak II), -1.32 (peak III), and -1.54 V (peak IV). In the reverse scan, two oxidation peaks appear at -0.03 V (peak V) and 0.35 V (peak VI). In the second
consecutive scan new reduction waves appear at -0.31 V (peak VII) and -0.74 V (peak I), with the rest of the peaks remaining approximately the same. By comparison with the CVs of \( \text{I}_2 \) in Reline 200 discussed above, peak VI can be assigned to the oxidation of \( \Gamma^- \) to \( \text{I}_3^- \) followed by formation of \( \text{I}_2 \) (eqs. 4.4 and 4.5), with peak VII being the reduction of \( \text{I}_2 \) to \( \Gamma^- \) (eq 4.1). The presence of \( \Gamma^- \) in the solution would occur upon reduction of \( \text{PdI}_2 \) to \( \text{Pd(0)} \) which frees \( \Gamma^- \). Some may also be released if ligand substitution occurs on \( \text{Pd(II)} \), leading to the loss of some \( \Gamma^- \) ligands and their replacement, most likely by \( \text{Cl}^- \) from (21).

**Figure 4.8** CVs of \( \text{PdI}_2 \) (50 mM) in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = \( \text{Ag}/\text{Ag}^+ \) (0.1 M \( \text{AgNO}_3 \) in \( \text{[BMIM]NO}_3 \)), Scan rate = 50 mV s\(^{-1} \), Temperature = 60 °C
Electrochemical data on Pd(II) iodide salts in the literature is not available, but the chloride and bromide analogues have been studied in DES and ILs. For example, Bando et al.\textsuperscript{113} dissolved PdBr\textsubscript{2} or PdCl\textsubscript{2} in [BMPyr]NTf\textsubscript{2} with added [BMPyr]X (X = Br or Cl) to form [PdX\textsubscript{4}]\textsuperscript{2-} anions. Using a Pt disc as the working electrode, the CVs of PdBr\textsubscript{2} showed a single reduction peak at -1.6 V and was assigned to the Pd(II)/Pd reduction of [PdBr\textsubscript{4}]\textsuperscript{2-} while anodic stripping of deposited Pd was observed at -0.4 V. For PdCl\textsubscript{2}, the CV had the reduction peak at -1.8 V. This more negative potential was attributed to the higher stability of the chloro-complex. Lanzinger et al.\textsuperscript{114} dissolved PdCl\textsubscript{2} in Reline 200 showing that it formed yellow solutions containing Pd(II)-chloride complexes of general formula [PdCl\textsubscript{4-x}]\textsuperscript{2-x}. It is assumed that PdI\textsubscript{2} dissolved in Reline 200 herein would form similar species incorporating Cl\textsuperscript{-} ligands from (21). Lanzinger et al. performed cyclic voltammetry of the PdCl\textsubscript{2}/Reline 200 solutions over glassy carbon, with scan rates of 25 and 150 mV s\textsuperscript{-1} and temperatures of 50, 75, and 100 °C. The CVs obtained showed one reduction peak, \textit{i.e.} Pd(II) to Pd(0), and an oxidative peak, associated with the stripping of bulk electrodeposits. Similarly, peaks II (-0.88 V) and V (0.03 V) in Figure 4.8 can be assigned to the reduction of Pd(II) to Pd(0) (eq. 4.7) and the stripping of the deposited Pd (eq. 4.8) respectively.

\[
\text{[PdX}_4\text{]}\textsuperscript{2-} + 2e^- \rightarrow \text{Pd} + 4X^- \quad \text{(eq. 4.7)}
\]

\[
\text{Pd} + 4X^- \rightarrow \text{[PdX}_4\text{]}\textsuperscript{2-} + 2e^- \quad \text{(eq. 4.8)}
\]

where X = Cl or I

Peaks III and IV are more difficult to assign as most literature data only shows one reduction peak for Pd(II). In some cases, however, other peaks have been observed. For example, Zhang et al.\textsuperscript{117} studied the electrodeposition of Pt nanoparticles in the IL N, N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate ([DEME]BF\textsubscript{4}), starting from either K\textsubscript{2}[PtCl\textsubscript{4}] or K\textsubscript{2}[PtCl\textsubscript{6}]. In the CVs over a GC working electrode, the reduction of [PtCl\textsubscript{4}]\textsuperscript{2-} to Pt(0) gave two peaks. The second process was attributed to the reduction of Pt(II) over Pt formed on the GC electrode surface during the first scan. An
alternative explanation is that of Jayakumar et al.,\textsuperscript{111} who studied the CV of PdCl\textsubscript{2} in [BMIM]Cl over GC. In this case, a reduction peak was observed at -0.61 V and, if the negative potential limit was extended, a second reduction peak could be observed at \textit{ca.} -1.13 V. Two oxidation waves were also present at -0.26 V and 0.31 V. The authors proposed that Pd(II) speciated into various stable Pd/chloro-complexes with the associated reduction peaks dependent on their stabilities and relative concentrations. They associated the first reduction peak to the reduction of [PdCl\textsubscript{4}]\textsuperscript{2-} to Pd(0) (eq 4.7), whereas the second would be the result of chloro-complexes that were more stable than [PdCl\textsubscript{4}]\textsuperscript{2-}, although the authors gave no examples.

Although the above two examples use different metal salts to PdI\textsubscript{2}, analogous assignments could be done for peaks III and IV. Deposition of Pd onto Pd may occur, but the additional reduction peaks can also be related to various chloro/iodo complexes which may exist in the PdI\textsubscript{2}/DES solution (\textit{e.g.} [PdClI\textsubscript{3}]\textsuperscript{2-}, [PdCl\textsubscript{2}I\textsubscript{2}]\textsuperscript{2-}, etc.). The fact that there is only one stripping peak (peak V) supports the latter explanation. If reduction of Pd(II) occurred over Pd deposited at the GC electrode, two stripping peaks would also be expected. From the above it then appears that dissolved PdI\textsubscript{2} in Reline 200 forms several mixed-halide anionic species that yield several reduction peaks in the CV.

\textit{4.2.2.5 PdCl\textsubscript{2} and K\textsubscript{2}[PdCl\textsubscript{4}]}

In order to confirm if the origin of any of the peaks observed in the PdI\textsubscript{2}/Reline 200 mixtures relates to the formation of Pd-chloride species, the cyclic voltammetry of PdCl\textsubscript{2} (50 mM) dissolved in Reline 200, was studied (Fig. 4.9). The first scan sweeping toward negative potential, shows a reduction peak at -0.96 V (peak II) followed by a smaller wave at -1.19 V (peak III). In the reverse scan, a small peak arises at -0.68 V (peak XI) with a much larger peak at 0.14 V (peak VIII). The second scan does not show significant differences with the first one. Lanzinger \textit{et al.}\textsuperscript{114} obtained an orange-red solution when PdCl\textsubscript{2} was dissolved in Ethaline 200, indicative of the formation of [PdCl\textsubscript{4}]\textsuperscript{2-}. In Reline 200, however, the authors observed a yellow colour which was attributed to the formation of other Pd(II) species, \textit{i.e.} [PdCl\textsubscript{4-x}]\textsuperscript{2-x}. In our case, orange-red solutions of PdCl\textsubscript{2}/Reline 200 where obtained, which indicates that [PdCl\textsubscript{4}]\textsuperscript{2-} is the dominant complex. The
difference with the literature is attributed to the larger concentration of PdCl$_2$ used herein (i.e. 50.0 mM, compared to ca. 17.0 mM used by Lanzinger et al.).

Figure 4.9 CVs of PdCl$_2$ (50 mM) in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

CVs of K$_2$[PdCl$_4$] (50 mM) in Reline 200 were also performed (Fig. 4.10) to further confirm that PdCl$_2$ formed [PdCl$_4$]$^{2-}$ when dissolved in the DES. As can be seen in Figure 4.10, the scans for [PdCl$_4$]$^{2-}$ are practically identical to those of PdCl$_2$, confirming that in Reline 200, PdCl$_2$ forms mainly [PdCl$_4$]$^{2-}$ at the concentrations used herein. Scans 1 and 2 for the latter, have reduction peaks at -0.93 and -1.20 V (peaks II and III respectively) with oxidation peaks at -0.67 and 0.11 V (peaks XI and VIII respectively). The main
peaks, II and VIII, are therefore attributed to the redox couple [PdCl₄]²⁻/Pd(0), i.e. eqs. 4.7-4.8, where X = Cl.

Unlike in the work of Lanzinger et al.,¹¹⁴ who described only one reduction and one oxidation peaks for PdCl₂/Reline 200, results herein show an additional, small, reduction (ca. -1.20 V) and oxidation peaks (ca. -0.67 V). As discussed earlier, the second reduction peak could be related to the deposition of Pd onto Pd, e.g. similarly to the deposition of Pt

**Figure 4.10** CVs of PdCl₂ and K₂[PdCl₄] in Reline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C
in ILs, as described by Zhang et al.,\textsuperscript{117} or to the existence of more stable chloro-complexes as explained by Jayakumar et al.\textsuperscript{111} Lanzinger et al.\textsuperscript{114} also observed two oxidation peaks of PdCl$_2$ in Ethaline 200, and assigned them to the stripping of bulk (-0.39 V) and surface (0.03 V, on the electrode) Pd electrodeposits. A similar assignment could be made herein, for the Reline 200 solutions.

4.2.2.6 Assigning the peaks of Pd(0) dissolved in Reline 200

In summary, the peaks observed in the CV of the Pd/I$_2$/Reline mixture are common with those found in the CV of PdI$_2$ in Reline with the exclusion of peak I. As mentioned before, the CVs of PdCl$_2$ and K$_2$[PdCl$_4$] in Reline 200 are the same confirming, as expected, that PdCl$_2$ forms mainly [PdCl$_4$]$^{2-}$, however none of the peaks related to [PdCl$_4$]$^{2-}$ are dominant in the Pd/I$_2$/Reline mixture CVs (Fig. 4.5). These peaks may however be hidden under the more intense, broader peaks observed in the CV of the Pd/I$_2$/Reline solution (for example, peak VIII in Figs. 4.5 and 4.10), but it shows that [PdCl$_4$]$^{2-}$ is not the main species formed in this system and is only seen in a relatively small proportion.

A final proposal for the origin of the peaks in Figure 4.5 can be made as follows. Starting with the first scan, peak I is due to the reduction of I$_3^-$ to 3I$^-$ (eq. 4.3). This is then followed by the reduction of Pd(II), mainly as an iodo- or a chloro/iodo-complex, to Pd(0) (peak II) as shown in equation 4.7. The other reduction waves observed in the region between -0.90 and -2 V may be related to formation of a film of (21) (ca. -1.05 V), to the reduction of Pd(II) over Pd, or to the reduction of more stable tetrahalide complexes of Pd(II). The oxidation peak V is assigned to the anodic stripping of Pd from the electrode (eq. 4.8), and peak VI to the oxidation of I$^-$ to I$_2$ (eq. 4.6). In the second scan a new reduction peak, VII, appears, corresponding to the reduction of I$_2$ (i.e. the reverse of VI, equation 4.1). A new oxidation peak, VIII, is also present and believed to be the anodic stripping of Pd (Fig. 4.9) to form chloro-complexes, e.g. equation 4.8 (X = Cl). It is unclear why this is only observed as a separate process on the second scan.
4.2.3 Electrodeposition

After successfully dissolving Pd in the presence of I\textsubscript{2} in Reline 200 to form a 50 mM solution (Fig. 4.5). Electrodeposition was carried out using glassy carbon as both working and counter electrodes with a Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}) reference. The reason for using glassy carbon as the counter electrode instead of Pt (as in the CVs above), was to prevent Pt from dissolving under the conditions employed. The temperature used throughout was 60 °C.

![Figure 4.11](image.png)

**Figure 4.11** Collected deposits following electrodeposition from Pd/I\textsubscript{2}/Reline 200 mixtures

As mentioned, Figure 4.5 shows the CVs for dissolved Pd (50 mM) in Reline 200 using I\textsubscript{2} (200 mM). Following the CV scans, the equipment was set up to hold a potential of -1.9 V for a total of 216 hours which was split into 18 hour periods. After every 18 hours the working electrode was removed and rinsed with deionised H\textsubscript{2}O to remove Pd deposits (Fig. 4.11). These deposits were either a black powder or a smooth bright silvery coating (mainly towards the latter part of the experiment). When no Pd was observed on the electrode, the electrodeposition process was ceased. Bando *et al.*\textsuperscript{113} have noted that the appearance of the deposit obtained during the electrodeposition of Pd from [BMPyr]NTf\textsubscript{2} using some [BMPyr]X (X = Br or Cl), depended on the current density experienced (black and powdery at higher densities, smooth and bright silver at lower densities). The H\textsubscript{2}O used to rinse the electrode was removed after the deposit had settled, typically after being
left overnight. The deposits were then rinsed thoroughly with acetone and then dried at 110 °C for 15 minutes. After this, SEM (Fig 4.12) and EDX spectroscopy (Fig. 4.13) were carried out.

![SEM image](image)

**Figure 4.12** SEM of deposited material at a magnification of x2075

The SEM image shows the deposit (Fig. 4.12) to consist of fragmented metal strands/sheets and small granular clusters. This suggests there are possibly two deposition mechanisms occurring. The strands/sheets are possibly caused by dendritic formation, as discussed below. Jayakumar et al. examined PdCl₂ in [BMIM]Cl and while investigating the electrodeposition of Pd, at 100 °C for 2 hours, the SEM images showed deposition of both the inner (on the surface of the working electrode) and outer layers (on the inner layer) to occur via dendrite formation after initial nucleation, with expansion in all directions with time. It was found that at higher negative applied potentials, dendrite growth increased and typically aggregated as large lumps leading to dense deposits. The SEM images of the outer Pd layer also showed a granular like deposit, the result of dendritic formation.
Lanzinger et al.\textsuperscript{114} carried out electrodeposition of Pd from Reline 200 at 70 °C, which led to deposits that were semi-bright grey (0.01 mA cm\textsuperscript{-2}) to dull dark grey (0.1 mA cm\textsuperscript{-2}) depending on the current density employed. It was found that current density used and electrolyte composition both affected the morphology of the deposit. In particular, from Reline 200 the deposit was a coarse grain, nodular, and less compact, before becoming fine grained and compact. Mehner et al.\textsuperscript{115} examined hydrogen embrittlement of deposited Pd from Reline 200 and an aqueous electrolyte. In Reline 200, large ‘droplets’ of ca. 500 nm formed via deposition. Unlike the deposit from the aqueous electrolyte, that obtained from the DES showed no significant cracking and brittleness indicating no H\textsubscript{2} incorporation.

![Map Sum Spectrum](image)

**Figure 4.13** EDX data showing elemental composition of the deposit obtained following electrodeposition from the Pd/I\textsubscript{2}/Reline 200 mixture.

EDX results (Figure 4.13) show other elements present in the deposit alongside Pd. It is believed these originate from residual Reline/I\textsubscript{2} which has not been sufficiently removed.
in the cleaning process. The presence of O at a high Wt% may indicate formation of PdO but can also originate from the C tape.\textsuperscript{183} C is not shown as it was chosen to be ignored due to the use of C tape for securing the sample.

![CVs of the Pd/I\textsubscript{2}/Reline 200 mixture after electrodeposition at -1.9 V (216 h); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C](image)

\textbf{Figure 4.14} CVs of the Pd/I\textsubscript{2}/Reline 200 mixture after electrodeposition at -1.9 V (216 h); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C

After carrying out electrodeposition of Pd as described above, the CVs were performed of the remaining solution (Fig. 4.14). These show a shortening of the ECW, which could be due to H\textsubscript{2}O being absorbed during the deposition process, as this was carried out in a cell open to the atmosphere. This absorbed H\textsubscript{2}O, which undergoes electrolysis, disrupts the homogenous nature of the DES creating polar and non-polar regions thus shortening the ECW.\textsuperscript{184,185} The CVs show broad reduction and oxidation peaks as \textit{ca.} -0.7 V (peak I)
and 0.5 V (peak VI), respectively. If the potential limits are increased in either direction no other peaks appear and the solvent undergoes either reduction (already occurring in Fig. 4.14 ca. -1.7 V) or oxidation. The observed peaks are assigned to the reduction of $I_3^-$ to $I^-$ (-0.57 V, peak I, Fig. 4.6, eq. 4.3) and the corresponding oxidation from $I^-$ to $I_3^-$ (eq. 4.4). These are slightly shifted from those discussed in 4.2.2.2 and 4.2.2.3. Importantly, no peaks can be seen related to the presence of Pd(II), *i.e.* peaks II-V, Fig. 4.6.

![Graph](image-url)

**Figure 4.15** CVs of the solution resulting from dissolving Pd metal in a recycled Reline/I$_2$ solution; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

The remaining Reline/I$_2$ solution was then re-used for the dissolution of more Pd (50 mM, Fig. 4.15). As in previous experiments, the metal took 24 hours to dissolve at 60 °C. The
CVs of the resulting solution show new peaks that can be related to the presence of Pd(II). In particular, compared with the CVs of PdI$_2$ and PdCl$_2$ (see sections 4.2.2.3 and 4.2.2.4) the reduction peak at ca. -0.95 V (peak II) can be related to the presence of Pd(II)-halide complexes. Anodic stripping of the reduced Pd, possibly into iodo-complexes (eq. 4.8, Fig. 4.8), is related to peak V at -0.01 V, whereas stripping of Pd through the formation of chloro-complexes (eq. 4.8, Fig. 4.9) results in peak VIII (0.14 V). On completion of the CVs the sample was set up to perform electrodeposition for a second time. The electrodes used were the same as in the first attempt, e.g. glassy carbon working and counter electrodes and Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$) reference. This second attempt was carried out for a total time of 306 hours (i.e. until no Pd was observed to deposit). Again this was separated into 18 hour periods and the potential was held at -1.9 V. Every 18 hours the working electrode was rinsed with deionised H$_2$O and the deposit collected.

Figure 4.16  SEM of second deposited material from the Pd/I$_2$/Reline 200 mixture at a magnification of x2075
The deposit was initially a black powder but would eventually become a smooth silver coat, which can be related to higher or lower current densities respectively. Again, after the Pd deposit had settled, the H₂O used was removed before rinsing thoroughly with acetone and drying for 15 minutes at 110 °C. SEM (Fig. 4.16) and EDX (Fig. 4.17) spectroscopy were then carried out on the deposit. Figure 4.16 shows a similar deposit to that in Figure 4.12, i.e. both fragmented sheets and clusters. The EDX data in Figure 4.17 shows the same elements as that of the first sample but now includes N (possibly from residual Reline/I₂), and the Wt% of Pd is higher compared to the other elements present.

![Image](image_url)

**Figure 4.17** EDX data showing elemental composition of the second deposit obtained from the Pd/I₂/Reline 200 mixture.

The CVs of the remaining solution after depositing Pd for the second time were carried out (Fig. 4.18). The first scan contains a reduction peak at -0.57 V together with a small second peak at -1.42 V. When the scan changes direction, oxidation peaks appear at -0.05 V and 0.56 V. On the second scan the first peak shifts slightly to -0.64 V while the other
three remain unchanged. No other peaks were observed upon increasing the potential limits. The reduction and oxidation peaks at \textit{ca.} -0.60 V and 0.56 V respectively, are related to I\textsubscript{2}, whereas the peaks at -1.42 and -0.05 V indicate that some Pd still remains in the system. It should be noted that every time the electrodes are removed from the electrochemical cell some of the solution is lost.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cv_example.png}
\caption{CVs of Reline/I\textsubscript{2} solution after second electrodeposition; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C}
\end{figure}

By the time the CVs of Figure 4.18 were carried out there was very little remaining. Despite this it was decided to try and re-use it for dissolving Pd again. Initially 2.7 mg of metal were added and these dissolved within 24 hours. A second addition of 3.7 mg also
dissolved within 24 hours, but when a further 5.7 mg were added there was no noticeable dissolution. As there was very little of the solvent remaining it was impossible to get good CVs and although attempts were made those produced consisted of noise and showed no discernible peaks.

Even though no CVs were obtained for the second re-cycling of the system, Pd did dissolve and shows that not only can Reline/I2 dissolve Pd in the first instance, but it is possible to recycle the solution at least twice. During the two electrodeposition experiments carried out, the amount of Pd recovered was estimated to be ca. 50 %, but the amounts used were small and loses throughout the experiment were relatively high, i.e. every time the working electrode was removed from the system or through the cleaning process.

4.3 Ethaline 200

The dissolution of Pd in Ethaline 200 was also investigated. Raman spectroscopy and cyclic voltammetry were used to characterise the Ethaline 200 solutions of I2 and Pd(II).

4.3.1 Raman Spectroscopy

On addition of I2 to Ethaline 200, the Raman spectrum in the region below 200 cm\(^{-1}\) shows two peaks at 112 cm\(^{-1}\) and 166 cm\(^{-1}\) (Fig. 4.19). As in the case of the I2 solution in Reline 200, discussed in section 4.2.1, the peaks at 112 and 166 cm\(^{-1}\) are related to the I\(_3^-\) and I\(_5^-\) anions respectively.\(^{96}\) The small peak at 268 cm\(^{-1}\) may relate to ICl\(_2^{-}\).\(^{180}\) Dissolving Pd (300 mM) in the I2/Ethaline mixture does not lead to much difference in the Raman spectrum below 200 cm\(^{-1}\), but the small peak at 268 cm\(^{-1}\) disappears.
4.3.2 Cyclic Voltammetry

4.3.2.1 Electrochemical Window (ECW) of Ethaline 200

The ECW of Ethaline 200 is shown in Figure 4.20. The limits are shown to be -1.8 V and 0.5 V, corresponding to an ECW of 2.3 V, when using a glassy carbon working electrode, Pt wire counter, and a Ag/Ag⁺ reference of 0.1 M AgNO₃ in [BMIM]NO₃ at 60 °C. At the same temperature, Costa et al.¹⁵¹ determined an ECW of 1.8 V using a hanging Hg working electrode, a glassy carbon counter electrode, and a Ag wire reference. When the temperature was lowered to 40 °C the ECW extended slightly to 1.9 V. As in the case of Reline 200, a larger ECW is obtained for Ethaline 200 at the conditions we used.
1 and 2 show small reduction waves at -0.86 and -1.38 V with oxidation peaks at -1.13 and -0.09 V. It could be that these are due to small amounts of impurities or that they relate to (23) in Ethaline and are similar to the peaks attributed to the thiourea film reported by Costa et al.\textsuperscript{151}

![Figure 4.20](image)

**Figure 4.20** CVs showing the ECW of Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C

As with Reline 200, the potential limits of the ECW for Ethaline 200 were expanded. Extending the negative potential to either -2.0 or -2.25 V leads to the solvent being reduced (Fig. 4.21), and if the positive limit is extended to 0.75 V then the solvent is oxidised.
This is indicated by the sharp rise of the black scans which precedes a broad reduction peak at 0.37 V also observed by Costa et al.\textsuperscript{151} at ca. 0.1 V. It is unknown what this relates to. Alongside the peaks still present at -0.86 and -1.38 V, another reduction peak appears at -0.25 V. New oxidation peaks are also present in scans 1 and 2 at -0.2 and 0.4 V. The second of these peaks is present when the negative limit is -2.0 V but neither appear in Figure 4.20. These peaks are therefore related to the reduction of the solvent.

\textbf{Figure 4.21} CVs showing extension of the ECW limits for Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\textsuperscript{+} (0.1 M AgNO\textsubscript{3} in [BMIM]NO\textsubscript{3}), Scan rate = 50 mV s\textsuperscript{-1}, Temperature = 60 °C
4.3.2.2 \textit{Pd(0)}

Using I$_2$ (200 mM), Pd was dissolved in Ethaline 200 to a concentration of 50 mM and the CVs of the resulting solution were performed at 60 °C within potential limits of -2.0 V and 1.25 V (Figure 4.22). Glassy carbon was used as the working electrode, Pt wire as the counter, and a Ag/Ag$^+$ reference of 0.1 M AgNO$_3$ in [BMIM]NO$_3$.

![CVs of I$_2$ (200 mM) and Pd (50 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C](image)

**Figure 4.22** CVs of I$_2$ (200 mM) and Pd (50 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

The voltammetries obtained are similar to those in Reline 200, discussed above. As the first scan is recorded toward negative potential, reduction peaks are present at -0.62 V.
(peak I), -0.86 V (peak II), -1.57 V (peak III) and -1.88 V (peak IV). After the scan changes direction the first oxidation peak appears at -0.12 V (peak V) with another three at 0.48, 0.69, and 0.94 V (peaks VI, IX, and X respectively). Once the second scan begins a new reduction peak appears at -0.35 V (peak VII). The rest of the peaks are similar to those in the first scan, with peaks I-III increasing in intensity. For comparison, I₂, PdI₂, PdCl₂, and K₂[PdCl₄] were dissolved in Ethaline 200 and their CVs recorded. As with Reline 200, it is believed that tetrahalide species are dominant, in particular iodo-complexes.

4.3.2.3 Addition of I₂

I₂ was dissolved in Ethaline 200 to a concentration of 200 mM. CVs were carried out at 60 °C using a glassy carbon working electrode, Pt wire counter, and Ag/Ag⁺ reference electrode of 0.1 M AgNO₃ in [BMIM]NO₃. The potential limits were set as -2.25 V and 1.25 V (Figure 4.23). The CVs in Ethaline 200 are similar to those obtained in Reline 200. For example, in the first scan in Figure 4.23, reduction peaks are present at -0.38 V (peak VII) and -0.59 V (peak I), with three oxidation peaks at 0.48 V (peak VI), 0.67 V (peak IX), and 0.92 V (peak X). These peaks remain mostly unchanged on the second scan.

Due to the similarities between the CVs of I₂ in Reline and Ethaline the processes are assigned in a similar manner. Thus, peak VII would relate to equations 4.1 and 4.2 for the two step reduction of I₂ to I⁻. After this I⁻ is reduced to 3I⁻ (eq. 4.3, peak I). Although with some overlapping, three oxidation waves can also be seen in the reverse scans which would correspond to iodide oxidations to form 3I⁻ or I₂ (eqs. 4.4-4.6) as well as other trihalides (e.g. I₂Cl⁻). Overlapping in the oxidation processes was also noted by Abbott et al.¹²² in the cyclic voltammogram of a 100 mM I₂/Ethaline 200 solution. As with Reline, the ECW of Ethaline increased when I₂ was added. The blank DES possessed an ECW of 2.3 V (-1.8 – 0.5 V) which increases to 6.0 V (-3.5 – 2.5 V) with an I₂ concentration of 1.2 M. When the I₂ concentration was 200 mM the ECW increased to 3.25 V (-2.25 – 1 V). The reason for the increase in the ECW may again be a result of the increased packing density or formation of channel inclusion features as discussed in 4.2.2.3.⁹⁴–⁹⁶
Figure 4.23 CVs of I$_2$ (200 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

Figure 4.24 shows the CVs of Ethaline 200 with I$_2$ dissolved at a concentration of 1.2 M. In scan 1, as the potential is swept towards negative values, two reduction peaks are present at -0.34 and -1.08 V. As the scan changes direction an ill-shaped, large oxidation peak is observed at 1.62 V, possibly overlapping with the potential limit of the solvent. In the second scan, two reduction peaks are present at -0.59 and -1.13 V and are more intense than in the first scan. As with scan 1 there is a single, large oxidation peak in the second scan. A larger potential gap between the oxidation a reduction processes with increased concentration was also observed in Reline 200, as discussed earlier.
Figure 4.24 CVs of I$_2$ (1.2 M) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C

4.3.2.4 PdI$_2$

The CVs of PdI$_2$ (50 mM) in Ethaline are shown in Figure 4.25. The first and second reduction peaks appear at -0.73 V (peak I) and -0.90 V (peak II), with a third reduction peak at -1.37 V (peak III). After the scan changes direction, oxidation peaks appear at -0.07 V (peak V) and 0.45 V (peak VI). When the second scan begins a new reduction peak is observed at -0.41 V, believed to be peak VII. The next three peaks appear at -0.76 V (peak I), -0.92 V (peak II), and -1.42 V (peak III). There seems to be another reduction peak at -1.84 V (peak IV). On the second half of the scan, the two oxidation peaks are observed at -0.04 and 0.45 V (peaks V and VI respectively). It must be noted that
additional peaks (e.g. VIII and IX) did not appear on extension of the positive potential limit to 1.25 V.

![Graph showing CVs of PdI₂ (50 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C]

**Figure 4.25** CVs of PdI₂ (50 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C

Overall, the CVs of PdI₂ in Ethaline 200 are analogous to those in Reline 200 (see Fig. 4.8) and the same assignments are therefore suggested. Thus, peaks I, VI and VII are related to the I₂/I⁻/I₃⁻ system, whereas II and V involve reduction of Pd(II) to Pd(0) and anodic stripping of the metal. Peaks III and IV are again thought to relate to the reduction of other, more stable, chloro/iodo complexes and/or the reduction of Pd(II) onto Pd.
4.3.2.5 \textit{PdCl}_2 and \textit{K}_2[\textit{PdCl}_4]

Figure 4.26 shows the CVs of PdCl$_2$ (50 mM) dissolved in Ethaline. In the first scan a reduction peak is present at -0.99 V (peak II) and as the scan direction changes, a nucleation loop appears \textit{ca.} -0.81 V, followed by a small oxidation peak at -0.5 V (peak XI). Another two peaks are present at -0.1 V (peak V) and 0.03 V (peak XII). There is again only one reduction peak on scan 2 at -0.96 V (peak II) and the nucleation loop appears again around -0.7 V. The small oxidation peak is at -0.5 V with the next two at -0.11 V (peak V) and 0.04 V (peak VII). All three oxidation peaks are more intense in the second scan than in the first. However, in the first scan peak V is more intense than peak XII but in scan 2 this is reversed.

\textbf{Figure 4.26} CVs PdCl$_2$ (50 mM) in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C
K$_2$[PdCl$_4$] was also dissolved in Ethaline 200 and CVs carried out (Fig. 4.27). Scan 1 has a reduction peak at -1.01 V with oxidation peaks at -0.51, -0.13, and 0.06 V. In the second scan the reduction peak is at -0.94 V and the oxidation peaks at -0.49, -0.07, and 0.09 V. These are similar to those of PdCl$_2$ (Fig. 4.27), showing that [PdCl$_4$]$^-$ forms in the PdCl$_2$/Ethaline solutions. These results are slightly different to those obtained in Reline 200 (for example Fig. 4.10).

**Figure 4.27** CVs of PdCl$_2$ and K$_2$[PdCl$_4$] in Ethaline 200; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Temperature = 60 °C
As reported by Lanzinger et al.\textsuperscript{114} an orange-red colour was noted when \(\text{PdCl}_2\) was dissolved in Ethaline 200, also indicative of the formation of \([\text{PdCl}_4]^{2-}\). The authors also reported one reduction and two oxidation peaks for \(\text{PdCl}_2\) in Ethaline 200. The latter were assigned to the stripping of bulk and surface Pd electrodeposits. Similar assignments can be made in our case, although two large oxidation peaks (V and XII) appear in addition to XI. It is suggested that V and XII may correspond to oxidation of Pd(0) to different halide complexes. In particular, peak V appears at the same potential as that in Figure 4.25 for \(\text{PdI}_2/\text{Ethaline}\) solutions and it may therefore be related to formation of a Pd(II) iodide (or iodide/chloride) complex. In addition, Lanzinger et al. reported the presence of a nucleation loop, which is also seen in Figs. 4.26-4.27. This loop indicates that for electrodeposition to occur, an overpotential is required. This potential is higher than thermodynamically expected, and provides the activation energy required for the reaction to proceed.

The peaks in Figure 4.22 can now be assigned. As in the case of Reline 200 solutions, the peaks observed in the \(\text{I}_2/\text{Pd}/\text{Ethaline}\) mixtures indicate that metal iodide species are dominant in the solution, rather than \([\text{PdCl}_4]^{2-}\). Thus, peak I corresponds to the reduction of \(\text{I}_3^-\) to \(3\text{I}^-\) (eq. 4.3), and peak II to Pd(II) being reduced to Pd(0) (eq. 4.7). Reduction peaks III and IV are believed to relate to the reduction of more stable tetrahalide complexes of Pd(II) or the reduction of Pd(II) onto electrodeposited Pd. Peak V is then the anodic stripping of Pd from the electrode possibly forming Pd(II) complexes with \(\text{I}^-\) or \(\text{I}^-/\text{Cl}^-\) ligands. Peaks VI, IX, and X relate to the oxidation of \(\text{I}^-\) to \(\text{I}_3^-/\text{I}_2^-\) (eqs. 4.4-4.6) or other trihalides.

\subsection*{4.4 Real World Catalytic Converter}

Extraction of metals from an automotive catalytic converter was tried using Reline/\(\text{I}_2\). An example of an unused catalytic converter is included in Figure 4.28 showing its honeycomb structure, which increases the total surface area. This kind of converter normally contains 1.0-2.0 g of all PGMs (Pd/Pt/Rh), with the total content always lower than 0.1\%.\textsuperscript{29,186}
As described in section 1.2.1, there are three main components of a catalytic converter; the honeycomb ceramic, the protective outer steel shell, and the fibre blanket buffer. The ceramic component is the most abundant and consists of a silicon-aluminium-magnesium oxide called cordierite (2MgO.2Al₂O₃.5SiO₂). Upon this, there is a washcoat of alumina with some combination of oxide additives (Ce, Zr, La, Ni, Fe, etc.; no PGMs) and this further increases the surface area. The oxides serve as support stabilizers, activity promoters, and selectivity improvers.³,²⁷,²⁹ It is clear then, that there exists a large amount of other material to deal with as well as the PGMs.

The first attempt at extracting metals from a catalytic converter involved using a monolith which contained 25.0 g ft⁻³ Pd (≈84 mg) and 5.0 g ft⁻³ Rh (≈17 mg). Enough I₂ (814 mg) was used to ensure 4 equivalents for every equivalent of Pd. The converter was broken up and ground using a mortar and pestle before being added to a round bottom flask containing 250 mL of Reline 200 and I₂ at 60 °C. The volume of Reline 200 used was the minimum needed in order to be able to stir the mixture, and this was left for 24 hours. After this time it was found that some material had dissolved, as the Reline had a beige/cream colour (Fig. 4.29). There also remained a large amount of solid at the bottom.
of the flask. The mixture was centrifuged for 20 minutes at 4400 RPM and then 4 mL of the supernatant liquid decanted. Cyclic voltammetry was carried out on this solution in an attempt to characterise any species dissolved (Fig. 4.30).

![Figure 4.29](image)

**Figure 4.29** Reline 200/I₂ mixed with ground catalytic converter, after 24 hours stirring

The first scan, swept toward the negative potential limit, shows a small reduction peak at -1.05 V and a second, large, peak at -2.4 V. On the return scan an oxidation peak appears at 0.63 V. In the second, a new reduction peak at -0.26 V is also observed. Compared to the first scan, the reduction wave at *ca.* -2.4 V increases in intensity, and the oxidation peak shifts to 0.55 V in scan 2. The reduction at -0.26 V may be related to the reduction of I₃⁻ to I⁻ (peak VII, eq. 4.3), whereas the reverse process (peak IX, eq. 4.4) occurs *ca.* 0.60 V. The small peak at -1.05 V could be related to the urea film that forms on the electrode surface (see 4.2.2.1). It is unknown what the peak at -2.4 V corresponds to; as there are many other compounds present in the converter which could have dissolved.\(^{186}\)
Dealing with large amount of material is an issue in this process. To address this, Kim et al.\textsuperscript{186} investigated the selective recovery of the washcoat by removing the ceramic via attrition scrubbing. This was achieved by adding 210 g of milled converter to 600 mL of pure H\textsubscript{2}O (solid:H\textsubscript{2}O ratio of 0.35) and stirring the mixture at 1800 RPM between 5 and 60 minutes. It was found that 60 minutes increased the percentage of washcoat particles less than 45 µm (68.77\%) compared to 5 minutes (37.27\%). The percentage of cordierite particles less than 45 µm also increased over this time (2.32-6.43\%) but this was relatively small in comparison. The greater brittleness of the washcoat, which results from the internal pores and fissures for increased surface area, was considered to be the cause of this difference. After wet sieving the particles, it was shown that the smaller ones had
greater PGM and metal oxide content, as these are present in the washcoat. A similar attrition scrubbing process was employed for the second attempt at recovering Pd from a catalytic converter containing 0.13 g of precious metal (Pd:Rh, 5:1). For this, the material was initially broken up and ground slightly in a mortar and pestle.

**Figure 4.31** Catalytic converter particles; A) pre-attrition scrubbing and B) post-attrition scrubbing

**Figure 4.32** EDX data showing elemental composition of ground catalytic converter; A) pre-attrition scrubbing and B) post-attrition scrubbing

The appearance of the converter particles at this stage is shown in Figure 4.31A. EDX (Fig. 4.32A) and SEM (Fig. 4.33A) analysis was carried out on these ‘large’ particles before attrition scrubbing. H₂O (50 mL) was then added to the catalytic converter (16.25
g, i.e. solid:H₂O ratio of 0.325) and stirred for 90 minutes at 1500 RPM. The larger time used, compared to the literature was chosen to compensate for the lower RPM. The solid was then wet sieved using a 75 µm sieve before filtering, obtaining 3.95 g of the ‘smaller’ particles, which were dried in an oven for 30 minutes at 110 °C (Fig. 4.31B), before performing EDX (Fig. 4.32B) and SEM (Fig. 4.33B) analysis.

**Figure 4.33** SEM of ground catalytic converter at a magnification of x100; A) pre-attrition scrubbing and B) post-attrition scrubbing
The range of particle sizes, as shown by SEM, before attrition scrubbing (Fig. 4.33A) is very large, between 165 and 625 µm, compared to those after the process (Fig. 4.33B), which range between 13 and 54 µm. There are some particles which if measured along a different axis are ≈100 µm but these are typically long and slender particles capable of passing through the sieve used as their length along the other axis is <75 µm. The EDX data shows that the elemental composition has changed. Specifically, the smaller particles have reduced content of some elements (e.g. Si, F, Fe), while Pd is now detected (4.32B) as well as several other elements. It is clear the attrition scrubbing has been a success in removing excess ceramic material and increasing the Pd concentration in the sample.

As mentioned before, 0.13 g of precious metal (Pd:Rh, 5:1) was present in the second catalytic converter. 2.64 g of the smaller, post-attrition scrubbing particles were added to 4 mL of Reline 200. It was estimated that this amount of converter contained 17.7 mg of Pd which would give a concentration of 41.5 mM. Excess I₂ was added to the mixture (5 eq; 210 mM) and this was stirred at 60 °C for 24 hours, before centrifuging (5000 RPM, 30 minutes) and decanting the supernatant (Fig. 4.34).

![Figure 4.34](image)

**Figure 4.34** Second attempt at extracting Pd from a catalytic converter; A) separated converter residue after decanting and B) decanted solution

The cyclic voltammogram of the decanted solution (Fig. 4.34B) was taken (Fig. 4.35). At the beginning of scan 1 a reduction peak is observed at -0.42 V (peak I). This is followed by two small reduction waves at -1.31 V (peak III) and -1.71 V. In the reverse scan, a
small oxidation peak is present at -0.36 V followed by larger ones at 0.01 V (peak V), 0.28 V (peak VI), 0.66 V (peak IX) and 0.88 V (peak X). The second scan shows a new reduction peak at -0.19 V (peak VII), with the rest remaining similar to the first scan.

**Figure 4.35** CVs of the decanted solution (Fig. 4.34B) after the second attempt at extracting Pd from a catalytic converter using Reline 200/I₂; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C

The CVs in Figure 4.35 are similar to those of Figure 4.5, and the main reduction (I, VII) and oxidation (VI, IX, X) waves can be assigned to the I₂/I⁻/I₂⁻ system, as discussed above. The smaller reduction peaks at *ca.* -1.31 V (peak III) and -1.71 V may be related to the reduction of tetrahalide Pd(II) complexes and/or a different metal dissolved from the
washcoat. The corresponding oxidation processes would then correspond to the peaks at -0.36 V, and *ca.* 0.01 V (peak V). Comparing Figures 4.5 and 4.35 the lack of the Pd(II) reduction peak (II), and the less intense peak V (suggesting less Pd) is apparent. This may be due to the small concentration of Pd in the mixture and/or the easier oxidation of other metals present in the solid catalyst.

![Image](image.png)

**Figure 4.36** Solid deposit obtained by electrodeposition from the Reline 200/I$_2$ solution used for extraction of metal from a catalytic converter (second attempt)

To obtain further information on the composition of the mixture, electrodeposition was carried out, with the potential being held at -1.9 V for 72 hours, separated into three 24 hour periods. After every 24 hours the working electrode was removed and rinsed with deionised H$_2$O to remove the black deposit (Fig. 4.36). Acetone was used to rinse the deposits thoroughly after removing H$_2$O before drying at 110 °C for 15 minutes. SEM (Fig. 4.37) and EDX spectroscopy (Fig. 4.38) were then carried out on the recovered solid. The SEM shown in Figure 4.37 is similar to those in Figures 4.12 and 4.16, particularly the latter. As can be observed in the figure there are both sheets of deposited material as well as small clusters. It is believed the sheets form on the surface of the glassy carbon working electrode creating a denser deposit before the clusters form on top creating an outer layer.\textsuperscript{111}
Figure 4.37  SEM of the solid electrodeposited from the Reline 200/I₂ solution following extraction of metal from a catalytic converter (second attempt); at a magnification of x2075

Figure 4.38  EDX data showing elemental composition of the deposit obtained from the Reline 200/I₂ solution following extraction of metal from the catalytic converter (second attempt)
Interestingly, the EDX data in Figure 4.38 also shows the presence of Pd at a relatively large concentration, although it is mixed with several other metals that are present in the washcoat; either as additives and stabilisers (Ba, La, etc.) or as the washcoat itself (Al₂O₃). There is also residual Reline/I₂ which was not fully removed during the cleaning process.

![Graph showing CVs of the Reline 200/I₂ solution after electrodeposition of metals following treatment of the catalytic converter (second attempt); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C.]

**Figure 4.39** CVs of the Reline 200/I₂ solution after electrodeposition of metals following treatment of the catalytic converter (second attempt); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Temperature = 60 °C

CVs were carried out after electrodeposition and are shown in Figure 4.39. The scans show the peaks corresponding to the I₂/I⁻/I₃⁻ system, with reduction peaks at -0.43 V and -0.22 V (scan 2), and oxidation peaks at 0.27, 0.63 and 0.87 V. Most importantly, the peaks relating to the presence of Pd (and possibly other metal(s)) are lost. This alongside
the EDX data in Figure 4.38 shows the successful recovery of Pd from a catalytic converter.

4.5 Conclusions

Raman spectroscopy shows that dissolution of I$_2$ in Reline 200 or Ethaline 200 leads to the formation of predominantly I$_3^-$ and I$_5^-$. The CVs of I$_2$ in either DES shows varying degrees of overlapping between the peaks, but it is possible to distinguish two reduction and three oxidation peaks. These are related to reduction of I$_2$ and I$_3^-$ to I, and the corresponding oxidations. The additional oxidation peak is suggested to correspond to formation of a different trihalide species, e.g. I$_2$Cl$^-$. The CVs of PdI$_2$ in Reline or Ethaline were similar with three Pd(II) reduction peaks and one Pd stripping peak. There are also two peaks related to the oxidation and reduction of iodide. Solutions of PdCl$_2$ produce CVs which differ slightly in each of the DESs, e.g. in Ethaline, the CVs show a nucleation loop which is not seen in Reline. In each DES, however, the CVs of K$_2$[PdCl$_4$] are nearly identical to those of PdCl$_2$, showing that the main species formed in the latter is [PdCl$_4$]$^{2-}$. Solutions of Pd (50 mM) and I$_2$ (200 mM) in either DES produce CVs that are similar to each other, as well as similar to those of PdI$_2$. Peaks related to the I$/I_2/I_3^-$ system can be seen, as well as to the reduction of Pd(II) and stripping of the metal. It is also apparent that [PdCl$_4$]$^{2-}$ is not one of the main species formed when Pd metal is dissolved in the DESs in the presence of I$_2$. It is suggested that mixed iodide/chloride square-planar Pd(II) complexes form instead. Recovery of the dissolved Pd by electrodeposition from Reline 200 containing I$_2$ has been successfully achieved. It also appears that the I$_2$/Reline mixture can be recycled at least twice. Work has also been performed on a real world catalytic converter. Removal of excess material of the converter (cordierite) has been effectively carried out via an attrition scrubbing process which allowed the separation of large particles containing predominately cordierite, from smaller particles with a larger washcoat content and therefore PGMs. From the smaller particles, Pd was successfully dissolved and deposited from the remaining washcoat. Overall, Pd has been successfully recovered from a catalytic converter as proven by cyclic voltammetry, SEM, and EDX spectroscopy.
4.6 Future Work

The studies described herein could be further expanded in several ways to develop a greater understanding and provide further confirmation on the conclusions made. For example:

- Perform a more in depth study of the speciation of I₂ in Reline 200 and Ethaline 200. This would be achieved by using a range of different I₂ concentrations and analysing them via Raman spectroscopy and cyclic voltammetry. Correlation of the Raman results with the voltammetries would allow a more accurate assignment of electrochemical processes. Complementary Raman and electrochemical studies would also be done adding Pd(0) and a variety of Pd(II) salts at various concentrations. In addition, dissolving and analysing Pd(IV) salts would add further information regarding the nature of the metal complexes that form in the DES/I₂ mixtures.

- Work on selectively depositing Pd as Figure 4.38 shows other metals are present. This will require testing a wide variety of metal salts to obtain their electrochemical data and at which potential these metals are deposited.

- Carry out electrodeposition of Pd from Ethaline 200 and test its capability of re-use. This would allow comparison to results obtained from Reline 200.

- Optimise the attrition scrubbing process to maximise removal of excess material (e.g. cordierite). Investigate the re-usability of Reline 200 with catalytic converters to see if the excess material has an effect on subsequent uses. Perform electrodeposition at different potentials and conditions (e.g. T, working electrode) in order to selectively deposit Pd.

- Test Ethaline 200 as the solvent for the removal of Pd from catalytic converters.

- Test other DESs, e.g. similar to Reline and Ethaline but using choline iodide rather than chloride and compare to results already obtained.
Chapter 5. Dissolution of Au in [BMIM]OTf: $^{31}$P-NMR spectroscopic and electrochemical investigation, and removal of Au from electronic components

5.1 Aims and Introduction

The aim of this Chapter was to investigate the properties of Au dissolved in [BMIM]OTf in the presence of Ph$_3$P and I$_2$, as the highest concentration of metal was achieved in this IL mixture, as described in Chapter 3. In particular, the nature of the species formed in solution has been investigated, as well as the electrochemical behaviour of the solutions. Solutions of Ph$_3$P (with and without added H$_2$O), Ph$_3$P:I$_2$ (1:1), Ph$_3$P=O, and Ph$_3$P=O.H$_2$O$_2$ in ILs were analysed by $^{31}$P-NMR spectroscopy to determine their speciation (both in samples closed and open to the air) over time. The oxides were synthesised according to literature procedures.\textsuperscript{187} The final aim was to test the extraction of Au from real world electronic components.

Part of this work was done in collaboration with Ms. Katharine Gregg, an undergraduate student who carried out her final year research project in our research group under my supervision. In particular, she focused on the initial monitoring of Ph$_3$P, Ph$_3$P:I$_2$ (1:1), Ph$_3$P=O, and Ph$_3$P=O.H$_2$O$_2$ solutions by $^{31}$P-NMR spectroscopy. She also performed the initial cyclic voltammetry and electrodeposition work.

Several considerations must be made when planning on performing NMR in ILs. As a signal is required to provide a lock in NMR, this can be achieved by use of a capillary containing a deuterated solvent helping avoid any dilution of the IL system being analysed. This is the easiest way but it is also possible to have the IL system in the capillary and the lock standard surrounding the capillary. To allow accurate determination of chemical shifts, a reference compound can be included in the capillary/IL as an internal reference. When using a capillary lock the bulk magnetic susceptibilities of the sample and reference are different, and because of the different natures of ILs and organic solvents (contains reference compound) referencing the exact chemical shift is of concern without application of a correction. In saying this, the correction is not required when describing relative trends in chemical shifts.\textsuperscript{188–190} Due to the higher viscosity of ILs, molecular
motion can be slow, thus increasing the efficiency of the quadrupole moment relaxation. This can lead to disappearance of multiplet structure at lower temperatures. There is also the fact that, depending on the type of NMR being performed, the IL being used may have peaks present in the spectrum, e.g. $^1$H-NMR in imidazolium ILs, and these could overlap with the species present in the solvent. By increasing the temperature the NMR is performed at, the signal width can be reduced and resolution improved, due to reduction of viscosity. It is also important to ensure all substrates are dissolved in the IL and may even require application of ultrasonic treatment.

As with DESs (see Section 4.1), there are some concerns associated with using ILs in electrochemical systems. These are their high viscosity, which affects laminar flow, and their limited conductivity, an issue when using ultramicroelectrodes. Due to the greater viscosities of ILs compared to conventional solvents, mass transport is significantly slower. Slower diffusion of metal ions within ILs, resulting from the higher viscosities, slows deposition rates, possibly altering the nature of the deposit. The nature of the IL can also affect the formal potential, electrodeposition mechanism, stripping processes, electrode kinetics, and the metal deposit structure.

ILs have been used for the recovery of common metals (Al, Zn, Cu, Fe, Co, Ni), light metals (Li, Na, Mg), rare earth metals (La, Dy, Ce, Sm, Eu, Yb), and noble metals (Pd, Pt, Ag, Au, Ru, Rh). Au recovery in ILs has been previously investigated. Some research focused on Au extraction, while other also look at depositing Au. For example Au (and Ag) was recovered from ore using [BMIM]HSO$_4$, with thiourea added and Fe$_2$(SO$_4$)$_3$ as oxidant. Selective extraction of Au was $\geq$85% (Ag $\geq$60%) from powdered ore, achieved within 50 hours at room temperature. Compared to an aqueous system, extraction of Au was similar, whereas Ag extraction was significantly better in the IL. An analogous system has been reported for Au extraction from sulfidic ore using [BMIM]Cl or [BMIM]HSO$_4$, with an oxidant and leaching agent. Au has also been recovered from copper anode slime using [EMIM]HSO$_4$. Using [BMIM]NTf$_2$, it was possible to extract Au(III) from an aqueous phase, while an IL in H$_2$O microemulsion was used for the extraction of Au(III) from an acidic chloride media. [P$_{66614}$]Cl impregnated onto ionic resin Amberlite XAD-1180
has been applied for the extraction of Au(III), Pd(II), and Pt(IV) from HCl solutions. One Cl⁻ ion in resin exchanged for [AuCl₄]⁻ or [PdCl₃]⁻ and two exchanged for [PtCl₆]²⁻.²⁰³ The same IL on Amberlite XAD-7 can also extract Au(III) as [AuCl₄]⁻.²⁰⁵ In another work, an imidazolium chloride–polyvinyl chloride ionomer was used to recover Au(III) from an acidic chloride solution. The Au was desorbed from the ionomer using thiourea as a stripping agent.²⁰⁸ All of these examples look at extracting Au complexes from one phase into another but do not look into recovering the metal as a Au(0) deposit. Using pure [OMIM]PF₆ as an extractant, Au(I) (>98%) was extracted from an aqueous phase before achieving 92% recovery of the Au in the IL via deposition.²⁰⁶ K[AuCl₄] has also been dissolved in an aqueous solution of HCl or HBr. The metal was then extracted into the ILs and deposited, via a three-electron one-step process.²¹¹

In contrast with previous literature work which use Au salts, the research described in this chapter focuses on the synthesis and application of an adduct which can be used at room temperature while open to air for the dissolution of Au(0) before recovering it electrochemically.

5.2 Monitoring Experiments using NMR spectroscopy

As stated in the Introduction (Section 1.4), iodophosphoranes can exist in several forms, e.g. Scheme 5.1 shows that a 1:1 mixture of Ph₃P and I₂ can produce (17a) (noted as (17) in Section 1.4), (17b), or (17c).

The species that can be found in equilibrium in solution depends partly on the solvent. For example, it has been reported than in acetonitrile only the salt [Ph₃PI]I (17b) is present, while in less polar pyridine, the pentavalent species Ph₃PI₂ (17c) predominates. In excess of I₂, tri-iodide compounds can also form (Scheme 5.1.).²¹² In addition, formation of phosphine oxide during the dissolution experiments is also possible, and therefore species such as Ph₃P=O and its adducts with I₂ and/or H₂O, e.g. Ph₃P=O.H₂O, should be taken into account.¹⁸⁷ Therefore, in order to better understand the species formed when Ph₃P and I₂ are dissolved in ILs and how these change with time, various NMR monitoring
experiments were carried out. Table 5.1 shows literature NMR data for the various possible species in solution.

Scheme 5.1 Some of the species that can be found in equilibrium in solutions of Ph\textsubscript{3}P and I\textsubscript{2}. Adapted from reference 212

Monitoring experiments were initially performed using 1:1 mixtures of Ph\textsubscript{3}P:I\textsubscript{2} in neat [BMIM]OTf, to determine the formation and stability of the adduct in the IL and study any changes that may occur over time in samples both closed and open to the air. Similar experiments were then carried out on Ph\textsubscript{3}P, Ph\textsubscript{3}P=O, and Ph\textsubscript{3}P=O.H\textsubscript{2}O\textsubscript{2}, as well as using Ph\textsubscript{3}P in [BMIM]OTf with various amounts of H\textsubscript{2}O added. All \textsuperscript{31}P-NMR spectra were performed with neat [BMIM]OTf as solvent. Each sample contained an internal reference consisting of a sealed capillary tube with 1, 2-bis(diphenylphosphino)ethane (28) dissolved in DMSO-d\textsubscript{6}. The signal for (28) was manually set at -14.44 ppm.
Table 5.1 Literature $^{31}$P NMR data for various phosphine species in solution

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical shift/ppm</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph$_3$P</td>
<td>Acetonitrile-d$_3$</td>
<td>-5.5</td>
<td>212</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_3$P</td>
<td>Pyridine-d$_5$</td>
<td>-6.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ph$_3$P</td>
<td>CDCl$_3$</td>
<td>-4.25</td>
<td>213</td>
</tr>
<tr>
<td>4</td>
<td>Ph$_3$P</td>
<td>[BMIM]BF$_4$</td>
<td>-5.5</td>
<td>214</td>
</tr>
<tr>
<td>5</td>
<td>Ph$_3$P</td>
<td>Pyridine-d$_5$</td>
<td>-21.0</td>
<td>212</td>
</tr>
<tr>
<td>6</td>
<td>Ph$_3$P$_2$ (17a)</td>
<td>1,2-Dichloroethane-d$_4$</td>
<td>-21.7</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>[Ph$_3$P]I (17b)</td>
<td>Acetonitrile-d$_3$</td>
<td>46.1</td>
<td>212</td>
</tr>
<tr>
<td>8</td>
<td>[Ph$_3$P]I (17b)</td>
<td>CDCl$_3$</td>
<td>44.8</td>
<td>48,51</td>
</tr>
<tr>
<td>9</td>
<td>[Ph$_3$P]I (17b)</td>
<td>1,2-Dichloroethane-d$_4$</td>
<td>44.8</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>Ph$_3$P$_4$</td>
<td>CDCl$_3$</td>
<td>48.8</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>Ph$_3$P=O</td>
<td>Benzene-d$_6$</td>
<td>25.16</td>
<td>187</td>
</tr>
<tr>
<td>12</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>29.1</td>
<td>187</td>
</tr>
<tr>
<td>13</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>30.6</td>
<td>213</td>
</tr>
<tr>
<td>14</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>29.8</td>
<td>214</td>
</tr>
<tr>
<td>15</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>29.61</td>
<td>215</td>
</tr>
<tr>
<td>16</td>
<td>Ph$_3$P=O</td>
<td>D$_2$O</td>
<td>25.2</td>
<td>216</td>
</tr>
<tr>
<td>17</td>
<td>Ph$_3$P=O</td>
<td>D$_2$O</td>
<td>24.2</td>
<td>217</td>
</tr>
<tr>
<td>18</td>
<td>Ph$_3$P=O</td>
<td>Benzene-d$_6$</td>
<td>27.52</td>
<td>187</td>
</tr>
<tr>
<td>19</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>30.15</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>30.2</td>
<td>215</td>
</tr>
<tr>
<td>21</td>
<td>Ph$_3$P=O</td>
<td>CDCl$_3$</td>
<td>41.2</td>
<td>218</td>
</tr>
<tr>
<td>22</td>
<td>[Au(PPh$_3$)$_2$]OTf</td>
<td>—</td>
<td>39.0</td>
<td>219</td>
</tr>
<tr>
<td>23</td>
<td>[Au(PPh$_3$)$_3$]</td>
<td>CDCl$_3$</td>
<td>-69.5 (Me$_3$P), 30.1 ([AuI$_3$(PMe$_3$))</td>
<td>47</td>
</tr>
<tr>
<td>24</td>
<td>[AuI$_3$(PMe$_3$)$_2$ (20)</td>
<td>—</td>
<td>-69.5 (Me$_3$P), 30.1 ([AuI$_3$(PMe$_3$))</td>
<td>47</td>
</tr>
<tr>
<td>25</td>
<td>[AuI$_3$(PMe$_3$)$_3$]</td>
<td>CD$_2$Cl$_2$</td>
<td>-11.2</td>
<td>220</td>
</tr>
<tr>
<td>26</td>
<td>[Au(PPh$_3$)] + I$_2$ (1:1)</td>
<td>CD$_2$Cl$_2$</td>
<td>39.3</td>
<td>220</td>
</tr>
<tr>
<td>27</td>
<td>[Au(P(P-tolyl)$_3$)]</td>
<td>CD$_2$Cl$_2$</td>
<td>39.5</td>
<td>220</td>
</tr>
<tr>
<td>28</td>
<td>[AuBr$_3$(PPh$_3$)]</td>
<td>CDCl$_3$</td>
<td>31.4</td>
<td>220</td>
</tr>
</tbody>
</table>
5.2.1 Initial experiments in [BMIM]OTf

The initial monitoring experiments involved dissolving Ph$_3$P and I$_2$ in a 1:1 ratio in [BMIM]OTf (10 mL) to a concentration of 40 mM before performing $^{31}$P-NMR spectroscopy. It should be noted that Ph$_3$P on its own in [BMIM]OTf has a $^{31}$P-NMR chemical shift between -6.8 and 3.5 ppm (see below). In some of the spectra shown in the figures below, a small peak can be seen at ca. 30.0 ppm, which is believed to be an impurity in the reference lock as it is present when the blank IL is analysed.

Figure 5.1 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-40.0 ppm region) monitoring an open sample of Ph$_3$P:I$_2$ (1:1; 40.0 mM) over 720 hours (30 days), a final spectra was taken after 1320 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
The $^{31}$P-NMR spectra of a sample that was kept open to the air during the process are shown in Figure 5.1. After 24 hours there is a single peak at 36.68 ppm which shifts to 32.60 ppm after 120 hours. The peak continues to fluctuate around 32.0-33.0 ppm for 720 hours at which point monitoring ceased. A final spectrum was performed after 1320 hours (still open) from the start of the experiment showing the peak at 33.99 ppm.

Figure 5.2 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-47.5 ppm region) monitoring a closed sample of Ph$_3$P:I$_2$ (1:1; 40.0 mM) over 720 hours (30 days); internal reference = (28) in DMSO-d$_6$, -14.44 ppm
Figure 5.2 shows the $^{31}$P-NMR spectra of a similar experiment, but in this case the sample was kept in a closed vial throughout the process. After 24 hours a singlet is seen at 45.84 ppm. Over the course of 720 hours this slowly shifts upfield where it reaches 44.29 ppm. As can be observed in both Figures 5.1 and 5.2 there is no peak associated with free Ph$_3$P indicating that the adduct is not undergoing any dissociation. The spectra of the open and closed samples are clearly different, with the former changing significantly over time. This may be related to oxidation of Ph$_3$P to Ph$_3$P=O and/or formation of H$_2$O adducts in the open-air sample. To investigate this, samples of Ph$_3$P and Ph$_3$P=O were monitored with time (both open and closed to the air Figures 5.3-5.6).

The $^{31}$P-NMR spectra of the open sample of Ph$_3$P in [BMIM]OTf (Fig. 5.3) show a single peak at 2.92 ppm, which shifts with time between ca. 2.0 ppm and 3.0 ppm, whereas the spectra of the closed sample (Fig. 5.4) exhibit a peak at 3.55 ppm which remains virtually unchanged over the course of 552 hours. Small peaks at higher frequency (20.0-32.0 ppm) can also be seen, which may be related to formation of oxide. It is unclear at this stage why the chemical shift of Ph$_3$P in the samples is different to the expected value between -4.0 ppm and -6.0 ppm (Table 5.1, entries 1-5) and why there is a variation with time in the open sample.
Figure 5.3 \(^{31}\)P-NMR spectra ([BMIM]OTf (10 mL), -16.0-34.0 ppm region) monitoring an open sample of Ph\(_3\)P (40.0 mM) over 648 hours (27 days); internal reference = (28) in DMSO-d\(_6\), -14.44 ppm
Figure 5.4 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-35.0 ppm region) monitoring a closed sample of Ph$_3$P (40.0 mM) over 552 hours (23 days); internal reference = (28) in DMSO-d$_6$, -14.44 ppm

Analogous, inconsistent results were also observed in the case of Ph$_3$P=O, prepared using the method of Hilliard et al.$^{187}$ The open sample (Fig. 5.5) shows a peak at 35.85 ppm which shifts over time, and the closed sample (Fig. 5.6) gives a singlet at 40.79 ppm which does not change much. There is, however, some resemblance between the spectra of Ph$_3$P=O (open, Fig. 5.5) and those of Ph$_3$P:I$_2$ (open, Fig. 5.1).
Figure 5.5 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-40.0 ppm region) monitoring an open sample of Ph$_3$P=O (40.0 mM) over 648 hours (27 days); internal reference = (28) in DMSO-$d_6$, -14.44 ppm
Figure 5.6 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-42.5 ppm region) monitoring a closed sample of Ph$_3$P=O (40.0 mM) over 576 hours (24 days); internal reference = (28) in DMSO-d$_6$, -14.44 ppm

To clarify if the behaviour seen in these spectra is due to formation of Ph$_3$P=O adducts with H$_2$O, the related derivative Ph$_3$P=O.H$_2$O$_2$ was prepared, following the method of Hilliard et al.,$^{187}$ and its NMR spectra in the IL monitored (Figures 5.7 and 5.8). As before, different behaviour was observed for the open and closed samples of Ph$_3$P=O.H$_2$O$_2$ in [BMIM]OTf. The open sample (Fig. 5.7) shows a singlet at 36.33 ppm, which shifts to 32.93 ppm over a period of 168 hours, and then remains around 32.0 ppm up to 648 hours.
The closed sample (Fig. 5.8) gives a peak initially at 41.05 ppm. This slowly moves upfield, i.e. to 40.42 ppm at 432 hours. It is then present at 36.71 ppm after 576 hours. Although there are some differences, the behaviour of Ph$_3$P=O$\cdot$H$_2$O$_2$ (open sample, Fig. 5.7) is comparable with that of Ph$_3$P=O and Ph$_3$P:I$_2$ (open, Figs. 5.5 and 5.1, respectively), and suggests that in the Ph$_3$P:I$_2$ mixture, a phosphine oxide/H$_2$O adduct forms. The closed samples shown in Figures 5.2, 5.6, and 5.8 (Ph$_3$P:I$_2$, Ph$_3$P=O, and Ph$_3$P=O$\cdot$H$_2$O$_2$)
respectively) are also similar to each other. An analogous process as that in the open samples may also be taking place, but at a slower rate.

Figure 5.8 $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-45.0 ppm region) monitoring a closed sample of Ph$_3$P=O.H$_2$O$_2$ (40.0 mM) over 576 hours (24 days); internal reference = (28) in DMSO-d$_6$, -14.44 ppm

Ph$_3$P=O was added to the sample from Figure 5.1 (Ph$_3$P:I$_2$, open) and is shown in Figure 5.9. It can be seen that a small shift has occurred and an increase in intensity, but only
one peak is present in the final spectrum, indicating that at the very least, Ph$_3$P=O appears to form in the Ph$_3$P:I$_2$ mixtures. Whether a H$_2$O adduct forms remains unclear.

**Figure 5.9** $^{31}$P-NMR spectra ([BMIM]OTf (10 mL), -15.0-35.0 ppm region) of an open sample of Ph$_3$P:I$_2$ (1:1, 40.0 mM) after 1320 hours (55 days, top) and with added Ph$_3$P=O (bottom); internal reference = (28) in DMSO-d$_6$, -14.44 ppm

5.2.2 NMR spectra of Ph$_3$P:I$_2$ (1:1) in other ILs ([BMIM]NTf$_2$, [HMIM]NTf$_2$, and [C$_{10}$MPyr]NTf$_2$)

Mixtures of Ph$_3$P and I$_2$ (1:1) were also dissolved in other ILs and their $^{31}$P-NMR spectra monitored to examine if the behaviour observed above could be related to the nature of the IL cation/anion. The ILs used were [BMIM]NTf$_2$, [HMIM]NTf$_2$, and [C$_{10}$MPyr]NTf$_2$ (C$_{10}$MPyr = N-decyl-N-methylpyrrolidinium), and spectra are shown in Figures 5.10-
5.14. The NMR spectra of Ph$_3$P:I$_2$ (1:1) in the imidazoliun ILs [BMIM]NTf$_2$ and [HMIM]NTf$_2$ (Figures 5.10-5.13) are similar to each other, and the signals shift with time as in the case of [BMIM]OTf.

\[\text{T = 24 hours}\]

\[\text{T = 48 hours}\]

\[\text{T = 96 hours}\]

\[\text{T = 192 hours}\]

\[\text{T = 336 hours}\]

**Figure 5.10** $^{31}$P-NMR spectra ([BMIM]NTf$_2$ (10 mL), -15.0-45.0 ppm region) monitoring an open sample of Ph$_3$P:I$_2$ (1:1, 40.0 mM) over 336 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
As discussed above for [BMIM]OTf, the peaks at higher frequency (40-50 ppm) could be related to iodophosphoranes, or even to Ph₃P=O and/or Ph₃P=O.H₂O. For the sealed samples, peaks at ca. 4.0 ppm can be seen in the initial spectra, indicating that free Ph₃P is still present. This suggests that oxidation of the phosphine in the NTf₂-ILs is slow, compared with [BMIM]OTf, which could be due to the higher H₂O content in the latter IL (i.e. as shown in Chapter 3 the amount of H₂O determined by Karl Fischer for
[BMIM]OTf, [BMIM]NTf₂, and [HMIM]NTf₂ is 0.611 Wt%, 0.007 Wt%, and 0.039 Wt% respectively).

Figure 5.12 ³¹P-NMR spectra ([HMIM]NTf₂ (10 mL), -15.0-50.0 ppm region) monitoring an open sample of Ph₃P:I₂ (1:1, 40.0 mM) over 336 hours; internal reference = (28) in DMSO-d₆, -14.44 ppm
Figure 5.13 $^{31}$P-NMR spectra ([HMIM]NTf$_2$ (10 mL), -15.0-55.0 ppm region) monitoring a sealed sample of Ph$_3$P:I$_2$ (1:1, 40.0 mM) over 336 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm

By contrast, the NMR spectra in [C$_{10}$MPyr]NTf$_2$ (Fig. 5.14) show only one broad peak at ca. 35.0 ppm which does not shift over time, indicating that the shifting of the signals with time is related to the imidazolium cation. For example, hydrogen bonding interactions between the H atoms in the imidazolium ring and the various species possible in solution (H$_2$O, Ph$_3$P, Ph$_3$P=O, Ph$_3$P.I$_2$, etc.) may play a role.
Figure 5.14 $^3$P-NMR spectra ([C$_{10}$MPyr]NTf$_2$ (10 mL), -15.0-45.0 ppm region) monitoring an open sample of Ph$_3$P:I$_2$ (1:1, 40.0 mM) over 192 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm

5.2.3 Further monitoring experiments in [BMIM]OTf

Overall, the results obtained so far from the NMR experiments were unclear and inconsistent. To further understand the observed behaviour, the $^3$P NMR spectrum of Ph$_3$P was repeated in a new batch of [BMIM]OTf, and was monitored over time (Fig. 5.15). The effect of adding 0.5% of H$_2$O to the sample was also studied (Fig. 5.16). In contrast with that observed above (Figures 5.3-5.4), in the new set of spectra, the signal
for Ph₃P appeared at *ca.* -6.8 ppm and did not change. Small peaks appeared at 26.0-29.0 ppm over time.

**Figure 5.15** ³¹P-NMR spectra (second [BMIM]OTf batch (2 mL), -15.0-40.0 ppm region) monitoring a closed sample of Ph₃P (100 mM) over 168 hours; internal reference = (28) in DMSO-d₆, -14.44 ppm
Figure 5.16 $^{31}$P-NMR spectra (second [BMIM]OTf batch (2 mL), -15.0-40.0 ppm region) monitoring a closed sample of Ph$_3$P (100 mM) over 168 hours, 0.5 % H$_2$O added; internal reference = (28) in DMSO-d$_6$, -14.44 ppm

The addition of increasingly higher amounts of H$_2$O (Fig. 5.17) in a closed sample or one left open to the air (Fig. 5.18) still resulted in an unique Ph$_3$P peak at -6.85 ppm which did not change, and a smaller peak between 26.0-29.0 ppm increasing with time.
Figure 5.17 $^{31}$P-NMR spectra (second [BMIM]OTf batch (2 mL), -15.0-40.0 ppm region) monitoring a closed sample of Ph$_3$P (100 mM) over 168 hours, % H$_2$O added noted above each spectrum; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
It was then decided to use the original batch of [BMIM]OTf and a new, third batch of the IL, and compare the $^{31}$P NMR spectra of Ph$_3$P in both ILs at 0 and 168 hours (Fig. 5.19). Using the first batch, the main peak for Ph$_3$P is found at 3.66 ppm which then shifts to ca. 3.00 ppm. A small peak at 20.76 ppm also develops. The spectra in the third IL batch shows the main peak for Ph$_3$P consistently at -6.86 ppm, together with a small peak that develops at 28.52 ppm.
The results above indicate that the inconsistent NMR spectra are related to a particular batch of [BMIM]OTf, and are not related to the presence of H$_2$O in the solvent. The $^1$H, $^{19}$F, and $^{31}$P-NMR spectra of all the ILs used were performed prior to use and these were as expected, showing that there were no significant amounts of impurities. However, small amounts of residual starting materials or other impurities could be present and remain undetected by NMR. Despite our efforts in this area, the nature of these impurities, if present, and how they affect the NMR spectra of the mixtures could not be clarified. For example, the NTf$_2$-ILs could contain residual LiNTf$_2$. 

**Figure 5.19** $^{31}$P-NMR spectra ([BMIM]OTf (3 mL), -15.0-35.0 ppm region) of closed samples of Ph$_3$P (40.0 mM) over 168 hours, IL batch noted above each spectrum; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
To determine if the metal salt had an influence in the NMR of Ph$_3$P, the $^{31}$P-NMR spectra of a 1:1 mixture of LiNTf$_2$:Ph$_3$P in DMSO-d$_6$ were carried out (Fig. 5.20). However, in all the spectra, the Ph$_3$P peak remained at -6.85 ppm, with a second peak at 25.75 ppm increasing with time. From this, it appears that residual LiNTf$_2$ has no influence on the positioning of the Ph$_3$P peak. Further experiments to clarify the $^{31}$P NMR data of Ph$_3$P:I$_2$ or Ph$_3$P=O in the ILs were not carried out.

![Figure 5.20](image-url)

**Figure 5.20** $^{31}$P-NMR spectra (DMSO-d$_6$, -15.0-35.0 ppm region) monitoring a closed sample of Ph$_3$P and LiNTf$_2$ (1:1, 90.0 mM) over 168 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
Due to the differences observed between batch 1 with 2 and 3, assignments could not be made from the first batch. However, the work presented above highlights the need for ILs to be pure and/or for the researcher to know how it was made when performing work like this. To allow accurate determination of relative chemical shifts, an external reference consisting on a DMSO solution of DPPE in a capillary tube, was used in all samples. However, inconsistencies on the NMR spectra could be due to various factors, in addition to the presence of small amounts of impurities. For example, solvent-solute equilibrium can take a long time to achieve and so the chemical shifts at earlier times in batch 1 may
not be accurate.\textsuperscript{221} Also, the NMR spectra were not performed at a fixed temperature. As a change in temperature can affect viscosity, this in turn may affect the chemical shift.\textsuperscript{188,191–193} Using the second and third batches some conclusions can be made. For example, Ph$_3$P gives a singlet at around -6.9 ppm ([BMIM]OTf, batches 2 and 3), and this is in the same region as those in Table 5.1, entries 1-5. The NMR spectra of a solution of Ph$_3$P with added amounts of H$_2$O using the second batch of [BMIM]OTf in a sealed NMR tube (Fig. 5.17), shows the development of a peak \textit{ca.} 25.0 ppm. The expanded region is shown in Figure 5.21. Also, as the amount of H$_2$O increases this peak moves to a slightly higher chemical shift, \textit{e.g.} \textit{ca.} 26.0 ppm at 2.0 \% and \textit{ca.} 29.0 ppm at 10.0 \%. It is believed this peak is Ph$_3$P=O and the extra H$_2$O present accelerates the oxidation of Ph$_3$P (Table 5.1, entries 12-18). However, distinguishing between the phosphine oxide and its adduct by NMR is difficult as evidenced by Hilliard \textit{et al.}\textsuperscript{187} For example Ph$_3$P=O and Ph$_3$P=O.H$_2$O$_2$ were found to have chemical shifts of 29.10 ppm and 30.15 ppm respectively.

5.2.4 NMR spectra of Au dissolved in [BMIM]OTf

Figure 5.22 shows the $^{31}$P-NMR spectra of dissolved Au (57 mM) in [BMIM]OTf (batch 3) using Ph$_3$P:I$_2$ (1:1; 115 mM). A peak can be seen at \textit{ca.} 41.0 ppm that does not shift with time. As Au was observed to have dissolved and no other peaks exist it would appear to relate to a Au complex. Comparing the chemical shift to those in Table 5.1 (entries 22-28) it would seem to match the Au(I) species well, \textit{ca.} 39.0-41.0 ppm, particularly entry 22 (41.2 ppm).\textsuperscript{218–220} This also ties in with the use of 2 equivalents of Ph$_3$P:I$_2$ (1:1) and the excess or OTf$^-$ present as part of the IL. It is unknown if in this work a Au-PPh$_3$ species is directly interacting with OTf$^-$, but it is possible the surrounding IL anions are exerting an influence. The Au species present also appears particularly stable in the IL. For example, [AuI$_3$(PMe$_3$)$_2$] (20) as reported by Godfrey \textit{et al.}\textsuperscript{47} (Table 5.1, entry 24) exhibited two NMR peaks indicating that, in solution, the trigonal bipyramidal Au(III) complex dissociated into a square planar complex [AuI$_3$(PMe$_3$)] ($\delta = 30.1$ ppm) and free Me$_3$P ($\delta = -69.5$ ppm). In contrast only one peak is observed in [BMIM]OTf. It should be noted that in molecular solvents, the oxidation of Au with Me$_3$P:I$_2$ to form (20) has to
be carried out in strictly anhydrous and anaerobic conditions.\textsuperscript{47} However in this work, the dissolution of Au with Ph$_3$P:I$_2$ in [BMIM]OTf is done in air, and the resulting complex remains unchanged for a long period, as shown by the NMR spectra depicted in Figure 5.22. Remarkably it has been shown that the oxidation of Au powder can be carried out using phosphine/I$_2$ in air and at room temperature.

**Figure 5.22** $^{31}$P-NMR spectra (third [BMIM]OTf batch (10 mL), -15.0-35.0 ppm region) monitoring of a closed sample of Ph$_3$P:I$_2$ (1:1; 115 mM, 2 eq.) and Au (57.0 mM, 1 eq.) over 168 hours; internal reference = (28) in DMSO-d$_6$, -14.44 ppm
5.3 Cyclic Voltammetry

All the cyclic voltammograms (CVs) were performed using a three electrode cell set-up, a working electrode of glassy carbon, a Pt wire counter electrode, and a Ag/Ag\(^+\) reference consisting of a Ag wire immersed in a 0.1 M solution of AgNO\(_3\) in [BMIM]NO\(_3\). Two consecutive scans were run for all CVs, starting from the OCP towards the left (reduction) before reversing the scan. All CVs were carried out at room temperature as this was the temperature at which Au dissolution was performed. In order to de-gas the mixture, N\(_2\) was bubbled through for 15 minutes before raising the N\(_2\) tube to just above the solvent, ensuring a N\(_2\) layer prevented any atmospheric gases from dissolving and showing up on any CVs obtained. Unlike in Chapter 4, electrodeposition was carried out using the same three electrode set-up as cyclic voltammetry. The temperature was also room temperature and the voltage was held at a particular voltage in order for the metal to deposit. The work in Sections 5.3.1 and 5.3.2 were performed using the second batch of [BMIM]OTf while Sections 5.3.3, 5.4, and 5.5 were completed using the third batch.

5.3.1 Electrochemical Window (ECW) of [BMIM]OTf

The ECW of [BMIM]OTf is shown in Figure 5.23, using two sets of potential limits. The smaller window between -2.2 V and 1.8 V (ECW = 4.0 V, black) gives the cleaner scan. An ECW of 5.3 V (room temperature, over GC) has previously been reported for [BMIM]OTf\(^2\).
Figure 5.23 CVs showing the ECW of [BMIM]OTf; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Room temperature

5.3.2 Addition of Ph₃P:I₂ (1:1)

Ph₃P followed by I₂ (1:1) was dissolved in [BMIM]OTf to a concentration of 100 mM, and its CVs at room temperature are shown in Figure 5.24. In scan 1, a reduction peak appears at 0.13 V (peak I), followed by a second reduction peak at -0.76 V (peak II). When the scan changes direction, two oxidation peaks at 0.26 and 0.48 V (peaks III and IV respectively), showing a degree of overlapping, can be seen. The same peaks are
observed in the second, consecutive scan, but the intensity of I increases. The positive potential limit appears to be lower than that observed for the blank IL, \textit{i.e.} 1.4 V \textit{vs} 1.8 V.

![Diagram of CVs](image)

**Figure 5.24** CVs of Ph$_3$P:I$_2$ (1:1, 100 mM) in [BMIM]OTf; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Room temperature

In order to determine what the peaks correspond to, both I$_2$ and Ph$_3$P were dissolved independently in [BMIM]OTf (100 mM) and the voltammetry of the solutions performed. These are shown in Figures 5.25 and 5.26, respectively. The CVs of I$_2$ in [BMIM]OTf are comparable to that of the Ph$_3$P:I$_2$ mixture and the first scan also shows peaks I (0.16 V), II (-0.77 V), III (0.22 V) and IV (0.43 V). There is, however, an additional small oxidation peak at 1.35 V. In the second scan, both reduction peaks increase in intensity.
and shift slightly (I: 0.06 V, II: -0.81 V.) It was also found that the upper potential limit is 1.5 V, greater than that when Ph₃P:I₂ (1:1) is dissolved (1.4 V, Fig 5.24) but still less than the blank IL (1.8 V, Fig. 5.23). It may be a result of H₂O absorbed during the dissolution process.

Figure 5.25 CVs of I₂ (100 mM) in [BMIM]OTf; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Room temperature

As mentioned in Chapter 4, two reduction and two oxidation peaks with some degree of overlapping are expected for I/I₂/I₃⁻ redox systems.¹²²,¹²³ For example, Bentley et al.¹⁸¹,¹⁸² examined these in various imidazolium ILs, a pyrrolidinium IL, and two ammonium ILs, using a Pt macrodisk (1.6 mm diameter) working electrode, a Pt counter electrode, and
Ag wire for a pseudo reference. Reduction of I₂ to I⁻ (eq 5.1) occurred at the first wave followed by reduction of I⁻ to I⁻ (eq. 5.2). These reactions are then reversed by equations 5.3 and 5.4 respectively. An analogous assignment can be made for peaks I-IV observed in Figure 5.24. It is unknown what the peak at 1.35 V could be. The lower intensity of peak I in the first scans shows that free I₂ is not present in a large amount in the initial mixtures.

\[
\begin{align*}
3I_2 + 2e^- & \rightarrow 2I_3^- \quad \text{(eq. 5.1)} \\
I_3^- + 2e^- & \rightarrow 3I^- \quad \text{(eq. 5.2)} \\
3I^- & \rightarrow I_3^- + 2e^- \quad \text{(eq. 5.3)} \\
2I_3^- & \rightarrow 3I_2 + 2e^- \quad \text{(eq. 5.4)}
\end{align*}
\]

The CVs of Ph₃P (100 mM) in [BMIM]OTf are shown in Figure 5.26. Both scan 1 and 2 show a large, broad oxidation peak at 1.23 V. The negative potential limit occurs at -1.85 V, i.e. before the potential limit of -2.2 V observed with the blank IL (Fig. 5.23). Literature reports have shown that electrochemical oxidation of Ph₃P or Ph₃P complexes in various solvents results in the elimination of one electron to form Ph₃P⁺ (eq. 5.5).²²³ It was also found that traces of H₂O in the solvent can lead to Ph₃P being oxidised to Ph₃P=O (eq. 5.6).

\[
\begin{align*}
\text{Ph}_3\text{P} & \rightarrow \text{Ph}_3\text{P}^+ + e^- \quad \text{(eq. 5.5)} \\
3\text{Ph}_3\text{P} + \text{H}_2\text{O} & \rightarrow \text{Ph}_3\text{P=O} + 2\text{Ph}_3\text{PH}^+ + 2e^- \quad \text{(eq. 5.6)}
\end{align*}
\]

Tsierkezos and Ritter²²³ performed CVs of Ph₃P in acetonitrile, DCM, and cyclohexane. They used a working electrode of glassy carbon, a Pt plate for the counter electrode, and the reference was Ag/Ag⁺ (0.1 M NBu₄Cl in acetonitrile). An irreversible oxidation peak was observed at 1.3 V corresponding to the oxidation of Ph₃P to Ph₃P=O (eq. 5.6). No peak for the reverse process was observed. Another oxidation peak was also found that
related to the formation of \( \text{PH}_3\text{P}^+ \) (eq. 5.5) with a reduction peak in the reverse process. According to this, the peak at 1.23 V in Figure 5.26 would correspond to equation 5.6, as there is no related reduction peak. It also makes sense due to the \( \text{H}_2\text{O} \) content noted in the IL (\textit{i.e.} 0.611 Wt%).

**Figure 5.26** CVs of \( \text{PH}_3\text{P} \) (100 mM) in [BMIM]OTf; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag\(^+\) (0.1 M AgNO\(_3\) in [BMIM]NO\(_3\)), Scan rate = 50 mV s\(^{-1}\), Room temperature

From the above CVs it is clear that on dissolution of \( \text{PH}_3\text{P}:\text{I}_2 \) (1:1) in [BMIM]OTf (Fig. 5.24) the electrochemical behaviour is dominated by that of \( \text{I}_2 \) (Fig. 5.25) which is reduced to \( \text{I}^- \) in two steps before the scan is reversed. A clear peak around 1.2 V for the oxidation
of phosphine, like that in Figure 5.26, is not seen, but the broad wave could be hidden in the region after peak IV (Fig. 5.24).

5.3.3 Dissolution of Au

Au was dissolved in [BMIM]OTf to a concentration of 56 mM using \( \text{Ph}_3\text{P}:\text{I}_2 \) (1:1) (116 mM). CVs were then carried out using a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/Ag\(^+\) reference of 0.1 M AgNO\(_3\) in [BMIM]NO\(_3\). These were performed at room temperature with potential limits between -2.5 V and 1.1 V and are shown in Figure 5.27.

As can be observed in Figure 5.27 there are many reduction and oxidation peaks present. At the start of scan 1, a reduction peak is present at -0.90 V (peak II). As the scan progresses a further peak is present at -1.54 V (peak V) followed by two smaller peaks at -1.89 V (peak VI) and -2.18 V (peak VII). In the reverse scan, a small oxidation peak is then observed at -1.3 V (peak VIII), followed by larger waves at -0.1 V (peak IX), 0.31 V (peak III) and 0.67 V (peak IV). As this scan changes direction, a reduction peak appears at 0.06 V (I). In scan 2, peaks II and V are observed at less negative potentials (-0.66 V and -1.45 V, respectively), with peak V also being of a lower intensity. At -1.81 V and -2.16 V are peaks VI and VII respectively, both at a slightly more positive potential than in the first scan. After the second scan changes direction there is no clear indication of peak VIII being present. The following three oxidation peaks however are still present, at -0.12 V (peak IX), 0.28 V (peak III), and 0.64 V (peak IV), also followed by I (0.06 V). By comparison with the CVs shown in Figures 5.24-5.25, four of the peaks can be related to I\(_2\) (or \( \text{Ph}_3\text{P}:\text{I}_2 \)). Therefore peak I would correspond to the reduction of I\(_2\) to I\(^-\), followed by formation of I\(_3^-\) as shown in equation 5.1; whereas peak II would relate to the reduction of I\(_3^-\) to I\(^-\) (eq. 5.2). The reverse process (eq. 5.3) is then assigned to peak III. Equation 5.4, which shows the regeneration of I\(_2\), is assigned to peak IV. This latter peak, however, is shifted with respect to peak VII in Figures 5.24 and 5.25 and is also more intense, indicating that it could be overlapped with another oxidation process, although the actual nature of this is still unclear.
To determine which of the remaining peaks are associated with each other, the negative potential limit was varied (Fig. 5.28). It can be observed that setting the negative potential limit at -2.1 V (blue), just before peak VII, also removes peak VIII (Fig. 5.27). It also shows a new small oxidation peak at -1.60 V in the first scan and then at -1.52 V in the second. Reversing the scan at -1.8 V (red), which is just before peak VI, removes the new oxidation peak at ca. -1.55 V. These sets of scans show that peak IX is solely related to peak V as its intensity is the same in the scans including or excluding peak VI. Peak IX is not present when the negative potential limit is set at -1.2 V (before peak V). This leaves only the peaks associated mainly with Ph$_3$P:I$_2$ (1:1).
Figure 5.28 CVs of Ph$_3$P:I$_2$ (1:1, 116 mM) and Au (56 mM) in [BMIM]OTf with varied negative potential limits; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Room temperature

Typically, the electrochemistry of Au involves either one reduction peak if it is Au(I), or two reduction peaks if it is Au(III) whereby it is first reduced to Au(I), e.g. eqs 5.7-5.8. However, there are occasions when Au(III) results in one three-electron reduction, e.g. eq. 5.9, as evidenced by Fu et al.,$^{224}$ who used a H$_2$O in [BMIM]PF$_6$ microemulsion to dissolve H[AuCl$_4$] and observed a single reduction peak at 0.059 V vs. Ag/AgCl over a GC working electrode. The Au(III) salt, H[AuCl$_4$], dissolved in the H$_2$O dispersed
throughout the liquid. H$_2$O nanopools then meet the working electrode surface via Brownian motion and Au(III) gets reduced to Au(0). The reaction stops when the nanopools, which have a surfactant coating, have dispersed from the electrode surface. Kaminska et al.$^{225}$ also reported a single reduction peak for H[AuCl$_4$] in [C$_{10}$MIM]NTf$_2$, over an indium tin oxide (ITO) working electrode.

\[ \text{[AuCl}_4]\text{]}^{-} + 2e^{-} \rightleftharpoons \text{[AuCl}_2]\text{]}^{-} + 2\text{Cl}^{-} \quad \text{(eq. 5.7)} \]

\[ \text{[AuCl}_2]\text{]}^{-} + e^{-} \rightleftharpoons \text{Au} + 2\text{Cl}^{-} \quad \text{(eq. 5.8)} \]

\[ \text{[AuCl}_4]\text{]}^{-} + 3e^{-} \rightleftharpoons \text{Au} + 4\text{Cl}^{-} \quad \text{(eq. 5.9)} \]

\[ 3\text{[AuCl}_2]\text{]}^{-} \rightleftharpoons \text{[AuCl}_4]\text{]}^{-} + 2\text{Au} + 2\text{Cl}^{-} \quad \text{(eq. 5.10)} \]

Oyama et al.$^{119,120}$ studied the reduction of Au(III) to Au(0) using Na[AuCl$_4$] in [EMIM]BF$_4$ and observed two reduction peaks corresponding to equation 5.7 followed by 5.8. The authors also reported that a disproportionation reaction occurred (eq. 5.10) and once the Au(0) was on the glassy carbon working electrode, the reduction of [AuCl$_4$]$^-$ can then occur more easily. The electrochemistry of Na[AuCl$_4$] has also been investigated in [BMIM]NTf$_2$, over gold, platinum or glassy carbon working electrodes.$^{121}$ In all cases, two reduction peaks are obtained. As mentioned in other studies, the second reduction peak shifted to more positive potentials after the first scan on GC and Pt electrodes, i.e. the reduction of Au(I) shifts due to deposition of Au taking place on active gold deposits formed on the electrode surface during the first scan. Monzon et al.$^{226}$ investigated the electrochemistry of K[AuCl$_4$] in DMSO-d$_6$ and [TBMA]NTf$_2$ (tributylmethylammonium bis(trifluoromethylsulfonyl)imide), reporting two reduction peaks associated with equations 5.7 and 5.8, but also evidence of a third process. This third reduction peak was attributed to reactivation of the working electrode by removing inhibitory species. This then frees the electrode for further reduction processes to occur. Yang et al.$^{206}$ examined the reduction of K[Au(CN)$_2$] in [OMIM]PF$_6$ over a glassy carbon working electrode and
noted two peaks. The first was assigned to the reduction of [Au(CN)\(_2\)]\(^-\) to AuCN\(_{ads}\). The second peak was then assigned to the direct reduction of [Au(CN)\(_2\)]\(^-\) to Au(0).

\[
\text{Au} + 2 \text{Ph}_3\text{PI}_2 \rightarrow [\text{AuI}_3(\text{PPh}_3)_2] + \frac{1}{2} \text{I}_2 \quad (\text{eq. 5.11})
\]

The Au dissolution process in [BMIM]OTf using Ph\(_3\)P:I\(_2\) appears to see the formation of [Au(PPh\(_3\))\(_2\)]OTf according to the NMR results in Section 5.2.4. Another possibility is [AuI\(_3\)(PPh\(_3\))\(_2\)] formed according to eq. 5.11. It has also been described that a similar Au(III) complex, (20), can react with excess H\(_2\)O to form the Au(I) species [(Me\(_3\)PO)\(_2\)H][AuI\(_2\)].\(^{47}\) In this case [(Ph\(_3\)PO)\(_2\)H][AuI\(_2\)] may form from [AuI\(_3\)(PPh\(_3\))\(_2\)] reacting with excess H\(_2\)O in the IL. It is believed that peaks V and IX are related to reduction/oxidation of gold species, but is unknown whether it is the direct reduction of Au(III) to Au(0) or the reduction of a Au(I) complex chemically formed in the mixture (e.g. [Au(PPh\(_3\))\(_2\)]OTf or [(Ph\(_3\)PO)\(_2\)H][AuI\(_2\)]). The nature of the smaller peaks VI and VII is unclear at this stage and a full assignment will require further work. They may be related to impurities present in the mixture, to Au(I) species adsorbed onto the working electrode (e.g. AuI) or to other metal complexes formed in the solution. The shift observed in the reduction peaks during the second consecutive scan (see Fig. 5.27, peaks II and V) is likely to be related to formation of Au deposits during the first scan which are not fully stripped during the oxidation scan, as discussed above and previously observed in other ILs.\(^{119–121}\)

### 5.4 Electrodeposition

After successfully dissolving Au (56.0 mM) and performing CVs (Fig. 5.27) in [BMIM]OTf, using Ph\(_3\)P:I\(_2\) (116 mM), electrodeposition was carried out. Ph\(_3\)P was first dissolved in the IL, followed by I\(_2\) (1:1). A potential of -2.0 V was chosen and held for a total of 144 hours separated into periods of 24 hours. After each period, the working electrode was taken out and rinsed with deionised H\(_2\)O in order to remove Au deposits. It
should be noted that very little Au was present on the electrode for the last two deposition periods and so the process was stopped as it appeared that most of the metal had been recovered. After the deposit suspended in H₂O had settled, typically overnight, the H₂O was removed. Acetone was then used to rinse the metal thoroughly before drying at 110 °C for 15 minutes. The recovered deposits were clear golden yellow as shown in Figure 5.29. Approximately 53% of dissolved Au was recovered but some loss may have occurred during the transfer and cleaning processes. EDX analysis and SEM images of the recovered metal are shown in Figures 5.30 and 5.31, respectively. The EDX data shows that the deposit is formed by 100 Wt% Au.

**Figure 5.29** Au deposits on the glassy carbon electrode and collected metal after rinsing the electrode with deionised H₂O

Figure 5.31 shows that the Au deposit consists of flat ‘flakes’ on one side and globular particles on the other. This is similar in a way to the deposit obtained for Pd but is more structurally intact as removal from the electrode was easier. The SEM image shown in Figure 5.31 is similar to that reported by Fu et al. on the deposit formed upon electrodeposition of Au from H₂O in [BMIM]PF₆ microemulsions, e.g. composed of Au nanoparticles of approximately 25 nm. The morphology of the deposits obtained herein can also be related to those reported by Yang et al. who described the Au deposit obtained from [OMIM]PF₆ as globular and uniformly flat on the working electrode.
Figure 5.30 EDX data showing elemental make up of Au deposit

Figure 5.31 SEM of Au deposit at a magnification of x2075

Bozzini et al.\textsuperscript{118} studied the morphology of Au deposits (from K[Au(CN)\textsubscript{2}] in [EMIM]NTf\textsubscript{2}) obtained after varying deposition times using SEM. After 20 minutes, the
deposits had a dendritic morphology of nanoscale spheroidal grains. After 60 minutes, the grains appear to expand to form what the authors call ‘micrometric islands’, and finally, micrometric acicular grains are observed after 180 minutes. It is believed that in this work formation occurs via the ‘nanoreactors’ formed between H$_2$O and the IL. When combined with the high voltage this leads to a dense deposit initially on the glassy carbon. Once complete a new layer seems to form on top. On completion of electrodeposition, CVs were performed to check for removal of Au (Fig. 5.32). Probably due to absorption of H$_2$O during the deposition process the ECW appears to have shortened to around -1.3 V but the negative potential was kept at -2.5 V for comparison with the CVs in Figure 5.27.

![Graph](image)

**Figure 5.32** CVs of the solution that remained after electrodeposition of Au from a solution initially containing Ph$_3$P:I$_2$ (1:1, 116 mM) and Au (56.0 mM) in [BMIM]OTf; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 50 mV s$^{-1}$, Room temperature
In scan 1 there is a reduction peak at -0.84 V (peak II) followed by a small wave at -1.45 V (peak V). Two oxidation peaks appear at 0.31 and 0.64 V (peaks III and IV respectively). Before completion of the first scan a reduction peak is also observed at -0.04 V (peak I). There are only some small variations in the second scan. By comparison with the scans shown in Fig. 5.27, it is clear that peaks V and VII are not significant after the electrodeposition process, and the peaks remaining relate mainly to Ph₃P:I₂ (1:1) as discussed in 5.3.2. The two waves seen at the most negative potentials in Fig. 5.32, believed to be Au related, indicate that not all of the metal had been recovered. This was expected as it was mentioned earlier how very little Au was deposited in the last two periods and that the process had to be stopped before completion. After this, the remaining solution was taken for re-use at dissolving a fresh Au sample (42.7 mg, 2.17x10⁻⁴ moles, 54 mM). Within 72 hours, and without the addition of Ph₃P:I₂ (1:1), the Au dissolved. No CVs could be performed due to loss of solvent over time as electrodes are moved and changed.

5.5 Recovery of Au metal from an electronic device

In order to test the effectiveness of Ph₃P:I₂ (1:1)/[BMIM]OTf as a tool for recovery of Au, the system was used on several spare electronics that were available. This included 2 SIM cards, 2 RAM cards, and a printer cartridge. One of each of the SIM and RAM cards were kept intact to allow a visual comparison. The other three items (the RAM card had to be broken up to allow everything to fit) were added to a beaker containing the dissolved Ph₃P followed by I₂ (1:1, 116 mM) in [BMIM]OTf (4 mL).

Figure 5.33 Comparison of SIM cards; left – not treated with Ph₃P:I₂ (1:1)/[BMIM]OTf, right - treated with Ph₃P:I₂ (1:1)/[BMIM]OTf
Everything was left stirring for 96 hours (extra time given to increase likelihood of Au dissolving) at room temperature. Removal of the items provided visual evidence that some metal had dissolved from the SIM (Fig. 5.33) and RAM cards (Fig. 5.34). There was no obvious change in the cartridge electronic strip. CVs were then performed on the resulting solution (Fig. 5.35). These were carried out between -2.5 and 1.1 V and are quite different to those shown in Figure 5.27. In the first, as it sweeps left toward the negative limit the first reduction peak is present at -1.60 V (possibly related to peak V due to position but size of oxidation peaks mean it could be a different metal), with no peaks related to the reduction of I\(_2\) or I\(^-\) observed at this stage. After changing direction, a nucleation loop appears, followed by two oxidation peaks at -0.82 and -0.69 V (peaks XI and XII respectively). Two more oxidation peaks are present further on at 0.27 (peak III) and 0.73 V (peak IV). As the second scan begins, two new reduction peaks can be seen at -0.48 and -0.89 V (peaks X and II) with a third further down at -1.64 V. There is also a hint of a fourth at -2.12 V. On the return sweep oxidation peaks can be found at -0.84 (XI) and -0.75 V (XII) with two more at 0.26 (III) and 0.70 V (IV).
Figure 5.35 CVs of a solution of Ph₃P:I₂ (1:1, 116 mM) in 4 mL of [BMIM]OTf after stirring for 96 hours at r.t. in the presence of electronics electronic devices; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Room temperature

The peaks at -0.48 and -0.89 V are approximately in the same positions as the reduction peaks observed for the I₂/I₃⁻/I⁻ system (see above, e.g. Fig. 5.27). The oxidation peaks ca. 0.27 and 0.72 V may then relate to the corresponding oxidation reactions. The reduction process at ca. -1.6 V is likely to relate to metal electrodeposition, with associated oxidation peaks at -0.82 and -0.69 V. However, at this stage the exact origin of these peaks is unclear and it may be that the peaks ca. -1.6 V and -2.12 V are related to Au as they are similar to those for peaks V (-1.54 V) and VII (-2.18 V) but the CVs in Figure 5.35 do not contain peak VI (Fig. 5.27), attributed to Au stripping.
Figure 5.36 Metal deposit formed on the glassy carbon electrode upon electrodeposition was carried out at -2.3 V on the solution obtained after treating electronic devices with Ph³P/I₂/[BMIM]OTf

On completion of the CVs, electrodeposition was performed on the sample at a potential of -2.3 V, using a glassy carbon plate as the working electrode. The process was carried out for 18 hours. The same electrode cleaning procedure as that described in section 5.4 was employed. The deposited material on the electrode is shown in Figure 5.36. It is not as obvious that Au is present as it is in Figure 5.29, but towards the bottom of the electrode (right hand side) there is a yellow deposit which could be recovered Au. The deposit was analysed by SEM (Fig. 5.37) and EDX (Fig. 5.38).

Figure 5.37 SEM of the metal deposit shown in Figure 5.36
The SEM image shows a deposit consisting largely of grains with some small particles on top, somewhere between the grains and islands described by Bozzini et al.\textsuperscript{118} EDX data shows that the deposit is composed mainly of Sn and O, suggesting that an oxide of Sn is present. Au is also listed on the EDX as 0.0 Wt\%. It could be that a tiny amount of Au is present and is enough for Au to be detected but not enough for a reading of its Wt\%. At this point in time it is unknown if Au has been dissolved and recovered. Figure 5.34 does suggest Au has been removed and 5.26 suggests it has been deposited but the EDX seems to counter this. The main electrodeposition peak at -1.6 V (Fig. 5.35) seems therefore to correspond to the reduction of various metals, but according to the EDX results, it may be dominated by the formation of Sn. For example, it has been shown that the cyclic voltammetry of SnO\textsubscript{2} shows a single reduction peak from Sn(IV) to Sn(0), and two oxidation peaks for Sn(0) to Sn(II) and Sn(II) to Sn(IV).\textsuperscript{227}

![Map Sum Spectrum]

**Figure 5.38** EDX data of the deposit shown in Figures 5.36 and 5.37

CVs were carried out on the remaining solution after electrodeposition (Fig. 5.39). The first scan has reduction peaks at -0.97 (peak II), -1.64, -1.99, and -2.17 V. Oxidation peaks appear at -0.69 V (XII, with a shoulder to its left), 0.21 V (III) and \textit{ca.} 0.7 V (broad wave).
At the beginning of the second scan there is a new reduction peak at -0.50 V (X). The rest of the peaks are similar to those in the first scan.

![Graph showing CVs of the remaining solution following electrodeposition at -2.3 V (18 hours) from the solution used to dissolve metals from electronic devices (CVs of the initial solution are shown in Fig. 5.35); working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag⁺ (0.1 M AgNO₃ in [BMIM]NO₃), Scan rate = 50 mV s⁻¹, Room temperature. The peak ca. -1.68 V is less intense than that reported in Figure 5.35 indicating that this indeed relates to metal deposition (possibly Sn). Its presence indicates not all metal has been removed from the solution. There has also been a reduction in one of the oxidation peaks highlighting the relationship between this process and the reduction at -1.68 V. It]
is not possible to fully assign the processes observed without further investigation, given the complexity of the solution composition. However, it is noted, that two small reduction peaks \(ca. -1.97\) and \(-2.18\) V can be seen in Figure 5.39, and may be associated with Au, \(i.e.\) peaks VI and VII in Figure 5.27.

5.6 Conclusions

The \(^{31}\text{P}\)-NMR investigation shows that the NMR of Ph\(_3\text{P}\) and its derivatives is dependent on the batch of [BMIM]OTf used. This may be due to small amounts of impurities undetected by NMR. Using NMR to determine successful synthesis of Ph\(_3\text{P}:\text{I}_2\) (1:1) is therefore difficult but results show that overtime, Ph\(_3\text{P}:\text{I}_2\) (1:1) appears to be oxidised to Ph\(_3\text{P} = \text{O}\) which itself can interact with H\(_2\)O. Despite this, the Ph\(_3\text{P}:\text{I}_2\) mixture in the IL is able to dissolve Au at r.t. without the need of anhydrous/anaerobic conditions, in contrast to that observed in conventional solvents. The nature of the Au complex formed in the solutions has not been confirmed but it seems to be a unique, stable product, \(i.e.\) it gives a singlet in its \(^{31}\text{P}\)-NMR spectrum which does not change with time. Possible species include [Au(PPh\(_3\))\(_2\)]OTf, [Au\(_3\)(PPh\(_3\))\(_2\)] or [(Ph\(_3\)PO)\(_2\)H][AuI\(_2\)]. CVs of Ph\(_3\text{P}:\text{I}_2\) (1:1) in [BMIM]OTf show that its electrochemical behaviour is dominated by that of I\(_2\). Initial studies of the CVs of dissolved Au in these mixtures show one main reduction and oxidation peak related to the deposition and stripping of the metal, respectively. Approximately 53\% of Au was successfully recovered through an electrodeposition process and the remaining solution was successfully re-used for further Au dissolution. Work has also been carried out investigating whether Au can be recovered from electronic devices. Using Ph\(_3\text{P}:\text{I}_2\) in [BMIM]OTf, metals could be dissolved from the devices and subsequently electrodeposited, but EDX data showed that the main component of the deposit was Sn. Results were inconclusive if Au had also been deposited. Overall, it has been proven that Au(0) can be dissolved and recovered at mild conditions and that the IL mixture can be recycled. There is also potential to recover Au from spare electronics.
5.7 Future Work

In order to develop a greater level of understanding on what is occurring herein, the investigations and studies described could be further expanded in several ways. For example:

- A more in-depth NMR study in order to clarify the behaviour of phosphines in ILs and the nature of the Au species formed, involving for example other ILs and NMR characterisation of isolated Au complexes.
- Cyclic voltammetry of different Au(I) and (III) salts in order to better map the redox processes observed and the nature of the Au compounds formed in the solutions.
- Further investigate the recyclability of the systems. So far, the IL mixture was successfully re-used once but no CVs could be performed as solvent was lost over time with the electrodes being moved and changed. In addition, the nature of the deposit obtained at various electrodeposition potentials could be explored, in order to identify the origin of the reduction peaks at ca. -1.5 V.
- Test the use of non-imidazolium ILs, e.g. pyridinium, pyrrolidinium, or ammonium ILs.
Chapter 6. Experimental

I₂, Ph₃P, dimethyl oxalate (3), N,N’-dimethylethylenediamine (4), N,N’-dimethyl-1, 3-propanediamine (5), choline chloride (21), urea (22), ethylene glycol (23), imidazole (24), and 2, 2'-bipyridine (26), 1, 10-phenanthroline (27), 1, 2-bis(diphenylphosphino)ethane (28), ethylenediaminetetraacetic acid (29), ethylene diamine (30), 1, 4-bis(diphenylphosphino)butane (31), 1, 6-bis(diphenylphosphino)hexane (32) were all bought from Sigma-Aldrich and used as received. Lawesson’s Reagent (8), Pd powder, Pt powder and wire, and Au powder were obtained from Alfa Aesar and used as received. ¹H and ¹³C NMR spectra were run on either a Bruker Advance DPX 300 (Chapter 2) or a DPX 400 (Chapter 4). SiMe₄ was used as standard. ³¹P NMR spectra (Chapter 4) were carried out using a capillary containing dimethyl sulfoxide (DMSO) as the solvent, and (28) as an internal reference. Infra-red spectra (IRs) were carried out on a Perkin Elmer Spectrum Two IR Spectrometer. Electronic Absorption spectra (UV-Vis) were run using a Perkin Elmer UV/Vis Spectrometer Lambda 300 or an Agilent Technologies Cary 60 UV-Visible Spectrophotometer. PXRD patterns were obtained using a PANalytical X’Pert PRO with a TCU 750 Temperature Control Unit. The scan range of the XRD was 5 – 50° and the wavelength was Cu K-Alpha1 (1.5405980 Å). SEM images were obtained using a Panalytical X’Pert Highscore Version 1. This was also used for EDX, alongside the Aztec 2.0 software. Cyclic voltammetry experiments were carried out using a µAutolab III potentiostat/galvanostat which used the GPES program in the Autolab 4.9 software. Electrodeposition was performed using an EG&G Princeton Applied Research potentiostat/galvanostat Model 273A alongside the Electrochemistry Power Suite Software. CHNS was performed in ASEP (School of Chemistry, Queen’s University Belfast) using a Perkin Elmer 2400 CHN microanalyser (measures C, H, N, S/O). H₂O content was determined via Karl Fisher titration using a Metrohm 899 Coulometer connected to a Metrohm 803 Ti Stand, and Raman spectra were obtained using a Perkin Elmer Raman Station 400F Raman Spectrometer (350 mW near infrared 785 nm laser), both performed in QUILL (School of Chemistry, Queen’s University Belfast). Mechanochemical experiments were carried out using a Retsch mm400 shaker ball mill.
(Fig. 6.1), the microwave experiments used a CEM Discover microwave reactor (Fig. 6.2), and the sonochemical experiments used a VWR ultrasonic cleaner sonic bath (Fig. 6.3).

**Figure 6.1** Shaker ball mill (Retsch mm400) used in this work

**Figure 6.2** Microwave reactor (CEM Discover) used in this work

**Figure 6.3** Sonic bath (VWR ultrasonic cleaner) used in this work
6.1 Synthesis of Me<sub>2</sub>pipd (1)

![Chemical structure](image)

6.1.1 Conventional Synthesis

(3) was added to a three-necked round bottom flask containing a stirring bar and septum. A condenser was attached before evacuating with N<sub>2</sub> three times. Dry toluene was added via a syringe followed by (4). The reaction mixture was refluxed for 2 hours, and then cooled to room temperature. Toluene was then removed under vacuum before recrystallizing the crude product from hot toluene. The product was then filtered and dried. The amounts of reagents used and yields were reported in Table 2.1 (Chapter 2).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 3.56 (s, 4H, CH<sub>2</sub>), 3.10 (s, 6H, CH<sub>3</sub>)

![NMR spectrum](image)

**Figure 6.4** <sup>1</sup>H-NMR spectrum of (1), obtained via conventional synthesis, in CDCl<sub>3</sub>
$^{13}$C-NMR (300 MHz, CDCl$_3$): δ 157.67 (C=O), 46.28 (CH$_2$), 35.14 (CH$_3$)

**Figure 6.5** $^{13}$C-NMR spectrum of (1), obtained via conventional synthesis, in CDCl$_3$

**Figure 6.6** IR spectrum of (1), obtained via conventional synthesis
Figure 6.7 UV/Vis spectrum of (1), obtained via conventional synthesis

Figure 6.8 PXRD pattern of (1), obtained via conventional synthesis

Table 6.1 Calculated and found CHNO elemental analysis of (1), obtained via conventional synthesis

<table>
<thead>
<tr>
<th></th>
<th>Calculated for C₆H₁₀N₂O₂/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>50.69</td>
<td>7.09</td>
</tr>
</tbody>
</table>

*a: The compound was not obtained analytically pure*
6.1.2 Mechanochemical Synthesis

(3) (0.2194 g, 1.86 mmol) was added to a 25 mL ball mill jar. If used, toluene (0.2 mL, 1.89 mmol) was then added, followed by (4) (0.2 mL, 1.86 mmol). A stainless steel ball, weighing 13.6 g and 11 mm in diameter, was added and the jar sealed. This is attached to the ball mill (Fig. 6.6) and the conditions set. After reaction is complete, toluene (5 mL) is added. The jar is shook and the toluene suspension is transferred to a sample vial. This is repeated once more. The remaining solid in the jar is collected and transferred to the vial. This is stirred for 15 minutes to ensure the product is successfully washed. It is first filtered before drying under vacuum. The amounts of reagents used and yields were reported in Table 2.2 (Chapter 2).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.56 (s, 4H, CH$_2$), 3.10 (s, 6H, CH$_3$)

![Figure 6.9 $^1$H-NMR spectrum of (1), obtained via mechanochemical synthesis, in CDCl$_3$](image-url)
$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 157.68 (C=O), 46.27 (CH$_2$), 35.15 (CH$_3$)

**Figure 6.10** $^{13}$C-NMR spectrum of (1), obtained via mechanochemical synthesis, in CDCl$_3$

**Figure 6.11** PXRD pattern of (1), obtained via mechanochemical synthesis
It is unknown if the differences observed relate to H\textsubscript{2}O present in the sample.

**Table 6.2** Calculated and found CHNO elemental analysis of (1), obtained via mechanochemical synthesis\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>Calculated for C\textsubscript{6}H\textsubscript{10}N\textsubscript{2}O\textsubscript{2}/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50.69</td>
<td>48.82</td>
</tr>
<tr>
<td>H</td>
<td>7.09</td>
<td>6.56</td>
</tr>
<tr>
<td>N</td>
<td>19.71</td>
<td>19.00</td>
</tr>
<tr>
<td>O</td>
<td>22.51</td>
<td>25.62</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The compound was not obtained analytically pure

6.2 Synthesis of Me\textsubscript{2}pipdt (6)

6.2.1 Conventional Synthesis

Compound (1) was prepared *in situ* in some cases. For this, (3) was added to a round bottom flask containing a stirring bar and septum. A condenser was attached before evacuating with N\textsubscript{2} three times. Dry toluene was added via a syringe followed by (4). The reaction mixture was refluxed for 2 hours, and then cooled to room temperature. (8) was then added and the mixture refluxed (See Table 2.3, Chapter 2). The toluene was removed under vacuum leaving a dark brown solid, which was dissolved in DCM before adding ethanol (4:1). The mixture was concentrated under vacuum, precipitating (6) as a dark red powder. It is first filtered before drying under vacuum. The amounts of reagents used and yields were reported in Table 2.3.

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \( \delta \) 3.74 (s, 4H, CH\textsubscript{2}), 3.58 (s, 6H, CH\textsubscript{3})
Figure 6.12 $^1$H-NMR spectrum of (6), obtained via conventional synthesis, in CDCl$_3$

$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 186.68 (C=S), 49.41 (CH$_2$), 44.88 (CH$_3$)

Figure 6.13 $^{13}$C-NMR spectrum of (6), obtained via conventional synthesis, in CDCl$_3$
Figure 6.14 IR spectrum of (6), obtained via conventional synthesis

Figure 6.15 UV/Vis spectrum of (6), obtained via conventional synthesis
Figure 6.16 PXRD pattern of (6), obtained via conventional synthesis

Table 6.3 Calculated and found conventional CHNS elemental analysis of (6), obtained via conventional synthesis

<table>
<thead>
<tr>
<th>Calculated for C$<em>6$H$</em>{10}$N$_2$S$_2$/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>41.35</td>
<td>5.78</td>
</tr>
</tbody>
</table>

6.2.2 Attempts to prepare (6) mechanochemically
(1) (0.2742 g, 1.93 mmol) was added to a 25 ml ball mill jar. If used, toluene (0.4 mL, 3.78 mmol) was then added, followed by (8) (1.5608 g, 3.86 mmol). Either a stainless steel ball, weighing 13.6 g and 11 mm in diameter, or three steel balls weighing 4.03 g and 9 mm in diameter, were added and the jar sealed. This was attached to the ball mill and the conditions set (15 Hz, 4 hours). None of the attempts were successful.

6.2.3 Microwave Synthesis
To a beaker is added (8) (0.4505 g, 1.0 mmol) and (1) (0.0711 g, 0.5 mmol). The solids are then thoroughly mixed before transferring to a glass test tube containing toluene (1 mL). More toluene (5 mL) is then used to rinse the beaker and added to the test tube. This
is then placed in the microwave reactor (Fig. 6.15) and the reaction parameters set (See Table 2.4, Chapter 2).

6.2.4 Sonochemical Synthesis

A sonic bath (Fig. 6.16) was set to a temperature of 80 °C and a power of 9. Compounds (8) and (1) are thoroughly mixed in a beaker before transferring to a round bottom flask containing toluene (1 mL). The beaker is then rinsed with toluene (9 mL) before adding. This is then placed in the bath and the reaction run for 4 hours. The toluene was removed under vacuum leaving a dark brown solid, which was dissolved in DCM and ethanol (4:1). The mixture was concentrated under vacuum, resulting in the precipitation of (6) as a dark red powder which was filtered and dried. The amounts of reagents used and yields were reported in Table 2.1 (Chapter 2).

\[ ^1\text{H-NMR (300 MHz, CDCl}_3\text{): } \delta 3.74 (s, 4H, CH}_2\text{), 3.58 (s, 6H, CH}_3\text{) } \]

Figure 6.17 \( ^1\text{H-NMR spectrum of (6), obtained via sonochemical synthesis, in CDCl}_3\text{) } \]
$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 186.65 (C=S), 49.40 (CH$_2$), 44.88 (CH$_3$)

**Figure 6.18** $^{13}$C-NMR spectrum of (6), obtained via sonochemical synthesis, in CDCl$_3$

**Figure 6.19** PXRD pattern of (6), obtained via sonochemical synthesis
Table 6.4 Calculated and found sonochemical CHNS elemental analysis of (6), obtained via sonochemical synthesis

<table>
<thead>
<tr>
<th>Calculated for C₆H₁₀N₂S₂/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>41.35</td>
<td>5.78</td>
</tr>
</tbody>
</table>

*a: The compound was not obtained analytically pure*

6.3 Synthesis of Me₂dazd (2)

![Chemical structure](image)

6.3.1 Conventional Synthesis

(3) was added to a three-necked round bottom flask containing a stirring bar and septum. A condenser was attached before evacuating with N₂ three times. Dry toluene (20 mL) was added via a syringe followed by (5). The reaction mixture was heated to reflux and then cooled to room temperature. The toluene was removed under vacuum and the precipitated product recrystallized from toluene. The amounts of reagents used, reaction times, and yields were reported in Table 2.6 (Chapter 2).

¹H-NMR (300 MHz, CDCl₃): δ 3.41 (t, 4H, ³J=6.3 Hz, NCH₂), 3.05 (s, 6H, CH₃), 1.99 (qnt, 2H, ³J=6.3 Hz, CH₂)
Figure 6.20 $^1$H-NMR spectrum of (2), obtained via conventional synthesis, in CDCl$_3$

$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 164.84 (C=O), 45.88 (NCH$_2$), 33.61 (CH$_3$), 26.26 (CH$_2$)

Figure 6.21 $^{13}$C-NMR spectrum of (2), obtained via conventional synthesis, in CDCl$_3$
Figure 6.22 IR spectrum of (2), obtained via conventional synthesis

Figure 6.23 UV/Vis spectrum of (2), obtained via conventional synthesis
Table 6.5 Calculated and found conventional CHNO elemental analysis of (2), obtained via conventional synthesis

<table>
<thead>
<tr>
<th>Calculated for C7H12N2O2/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>53.83</td>
<td>7.74</td>
</tr>
</tbody>
</table>

*a: The compound was not obtained analytically pure. Calculated C7H12N2O2:2H2O (5:2): C = 51.46%, H = 7.9%, N = 17.15%, O = 23.5%*

6.3.2 Mechanochemical Synthesis

(3) (0.1880 g, 1.59 mmol) added to a 25 mL ball mill jar. Toluene (0.17 mL, 1.61 mmol) added followed by (5) (0.2 mL, 1.60 mmol). A stainless steel ball, weighing 13.6 g and 11 mm in diameter, was added and the jar sealed. This is attached to the ball mill (Fig. 6.6) and the conditions set. After reaction is complete, toluene (5 mL) is added. The jar is shook and the toluene is transferred to a sample vial. This is repeated once more. The remaining solid in the jar is collected and transferred to the vial. This is stirred for 15 minutes to ensure the product is successfully washed. It is first filtered and then dried under vacuum. The amounts of reagents used, reaction times, and yields were reported in Table 2.7 (Chapter 2).

![Figure 6.24 PXRD pattern of (2), obtained via conventional synthesis](image)
$^{1}$H-NMR (300 MHz, CDCl$_3$): δ 3.41 (t, 4H, $^{3}$J=6.3 Hz, NCH$_2$), 3.05 (s, 6H, CH$_3$), 1.99 (qnt, 2H, $^{3}$J=6.3 Hz, CH$_2$)

Figure 6.25 $^{1}$H-NMR spectrum of (2), obtained via mechanochemical synthesis, in CDCl$_3$
$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 164.84 (C=O), 45.61 (NCH$_2$), 33.62 (CH$_3$), 26.26 (CH$_2$)

**Figure 6.26** $^{13}$C-NMR spectrum of (2), obtained via mechanochemical synthesis, in CDCl$_3$

**Figure 6.27** PXRD pattern of (2), obtained via mechanochemical synthesis
Table 6.6  Calculated and found CHNO elemental analysis of (2), obtained via mechanochemical synthesis\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>Calculated for C\textsubscript{7}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53.83</td>
<td>49.31</td>
</tr>
<tr>
<td>H</td>
<td>7.74</td>
<td>8.15</td>
</tr>
<tr>
<td>N</td>
<td>17.94</td>
<td>16.04</td>
</tr>
<tr>
<td>O</td>
<td>20.49</td>
<td>26.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The compound was not obtained analytically pure. Calculated C\textsubscript{7}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}·H\textsubscript{2}O (5:4): C = 49.28\%, H = 8.04\%, N = 16.42\%, O = 26.26\%

6.4 Synthesis of Me\textsubscript{2}dazdt (7)

\[
\text{(2)} + \text{(8)} \rightarrow \text{(7)} + 2 \text{OCH}_3
\]

6.4.1 Conventional Synthesis

(8) was added to a round bottom flask containing a stirring bar and septum followed by (2). A condenser was attached before evacuating with N\textsubscript{2} three times. Dry toluene (20 mL) was added via a syringe. The reaction mixture was refluxed for 72 hours, and then cooled to room temperature. Toluene was removed under vacuum. Attempts to purify the crude product by recrystallizing from DCM and ethanol (4:1), or column chromatography using silica (methanol/DCM eluent) were unsuccessful. The amounts of reagents used, reaction times, and yields were reported in Table 2.8 (Chapter 2).

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 3.54 (t, 4H, NCH\textsubscript{2}), 3.49 (s, 6H, CH\textsubscript{3}), 2.18 (qnt, 2H, CH\textsubscript{2})
Figure 6.28 $^1$H-NMR spectrum of (7), obtained via conventional synthesis, in CDCl$_3$

$^{13}$C-NMR (300 MHz, CDCl$_3$): $\delta$ 195.50 (C=O), 51.13 (NCH$_2$), 40.83 (CH$_3$), 27.69 (CH$_2$)

Figure 6.29 $^{13}$C-NMR spectrum of (7), obtained via conventional synthesis, in CDCl$_3$
6.4.2 Attempt to obtain (7) via sonochemical synthesis

A sonic bath (Fig. 6.16) was set to a temperature of 80 °C and a power of 9. To a beaker was added (8) (3.2754 g, 8.10 mmol) and (2) (0.2443 g, 1.56 mmol). These were thoroughly mixed then transferred to a round bottom flask containing toluene (1 mL). The beaker was rinsed with toluene (9 mL) then added. This is placed in the sonic bath and the reaction run for 4 hours. NMR data showed that compound (7) was not obtained. The amounts of reagents used and reaction times were reported in Table 2.9 (Chapter 2).

6.5 Synthesis of [Me₂pipdtH]I₃ (12)

I₂ (0.0372 g, 0.15 mmol) was dissolved in DCM/CHCl₃ (15 mL) and added to a beaker containing a stirring bar and (6) (0.0130 g, 0.0075 mmol). The solution was left stirring for 2 hours until all DCM/CHCl₃ had evaporated off. Stirring was then stopped and the shiny black crystals were left overnight in air, and collected. The solvent, reaction times, and yields were reported in Table 2.10 (Chapter 2).

Figure 6.30 PXRD pattern of (12)
Table 6.7 Calculated and found CHNS elemental analysis of (12)

<table>
<thead>
<tr>
<th>Calculated for C₆H₁₁N₂S₂I₃/%</th>
<th>Found/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>12.96</td>
<td>1.99</td>
</tr>
</tbody>
</table>

*a: The compound was not obtained analytically pure. Calculated C₆H₁₁N₂S₂I₃:DCM (2:3): C = 13.18%, H = 2.06%, N = 4.10%, S = 9.38%*

6.6 Synthesis of Ph₃P=O.H₂O₂ and Ph₃P=O

Ph₃P=O.H₂O₂ and Ph₃P=O were synthesised according to known literature procedures.¹⁸⁷

6.6.1 Synthesis of Ph₃P=O.H₂O₂

Ph₃P (2.0 g, 7.63 mmol) was dissolved in toluene (150 mL) in a sealed round bottomed flask and cooled to 0 °C. 50% H₂O₂ was syringed into the flask dropwise with vigorous stirring. After 10 minutes white, needle-like crystals were observed. The reaction mixture was stirred overnight and slowly brought to room temperature. Solvent was removed in vacuo, and the white precipitate was washed with toluene (3 x 20 mL). The precipitate was dried to form the Ph₃P=O.H₂O₂ adduct which was a white crystalline powder.
Figure 6.32 $^{31}$P-NMR spectrum of Ph$_3$P=O.H$_2$O$_2$ in CDCl$_3$; internal reference = (28) in DMSO-d$_6$, -14.44 ppm

Figure 6.33 IR spectrum of Ph$_3$P=O.H$_2$O$_2$
Figure 6.34 Comparison of calculated (top) and experimental (bottom) PXRD patterns of Ph₃P=O·H₂O₂

It is unknown if the differences observed relate to H₂O present in the sample.

6.6.2 Synthesis of Ph₃P=O
Ph₃P=O·H₂O₂, synthesised as in 6.6.1, was added to a round bottomed flask and dissolved in toluene (150 mL). Molecular sieves (5.0 g, activated by heating to 200 °C overnight) were added to the flask and then stirred vigorously for 4 hours. The molecular sieves were
extracted and the solvent was removed \textit{in vacuo} at 60 °C to produce a white crystalline powder.

\textbf{Figure 6.35}  $^{31}$P-NMR spectrum of Ph$_3$P=O in CDCl$_3$; internal reference = (28) in DMSO-d$_6$, -14.44 ppm

\textbf{Figure 6.36}  IR spectrum of Ph$_3$P=O
Figure 6.37 Comparison of calculated (top) and experimental (bottom) PXRD patterns of Ph$_3$P=O
6.7 Synthesis of Ionic Liquids

6.7.1 Synthesis of [BMIM]Cl

[BMIM]Cl was synthesised using a method similar to that in the literature.\(^{228}\) To a round bottomed flask containing 1-chlorobutane (150 mL, 1.43 mol) and acetonitrile (100 mL) was added 1-methylimidazole (75 mL, 0.95 mol). The reaction mixture was stirred at room temperature for 24 hours, before refluxing for 168 hours. This was then cooled to room temperature and excess solvent was removed \textit{in vacuo}. Excess 1-chlorobutane was removed by washing with dry ethyl acetate (5 x 100 mL). Ethyl acetate (100 mL) was added to the flask followed by acetonitrile (50 mL). The round bottomed flask was placed in the freezer overnight to ensure full crystallisation. The solvent was removed using Schlenk techniques and the white crystalline solid was dried \textit{in vacuo} to yield 1-butyl-3-methylimidazolium chloride.

![Figure 6.38 Pure [BMIM]Cl](image)

\(^1\text{H-}\text{NMR (300 MHz, (CD}_3\text{)}_2\text{SO): }\delta 9.36 (s, 1H, H_a), 7.83 and 7.75 (2s, 2H, H_{b+c}), 4.18 (t, 2H, ^3J= 7.2, 6.9 Hz, H_d), 3.86 (s, 3H, H_e), 1.76 (qnt, 2H, ^3J= 7.5, 7.2 Hz, H_f), 1.23 (sxt, 2H, ^3J= 7.5, 7.2 Hz, H_g), 0.89 (t, 3H, ^3J= 7.5, 7.2 Hz, H_h)}
6.7.2 Synthesis of [OMIM]Cl

The same procedure as in the case of [BMIM]Cl was followed, but using 1-chlorooctane instead of 1-chlorobutane. Purification involved washing the resulting liquid with dry ethyl acetate (15 x 100 mL) before removing any remaining ethyl acetate on a rotary evaporator. The compound was further dried overnight (at 80 °C) using Schlenk techniques.
$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 10.96 (s, 1H, Ha), 7.36 and 7.28 (2s, 2H, H$_b$ + c), 4.32 (t, 2H, $^3$J = 7.5 Hz, H$_d$), 4.14 (s, 3H, H$_e$), 1.94-1.87 (m, 3H, $^3$J = 7.5, 6.3, 5.7 Hz, H$_f$), 1.33-1.26 (dd, 10H, $^3$J = 9.6, 9.3, 3 Hz, H$_g$), 0.88 (t, 3H, $^3$J = 6.9, 5.1 Hz, H$_h$)

Figure 6.41 $^1$H-NMR spectrum of [OMIM]Cl in CDCl$_3$

6.7.3 Synthesis of [BMIM]NTf$_2$

[BMIM]NTf$_2$ was synthesised using a method similar to that in the literature.$^{229}$ LiNTf$_2$ (229.7 g, 0.8 mol) was added to a round bottomed flask containing [BMIM][Cl] (108.3 g,
0.62 mol) and H₂O (50 mL). This was stirred at room temperature for 24 hours. The upper layer was decanted and the remaining ionic liquid layer washed with H₂O (2 x 50 mL). Acetonitrile (50 mL) was added and the solution dried using MgSO₄. Using a rotary evaporator, the acetonitrile was removed before further drying the resulting liquid overnight (at 80 °C) using Schlenk techniques.

\(^{1}\text{H-NMR} (300 MHz, (CD₃)₂SO): \delta 9.10 \text{ (s, 1H, Hₐ), 7.76 and 7.69 (2s, 2H, Hₖ + c), 4.15 (t, 2H, } ^{3}\text{J} = 7.2, 6.9 \text{ Hz, H₈), 3.84 (s, 3H, H₅), 1.76 (qnt, 2H, } ^{3}\text{J} = 7.5, 7.2 \text{ Hz, H₇), 1.24 (sxt, 2H, } ^{3}\text{J} = 7.8, 7.5, 7.2 \text{ Hz, H₉), 0.90 (t, 3H, } ^{3}\text{J} = 7.5, 7.2 \text{ Hz, H₁₀)}}

\[\begin{array}{c}
\text{ppm} \\
9.10 & 7.76 & -4.15 & 3.84 & -2.50 & -1.76 & -1.24 & 0.90 \\
\end{array}\]

\[\begin{array}{cccccccc}
9.0 & 8.0 & 7.0 & 6.0 & 5.0 & 4.0 & 3.0 & 2.0 & 1.0 \\
\end{array}\]

\textbf{Figure 6.42} \(^{1}\text{H-NMR spectrum of [BMIM]NTf₂ in (CD₃)₂SO}\)

\[\textit{6.7.4 Synthesis of [BMIM]OTf}\]

[BMIM]OTf was synthesised using a method similar to that in the literature.\textsuperscript{230} LiOTf (25 g, 0.16 mol) was added to a round bottomed flask containing [BMIM][Cl] (26.97 g, 0.15 mol) and DCM (35 mL). This was stirred at room temperature for 108 hours before filtering. The separated solid was then washed with DCM (2 x 20 mL) and the organic phase of the filtrate separated. This organic phase was washed with H₂O (2 x 5 mL) before
drying with MgSO₄. The organic phase was filtered and the DCM removed on a rotary evaporator. Further drying was carried out overnight (at 80 °C) using Schlenk techniques.

¹H-NMR (300 MHz, (CD₃)₂SO): δ 9.10 (s, 1H, Hₐ), 7.76 and 7.70 (2s, 2H, Hₐ+c), 4.15 (t, 2H, J = 7.2, 6.9 Hz, H₆), 3.84 (s, 3H, H₇), 1.76 (qnt, 2H, J = 7.5, 7.2 Hz, H₈), 1.24 (sxt, 2H, J = 7.5, 7.2 Hz, H₉), 0.90 (t, 3H, J = 7.5, 7.2 Hz, H₁₀)

![Figure 6.43 ¹H-NMR spectrum of [BMIM]OTf in (CD₃)₂SO](image)

6.8 Synthesis of DESs

Choline chloride was added to a round bottom flask containing a stirring bar followed by 2 eq. urea (Reline 200) or ethylene glycol (Ethaline 200).²³¹ A swan-neck tap was added and left open as the mixture was heated to 80 °C and left stirring until a clear homogenous liquid had formed. Imiline 700 was synthesised in a similar way but now using 3 eq. choline chloride and 7 eq. imidazole as well as a temperature of 100 °C.¹⁰⁴

6.8.1 Reline 200

¹H-NMR (300 MHz, CD₃OD): δ 4.86 (s, 11H, OH and NH₂), 4.03-3.98 (m, 2H, OCH₂), 3.51-3.47 (m, 2H, NCH₂), 3.22 (s, 9H, CH₃)
Figure 6.44 $^1$H-NMR spectrum of Reline 200 in CD$_3$OD

$^{13}$C-NMR (300 MHz, CD$_3$OD): $\delta$ 54.70 (CH$_3$), 57.08 (OCH$_2$), 69.04 (NCH$_2$), 163.58 (C=O)

Figure 6.45 $^{13}$C-NMR spectrum of Reline 200 in CD$_3$OD
6.8.2 Ethaline 200

$^1$H-NMR (300 MHz, CD$_3$OD): δ 4.86 (s, 6H, OH), 4.03-3.98 (m, 2H, OCH$_2$), 3.60 (s, 8H, CH$_2$), 3.52-3.49 (m, 2H, NCH$_2$), 3.22 (s, 9H, CH$_3$)

Figure 6.46 Raman spectrum of Reline 200

Figure 6.47 $^1$H-NMR spectrum of Ethaline 200 in CD$_3$OD
6.8.3 Imiline 700

$^1$H-NMR (300 MHz, CD$_3$OD): δ 7.68 (s, 7H, NCHN), 7.05 (s, 14H, NCH), 5.01 (s, 11H, OH and NH), 4.02-3.97 (m, 6H, OCH$_2$), 3.51-3.48 (m, 6H, NCH$_2$), 3.22 (s, 27H, CH$_3$)

![Figure 6.48 Raman spectrum of Ethaline 200](image1)

![Figure 6.49 $^1$H-NMR spectrum of Imiline 700 in CD$_3$OD](image2)
6.9 Dissolution Studies

6.9.1 Pd and Pt

Dissolution studies were performed in a glass vial (23 mm x 46 mm) with most experiments using 4 mL of solvent, at several temperatures (r.t., 60 °C, or 90 °C), open to the air, and normally for 168 hours. The metal and ligand/oxidant were added simultaneously, with (normally) only ≈0.5 mg of metal added. This small amount made it challenging to be accurate (±0.2 mg), and at times reproducibility was difficult. Details of results are included in Tables 3.1-3.4 and 3.7 (Chapter 3). A list of the various ligands used is shown in Figure 3.4 (Chapter 3).

6.9.2 Au

The IL (4 mL) was added to a glass vial (23 mm x 46 mm) followed by Ph₃P (13.3 mg, 0.05 mmol) and left stirring until completely dissolved. I₂ (12.9 mg, 0.05 mmol) was then added. When dissolved, Au (5 mg, 0.025 mmol) was added. The sample vial was then capped and stirred. Details of times and results are included in Table 3.8 (Chapter 3).

6.10 Monitoring Experiments

6.10.1 Ph₃P:I₂ (1:1) (17) monitoring experiments

The IL (10 mL) was added to a glass vial (23 mm x 46 mm) followed by Ph₃P (105 mg, 0.04 mmol) and left stirring until completely dissolved. I₂ (102 mg, 0.04 mmol) was then added and stirred until dissolved. The sample vial was capped if required and stirred for the duration of the experiment. The adduct formation was monitored by ³¹P NMR spectroscopy using a capillary containing DMSO/DPPE (28) as a reference (See Chapter 5, Section 5.2).

6.10.2 Ph₃P, Ph₃P=O, and Ph₃P=O.H₂O₂ monitoring experiments in [BMIM]OTf

The IL (10 mL) was added to a glass vial (23 mm x 46 mm) followed by either Ph₃P (105 mg, 0.04 mmol), Ph₃P=O (105 mg, 0.04 mmol), or Ph₃P=O.H₂O₂ (105 mg, 0.04 mmol) and stirred until dissolved. The sample vial was capped if required and stirred for the duration of the experiment. The adduct formation was monitored by ³¹P NMR
spectroscopy using a capillary containing DMSO/DPPE (28) as a reference (See Chapter 5, Section 5.2).

6.10.3 Ph₃P monitoring experiments in [BMIM]OTf with known amounts of H₂O
De-gassed [BMIM]OTf (10 mL) was added to a glass vial (23 mm x 46 mm) followed by Ph₃P (105 mg, 0.04 mmol) and left stirring until completely dissolved. The amount of H₂O required was then added. Some of the solution was transferred to a NMR tube containing a DSMO/DPPE (28) capillary in a Schlenk bomb maintained under an inert N₂ atmosphere (See Chapter 5, Section 5.2.3).

6.11 Cyclic Voltammetry
CVs were run using a three electrode set-up (Fig. 6.50) and an AUTOLAB-Type III potentiostat (Fig. 6.51). A glassy carbon disc electrode (0.07068 cm²) was used as working electrode, coiled Pt wire as the counter, and Ag/Ag⁺ as the reference. The glassy carbon electrode was polished before each run using alumina on a wet polishing pad and rinsing with H₂O. CVs were run in a glass vial (25 mm x 50 mm) with 4 mL of IL/DES, at the desired temperature (r.t., 60 °C, or 90 °C) at a scan rate of 50 mV s⁻¹. Higher temperatures were maintained using a thermostat. N₂ (dried by passing through a column of silica gel) was also used to purge the sample for 15 minutes prior to running CVs, and used to maintain an inert atmosphere.

The reference electrode was made in-house by immersing a silver wire on a 0.1 M solution of AgNO₃ in [BMIM]NO₃. The solution was contained on a glass tube with a partially solvent-permeable glass frit at the base (Fig. 6.50). To ensure that the reference electrode had been built correctly, it was tested in the cell set-up mentioned above, using an acetonitrile solution of ferrocene (0.1 M) and tetrabutylammonium tetrafluoroborate (0.1 M, supporting electrolyte). A well-defined reversible wave was obtained for the Fc/Fc⁺ couple, and the cyclic voltammetry parameters were comparable to those expected in an organic solvent, i.e. iₚₐ /iₚₖ = 0.97; ΔE= 0.13 V; E₁/₂ = 0.06 V; at a scan rate of 100 mV s⁻¹, Fig. 6.52.\(^{232}\)
Figure 6.50  Three electrode electrochemical cell used in this work

Figure 6.51  Potentiostat used for cyclic voltammetry in this work
Figure 6.52 CVs of ferrocene (0.1 M) and tetrabutylammonium tetrafluoroborate (0.1 M, supporting electrolyte) in acetonitrile; working electrode = glassy carbon, counter electrode = Pt wire, reference electrode = Ag/Ag$^+$ (0.1 M AgNO$_3$ in [BMIM]NO$_3$), Scan rate = 100 mV s$^{-1}$, Room temperature

6.12 Electrodeposition

Electrodeposition was performed using a PC controlled Potentiostat/Galvanostat EG&G Model 273A (Fig. 6.53). The same three electrochemical cell set up described in 6.11 (Fig. 6.50) was used, but now with a glassy carbon plate (40 mm x 10 mm) (Fig. 6.54) as the working electrode. A potential of -1.9 V was applied for Pd, and -2.0 or -2.3 V applied for Au. Electrodeposition times can be found in Chapter 4 for Pd and Chapter 5 for Au.
**Figure 6.53** Potentiostat/Galvanostat used for electrodeposition in this work

**Figure 6.54** Glassy carbon plate used in this work
References


64. L. Takacs, *JOM*, 2000, **52**, 12.


