Biphasic Chemistry Utilising Ionic Liquids[a]

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Abstract: Biphasic and multiphasic processes have emerged as effective methods to reduce the amount of volatile organic solvents used in the manufacture of chemicals. In this article some of the research conducted in my laboratory in this domain utilizing ionic liquids is described. Other dimensions to our research interests in ionic liquids are also discussed including their conversion to porous nanomaterials.

Keywords: Biphasic catalysis · Catalysis · Ionic liquids · Reaction mechanisms · Nanoparticles

Introduction

Decreasing the use of volatile organic solvents represents one of the major challenges of the chemical and pharmaceutical industries [1][2]. While solvents are used to facilitate reactions (allowing reactants to mix and supplying or dissipating heat), their use is inherently wasteful as the solvent is subsequently removed from the chemical product and then disposed of, often by incineration. Solvents tend to be highly volatile as this property facilitates their removal from chemical products, but unfortunately their volatility has led to major environmental and toxicological problems. Atmospheric pollution resulting from the evaporation of solvents represents one of the major global environmental issues of our time, with emissions of some categories of volatile organic solvents implicated in the depletion of the ozone layer and in the greenhouse effect. Ongoing legislation including the

Montreal, Geneva and Kyoto Protocols set targets for reducing and eventually phasing out many solvents [3]. Considerable efforts are being made to find alternative solvents that will conform to future controls, and in particular, there has been an explosion of interest in the use of non-volatile, ionic liquids as alternative media in which to conduct reactions. In our laboratory we are interested in fundamental aspects of ionic liquids chemistry, including method development and the elucidation of reaction mechanisms in ionic liquids, and based on these basic data we attempt to develop new catalysts and new ionic liquids that are superior to those in current use, and superior to other catalyst–solvent regimes.

Ionic Liquids – Composition, Uniqueness and Applications

Ionic liquids, which until recently were referred to as room-temperature molten salts, are merely salts with low melting points, by definition being below 100 °C [4]. The first ionic liquid, at least the first substance being recognised as such, was [EtNH$_3$][NO$_3$], with a melting point of 12 °C, discovered in 1914 [5]. About thirty years later the next ionic liquids were discovered, being composed of alkylpyridinium cations with tetra chloroaluminate(III) and related anions [6]. Today the most widely studied class of ionic liquids is based on 1,3-dialkylimidazolium cations and many of these liquids have very low melting points, some approaching –100 °C [7]. It is these 1,3-dialkylimidazolium cation based ionic liquids that are most frequently encountered in synthetic and cata-

lytic applications, usually incorporating a methyl group in combination with an alkyl chain. A wide range of cations now give rise to low melting salts and some examples are illustrated in Fig. 1. The nature of the anion is also important; halides giving relatively high melting points, with anions such as BF$_4^-$, PF$_6^-$, AsF$_6^-$, SbF$_6^-$, NO$_3^-$, CH$_3$CO$_2^-$, CF$_3$SO$_3^-$, (CF$_3$SO$_2$)$_2$N$^-$, (CF$_3$SO$_2$)$_3$C$^-$ providing low melting salts.

Ionic liquids are finding applications in separation processes [8], in electrochemistry [9], as electrolytes in solar cells [10], as lubricants [11], as matrices in MALDI mass spectrometry [12] and even as propellants in small satellites [13]. However, the most active area of ionic liquid research involves their use as alternative solvents in which to conduct synthetic chemistry [14]. The general properties of ionic liquids that make them suited to synthesis and catalysis include the following:

– They have no (or negligible) vapour pressure and therefore do not evaporate.
– They have favourable thermal properties.
– They dissolve many metal complexes, catalysts, organic compounds and gases.
– They are immiscible with many organic solvents and water.

In particular, it is the first property, viz. the fact that they do not evaporate, which makes them particularly attractive, due to the problem associated with volatile solvents mentioned in the introduction. However, what really makes ionic liquids such fascinating solvents for synthetic chemists is that there is no limit to the number of

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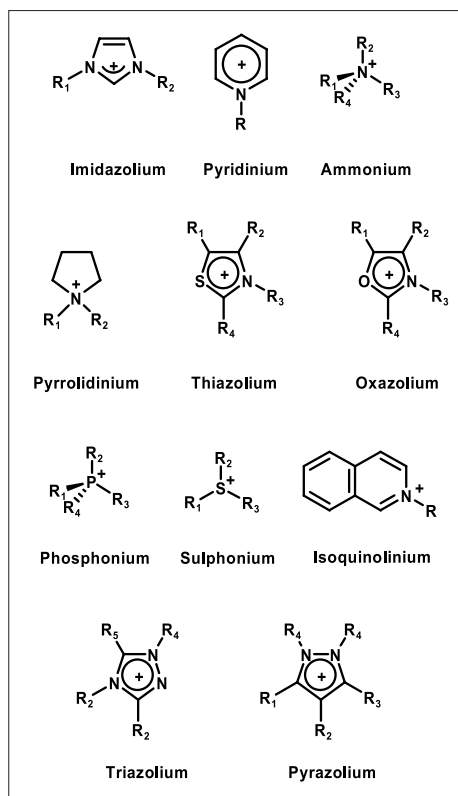Fax: +41 21 693 98 85
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Fig. 1. Examples of cations used to provide low melting salts (ionic liquids)

different liquids that can be made, and as our fundamental understanding of them increases, it should be possible to design specific ionic liquids for specific reactions and processes. A relatively detailed list of the physical properties of ionic liquids relevant to their applications in synthesis and catalysis may be found elsewhere [15].

Catalysed Reactions in Ionic Liquids

A large and diverse range of chemical reactions, in particular, those catalysed by metal compounds, have been conducted in ionic liquids, and several useful features have been documented. It would appear that the non-nucleophilic environment provided by many ionic liquids is conducive to stabilising the lifetime of sensitive homogeneous catalysts, leading to increased yields and enantioselectivities. It has also been found that ionic liquid or ionic liquid–catalyst systems can be recycled and reused a large number of times. Products can often be extracted from ionic liquids directly, although a co-solvent may be necessary, and the amount of ionic liquid and catalyst present in the product is usually low (a particularly important parameter in the manufacture of pharmaceuticals [16]). Despite these significant benefits, very few studies have addressed in detail the mechanisms of

reactions conducted in ionic liquids, which will ultimately lead to improved processes. The reason for the lack of mechanistic data is due, at least in part, to the new set of problems associated with non-volatile solvents, which are largely alien to most chemists. However, some simple solutions have been devised, for example, an elegant approach using entirely labelled substrates, as opposed to preparing labelled ionic liquids allow reactions in ionic liquids to be monitored *in situ* by NMR spectroscopy [17], and various mass spectrometric methods can be used to analyse catalysts present in extremely low concentrations directly in ionic liquids [18]. Clearly, there is considerable interest in showing why a reaction may be superior (or less effective) in an ionic liquid, in order to remove the guesswork from the field.

It has been shown that some catalysed reactions that operate in water are less effective in ionic liquids, or do not even proceed in an ionic liquid [19], while other papers indicate that addition of water to ionic liquids improves activity [20]. Recently, we have proposed an explanation for these observations derived from the detailed mechanistic analysis of a series of ruthenium(II) hydrogenation catalysts [21]. Based on an investigation of catalysts of general formula $[Ru(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-}P\text{-}P)Cl]^+$ (where P-P is a bisphosphine) in aqueous solution, using

in situ NMR spectroscopy and electrospray ionisation mass spectrometry, it has been possible to show that the active complex in the catalytic hydrogenation of styrene is a dihydrogen species with the dihydrogen undergoing heterolytic cleavage. The arene ligand may also undergo exchange, but it is not a prerequisite for catalysis, and the arene does not undergo hydrogenation (although at high pH arene hydrogenation is observed, but the active catalyst has been identified as nanoparticulate) [22]. Based on our experiments the catalytic cycle shown in Scheme 1 was devised, and from bite angle effects arising from the use of different bisphosphine ligands, the rate determining step has been identified as dissociation of the chloride ligand.

Subsequently, using NMR methods, the solvation enthalpy of chloride in 1,3-dialkylimidazolium ionic liquids was quantified and found to be eight-fold lower than in water [23]. Thus, catalysis does not take place in these ionic liquid as loss of a chloride ligand, a prerequisite for the ruthenium compound to enter the catalytic cycle, is disfavoured. Catalytic activity may be restored by exchange of chloride by another ligand providing the impetus for future catalyst design, or by the addition of water, which solvates the chloride and explains why the presence of water facilitates certain reactions (see above). In fact, ionic liquids can
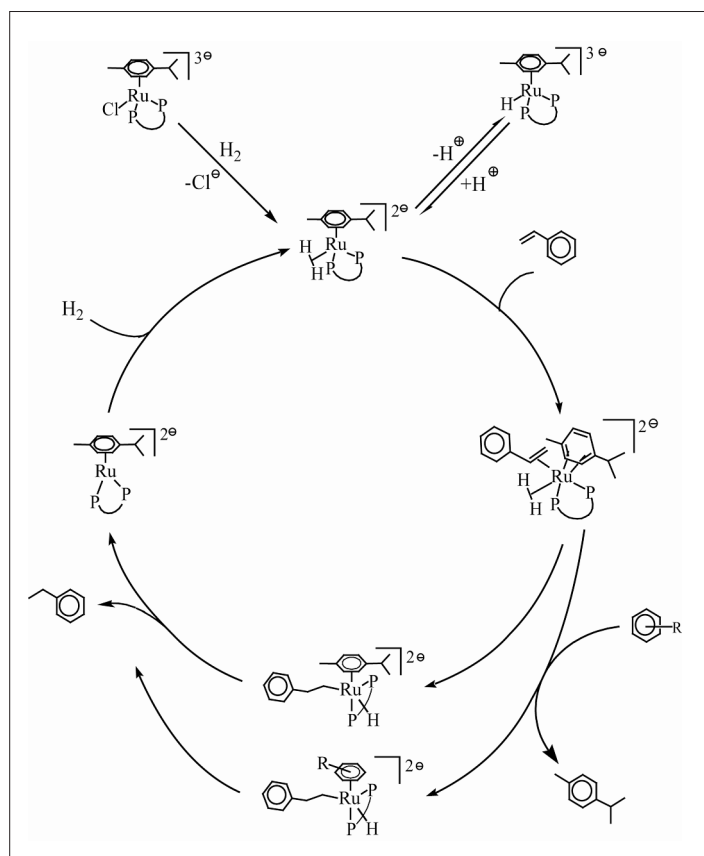
Scheme 1. Proposed mechanism of styrene hydrogenation using $[Ru(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-}P\text{-}P)Cl]^+$; P-P is a bisphosphine ligand.

be used in combination with water for the hydrogenation of water soluble substrates which not only eliminates organic solvents, but also provides excellent catalyst recycling [24].

Hydrogenation is a particularly promising reaction in ionic liquids with the differences in polarity between unsaturated substrates and hydrogenation products providing pseudo homogeneous reactions conditions (as substrate solubility tends to be high in ionic liquids) combined with excellent phase separation of the products (which are generally less polar than their unsaturated counterparts and therefore less soluble in ionic liquids) [25]. Early studies also demonstrated that for hydrogenation reactions increased reaction rates were also possible when using an ionic liquid in place of a molecular solvent [26]. One commonly cited explanation for the increased reaction rates was that hydrogen solubility was high in ionic liquids, by analogy to CO_2 [27]. However, since reliable data was not available, we set out to measure hydrogen solubility [28] (and subsequently CO [29]) in a series of ionic liquids using high pressure NMR spectroscopy. To our surprise, we discovered that the solubility of H_2 in most ionic liquids is low, comparable to water (*ca.* <1 M at 0.101 MPa). However, as long as substrate solubility is high in the ionic liquid, then hydrogen solubility is also higher and mass transport problems appear to be considerably reduced.

Another attractive feature stemming from the differences in substrate and product solubility in ionic liquids is that partial reduction reactions often take place with high selectivities. For example, various diene substrates can be reduced to monoenes in ionic liquids using catalysts that give the fully hydrogenated product under homogeneous conditions [30][31]. The partial reduction of benzene has even been achieved using heterogeneous catalysts [32] as predicted from analogies with the industrially important aqueous process [33].

In recent years transfer hydrogenation has proven to be a particularly attractive method for the enantioselective reduction of C=O bonds. Attempts to conduct these reactions under biphasic conditions have been met with some success [34], but not using ionic liquids. We have designed a new catalyst for transfer hydrogenation reactions in ionic liquids that does not impede the high enantioselectivities characteristic of the homogeneous (monophasic) catalysts [35]. In general, catalysts are made compatible with a particular solvent by derivatising it with an appropriate functional group. For example, hydrophilic groups, such as sulfates and carbohydrates, attached to phosphines are widely employed to induce water solubility (the phosphine also imparts other features crucial to the activity of the catalyst). Our

approach involves derivatising the compound with an imidazolium group at a peripheral site, which provides the necessary solubility properties, but does not interfere with the active part of the catalyst. In the example shown in Scheme 2 the imidazolium-tagged compound could be converted to catalysts suitable for transfer hydrogenation as well as other types of reactions.

The transfer hydrogenation catalysts shown in Scheme 2 have been evaluated in the reduction of several substrates, with attention focussed on product yield and enantioselectivity, as well as on catalyst leeching and recycling. It was found that the optimum ionic liquid for use in this reaction is 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (a methyl group is essential in the 2-position to prevent reaction with base) in combination with formic acid-triethylamine. In such biphases acetophenone, for example, can be reduced in yields exceeding 90% with an ee exceeding 99%.

Anchoring catalysts employing the type of strategy described above is very effective, although, extraction of the catalyst from the ionic liquid is not a trivial task. In aqueous-organic catalysis the solubility of the catalyst may be modulated by pH. Catalysts containing ligands with pendant basic functionalities are preferentially soluble organic solvents, but if the basic

group is protonated, the catalyst becomes more water soluble [36]. Such an effect has even been exploited in a biological context involving compounds related to those described above [37]. We have attempted to translate this technique into the ionic liquid arena, replacing the pH controlled system with ion control. Essentially, in place of a basic ligand, we employ a moiety such as a crown or calixarene that can reversibly bind an ion, thus, when empty the compound is insoluble in ionic liquids, but on uptake of an appropriate ion into the cavity, solubility is induced in the ionic liquid. Removal of the ion, by washing with water, for example, then facilitates the extraction of the catalyst from the ionic liquid phase.

Ionic Liquids by Design

The application of ionic liquids in catalysis is not without problems; one being that yields and selectivities can vary according to the batch of ionic liquid used. Impurities such as halides, and to lesser extent organic compounds of low volatility, have been implicated in reproducibility problems [38]. Halide contamination originates from the salt metathesis reaction frequently used to prepare ionic liquids, although many alternative 'halide-free' routes are now available
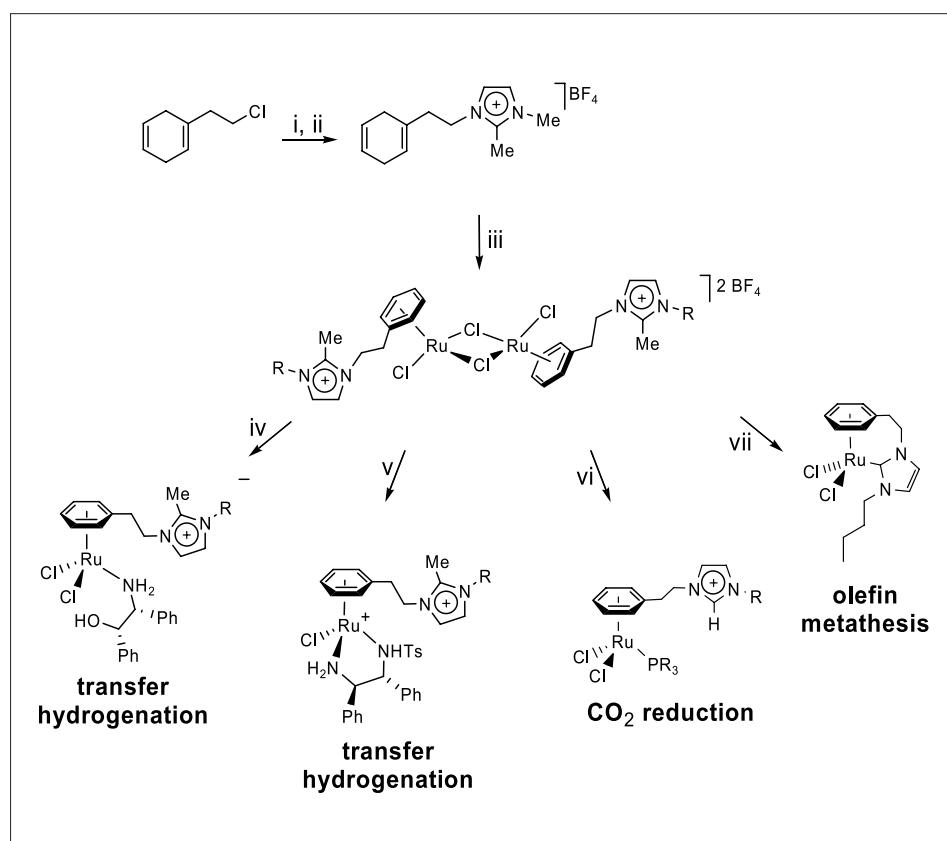
Scheme 2. Synthesis of the imidazolium tagged dimer and subsequent catalysts: Reagents and conditions: (i) 1,2-dimethyl imidazole, toluene, 110 °C; (ii) NaBF$_4$, CH$_2$Cl$_2$; (iii) RuCl$_3$, MeOH, 80 °C; (iv) (1(*S*),2(*R*))-2-amino-1,2-diphenylethanol, DMF, RT; (v) (*R*,*R*)-N-tosyl-1,2-diphenylethylenediamine, DMF, RT: (vi) PR$_3$, MeOH-CH$_2$Cl$_2$, RT, 1 h; (vii) Ag$_2$O, DMF.

[39]. In addition to the synthesis of highly pure ionic liquids, the prospect of designing ionic liquids that exhibit specific properties to enhance catalytic activity opens up new dimensions and possibilities in catalysis. Conceptually, an ionic liquid cation modified to incorporate a Lewis base functionality, such as a nitrile group, represents a simple method of anchoring a catalyst, *via* coordination, in the ionic liquid phase. We have prepared a series of nitrile functionalised ionic liquids in order to test such a hypothesis [40] and some representative cation structures are illustrated in Fig. 2.
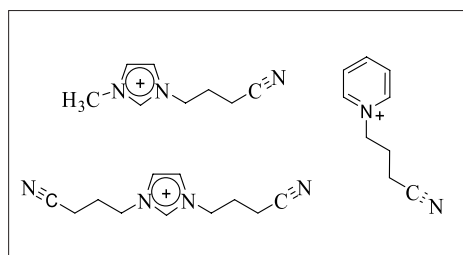

Fig. 2. Some nitrile functionalised cations that in combination with anions such as BF_4^-, PF_6^- and Tf_2N^- afford ionic liquids with melting points as low as –80 °C.

A number of different catalysed reactions have been conducted in these ionic liquids, notably palladium catalysed carbon–carbon cross coupling reactions including Heck, Suzuki and Stille reactions, all of which have been evaluated in non-functionalised ionic liquids for comparison purposes. In the reactions undertaken in our laboratory we noticed a number of major benefits when using the nitrile-functionalised liquids. Indeed, catalyst retention is considerably improved, reduced from typically 70–100 ppm to between 1–4 ppm per cycle in the nitrile-functionalised ionic liquids. Not only is palladium leeching considerably reduced, but the catalyst is also stabilised and does not decompose to give palladium deposits, which contrasts to that observed for the non-functionalised systems. Consequently, the nitrile-functionalised ionic liquid solution can be reused repeatedly without significant decrease in activity. The actual situation in Stille reactions is more complicated than that predicted. While a simple complex is formed between the palladium(II) centre and the nitrile functionality of the ionic liquid in the first instance, the palladium(II) species is reduced to palladium(0), presumably also stabilised by coordination of the nitrile groups, and following catalysis condense to form nanoparticles, which also appear to be stabilised in the nitrile-functionalised ionic liquid. The nitrile-functionalized ionic liquid probably forms a protection shell similar to those observed for related ammonium salts [41]. The nanoparticles isolated from a nitrile functionalised ionic liquid are shown in Fig. 3 and their proposed composition is represented schematically.

One potential problem with the nitrile-functionalised ionic liquids is that their viscosities tend to be higher than non-functionalised analogues, despite maintaining very low melting points. We have recently found that the viscosity of these ionic liquids can be reduced by using an asymmetric functionalised anion in combination with the functionalised cation [42]. In addition, a functionalised anion could provide a complementary function giving what we have termed, 'dual functionalised ionic liquids'.

Inorganic and Hybrid Materials from Ionic Liquids

The unusual environment presented by ionic liquids has also been exploited in the synthesis of organometallic and inorganic compounds, including those with compl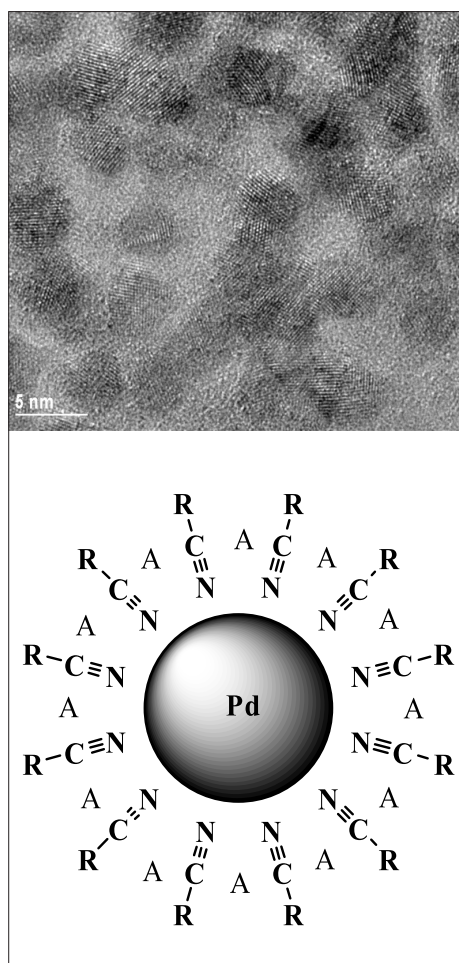ex architectures. We demonstrated that the Lewis acidic properties of chloroaluminate ionic liquids could be used to facilitate certain organometallic reaction, such as arene exchange processes [43], and subsequently expanded their utility to other systems [44]. In addition, we demonstrated that anionic transition metal organometallic complexes could replace the usual anions in ionic liquids providing a new range of liquid materials [45], suitable for painting onto surfaces to give heterogeneous supported catalysts. Also, ionic liquids with alkyne functionalised cations have been reacted with organometallic species, to give low melting salts [46], thus ionic liquids composed of organometallic cations and anions are available, which could be used as precursors to materials with novel properties.

A series of carboxylic acid-functionalised ionic liquids prepared in our laboratory using the route shown in Scheme 3 can be converted into porous materials [47]. As mentioned above, halide contamination in ionic liquids prepared by the traditional salt metathesis route can lead to marked differences in their properties. The strategy used to prepare the carboxylic acid-functionalised ionic liquids efficiently eliminates halide impurities by progressing through a zwitterionic anion-free intermediate. Protonation of the zwitterions with acids such as HBF_4 and HOTf affords highly pure ionic liquids.

Due to the very low pKa of these acids (*ca.* 1.3 where n = 1) they react directly with, for example, zinc metal to form the zwitterionic, helical coordination polymer shown in Fig. 4 [48]. Although not shown in the Figure, the channel contains a chain of water that form hydrogen bonds with the walls of the polymer, instead of hydrogen bonding to each other. Combined with the internal diameter of the tube, and its zwitterionic nature, the compound may be described as an artificial water channel by analogy to aquaporin water channels [49]. While other groups have reported the synthesis of porous materials from ionic liquids [50], we believe this represents the first example in which the ionic liquid constitutes part of the porous material, and many further examples have since been prepared in our laboratory.

Fig. 3. (Top) TEM image of the palladium nanoparticles isolated after the Stille reaction from $PdCl_2$-[C_3CNpy][Tf_2N]. (Bottom) Representation of the nitrile-functionalised ionic liquid stabilised palladium nanoparticles catalyst; R = 1-propyl-pyridinium, A = Tf_2N^-.

Outlook

Ionic liquids provide chemists with the opportunity of studying reactions in a fascinating new environment. While the fundamental properties are being unravelled chemists are developing new methods to handle and study them. In terms of their application as solvents in biphasic catalysis many notable achievements have already been made [14], but what is particularly fascinating is that not only is the catalyst
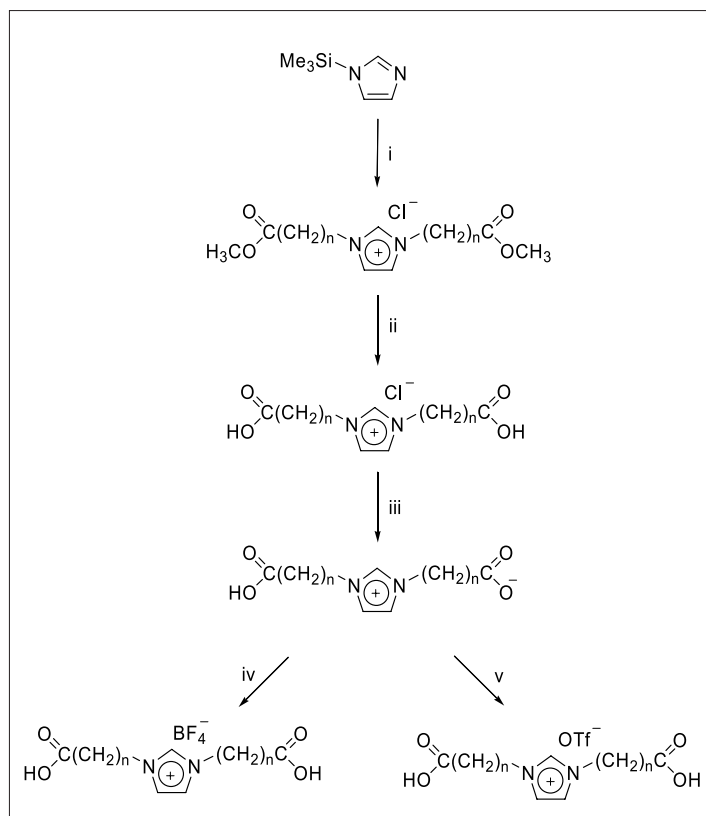
Scheme 3: Synthesis of carboxylic acid functionalised ionic liquids. Reagents and conditions (i) 2 equiv. $Cl(CH_2)_nCO_2CH_3$, 60 °C, 24 h; (ii) 37% aqueous HCl solution, 100 °C, 2 h; (iii) NEt_3, CH_2Cl_2, RT, 24 h; (iv) HBF_4, RT; (v) HOTf, RT.
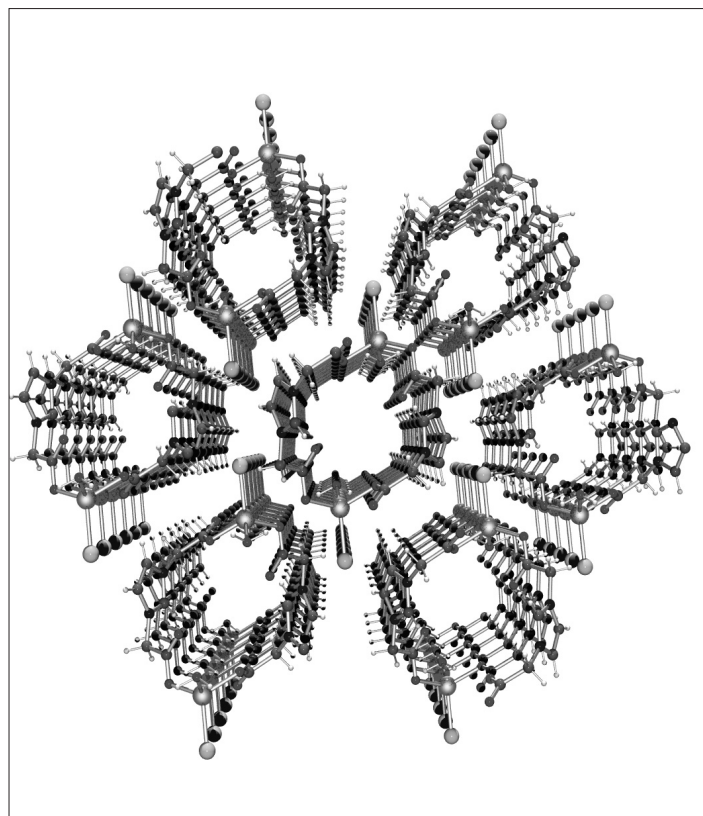

Fig. 4. View into the helical tube of the zwitterionic coordination polymer with the free water-molecules removed for clarity.

modified to improve its performance in the ionic liquids, but the ionic liquid can also be modified and fine-tuned to enhance the performance of the catalyst.

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