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Ionic liquids: perspectives for organic and catalytic reactions

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Abstract

Ionic liquids are attracting a great deal of attention as possible replacement for conventional molecular solvents for catalytic and organic reactions. They complete the use of environmentally friendly water, supercritical fluids or perfluorinated solvents. Features that make ionic liquids attractive include their lack of vapor pressure and the great versatility of their chemical and physical properties. By a judicious combination of cations and anions, it is possible to adjust the solvent properties to the requirement of the reactions, thus creating an almost indefinitely set of "designer solvents". Besides the possibility of recycling the catalytic system, one main potential interest in using ionic liquids results in the unique interactions of these media with the active species and in the possibility to modify the reaction activity and selectivity. Their successful use as solvents has been demonstrated for a wide range of organic reactions including acid catalyzed reactions and transition metal catalyzed transformations. © 2002 Published by Elsevier Science B.V.

Keywords: Ionic liquids; Biphasic catalysis; Imidazolium salts; Weakly coordinating anions

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1. Introduction

Because the constraints of environment are becoming more and more stringent, organic reactions, catalytic processes and separation technologies require the development of alternative solvents and technologies. The ideal solvent should have a very low volatility, it should be chemically and physically stable, recyclable and reusable and eventually easy to handle. In addition, solvents that allow more selective and rapid transformations will have a significant impact.

During these last 20 years, water has emerged as a new useful reaction media [1]. It has been successfully used in biphasic industrial metal catalyzed reactions [2,3]. However, its application is still limited due to the low miscibility of organic substrates in water which often conducts to low reaction rates. Moreover, water is a protic coordinating solvent and so it can react with organometallic complexes by halide–carbon bond protolysis or metal–carbon bond split, for example. If water represents a very interesting solvent for two-phase catalysis, it cannot be

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Abbreviations: [EMI], 1-ethyl-3-methylimidazolium; [EEI], 1-ethyl-3-ethylimidazolium; [BMI], 1-butyl-3-methylimidazolium; [HMI], 1-hexyl-3-methylimidazolium; [OMI], 1-octyl-3-methylimidazolium; [DMI], 1-decyl-3-methylimidazolium; [BDMI], 1-butyl-2,3-dimethylimidazolium; [N_{6444}], tributylhexylammonium; [1-BuPy], 1-butylpyridinium; [HPy], 1-Hpyridinium; [4-MBP], 4-methyl-1-butylpyridinium; MeDBU, 8-methyl-1,8-diazobicyclo[5,4,0]-7-undecenium; OTs, tosylate; OTf, trifluoromethanesulfonate; NFO, nonafluorobutanesulfonate; NTf_2, bis(trifluoromethanesulfonyl)amide; TsOH, *p*-toluenesulfonic acid; TfOH, trifluoromethanesulfonic acid; $ScCO_2$, supercritical carbon dioxide; SAPC, supported aqueous phase catalysis; dba, dibenzylideneacetone; acac, acetylacetonate; TPPTS, triphenylphosphine trisulfonate sodium salt; cod, cyclooctadiene; nbd, norbornadiene

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used for all catalysts and substrates without modifications.

More recently, perfluorinated solvents have proven their utility for many organic and catalytic reactions [4,5]. Nevertheless, specific ligands must be designed to solubilize catalyst in the perfluorinated phase. Moreover, decomposition of fluorous solvents at high temperature yields to toxic compounds and fluorous derivatives are often detected in the organic phase.

Supercritical fluids (e.g. $ScCO_2$) were also described as new solvents for organic and catalytic reactions [6]. Their physical and chemical stability make them described as particularly green solvents. Unfortunately, critical conditions needed for their use is still a limitation.

These last 10 years, ionic liquids were recognized as a novel class of solvents. Initially developed by electrochemists, who were looking for ideal electrolytes for batteries, they are now implied in a lot of applications which continue to expand such as electrolytes for electrochemical devices and processes, solvents for organic and catalytic reactions, new material production, solvents for separation and extractions processes. They now find additional use in enzyme catalysis or in multiphase bio-process operations. Because they impose an ionic environment on chemical reactions, they may change their course, and so one could expect to see a general ionic liquid effect.

We report herein, recent developments in the field of ionic liquids with special attention on new structures, properties and applications. Taking into account the rapid evolution of applications in this topic, those presented herein cover the period from the last Wasserscheid's review [7] to September 2001.

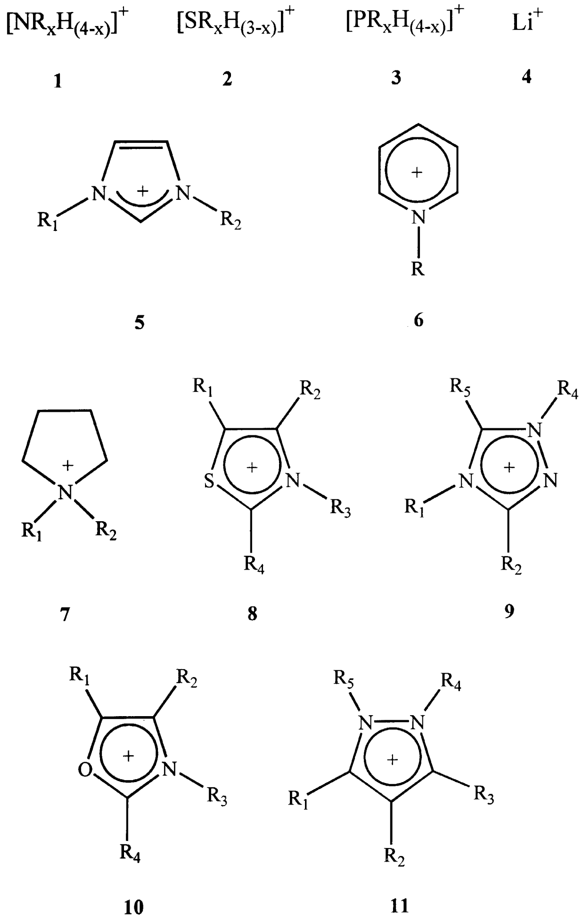
2. Some examples of recent combination of cations and anions

In the literature, it has been mentioned a lot of cation–anion associations able to yield room temperature ionic liquid. They have already been described in a number of reviews [7–10]. Like inorganic molten salts (e.g. Na_3AlF_6; m.p. = 1010 °C), they are composed solely of ions (cations and anions) but they are liquid at low temperature (melting point typically below 100 °C).

2.1. Cations

The cations are generally bulk, organic with low symmetry. Those described until now are based on ammonium **1** [11–13], sulfonium **2** [14], phosphonium **3** [15], lithium **4** [16], imidazolium **5** [17–20], pyridinium **6** [21–23], picolinium, pyrrolidinium **7** [24], thiazolium **8** [25], triazolium **9** [26], oxazolium **10** [27] and pyrazolium **11** [28] differently substituted (Scheme 1).

Of particular interest are the salts based on the *N*,*N*′-dialkylimidazolium cation **5** because of the wide spectrum of physico-chemical properties available in that class. Liquid imidazolium salts are generally obtained by anion exchange from imidazolium



Scheme 1. Some examples of cations described in ionic liquids.

halide precursors. Reported preparations of those precursors involve long reaction times. Recently, improved synthetic methods for the preparation of 1-alkyl(aralkyl)-3-methyl(ethyl)imidazolium halides have been described [29]. In this paper, the synthesis of 1-alkyl-3-methylimidazolium bromides is described with advantage of short reaction time giving high yields (94–99%) without purification step. The availability of such precursors will provide easier access to room temperature ionic liquids with widely varying structures.

It has very often been assumed that non-symmetrical *N,N′*-dialkylimidazolium cations give lower melting point salts. Very surprisingly, 1,3-dialkylimidazolium hexafluorophosphates with dibutyl, dipentyl, dioctyl, dinonyl and didecyl substituents are found to be liquid at room temperature [30].

The alkyl chain on the imidazolium can also bring a fluorous tail [31]. In that way, the fluorinated salts, when added to a conventional ionic liquid, can act as surfactants and facilitate the emulsification of perfluorocarbons in ionic liquids. It can also include task-specific functional groups [32]. Such imidazolium derivatives when used as part of the solvent or doped into less expensive ionic liquids, can be used to extract metal ions from water phases. Free amine groups have also been incorporated on the imidazolium cation and have been used to sweeten natural gas by sequestration of H_2S or CO_2 [33].

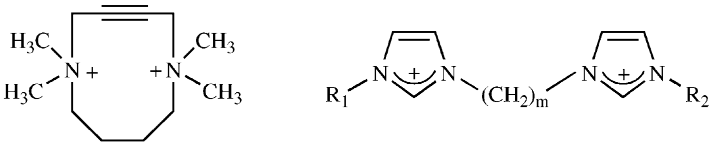
Alkoxy groups have also been attached to the imidazolium cation giving a large number of new ionic liquids which display particularly excellent antielectrostatic effect [34].

Besides the *N,N′*-dialkylimidazolium cations, pyrrolidinium cations **7** have gained attention first as plastic crystal former with anions such as BF_4^- or NTf_2^-. These low melting salts exhibit interesting ionic conductivity and, therefore, have received attention for use as electrolytes in a range of applications including solar cells and batteries [24,35]. Other recently developed cations are the planar trialkylsulfonium ones such as **2**. When combined with the NTf_2^- anion, they give low melting salts with very high conductivity and the lowest viscosity of all the NTf_2^- based room temperature ionic liquids ($[SEt_3][NTf_2]$: m.p. = −35 °C and 30 mPa s at 25 °C). Their high conductivity can be ascribed to a little stronger degree of association between SEt_3^+ and NTf_2^- than that of 1-ethyl-3-methylimidazolium (EMI^+) and NTf_2^- salt [36].

Organic polycations such as **12** and **13**, have also been envisioned (Scheme 2). Associated with bromide anions, the dication **13** ($m = 4$, $R_1 = R_2 =$ methyl) gives a salt melting at 67–69 °C [37]. Based on these polycations, new category of phosphate ionic liquids was described and presented as good candidates for organic electrochemical processes [38].

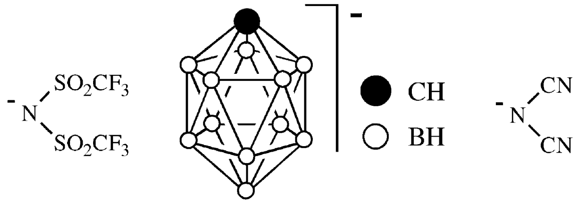
Besides organic cation based ionic liquids, lithium salts are increasingly developed particularly for secondary batteries and storage of energy. They often have lower lattice energy and, therefore, lower melting points than their neighboring elements of the periodic table. Their use to form ionic liquids can be considered. As an example, the mixture of LiCl and $EtAlCl_2$ gives a liquid, on a large range of composition, at temperatures lower than 0 °C [39].

In most chemical applications of ionic liquids, cations influence the physical properties of the medium. However, a chemical effect of the cation is also possible. For example, for the hydrovinylation of styrene catalyzed by Ni organometallic complexes, 4-methylpyridinium salts proved to give higher enantioselectivity than their 1-ethyl-3-butylimidazolium homologue [40]. On the other hand, when used as solvents for the regioselective alkylation of indole, 1,3-dialkyl or 1,2,3-trialkylimidazolium based salts



12 **13**

Scheme 2. Some examples of polycations.



14 **15** **16**

Scheme 3. Some examples of anions.

proved to be superior to the alkylpyridinium ones [41,42].

2.2. Anions

Concerning the anions, they can be classified in two parts: those which give polynuclear anions, e.g. $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Au_2Cl_7^-$, $Fe_2Cl_7^-$, $Sb_2F_{11}^-$. These anions are formed by the reaction of the corresponding Lewis acid, e.g. $AlCl_3$ with the mononuclear anion, e.g. $AlCl_4^-$. They are particularly air and water sensitive. The second class of anions corresponds to mononuclear anions which lead to neutral, stoichiometric ionic liquids, e.g. BF_4^-, PF_6^-, SbF_6^-, $ZnCl_3^-$, $CuCl_2^-$, $SnCl_3^-$, $N(CF_3SO_2)_2^-$, $N(C_2F_5SO_2)_2^-$, $N(FSO_2)_2^-$, $C(CF_3SO_2)_3^-$, $CF_3CO_2^-$, $CF_3SO_3^-$, $CH_3SO_3^-$, etc.

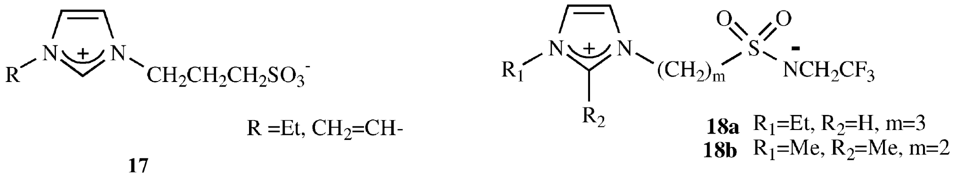
Of particular interest is the trifluoromethylsufonylamide anion $[NTf_2^-]$ **14** [43,44] which gives particularly thermally stable salts (up to 400 °C) (Scheme 3). Salts based on this anion can be easily prepared by anion exchange reactions using the commercially available lithium trifluoromethylsufonylamide. Because of the delocalization of the negative charge, the anion is probably less associated with the cation and then more mobile than the triflate one. For reasons that are not completely elucidate, this imide anion strongly lower the melting points of salts such as quaternary ammonium, surprisingly in the case of small symmetric ammonium such as Et_4N^+ ($[Et_4N][NTf_2]$: m.p. = 105 °C). $LiNTf_2$ and $LiCTf_3$ salts are considered as attractive alternatives to $LiPF_6$ in high voltage ion cells due to the hydrolytic instability of $LiPF_6$ [45].

The last innovation in the ionic liquid repertoire is the carborane-based salts [46,47]. Carborane anions **15** ($CB_{11}H_{12}^-$, Scheme 3) are one of the most inert anions in modern chemistry. Nevertheless, despite their great stability, the position 1 of the $CB_{11}H_{12}^-$ ion can be alkylated leading to new derivatives having melting points just above room temperature. An example is the [1-ethyl-3-methylimidazolium][1-C_3H_7-$CB_{11}H_{11}$] salt which melts at 45 °C. It appears also feasible to substitute the B–H bond with strong electrophiles which allows a systematic variation of the properties of the anion which is unavailable in most traditional anions. Moreover, their very weak nucleophilicity and redox inertness allowed the exploration of new extreme cation reactivity and the isolation of new superacids. Their incorporation in ionic liquids should expand these properties.

Ionic liquids developed until now often present higher viscosities than common organic solvents used in synthesis. Driven by the need to find materials with lower viscosity, dicyanamide anions **16** have recently been described [48]. This anion associated with *N*-butyl-*N*-methylpyrrolidinium, tetra-alkylammonium (N_{6444}), or with 1-ethyl-3-methylimidazolium, gives ionic salts with melting point below −10 °C. Viscosity for the [EMI][$N(CN_2)$] liquid salt is only 21 mPas at 25 °C with respect to 34 mPas for [EMI][NTf_2] at 20 °C.

2.3. Zwitterionic-type ionic liquids

A series of zwitterionic-type ionic liquids consisting of an imidazolium cations containing a covalently bound counter anionic sites, such as a sulfonate **17** or



Scheme 4. Some examples of zwitterionic salts.

a sulfonamide **18** group were prepared (Scheme 4). Compound **17** is a white powder which melts at 150 °C. However, by adding equimolar amounts of $LiNTf_2$, the mixture presents a glass transition temperature of −16 °C. These zwitterionic imidazolium salts (**18a**: $T_g = -61\,^{\circ}C$; **18b**: $T_g = -23\,^{\circ}C$) show unique characteristics [49]. For example they present very high ion density but their component ions cannot migrate. They act as an excellent ion conductive matrix, in which only added ions can migrate.

3. What features make ionic liquids so attractive?

3.1. The versatility of their chemical and physical properties

Besides their very low vapor pressure which makes ionic liquids good alternative solvents to volatile organic solvents, they display a large operating range (typically from −40 to 200 °C), a good thermal stability [50], high ionic conductivity [51], and large electrochemical window [52]. However, the key property of these solvents is the possibility to tune their physical and chemical properties by varying the nature of the cations and anions [53,54]. The spectrum of their physical and chemical properties is much larger than that of organic solvents. Some typical physical characteristics of the more currently used salts are given in Table 1. It has recently been demonstrated that the viscosity of 1-alkyl-3-methylimidazolium salts can be decreased by using highly branched and compact alkyl chain but more importantly by changing the nature of the anion [55]. For the same cation the viscosity decreases as follows: $Cl^- > PF_6^- > BF_4^- \approx NO_3^- > NTf_2^-$.

An illustration of their versatility is given by their exceptional solubility characteristics [56] which make them good candidates for multiphasic catalysis. For example, their solubility with water depends on the nature of the anions, on the temperature and on the length of the alkyl chain on the dialkylimidazolium cation.

For the same 1-butyl-3-methylimidazolium cation, the BF_4^-, $CF_3SO_3^-$, $CF_3CO_2^-$, NO_3^-, and halide salts display a complete miscibility with water at 25 °C. However, upon cooling the $[BMI][BF_4]$/water solution to 4 °C, a water-rich phase separates. In a similar way, changing the [BMI] cation for the longer chain [HMI] (1-hexyl-3-methylimidazolium) leads to a BF_4^- salt which presents a low co-miscibility with water at room temperature. On the other hand, the PF_6^-, SbF_6^-, NTf_2^-, BR_4^- show a very low miscibility with water. But for the PF_6^- based melt, the shorter symmetric substituted 1,3-dimethylimidazolium PF_6^- salt becomes water-soluble.

Salts based on 1,3-dialkylimidazolium cation remain preferred as they generally interact weakly with the anions and are more thermally stable than other quaternary ammonium cations. Recently, Huddleston et al. [57] have examined physical properties (rarely systematically explored in the literature) of different hydrophobic and hydrophilic 1-alkyl-3-methylimidazolium room temperature ionic liquids. It is demonstrated that water content, density, viscosity, surface tension, melting point, and thermal stability were affected by changes in alkyl chain length of the imidazolium cations and by the nature of the anion. As expected, the anion mainly determines water miscibility and has the most dramatic effect on the properties. For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length from butyl to octyl increases the hydrophobicity and the viscosity of the ionic liquid, whereas densities and surface tension values decrease. As a result, one could expect that modifications of alkyl substituents of the imidazolium

Table 1
Some physical characteristics of more currently used 1-butyl-3-methylimidazolium ionic liquids

Anion	Melting point (°C)	Density ($g\,cm^{-3}$)	Viscosity (mPas)	Conductivity ($S\,m^{-1}$)
BF_4^-	−82/−83	1.17 (30 °C)	233 (30 °C)	0.173 (25 °C)
PF_6^-	−61	1.37 (30 °C)	312 (30 °C)	0.146 (25 °C)
$CF_3SO_3^-$	16	1.290 (20 °C)	90 (20 °C)	0.37 (20 °C)
$CF_3CO_2^-$	−50/−30	1.209 (21 °C)	73 (20 °C)	0.32 (20 °C)
NTf_2^-	−4	1.429 (19 °C)	52 (20 °C)	0.39 (20 °C)

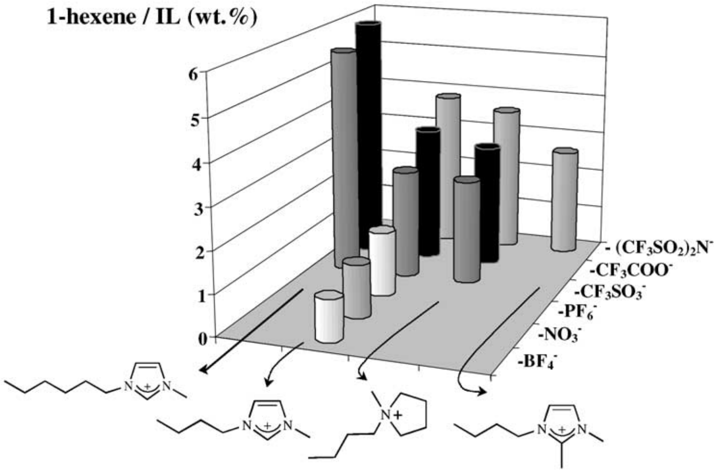


Fig. 1. Solubility of 1-hexene (wt.%) in different combinations of ionic liquids.

ring yields to different and very tunable solvent properties.

The solubility of 1-hexene in different *N*,*N*′-dialkylimidazolium and *N*,*N*-methylethylpyrrolidinium salts has been measured (Fig. 1). Interestingly, increasing the length of the alkyl chain on the cation but also by tuning the nature of the anion can increase the solubility of 1-hexene in the melt.

3.2. The importance of the purity of ionic liquids

The physical and chemical properties of ionic liquids can be altered by the presence of impurities arising from their preparation [58]. Purification of the ionic liquids is then essential. The main contaminants are halide anions or organic base that generally provide from unreacted starting material and water [59]. A colorimetric method has been recently developed to determine the level of unreacted alkylimidazole (<0.2 mol%) in the ionic liquid [59]. As halide impurities can have a detrimental effect on transition metal catalyzed reactions, alternative methods of preparations have been proposed to avoid the use of halide containing starting materials. Examples are given by the direct alkylation of alkylimidazole derivatives [60–62]. Even hydrophobic ionic liquids are hygroscopic [63]. Ionic liquids are usually dried by heating under vacuum. However, water is difficult to remove probably due to the existence of hydrogen bonding. The presence of water can reduce the density and the viscosity but can also modify the chemical properties. In some cases, e.g. PF_6^- based salts, traces of water can generate the decomposition of the anion and the formation of HF.

3.3. How do ionic liquids compare with conventional solvents?

At the present time, there is still an empirical knowledge of these media mainly developed on the basis of their solvent effect on organic reactions compared to that of well-know conventional solvents. The challenge would be to be able to predict their properties in order to optimize the choice for a given application [53].

Solvent polarity has often a strong influence on the outcome of reactions. However, the exact meaning of polarity is already complex, but even more complicated in the case of ionic solvents, as many interactions can be involved. Different investigations of solvent–solute interactions in ionic liquids using solvatochromic dyes have been reported [64,65]. The data indicate that polarities of 1,3-dialkylimidazolium salts based on the PF_6^-, BF_4^-, $CF_3SO_3^-$ and NTf_2^- anions can be compared to that of short chain primary alcohol with a little lower polarity for the NTf_2^- anion. This is in agreement with the ionic liquid solvent effect described in the Diels–Alder reactions of cyclopentadiene with methyl acrylate [66]. The endo/exo selectivity, which may be viewed as being dependent on the polarity of the solvent, is high (6.1:1) when using [BMI][BF_4] and compare quite well to that obtained with methanol (6.7:1). These selectivities are characteristic of hydrogen-bonded polar organic solvents.

The ionic liquid nucleophilicity [67] is only anion dependant and much lower than that of polar solvents which makes ionic liquids unique. Surprisingly, NTf_2^- based salt appears more coordinating than the PF_6^- analog relative to the [Cu(acac)tmen][BPh_4] solvatochromic system (acac: acetylacetonate, tmen: *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). This degree of coordination has been correlated to solvent effect observed in Ni catalyzed oligomerization of ethene [68].

4. Some examples of applications of ionic liquids

4.1. Electrochemical devices

Molten salts and ionic liquids were primarily developed by electrochemists for use in power systems, more than 20 years ago. Since ionic liquids are characterized by fairly large window of electrochemical stability, high conductivities, wide thermal operating ranges, they proved to be excellent candidates for electrochemical devices including supercapacitors, fuel cells, photovoltaics cells, electroplating, etc.

The increasing need for high performance batteries in various applications (portable electronics, cellular phones, electrical vehicles, etc.) has prompted the search for non-aqueous improved electrolytes solutions. The challenge for Li-ion rechargeable batteries was to identify a highly conductive electrolytes which is electrochemically stable (positive limit in the range of 4.5 V vs. Li) and allows high reversible capacity over cycling. Low temperature ionic liquids are proved to be good electrolytes for Li (lithium ion) rechargeable batteries. Their electrochemical window—the electrochemical potential range over which the electrolyte is not reduced or oxidized at an electrode—can be in excess of 4.5 V compared with 1.2 V for aqueous electrolytes. In addition, they offer greater thermal stability, higher conductivity and greater solubility than quaternary ammonium commonly used. As an example, conductivities can be five times higher than that obtained by non-aqueous solvent/salt combinations used in Li-batteries [69,70].

4.2. Solvents for organic and catalyzed reactions

The applications of ionic liquids in a range of reactions continue to expand. Table 2 gives some recent examples that can be classified in two classes: solvents for organic reactions (nucleophilic and electrophilic reactions including acidic catalyzed reactions) and solvents for reactions catalyzed by transition metal complexes.

From a chemical point of view, the main potential benefits of using ionic liquids are to enhance reaction rates and improve chemo- and regioselectivities relative to other organic solvents. It is probably worth mentioning here that ionic liquids can be very efficiently used in microwave assisted chemical transformations. Small amount of ionic liquids can insure an efficient absorption of microwave energy and a good distribution of heat. Reactions can proceed in a much faster way than in conventional organic solvents. As an example, the synthesis of imidazolium salts promoted by microwaves can be achieved within minutes instead of several hours when heated in refluxing solvent [37,71].

From an economic and practical point of view, the use of ionic liquids can of course be beneficial if the separation of the products and the recovery of the catalyst are simple enough. We can find different modes of operation of ionic liquids.

4.2.1. Operability of ionic liquids. Separation of the products and recycling of the catalyst

The ideal case of operability is when the ionic liquid is able to dissolve the catalyst and displays a partial miscibility with the substrate (for optimal reaction rate) and when the products have a negligible miscibility in the ionic liquid and can be removed, by simple decantation, without extracting the catalyst. This mode of operation does not require heating and therefore results in energy saving and reduced loss of catalyst by thermal decomposition.

If the products are partially or totally miscible in the ionic liquid, separation of the products is more complicated. Thanks to the low vapor pressure of the ionic liquids, distillation can be envisioned without azeotrope formation [72]. However, it is often limited

Table 2
Examples of applications of ionic liquids as solvents for chemistry

Reaction	Nature of the ionic liquid	Catalyst	Ref.
Organic reactions			
Diels–Alder reactions	[BMI][BF$_4$], [BMI][PF$_6$], [BMI][lactate], [BMI][Otf]	–	[108]
	[EtNH$_3$][NO$_3$]	–	[109]
	[EEI][Br], [EEI][CF$_3$CO$_2$]	–	[110]
	[EMI][OTf], [BMI][ClO$_4$], [BMI][BF$_4$], [EMI][NO$_3$], [EMI][PF$_6$], [EtNH$_3$][NO$_3$]	–	[66]
	[1-BuPy][Cl]/AlCl$_3$, [EMI][Cl]/AlCl$_3$	–	[111]
	[R$_3$PR$'$][TsO]	–	[112]
	[BMI][PF$_6$], [BMI][SbF$_6$], [BMI][OTf]	Sc(OTf)$_3$	[113]
Aza Diels–Alder reaction	[EtDBU][Otf]	Sc(OTf)$_3$	[114]
N or O regioselective alkylation	[BMI][PF$_6$], [BMI][BF$_4$]	KOH	[41]
	Ammonium and phosphonium	–	[115]
Nucleophilic displacement: Cl → CN	[BMI][PF$_6$]	–	[116]
Biginelli reaction	[BMI][PF$_6$], [BMI][BF$_4$]	–	[117]
Wittig reaction	[BMI][BF$_4$]	–	[118]
Preparation of polymer-supported thionating reagent	[EMI][PF$_6$]	Microwave	[119]
Allylation of alcohols	[BMI][BF$_4$], [BMI][PF$_6$]	R$_4$Sn	[120]
Reduction of aldehydes	[EMI][PF$_6$], [EMI][BF$_4$], [BMI][BF$_4$]	BR$_3$	[121]
Stereoselective syntheses of spirocyclopropanes	[NBu$_4$][Br]	NaOAc NaHCO$_3$	[122]
Benzoin condensation	[Thiazolium][BF$_4$]	NEt$_3$	[25]
Fluorodediazoniation (Balz–Shiemann reaction)	[EMI][BF$_4$], [BMI][PF$_6$], [EMI][CF$_3$CO$_2$], [EMI][OTs], [EMI][OTf]	Addition of NOBF$_4$ or NOPF$_6$	[123]
One pot synthesis of heterocyclic compounds	[EtDBU][OTf], [MeDBU][OTf], [EMI][OTf], [BMI][PF$_6$], [BMI][BF$_4$]	–	[124]
Preparation of α-fluoro-α,β-unsaturated esters	[EtDBU][OTf]	Base	[125]
α-Halo esters + carbonyl substrates: Reformatsky reaction with Zn reagents	[EtDBU][OTf], [EtDBU][BF$_4$], [EtDBU][PF$_6$], [BMI][PF$_6$], [BMI][BF$_4$]	Zn	[126]

Table 2 (*Continued*)

Reaction	Nature of the ionic liquid	Catalyst	Ref.
1,3-Dipolar cycloadditions	[EMI][PF$_6$], [EMI][BF$_4$], [EMI][NFO]	AcOH	[127]
Cycloaddition of CO$_2$ to propylene oxide	[BMI][BF$_4$], [BMI][PF$_6$], [1-BuPy][Cl]	–	[128]
Electrophilic reactions. acidic reaction			
Nitration of aromatics	[EMI][CF$_3$CO$_2$], [EMI][OTf], [HNEtPr$^i{}_2$][CF$_3$CO$_2$]	TfOH with isoamylnitrate	[78]
Beckmann rearrangement	[BMI][BF$_4$], [BMI][CF$_3$CO$_2$], [1-BuPy][BF$_4$]	PCl$_5$ or P$_2$O$_5$ or POCl$_3$	[129]
Aromatic benzoylation	[1-BuPy][Cl]/AlCl$_3$	–	[130]
Fischer indole synthesis of ketones	[*n*-BuPy][Cl]/AlCl$_3$	–	[131]
Isomerization and cracking of paraffins	Acidic chloroaluminates	Acidic chloroaluminates	[85]
Cracking of alkanes and cycloalkanes	[HPy][Cl]/AlCl$_3$, [BMI][Cl]/AlCl$_3$, [Me$_3$S][Br]/AlCl$_3$	Acidic chloroaluminates	[132]
Catalytic cracking of polyethylene	[EMI][Cl]/AlCl$_3$, [BMI][Cl]/AlCl$_3$, [1-BuPy][Cl]/AlCl$_3$, LiCl/AlCl$_3$	–	[133]
Alkylation of isobutane with olefin	[BMI][Cl]/AlCl$_3$	–	[99]
Friedel–Crafts alkylation of aromatics	[BMI][PF$_6$], [PMI][PF$_6$], [HMI][PF$_6$], [BMI][SbF$_6$], [EMI][BF$_4$], [EMI][SbF$_6$], [EMI][OTf], [BMI][OTf]	Sc(OTf)$_3$	[86]
	[BMI][Cl]/AlCl$_3$ supported on silica	–	[83]
	[BMI][PF$_6$], [EMI][Cl]/AlCl$_3$	–	[42]
	[EMI][Cl]/AlCl$_3$	–	[84]
Friedel–Crafts acylation	Acidic chloroaluminates	–	[80]
	Silica supported [BMI][Cl]/FeCl$_3$	–	[134]
	[EMI][I]/AlCl$_3$	–	[81]
	[EMI][I]/AlCl$_3$	–	[82]
		–	[135]
	[EMI][Cl]/AlCl$_3$	–	[84]
Acylative cleavage of ethers	[EMI][I]/AlCl$_3$	–	[136]
Organometallic synthesis of iron complexes	[BMI][Cl]/AlCl$_3$	[BMI][HCl$_2$] as H$^+$ source	[137]
Synthesis of cyclotriveratrylene	[N$_{6444}$][NTF$_2$]	–	[79]
Synthesis of transition metal-cyclophane complexes	[BMI][Cl]/AlCl$_3$	–	[138]

Table 2 (*Continued*)

Reaction	Nature of the ionic liquid	Catalyst	Ref.
Condensation of alcohol (synthesis of cyclotriveratrylene)	[NR_4][NTf_2]	H_3PO_4, TsOH	[79]
Sequential reactions: Claisen rearrangement and cyclization	[EtDBU][Otf], [MeDBU][OTf], [BMI][BF_4], [BMI][PF_6]	Sc$(OTf)_3$	[139]
Transition metal catalyzed reactions			
Olefin hydroformylation	[BMI][BF_4], [EMI][BF_4], [BMI][PF_6], [BMI][SbF_6]	$Rh(CO)_2$(acac) with PPh_3	[140,141]
	[BMI][PF_6], [BMI][BF_4]	$Rh(CO)_2$(acac) with guanidinium or cationic phosphine and phosphite ligands	[94]
	[BMI][PF_6]	$Rh(CO)_2$(acac) with phosphite ligand	[72]
	[Ph_3PEt][OTs], [Bu_3PEt][OTs]	[$Rh_2(OAc)_4$]/PPh_3	[142]
	[BMI][PF_6]	$Rh(CO)_2$(acac) with guanidinium modified diphosphine	[93]
	[BMI][PF_6]	$Rh(CO)_2$(acac) with cobaltocenium salt	[95]
	[BMI][PF_6] in $ScCO_2$	[$Rh_2(OAc)_4$]/P(OPh_3)	[76]
	[4-MBP][Cl]/$SnCl_2$	$PtCl_2(PPh_3)_2$	[143]
Olefin hydrocyanation	[BMI][$CuCl_2$]	[BMI][$CuCl_2$]	[144]
	[Et_3NH][$CuCl_2$], [BMI][$CuCl_2$], [Li][$CuCl_2$]	Cu	[145]
Carbonylation	[BMI][BF_4], [BMI][PF_6]	$Pd(OAc)_2/NEt_3$	[146]
Oxycarbonylation of MeOH	CuCl/KCl	Cu	[147]
Allylic alkylation	[BMI][BF_4]	$Pd(OAc)_2$/phosphine	[148]
	[BMI][BF_4]	$Pd(OAc)_2/PPh_3$	[149]
Enantioselective allylic substitution	[BMI][PF_6]	$Pd(dba)_2$ with ferrocenylphosphine	[150]
Negishi cross-coupling	[BDMI][BF_4]	$Pd(dba)_2$	[92]
Trost–Tsuji C–C coupling	[BMI][Cl]-SAPC	$Pd(OAc)_2$/TPPTS	[151]
Suzuki cross-coupling	[BMI][BF_4]	$Pd(PPh_3)_4$ with Na_2CO_3	[90] [152]
Heck reaction	[BMI][BF_4], [BMI][Br]	$Pd(OAc)_2$/NaOAc	[96]
	[n-Bu_4N][Br]/base	“Pd-benzothiazole carbene”	[153]
	[n-Bu_4N][Br]/base	Phosphapalladacycle	[154]
		$PdCl_2$, $Pd(OAc)_2$, $PdCl_2(PPh_3)_2$	[155]
	[BMI][X], [1-hexylPy][X]	$Pd(OAc)_2$ eventually with base and/or phosphine	[156]
	[BMI][PF_6]	Heterogeneous Pd/C	[157]
1,3-Butadiene telomerization	[BMI][BF_4], [BMI][PF_6]	$Pd(OAc)_2$, $[BMI]_2[PdCl_4]$	[158]

Table 2 (*Continued*)

Reaction	Nature of the ionic liquid	Catalyst	Ref.
Hydrogenation of olefins and diolefins	[BMI][BF$_4$], [BMI][PF$_6$]	Pd(acac)$_2$	[159]
	[Et$_4$N][SnCl$_3$], [R$_4$N][GeCl$_3$], [Ph$_3$MeP][SnBr$_3$]	PtCl$_2$	[91,160]
	[BMI][BF$_4$], [BMI][PF$_6$], [BMI][Cl]/AlCl$_3$	RhCl(PPh$_3$)$_3$, [Rh(cod)$_2$][BF$_4$]	[161]
	[BMI][BF$_4$], [BMI][PF$_6$], [BMI][SbF$_6$]	[Rh(nbd)(PPh$_3$)$_2$][PF$_6$]	[141]
	[BMI][BF$_4$], [BMI][PF$_6$]	RuCl$_2$(PPh$_3$)$_2$, K$_3$Co(CN)$_5$	[162]
	[EMI][NTF$_2$], [EMI][CF$_3$SO$_3$], [EMI][BF$_4$], [BMI][PF$_6$] supported ionic liquid membranes	[Rh(nbd)(PPh$_3$)$_2$][PF$_6$]	[104]
	[BMI][PF$_6$] over polymer gel	Pd/C	[103]
Arene hydrogenation	[BMI][BF$_4$]	[H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$][BF$_4$]$_2$	[88]
Asymmetric hydrogenation	[BMI][PF$_6$]	[Rh(cod){(−)-diop}][PF$_6$]	[141]
	[BMI][BF$_4$]	[RuCl$_2$-{(*S*)-BINAP}]$_2$·NEt$_3$	[163]
	[BMI][PF$_6$]/ScCO$_2$	Ru(O$_2$CMe)$_2$(BINAP)	[74]
Hydrogenation of acrylonitrile–butadiene rubber	[BMI][BF$_4$]	HRuCl(CO)(PCy$_3$)$_2$	[164]
Esterification	[BMI][BF$_4$]	PdCl$_2$(PhCN)$_2$, (+)-NMDPP/TsOH	[165]
Coupling of aryl halides	[BMI][PF$_6$]	[(PPh$_3$)$_n$Ni(0)]	[166]
Olefin polymerization	[BMI][Cl]/AlCl$_3$	NiCl$_2$(diimine)	[167]
	[EMI][Cl]/AlCl$_3$/AlCl$_{3-x}$R$_x$	Cp$_2$TiCl$_2$	[168]
Olefin dimerization	Acidic chloroaluminates	Ni	[89,169,170]
	[4-MBP][Cl]/AlCl$_3$, [4-MBP][Cl]/EtAlCl$_2$, [4-MBP][Cl]/AlCl$_3$/EtAlCl$_2$	(cod)Ni(hfacac)	[171,172]
	[BMI][Cl]/AlCl$_3$/AlEtCl$_2$	[Ni(MeCN)$_6$][BF4]$_2$, [Ni(MeCN)$_6$][AlCl$_4$]$_2$, [Ni(MeCN)$_6$][ZnCl$_4$]$_2$, [Ni(PhCN)$_6$][BF$_4$]$_2$, NiCl$_2$(PBu$_3$)$_2$	[173]
	[BMI][Cl]/AlCl$_3$/AlEtCl$_2$	NiCl$_2$(PCy$_3$)$_2$, [Ni(MeCN)$_6$][BF$_4$]$_2$	[174]
	[BMI][Cl]/EtAlCl$_2$	WCl$_6$ with aniline/EtAlCl$_2$ or Cl$_2$W=NPh(PMe$_3$)$_3$	[175]
	[BMI][PF$_6$], [HMI][PF$_6$], [OMI][PF$_6$], [DMI][PF$_6$]	[(allyl)(NiL$_2$)][SbF$_6$]	[68]
	[EMI][BF$_4$], [EMI][NTF$_2$], [EMI][Al{OC(CF$_3$)$_2$Ph}$_4$], [EMI][BARF], [4-MBP][BF$_4$], [4-MBP][NTf$_2$], all in ScCO$_2$	Wilkes's Ni catalyst	[40]
1,3-Butadiene dimerization	[BMI][BF$_4$], [BMI][PF$_6$], [BMI][OTf]	PdCl$_2$, Pd(OAc)$_2$, Pd(acac)$_2$, PdCl$_2$(PhCN)$_2$	[176]
Olefin metathesis	Chloroaluminates	W(OAr)$_2$Cl$_4$	[177]
	[EMI][Cl]/AlCl$_3$, [EMI][PF$_6$]	Ruthenium carbene	[178]

Table 2 (*Continued*)

Reaction	Nature of the ionic liquid	Catalyst	Ref.
Oxidation	[BMI][PF_6]	Mn(salen) complex	[179]
	CuCl/KCl over silica	$PdCl_2$/$CuCl_2$	[180]
	[BMI][PF_6], [BMI][SbF_6], [BMI][BF_4], [BMI][OTf]	Cr(salen)	[181]
	[EMI][BF_4]	$MeReO_3$	[182]
Radical polymerization	[BMI][PF_6]	Radical initiators	[183]
	[BMI][BF_4], [1-BuPy][BF_4]	Benzoyl peroxide	[184]
	[BMI][PF_6]	Cu^IBr	[185]
Arylation of α-substituted acrylates	[NBu_4][Br]	"Pd–benzothiazole carbene"	[186]
Radical reaction	[BMI][BF_4]/$CHCl_3$, [BMI][BF_4]/CH_2Cl_2	$Mn(OAc)_3$	[187]
Electrochemical polymerization	[EMI][Cl]/$AlCl_3$	Addition of NaCl and use of $ImHCl_2$ as H^+ source	[188]
	[1-BuPy][Cl]/$AlCl_2(OEt)$	No	[189]
Biotransformations			
Transesterification	[4-MBP][BF_4], [BMI][BF_4], [HMI][BF_4], [OMI][BF_4], [BMI][PF_6], [BMI][OTf], [BMI][NTf_2]	Lipase	[190]
Alcoholysis, ammoniomysis, perhydrolysis	[BMI][BF_4], [BMI][PF_6]	Lipase	[191]
Synthesis of *Z*-aspartame	[BMI][PF_6]	Enzyme	[192]

to highly volatile or thermally labile products because of the general thermal instability of organometallic catalysts. Extraction with a co-solvent poorly miscible with the ionic liquid (water or organic solvent) is often used although cross-contamination may occur.

Extraction with supercritical CO_2 proved to be promising technique mainly because of its complementary properties with ionic liquids [73]. $ScCO_2$ dissolves quite well in ionic liquids to facilitate extraction (e.g. 60% of CO_2 dissolves in [BMI][PF_6] at 80 bar), but ionic liquids do not dissolve in carbon dioxide, so pure products can be recovered. Continuous-flow catalytic system based on the combination of the two solvents systems, e.g. ionic liquids and $ScCO_2$ have been reported for hydrogenation [74,75], hydroformylation [76], and hydrovinylation reactions [40].

A more complex example of separation of the products can be illustrated by the nucleophilic cyanide displacement on benzyl chloride to yield phenylacetonitrile. This reaction is usually performed using phase transfer catalyst, e.g. a tetra-alkylammonium salt, to facilitate the reaction between the organic reagents and the inorganic KCN salt that provides the nucleophile. Ionic liquids, e.g. [BMI][PF_6] can act as both the solvent and the catalyst in promoting the contact of the reactants and providing the activation of the nucleophile. In a first step, the reaction proceeds. The products are removed in a second step via vaporization or supercritical fluid extraction. Washing with water can be used to remove the inorganic salt by-product. The ionic liquid can be reused after decantation thanks to its low solubility with water and $ScCO_2$.

Although, $ScCO_2$ extraction is an efficient separation technique applicable to a wide range of separation problem, it remains technically demanding. It has recently been demonstrated that solutes can be extracted from ionic liquids by pervaporation. This technique is based on the preferential partitioning of the solute from a liquid feed phase into a dense, non-porous membrane. The ionic liquids do not permeate the membrane. This technique can be applied to the recovery of volatile solutes from heat sensitive reactions carried out in ionic liquids such as bio-conversions [77].

4.2.2. Organic reactions

Nice examples of ionic liquid properties and solvent effect are given by Diels–Alder reactions of oxygen containing dienophiles. Reaction rates are comparable to that described in water. The endo selectivities can be higher, particularly by adding Lewis acid such as ZnI_2 or $Sc(OTf)_3$ (for references, see Table 2).

4.2.2.1. Nucleophilic reactions. General ionic liquid effect can be expected for reactions involving polar or charged intermediates such as carbocations or carbanions which could become more long-lived in these media. This is the case of the nucleophilic alkylation of nitrogen or oxygen atoms by haloalkanes in the presence of a base which involves the preformation of an anionic intermediate. In $[BMI][PF_6]$, the alkylation of indole or naphthol occurs with similar reaction rates compared to organic polar solvents but with very good regioselectivity [42].

4.2.2.2. Electrophilic reactions. The other interesting applications are related to that which use *acidic reagents or catalysts*. Because of their low nucleophilicity, ionic liquids provide unique environment in stabilizing electron deficient intermediates. Another practical advantage of ionic liquids is that they could avoid problems associated with the neutralization of large quantities of acids generally needed in the classical routes. Examples are given by the nitration of aromatics carried out in $[EMI][CF_3CO_2]$ with $(CF_3CO)_2O$ and $[NH_4][NO_3]$ without the need of aqueous work-up [78]. The CF_3COOH by-product is separated by reaction with the Et-iPr$_2$N amine creating the [Et-iPr$_2$NH][CF_3COO] salts.

Condensation methods of alcohols usually involve strong acid or acid/solvent combination as reaction media and dehydrating conditions. Catalytic amount of Bronsted acids such as H_3PO_4 proved to be soluble in $[NRR'_3][NTf_2]$ (R = hexyl, R' = butyl) without the addition of chlorinated solvents [79]. The condensation of veratryl alcohol is facilitated, the water formed is continuously lost to vapor which assists in driving the reaction to high yields. However, the product (cyclotriveratrylene) separation require the addition of a co-solvent.

Acidic chloroaluminates have already been largely described as both catalysts and solvents for reactions conventionally promoted by $AlCl_3$, e.g. stoichiometric Friedel–Crafts acylation [80–82], catalytic alkylation of aromatics [83,84], isomerization and cracking of paraffins [85]. Due to the powerful ability of $Al_2Cl_7^-$ to accept chloride ions, acidic chloroaluminates are the source of high Lewis acidity and can even be superacids in the presence of protons. The advantages over solid $AlCl_3$ reside in the possibilities to minimize the undesirable side reactions by controlling the concentration of polynuclear $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ anions and to recycle and reuse the ionic liquid catalyst. The main limitation of these chloroaluminates acids is that they can generate organic chloride impurities and contaminate the products.

Non-chlorinated Lewis acids, such as scandium triflate, have also been used to catalyze Friedel–Crafts alkylation reactions [86]. While no alkylation of aromatic hydrocarbon occurs in dichloromethane, in $[BMI][PF_6]$, $Sc(OTf)_3$ catalyzes the alkylation of benzene with high yield for the monoalkylated product. In addition, the products can be separated by simple decantation and the catalyst reused.

The imidazolium cation may also exhibit by itself some Lewis acidity but it remains very weak [87]. An example is the Friedel–Crafts alkylation of 1-(2-(*N*-morpholino)ethyl)-2-methylindole with benzoyl chloride in $[BMI][PF_6]$ without the addition of Lewis acid [42]. The lower acidity of the medium compared with usual acidic catalysts, leads to fewer by-products and therefore higher yields.

4.2.3. Solvents for transition metal catalysis

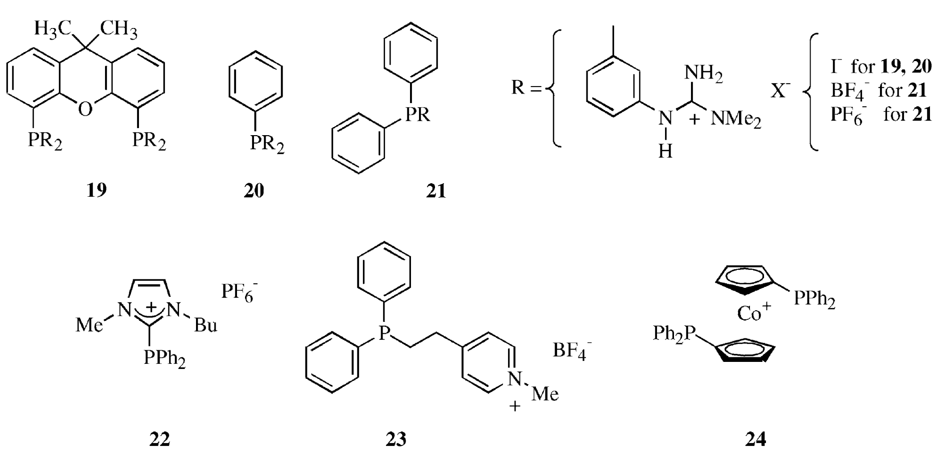
One of the major problem with transition metal catalyzed reactions is the recycle of expensive catalysts and ligands. In Table 2, we can find different examples of immobilization and recycling of the catalyst. When the active catalytic species is ionic, it can be retained in the ionic liquid without the need of specially designed ligand. This is the case of olefin hydrogenation reactions catalyzed by the cationic $[HRh(PPh_3)_2(L_2)][PF_6]$ complexes. The cationic $[H_4Ru_4(C_6H_6)_4][BF_4]$ cluster is also soluble and stable in $[BMI][BF_4]$ ionic liquid [88]. In the presence of hydrogen, it probably forms the $[H_6Ru_4(C_6H_6)_4][BF_4]_2$ complex which is arene hydrogenation effective catalyst. Another example is given by the olefin dimerization catalyzed by the active cationic [HNi(olefin)][A] complexes. This active species can be formed by in situ alkylation of a nickel(II) salt using an acidic alkylchloroaluminate ionic liquids as both the solvent and the co-catalyst [89]. The cationic [(methallyl)NiPh$_2$-PCH$_2$PPh$_2$(O)][SbF$_6$] complex proved to be stable and active for ethene oligomerization in PF$_6$$^-$ based ionic liquids without the addition of Lewis acid. The high electrophilicity of the Ni center, which is responsible for the activity of the catalyst, is probably not altered by the ionic solvent [68]. In the Suzuki reaction, the active species in [BMI][BF$_4$] is supposed to be the tricoordinated [Pd(PPh$_3$)$_2$(Ar)][X] complex which forms after oxidative addition of the aryl halide to the [Pd^0(PPh$_3$)$_4$] [90]. Therefore, thanks to their low nucleophilicity, ionic liquids do not compete with the unsaturated organic substrate for the coordination to the electrophilic active metal center.

The anionic active [HPt(SnCl$_3$)$_4$]$^{3-}$ species have been isolated from the [NEt$_4$][SnCl$_3$] solvent after hydrogenation of ethylene [91]. The PtCl$_2$ precursor used in this reaction is stabilized by the ionic salt (liquid at the reaction temperature) since no metal deposition occurs at 160 °C and 100 bar. The catalytic solution can be used repeatedly without apparent loss of catalytic activity.

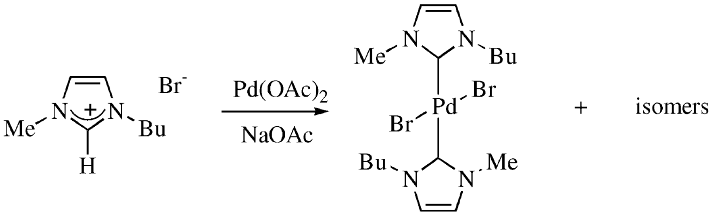
When the active catalytic species is assumed to be non-charged, leaching of the transition metal in the organic phase can be limited by the use of functionalized ligands. The ligands have to be specially tuned to the ionic liquid and vice versa. Examples of ionic liquid soluble phosphorous ligands are given in Scheme 5 (ligand **22** [92], ligands **19** and **20** [93], ligands **21** and **23** [94], ligand **24** [95]). These ligands have been used to immobilize Rh complexes for the olefin hydroformylation.

In the case of Pd-mediated reactions, the loss of Pd by the formation of Pd black is often a main difficulty to recover the catalyst. The imidazolium cation is presumed to be a simple inert component of the solvent system. However, the C(2) proton of the imidazolium is acidic and can be deprotonated, by basic ligands of the metal complex, to form carbenes (Scheme 6). The ease of formation of the carbene depends on the nucleophilicity of the anions associated with the imidazolium. For example when Pd(OAc)$_2$ is heated in the presence of [BMI][Br] the formation of a mixture of Pd imidazolylidene complexes occurs. The Pd–carbene **25** complex have been shown to be active and stable catalysts for Heck and C–C coupling reactions [96]. The highest activity and stability of Pd is observed in [BMI][Br] ionic liquid.

Carbene complexes can be formed not only by deprotonation of the imidazolium cation but also by direct oxidative addition on metal(0) (Scheme 7). Oxidative addition of 1,2,3-trimethylimidazolium cation to Pt(0) has not been observed. However, oxidative addition of C–H bond, which is known to proceed with a lower barrier, has been demonstrated. Heating 1,3-dimethylimidazolium tetrafluoroborate with Pt(PPh$_3$)$_4$ in refluxing THF resulted in the formation of the oxidative addition complex **26** [97]. A way



Scheme 5. Some examples of ligands used in ionic liquids.



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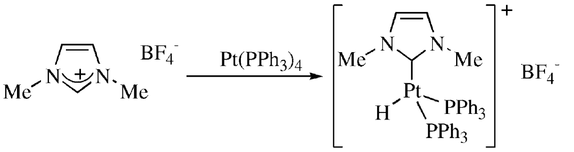
Scheme 6. Formation of carbene Pd complex by deprotonation of the imidazolium cation.



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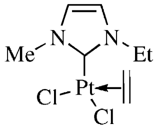
Scheme 7. Formation of carbene Pd complex by oxidative addition with Pt(0).

to limit decomposition of this carbene–metal-alkyl complex by reductive elimination, is to perform the reaction in imidazolium salts as the solvent of the reaction. The large excess of imidazolium present in these conditions can be expected to drive the oxidative reaction.

The N-heterocyclic carbene **27** has also been isolated in the reaction of $PtCl_2$ and $PtCl_4$ with ethylene in the basic [EMI][Cl]/$AlCl_3$ ionic liquid (Scheme 8). The basicity of the ionic liquid (presence of Cl^- anion in excess) and the ethylene pressure are essential for the reaction to occur. Complex **27**, which can be considered as an analog to the Pd(II) carbene intermediate in the Heck reaction, crystallizes from the ionic liquid [98].



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Scheme 8. Isolated carbene after reaction of $PtCl_2$ and $PtCl_4$ with ethylene in [EMI][Cl]/$AlCl_3$.

5. Supported ionic liquids as catalysts and solvents

In the few years, one of the challenges in the field of catalysis was to replace the existing acidic liquid catalysts by non-toxic, non-corrosive easy to handle and environmentally friendly ones. Liquid chloroaluminates based ionic liquids have been used to perform olefin or aromatic hydrocarbon alkylation [99]. Undesirable side reactions could be minimized by adjusting the $Al_2Cl_7^-$ concentration in the liquid.

The immobilization of chloroaluminates on a solid support can bring some advantages such as the ease of separation of the products and the better dispersion of the catalyst [83,100]. However, the deactivation of the catalyst, which is mainly due to the adsorption of heavy products on the surface of the solid, leads to loss of conversion with time. In order to facilitate the immobilization of the acidic ionic liquids, an alternative method is to chemically bond the Lewis acid, e.g. $AlCl_3$, $SnCl_4$ [101,102] on an inorganic support already functionalized with an imidazolium chloride moieties. This method has been applied for the alkylation of benzene with dodecene.

Another different method has been developed by Carlin et al. which consists in using the ionic liquids as solvents of transition metal complexes and support them on polymers such as poly(vinylidene fluoride)-hexafluoropropylene. The ionic liquid gives ionic conductivity and flexibility to the otherwise rigid co-polymer. Palladium [103] or rhodium catalysts were incorporated in these supported ionic liquid membranes, those with rhodium were employed to examine the catalytic hydrogenation of propylene [104].

Interestingly, ionic liquids can be used as novel phase in liquid-phase organic synthesis compatible with high-throughput synthesis and automation technology [105]. An example is given by the reaction of ionic liquid bounded benzaldehyde in Knoevenagel reactions and 1,3-dipolar cycloadditions using solvent free conditions assisted by microwave irradiations. The advantages offered by the use of ionic liquid technology are the routine product isolation, the ease for removing side products and the possibility to use standard analytical methods to monitor reaction progress.

6. Conclusion and outlook

The possibility to adjust the solubility characteristics of ionic liquids is one of their key advantages. Multiphasic (biphasic) catalysis can be performed and optimized. Reactions which cannot be performed in biphasic aqueous systems, due to the lack of solubility of the organic substrates, can be now envisioned in ionic liquids. An example is the hydroformylation of long chain olefins. In addition, because of the tunable coordinating ability of the anions, highly electrophilic metal center, involved as the active species in many reactions, can be stabilized and immobilized in the solvent, without loss of their activity. The product selectivity can also be improved. An example is the butene dimerization catalyzed by nickel complexes in acidic chloroaluminates [106]. This reaction has been performed on continuous pilot scale by IFP (Difasol process). Compared to the homogeneous industrial process (Dimersol process), the overall yield in dimers is increased. In a similar way, selective hydrogenation of diene can be performed in ionic liquids since the solubility of dienes is higher than that of monoene which is higher than that of paraffins. Due to these differences, ionic liquids offer the interesting option to make possible the transformation of feed diluted with inert components (such as butane or isobutane).

Besides the chemical advantages, it is worth mentioning the engineering one. Because the catalyst is concentrated and operates in the ionic phase, reaction volume can be much smaller than in classical homogeneous process in which catalyst concentration is often very low. In the case of Difasol process, a reduction of the reaction section volume by a factor up to 40 can be achieved. For this application, well-stirred carbon steel reactors that provide thorough mixing of the two phases, can be used with no problem of corrosion. The decantation of the phases is operated at the outlet of the reactor in a settler. This new Difasol technology enable lower dimer (e.g. octenes) production cost [106].

Concerning new horizons for ionic liquids, the discovery of enzyme activity in these media extends their potential use in bioinorganic applications [107]. Their use in enantioselective reactions promoted by chiral catalysts is an open field of great interest.

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