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Ionic liquids: applications in catalysis

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Abstract

The use of room temperature ionic liquids as either solvents or catalysts has been the subject of considerable recent attention because of the prospects for “green” catalysis. This paper presents a review of the potential applications of these unique liquid materials in industrial catalysis. © 2002 Published by Elsevier Science B.V.

Keywords: Ionic liquids; Catalysis; Synthesis

1. Introduction

In recent years, significant progress has been made in the application of room temperature ionic liquids in catalytic processes. Ionic liquids are salts consisting of ions, which exist in the liquid state at ambient temperatures, i.e. they are salts that do not normally need to be melted by means of an external heat source. Ionic liquids typically consist of organic nitrogen-containing heterocyclic cations and inorganic anions. Some typical cation/anion combinations comprising the main families of ionic liquids are illustrated in Table 1. The physical properties and solubilities of some ionic liquids frequently used in catalytic studies are given in Table 2. (All the data are based on experiments in our laboratories.)

The most widely used methodology in the preparation of ionic liquids is metathesis of a halide salt of the organic cation with a group 1 or ammonium salt containing the desired anion [1–5]. Alternatively the halide salt of the organic cation may be reacted with a Lewis acid. Fig. 1 illustrates preparation routes for some typical ionic liquids. Recently, some new categories of ionic liquids have been developed. For example, ionic liquids based on polyammonium halide

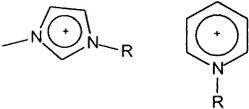
salts can be synthesized by replacing the halide ions with phosphate ions [6a]. Other ionic liquids with dicyanamide anions [6b] and C_2 -symmetrical imidazolium cations [6c], and even duplex DNA [6d] anions have also been synthesized.

Application of ionic liquids in chemical processes has blossomed only within the last decade. Comprehensive information about this field may be found in the recent reviews by Seddon and Holbrey [7a] and Welton [7b] and by Wasserscheid and Keim [8a] and Hagiwara and Ito [8b]. Many details of recent developments may be found in a series of articles by Freemantle [9–20]. These provide an excellent and essential source of the physical and chemical properties of ionic liquids and catalog a range of reactions that can be carried out in ionic liquids. The focus of this review is on the catalytic applications of ionic liquids, in particular on the principles involved and analogies with catalytic reactions in conventional media. Among the topics to be discussed are: how can ionic liquids be used in “green” catalysis and what potential do ionic liquids have for catalysis? To answer these questions, we may take a short look at the advantages that ionic liquids have in respect of their properties.

1. A wide liquid range of about 300 °C with a melting point around room temperature.

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Table 1
Typical cation/anion combinations in ionic liquids^a

Cations ^a	Anions	Coordination ability of anions
	$[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CuCl}_2]^-$, $[\text{AlCl}_4]^-$, $[\text{AlBr}_4]^-$, $[\text{AlI}_4]^-$, $[\text{AlCl}_3\text{Et}]^-$, $[\text{NO}_3]^-$, $[\text{NO}_2]^-$, $[\text{SO}_4]^{2-}$	Weak (neutral)
PR_4^+ , SR_4^+ , NR_4^+	$[\text{Cu}_2\text{Cl}_3]^-$, $[\text{Cu}_3\text{Cl}_4]^-$, $[\text{Al}_2\text{Cl}_7]^-$, $[\text{Al}_3\text{Cl}_{10}]^-$	None (acidic)

^a R = alkyl.

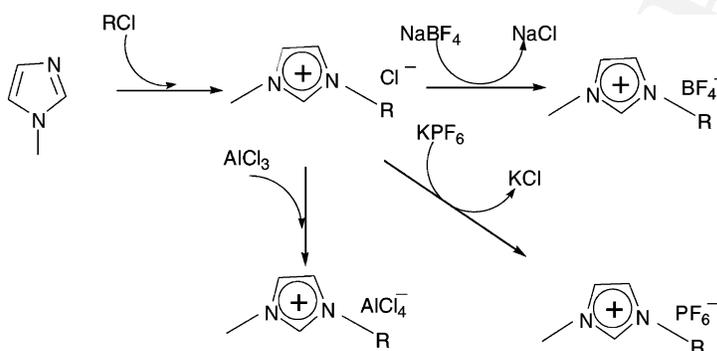


Fig. 1. Typical preparation routes for ionic liquids.

- 63 2. A wide range of materials including inorganic, or-
 64 ganic and even polymeric materials are soluble in
 65 ionic liquids.
 66 3. Excellent and variable Lewis/Brønsted acidity.
 67 4. High polarity [21].
 68 5. Negligible vapor pressure.
 69 6. Potential to be reused and recycled.

70 Ionic liquid are generally thought to have another
 71 advantage in that they display a low coordination
 72 tendency, however, direct experimental evidence of
 73 this is still lacking, that is to say, the structure of the
 74 solute entities in ionic liquids is still unclear. Inter-
 75 conversion of coordinatively unsaturated–saturated
 76 species is a key feature in catalyst function, fun-
 77 damental studies on the coordination behavior of
 78 ionic liquids with different materials such as metal
 79 clusters, oxides nanoparticles and coordination com-
 80 plexes are required in order to understand this area
 more clearly.

2. Current applications

81

82 What a role that ionic liquids have currently played
 83 for catalysis? A simple answer is for green catalysis.

84 More than 60% of products and more than 90%
 85 of processes worldwide rely on the rapidly expanding
 86 field of catalysis. High specificity and/or efficiency is
 87 the most important feature of “green” catalysis. Two
 88 concepts frequently discussed in “green” chemistry
 89 are atom economy and chemical specificity. Few of
 90 the many catalytic reactions can be atom economic.
 91 Furthermore, even for such reactions, in most cases
 92 it is hard to reach 100% conversion with 100% se-
 93 lectivity due to thermodynamic obstacles and/or the
 94 competition of parallel reactions. In order to measure
 95 the quality of a synthetic method, chemical speci-
 96 ficity is more fundamental and important. High speci-
 97 ficity, for example by accelerating the target reaction
 98 to reach equilibrium as fast as possible while elimi-
 99 nating or minimizing side reactions (high selectivity),

Table 2
Physical properties and solubilities of commonly used ionic liquids

Ionic liquid ^a	x^b	MW (g/mol)	Color (with impurities)	Density (g/ml)	Liquid temperature (°C)		Solubility in common solvents ^c							
					Lowest	Highest	Water	Methanol	Acetone	Chloro- form	Petroleum ether	Hexane	Acetic anhydride	Toluene
[bmim]BF ₄		226.02	Light yellow	1.320	−48.96	399.20	s	s	s	s	i	i	i	i
[bmim]PF ₆		284.18	Light yellow	1.510	13.50	388.34	i	s	s	s	i	i	s	i
[bmim]Cl/AlCl ₃	0.50	154.01	Light brown	1.421	−88.69	263.10	r	r	s	s	i	i	s	s
	0.55	151.94	Light brown	1.456	−94.44	286.59	r	r	s	s	i	i	s	s
[emim]Br/AlCl ₃	0.60	149.87	Light brown	1.481	−95.87	316.34	r	r	s	s	i	i	s	s
	0.50	162.21	Purplish black	1.575	13.61	272.51	r	r	s	i	i	i	s	i
[emim]PF ₆	0.55	159.32	Brownish black	1.656	6.45	294.02	r	r	s	i	i	i	s	i
	0.60	156.43	Brownish black	1.995	−19.08	345.34	r	r	s	i	i	i	s	i
<i>N</i> -butylpyridine/ AlCl ₃	0.50	152.50	Yellow	1.426	2.71	304.65	i	i	s	s	i	i	s	i
	0.50	152.50	Yellow	1.412	18.80	240.00	r	r	s	i	i	i	s	s
	0.55	150.59	Brownish yellow	1.430	33.73	245.39	r	r	s	i	i	i	s	s
(CH ₃) ₃ NHCl/ 2AlCl ₃	0.60	148.67	Brownish yellow	1.497	18.11	260.24	r	r	s	i	i	i	s	s
	0.66	362.25	Brownish yellow	1.621	−67.90	80.25	r	r	s	i	i	i	s	s

^a [bmim] = 1-butyl-3-methylimidazolium, [emim] = 1-ethyl-3-methylimidazolium.

^b Apparent mole fraction of AlCl₃.

^c s: soluble, i: insoluble, r: may react with each other.

100 or via reducing long synthetic routes to one or two
101 steps (high efficiency), is usually our only choice. Us-
102 ing ionic liquids as replacement for organic solvents
103 is one way to make a catalytic process “green”, how-
104 ever, making a process highly specific is a more im-
105 portant concern from the view of “Green Chem.”. As
106 shown in this review ionic liquids, as a consequence
107 of their unique properties, have a great potential to
108 help in reaching these goals. However, the mechanis-
109 tic role that ionic liquids play is still far from clear at
110 present. The questions presented here will, it is to be
111 hoped, stimulate the continuing growth of catalysis by
112 ionic liquids.

113 Current applications of ionic liquids in catalysis as
114 alternatives to conventional media are concentrated
115 in two directions. One is to take the place of or-
116 ganic solvents due to their unique solvent proper-
117 ties and the other is to take the place of liquid acids
118 due to their variable acidities. The former applica-
119 tions include dimerization reactions, Heck reactions
120 and hydroformylation, while the latter includes alky-
121 lation reactions and Friedel–Crafts reactions. Many
122 of these studies have significant commercial appli-
123 cations but fundamental studies of the relationship
124 between the properties of ionic liquids and the im-
125 proved performance compared with conventional sol-
126 vents are still rare. For example, many studies have
127 found that reaction rate, conversion and selectivity
128 are enhanced to different degrees (see Tables 3–5),
129 but the reason, i.e. why the liquids show higher ef-
130 ficiency/specificity in the reactions, is still an open
131 question.

132 Improvement of current biphasic aqueous–organic
133 systems by using ionic liquids in place of water has
134 received significant recent attention. The disadvan-
135 tage of traditional aqueous–organic systems is that
136 the ligands have to be modified in order to give the
137 catalyst the desired solubility in water [22–37]. In
138 addition, the poor solubility of some organic sub-
139 strates in water giving rise to low reaction rates is
140 another limitation. Water is a coordinating protic
141 solvent with high polarity, i.e. water itself in many
142 cases is rather reactive with organometallic catalysts.
143 Ionic liquids do not suffer from these limitations.
144 When used in place of water, ionic liquids can form
145 ionic liquid–organic solvent systems without requir-
146 ing any change or modification in either ligand or
organic phase.

3. Significant examples of the use of ionic liquids in catalysis 147 148

149 Tables 3–5 present fairly complete lists of re-
150 search reported on catalysis using ionic liquids up to
151 mid-2001. As indicated in the tables, ionic liquids
152 have been employed in a wide range of reactions.
153 Based on the key steps involved, we suggest these
154 reactions can be divided into three types, i.e.:

- 155 1. Hydrogen addition and rearrangement reactions
156 (Table 3).
- 157 2. C–C and C–O cleavage reactions (Table 4).
- 158 3. C–C or C–heteroatom coupling reactions (Table 5).

159 In addition to the data in the tables, some general
160 points are discussed in more detail below.

3.1. Hydrogen addition and rearrangement reactions 161 162 (see Table 3)

3.1.1. Hydrogenation 163

164 Many attempts have been made to develop bipha-
165 sics processes for homogeneous hydrogenation cat-
166 alyzed by transition metal complexes. In traditional
167 aqueous–organic solvent system, modification of
168 the ligands to introduce water-solubility is gen-
169 erally necessary but the cost is a great problem.
170 [RuCl₂-(S)-BINAP]₂-NEt₃ as an asymmetric hydro-
171 genation catalyst can be dissolved in the ionic liquid
172 [bmim]BF₄ directly without any modification how-
173 ever and used in a biphasic system with isopropanol
174 as the organic phase. Hydrogenated products Ibupro-
175 fen/Naproxen (2-acrylacrylic acids) have been ob-
176 tained with high enantioselectivity (96 ee%). The
177 products remain in the isopropanol phase and can be
178 separated by simple decantation [41]. The recovered
179 ionic liquid phase containing the catalyst can then be
180 reused several times without any significant loss in
181 catalytic activity or enantioselectivity.

182 Stereoselective hydrogenation of aromatic com-
183 pounds in [bmim]Cl–AlCl₃ ionic liquid systems has
184 also been investigated [42], showing that carbocyclic
185 aromatic compounds are readily protonated [43].

186 Recently, supercritical CO₂ has been employed
187 with ionic liquids to form ionic liquid/scCO₂ bipha-
188 sics systems. By avoiding the use of organic solvent
189 completely, the systems are the environmentally to-
190 tally benign whilst having high reaction rates [44].

Table 3
Survey of catalytic hydrogen addition and rearrangement reactions

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
1	Hydrogenation	Hydrogenation of cyclohexene catalyzed by rhodium complexes	[bmim]Cl/AlCl ₃ PF ₆ , BF ₄	In 180 cm ³ autoclave	At room temperature, under argon protection the ionic liquid and rhodium complex are added by Schlenk technique to the autoclave, cyclohexene is then introduced and the autoclave is pressurized with 10 atm of hydrogen	Immobilization of Ru complex in ionic liquids	[38]
		Hydrogenation of non-activated alkenes catalyzed by ruthenium catalyst	[bmim]BF ₄	In 300 ml autoclave	In a stainless steel autoclave (300 ml) containing catalyst and water, the substrate is added with syringe. (The temperature and pressure are not mentioned). After reaction, the autoclave is cooled the pressure released, and the mixture separated into two phases	Easy product separation and catalyst recycling	[40]
		Asymmetric hydrogenation of 2-phenylacrylic acid with [RuCl ₂ -(S)-BINAP] ₂ -NEt ₃	[bmim]BF ₄	3 ml	At room temperature, the reactor is pressurized with H ₂ to the desired pressure followed by stirring for 20 h. The organic phase (upper layer) is separated and the ionic catalyst phase is reused	Easy product separation and catalyst recycling, high enantioselectivities	[41]
		Stereoselective hydrogenation of aromatic compounds	[bmim]Cl/AlCl ₃			Excellent yields and selectivities, efficient under mild conditions	[42]
		Asymmetric hydrogenation of tiglic acid	[bmim]PF ₆	30 g	At 25 °C, ionic liquid (30 g), water (10 ml), Ru complex (22 μmol), tiglic acid 1.1 mmol mixed up in 160 ml vessel under N ₂ , 5 bar of H ₂ , stirred for 18 h, then warmed to 35 °C and scCO ₂ bubbled through into a cold trap for about 18 h	No need of organic solvents and catalyst redesign, immobilization of catalyst in IL	[44]
2	Hydrogenation, isomerization	Hydrogenation of 1-pentene with isomerization to 2-pentene using rhodium catalyst	[bmim]BrF ₄ , PF ₆ , SbF ₆	4 ml	The hydrogen pressure is set to 0.1 MPa in Fischer–Porter glass flask containing 0.05 mmol catalyst, ionic liquid (4 ml) and 1-pentene. After reaction, the remaining upper organic phase is removed and ionic liquids is reused	Liquid–liquid biphasic protocol realized	[45]

Table 4
Survey of catalytic C–C and C–O cleavage reaction

Entry	Reaction	Reaction description	Ionic liquid	Scale	Brief details	Advantages	Reference
1	Catalytic cracking of polyethylene	Catalytic cracking of high/low density polyethylene to give light alkanes	[emim]Cl/AlCl ₃ , [N-butylpyridine]Cl/ AlCl ₃ , [bmim]Cl/AlCl ₃ , LiCl/AlCl ₃		At 130–180 °C the polyethylene must be finely powdered for the reaction to succeed. The polyethylene melts and the surface area in contact with the ionic liquid is reduced. Above 180 °C, efficient stirring is employed to disperse the molten polyethylene in the ionic liquid	Easy separation and ionic liquid reusable	[48]
2	Acylative cleavage of a series of cyclic and acyclic ethers	Acylative cleavage of a series of cyclic and acyclic ethers to afford ester	[emim]I–AlCl ₃	5 g	At room temperature, drofuran (0.20 ml, 2.5 mmol) freshly distilled from potassium/benzophenoune ketyl is added via a syringe to the ionic liquid, and allowed to stir for 15 min. Freshly distilled benzoyl chloride (0.58 ml, 5 mmol) is then added via a syringe to the solution and stirred under argon atmosphere for 2 h. Aqueous workup involved the careful addition of 20 ml of 0.1 M HCl or distilled water followed by extraction with chloroform three times. The combined organic extracts were then washed with 50 ml of saturated sodium bicarbonate followed by drying with anhydrous MgSO ₄ filtration through fluted filter paper, and concentration in vacuum. The crude reaction mixture is then purified using flash column chromatography on silica gel using 10:1 hexanes/ethyl acetate eluent to afford 0.72 g, 95% yield of 4-iodobutyl benzoate		[49]
3	Dissolution of kerogen and heavy oil.	Cleavage of heterocyclic compounds	[bmim]Cl/AlCl ₃ , PF ₆				[18]
4	Asymmetric ring opening reaction	Ring opening reactions of epoxides catalyzed by Cr(salen)	[bmim]PF ₆ /SbF ₆ / BF ₄ /OTf	1 ml	At 20 °C, of epoxide (2 mmol) and 3 mol% complex are stirred for 10 min, then hexane (15 ml) is added and stirred for 10 min, and the Cr(salen) complex (upper phase) is separated from the ionic liquid phase by simple decantation	No hazardous workup stages like distillation of azide, catalyst re-design, easy catalyst recycling	[50]

Table 5
Survey of catalytic C–C and C–heteroatom coupling reactions using ionic liquids systems

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
1	Friedel–Crafts reaction	Alkylation or acylation of aromatic rings catalyzed by acid catalyst	[bmim]PF ₆		At 70–110 °C, alkylation and acylation of lignin and carbohydrate		[51]
			[emim]Cl/AlCl ₃	0.1–5 g	At room temperature or the reflux temperature of the alkyl chloride. Reaction mixture is extracted with diethyl ether (5 ml) then dried over anhydrous MgSO ₄		[52]
			[emim]Cl/AlCl ₃		Acylation of toluene, chlorobenzene and anisole	Excellent yields and selectivities	[53]
			[emim]Cl/FeCl ₃	2.93 g of [emim]Cl and 3.66 g FeCl ₃	At 80 °C, the mixture of benzene/acetyl chloride in a molar ratio of 10:1 is dropped through a funnel into a flask containing ionic liquid. The acetophenone, in benzene, solution drips slowly into the collection flask	No need for aqueous treatment, and consequently no salt-laden aqueous waste for disposal	[59]
			[emim]SbF ₆ , BF ₄ OTf	1 ml	At 20 °C, a two phases mixture of alkene (1 mmol), aromatics (2 ml) and Sc(OTf) ₃ and 1 ml ionic liquid is stirred for 12 h. The organic layer is separated to leave the ionic liquid phase containing the catalyst which can be reused	Simple, easy recovery and reusable catalyst	[58]
2	Diels–Alder reaction	Cycloaddition reaction catalyzed by acid catalyst	[bmim]PF ₆ , SbF ₆ , BF ₄ OTf [pmim]PF ₆ [hmim]PF ₆				
			[emim]Cl/AlCl ₃			Good reaction rate, endo/exo selectivity and product yield and also high solubility	[60]
			[emim]BF ₄ , ClO ₄ , CF ₃ SO ₃ , NO ₃ , PF ₆ , NO ₃ [−]		At 25 °C, the diene and dienophile mixture is stirred for 72 h. Organic layer is separated and extracted by either diethyl ether or petrol (60–80 °C) to leave the pure ionic liquid	Biphasic with easy separation	[61]
			[diethylimidazolium]Br, CF ₃ COO, [bmim]Br		Similar to above but the temperature is −25 °C and under nitrogen protection, in dichloromethane	Biphasic with easy separation	[62]
			[bmim]PF ₆ /SbF ₆ /OTf		At room temperature, 1,4-naphtoquinone treated with 3.0 equiv. of 1,3-dimethylbutadiene in 0.1 mol% of Sc(OTf) ₃	Significant rate acceleration, selectivity improvement and easy recycling of catalyst	[63]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
		Aza-Diels–Alder reaction	8-Ethyl-1,8-diazabicyclo [5,4,0]-7-undecenium trifluoromethanesulfonate, 8-methyl-1,8-diazabicyclo [5,4,0]-7-undecenium trifluoromethanesulfonate	1 g	At room temperature, a mixture of benzaldehyde (318 mg) and aniline (279 mg) in ionic liquid (1 g) was stirred for 30 min and then 1-methoxy-3-(trimethylsilyloxy)butyl,3-diene (1207 mg) and Lewis acid (50 mg) was added to the mixer, and stirred for 20 h, the product was extracted with diethyl ether (10 × 20 ml), then ionic liquid and Lewis acid was recovered by biphasic extraction	No problem of organic solvent waste or Lewis acid waste	[64]
		Dimerization of propene catalyzed by cationic nickel–phosphine complexes	[bmim]Cl/AlCl ₃ , AlEtCl ₂	4 ml	45 mg of [NiCl ₂ (P(I–Pr) ₃) ₂] is used as catalyst. At –15 °C, the propene pressure is set to 1 atm in the reactor containing ionic liquid (4 ml) and heptane (4 ml). The resulting organic mixture is separated as an upper layer and the reaction is repeated seven times	Easy recycling of catalyst and separation of the products	[66]
		Oligomerization of <i>n</i> -butene catalyzed by nickel complexes	[bmim]Cl/AlCl ₃ , AlEtCl ₂	3 ml	At 10 °C, the oligomerization is carried out in Fischer–Porter flask with magnetic stirrer, 0.1 mmol of nickel complex and 7 ml of heptane, 3 ml of ionic liquid and 50 ml of liquid <i>n</i> -butene	Easy separation because of product insolubility, good selectivity, and being adjustable to Dimersol process	[67]
3	Dimerization, oligomerization and polymerization	Ethylene polymerization by Ziegler–Natta catalysts	[emim]Cl/AlCl ₃	6.8 g	At 25 °C and 1 atm, ethylene is bubbled through ionic liquid containing Cp ₂ TiCl ₂ catalyst and Al ₂ Me ₃ Cl ₃ (as co-catalyst). Solid polyethylene is separated by centrifugation		[68]
		Polymerization of raffinate	[bmim]Cl/AlCl ₃ , GaCl ₃	5 ml	At 1 atm and 10 °C, raffinate and ionic liquid mixture are stirred for 180 min resulting in an exothermic reaction. The temperature rise is limited to less than 10° by cooling		[69]
		<i>n</i> -Butene dimerization by nickel complexes	[bmim]Cl/AlCl ₃	3 ml	At 281 K and 1.08 bar, 1-butene is fed to a 120 ml double-walled glass reactor containing 0.1 mmol of nickel complex and 3 ml of ionic liquid and 5 ml of cyclohexane		[70]
		Selective catalytic hydrodimerization of 1,3-butadiene by palladium compounds	[bmim]BF ₄ , PF ₆	3 ml	At 70 °C in an autoclave pressurized to 10 bar by CO ₂ , palladium catalyst (53 mg) with of ionic liquid (3 ml) and of water (2.3 ml) and 1,3-butadiene (10 ml) are stirred for 3 h. The resulting mixture is cooled to –5 °C to form 2 phases. The upper phase is taken off and analyzed by GC	Easy separation of products and reaction effective even in the absence of carbon dioxide	[71]
		Linear dimerization of 1-butene	[bmim]Cl/AlCl ₃		In a glass autoclave, no brief details mentioned	Easy catalyst recycling	[72]

4	Alkylation	Olefin oligomerization	[emim]/[bmim]Cl/AlCl ₃ , AlEtCl ₃	4 g	Pyrrole (0.072 g) is added to ionic liquid (4 g) to form a buffered ionic liquid. Catalyst Ni-hexafluoroacetylacetonate (0.04 g) is added to this liquid in a vessel cooled down to -30 °C containing 1-butene (20 ml). After reaction, the organic layer is decanted off and further centrifugation at 2000 rpm to remove small drops of ionic liquid	High linear selectivities, high catalyst activities and easy separation of ionic liquid/catalyst from products	[73]
		Oligomerization of ethane to higher α-olefin with cationic Ni complexes	[bmim]/[hmim]/[omim]/[demim]-PF ₆	10 ml	At 25 °C, in a 150 ml autoclave, Ni (0.05 ml) complex, heptane (20 ml), ionic liquid (10 ml), 50 bar ethylene pressure, stirred for 2 h	Better reactivity and selectivity	[74]
		Alkylation of isobutane with 2-butene	[bmim]Cl/AlCl ₃	7 ml	In a 250 ml Fischer–Porter flask immersed in a cooling bath (~0.5 °C), isobutane and 2-butene are charged in the liquid phase. Magnetic stirring bar is used to give constant agitation. After the reaction, the hydrocarbon upper phase is decanted off, while the ionic liquid is reused	Precise acidity control of ionic liquid, good alkylate. No need for good agitation. No formation of “red oil”	[78]
		Preparation of linear alkyl benzenes	[bmim]Cl/AlCl ₃ , trimethylammonium chloride or triethylammonium chloride	1–2 g	Acidic ionic liquid (1–2 g) is impregnated onto 3.62 g of ACCUREL microporous polymer (Akzo Nobel). Benzene (17.88 g) and dodecene (3.22 g) is mixed in a round-bottom flask with a stirrer to carry out the reaction	Higher catalytic activity and recycling possible	[81]
5	Alkylation	Preparation of linear alkyl benzenes	[bmim]Cl/AlCl ₃ , trimethylammonium chloride or triethylammonium chloride	0.04 g	At 80 °C under nitrogen protection, dodecylene (5 g) and benzene (30 g) is mixed with ionic liquid (0.04 g). The reaction is carried out for 15 min	Easy recycling of ionic liquid, environmentally friendly process	[82]
			Et ₃ NHCl/AlCl ₃	1.2 g of AlCl ₃ and 0.42 g of Et ₃ NHCl	At 25 °C under nitrogen protection, benzene (18.7 g) and 1-dodecene (5.1 g) is charged into a three-neck flask. AlCl ₃ (1.2 g) and of Et ₃ NHCl (0.42 g) are then introduced. The desired alkylation reaction took place instantaneously	In situ formation of ionic liquid; no corrosion	[83]
			Ionic liquid free of Lewis acidity Et ₃ NHCl/HSO ₄ , [bmim]HSO ₄ , etc		Benzene (5 g) and 1-decene (5.6 g) in a glass batch reactor with stirring bar. Samples of the reaction medium are taken by pipette at intervals of 10 min for GC. After 5 h, the catalyst is separated from reaction mixture by decantation		[84]
			Et ₃ NHCl/AlCl ₃	0.04 g	At 80 °C under nitrogen protection, dodecene (5 g) and benzene (30 g) and of ionic liquid (0.04 g) are mixed. After 15 min the conversion of dodecene was 100%	No solid materials to handle, no sludge by-product; easy separation and recycling	[85]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
		Regioselective alkylation at the heteroatom of indole and 2-naphthol	[bmim]PF ₆ , BF ₄		Typical reaction is carried out using 1.3–2 equiv. of alkyl halide and 2 equiv. of KOH as 10% w/v solutions of substrates in ionic liquid. Reaction is complete in 2–3 h with almost quantitative extraction of products	Simplicity of the method, easy product isolation, with potential for recycling	[86]
6	Allylation	Palladium-catalyzed allylic alkylation and amination reactions	[bmim]BF ₄		At 80 °C the catalyst or catalyst precursor is formed by heating Pd(OAc) ₂ with PPh ₃ in [bmim]BF ₄ for 20 min. The ionic liquid is then cooled to ambient temperature and the reaction started by adding the substrates and K ₂ CO ₃ . ¹ H-NMR monitoring showed that the alkylation is complete after 5 h at ambient temperature	Easy separation and potential for catalyst/solvent reuse and recycling	[87]
		Preparation of homoallylic alcohols from tetraallylstannane and a range of aldehydes	[bmim]BF ₄ , PF ₆	2 ml	At room temperature, benzaldehyde (106 mg), ionic liquid (2 ml) and of tetraallylstannane (70.7 mg) are mixed in reactor and then stirred vigorously for 16 h. The mixture is extracted three times with Et ₂ O (10 ml). The organic extracts are combined and dried over anhydrous MgSO ₄ . The Et ₂ O is removed in vacuum. Ionic liquid can be reused without any further treatment	Easy solvent separation and recycling	[88]
		Enantioselective allylic substitution reaction of (rac)-(E)-1,3-diphenyl-3-acetoxyprop-1-ene with dimethyl malonate (DMM)	[bmim]PF ₆	1 ml	At 80 °C, Pd ₂ (dba) ₃ CHCl ₃ (10.4 mg, 2 mol%Pd) and ferrocenylphosphine ligand (0.04 mmol, 8 mol%P) were added to [bmim]PF ₆ and resulting mixture was stirred under an Ar atmosphere for 20 min. Substrate (252 mg, 1 mmol), DMM (0.17 ml, 1.5 mmol) and K ₂ CO ₃ (276 mg, 2 mmol) were added to the cooled reaction mixture which was stirred at room temperature under Ar for 5 h. Two milliliter of toluene was added and stirred for 5 min. The toluene layer collected and extraction repeated until no product was detected in the toluene layer. The toluene extracts were washed with water (20 ml), dried and the solvent was evaporated. The residue was purified by chromatography on a SiO ₂ column. The ionic solvent was washed with water (2 × 2 ml) and dissolved in EtOAc (10 ml), dried, solvent evaporated, dried at 40 °C/1 mmHg for 3 h and stored under Ar in the freezer before reuse	Encouraging enantioselectivity, effective reuse of catalyst	[89]

7	Heck Reaction	Heck reaction of chlorobenzene with styrene, and 0.5 mol% palladacycle as catalyst	[Nbu ₄]Br, [bmim]Br	1.5 g	At room temperature, aryl halide (1.0 mmol), mmol olefin (1.5), base (1.2 mmol), diethleneglycol-di- <i>n</i> -butylether (0.05 g) and catalyst are added under an inert reaction atmosphere. The mixture is diluted with water, the products are extracted with CH ₂ Cl ₂ and filtered. Yields are determined by GC/MS	Easy catalyst recycling	[91]
		Heck reaction of aryl halides with butyl acrylate in the presence of triethylamine	Tetraalkylammonium and phosphonium halides	Not mentioned		Simple, efficient and practical procedure for the generation of long-term active palladium(0), no need for additional phosphine ligands, stable catalyst activity after several runs	[92]
	Heck olefination of aryl halides with acrylates or styrene	[bmim]Br, BF ₄	5 ml	Aryl halide (5.0 mmol), anhydrous sodium acetate (451 mg), and palladium acetate (1 mol% with respect to the aryl alide). An acrylate or styrene (7.0 mmol) is injected through the septum, and the mixture heated to the reaction temperature for 24 h, the mixture is cooled to room temperature and diluted with water. The product is then extracted with ethyl acetate. The combined organics are washed with water and brine, and dried over MgSO ₄		[93]	
	Suzuki cross-coupling	Suzuki reaction of aryl halide with arylboronic acid by Palladium catalyst	[bmim]BF ₄	Not mentioned		Increased catalyst activity, homo-coupled products eliminated, no catalyst decomposition, repetitive catalytic runs	[94]
	Trost–Tsuji C–C coupling	C–C coupling of ethyl cinnamyl carbonate with ethyl acetoacetate by palladium catalyst	[bmim]Cl/AlCl ₃	0.51 ml		High solubility, cheaper catalyst, suppression of side reactions. Simple alkanes as organic layer	[95]
8	Hydroformylation	Rh-catalyzed hydroformylation of methyl-3-pentenoate	[bmim]PF ₆	75 ml steel autoclave	At 110 °C and 0.01 mbar of syngas pressure, the catalyst precursor, the ligand and the ionic liquid are stirred for 1 h. The organic compound is distilled out of the autoclave at 110 °C	Immobilization of catalyst in ionic liquid	[97]
		Hydroformylation of hex-1-ene	High temperature ionic liquids: phosphonium tosylates (melting point: 70–140 °C)			No corrosion, easy manipulation of reaction system, simple product separation	[98]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
		A process for preparing aldehydes by hydroformylation of olefins or olefinically unsaturated compounds in the presence of a rhodium catalyst	1-amino-3-(di- <i>i</i> -nonyl)aminopropane/trisulfo-phenyl-phosphine	400–500 g	At 125 °C and 4 MPa syngas pressure, ionic ligand liquid (420 g) mixed with rhodium 2-ethylhexanoate solution in 2-ethylhexanol with an amount of phosphorus(III) to rhodium of 136 to 1, 400 ppm <i>n</i> -hexene is added. The reaction took place in a liter autoclave for 1.5 h. The organic phase is removed via an immersed tube and the ionic liquid system is reused	Easy separation and potential of reuse and recycling; more recycling times	[99]
		Hydroformylation of olefinic compounds by rhodium catalyst	[bmim]PF ₆ /BF ₄	4 ml	At 82 °C and syngas (2 MPa), ionic liquid (4 ml), Rh(acetylacetonate)(CO) ₂ (19.3 mg) complex and 186 mg of triphenylphosphine dissolved in 2 ml of toluene, heptane (2 ml) and of 1-pentene (7.5 ml) are mixed. After 2 h reaction, the upper organic phase is extracted	Easy separation and high reaction selectivity	[45]
		Hydroformylation of 1-hexene with rhodium	1,2-Dialkylimidazolium, 1,2,3-trialkylimidazolium and <i>N</i> , <i>N</i> -dialkylpyrrolidinium with BF ₄ ⁻ , PF ₆ ⁻ , CF ₃ CO ₂ ⁻ , CF ₃ SO ₃ ⁻ , and N(CF ₃ SO ₂) ₂ ⁻	4 ml	At 80 °C, Rh(CO) ₂ (acac) 0.075 mmol, 1-hexene/Rh = 800, CO/H ₂ (molar ratio) = 1, <i>P</i> (CO/H ₂) = 2 MPa, heptane(internal standard) = 2 ml, 1-hexene = 7.5 ml, ionic liquids = 4 ml are mixed to react for 180–330 min. At the end of reaction, the organic phase is decanted and separated from ionic liquid which is reused	Minimized Rh leaching problem by adjusting the ligand and the ions of the ionic liquids	[102]
		Hydroformylation of oct-1-ene by Rh complex of cationic guanidinium modified phosphine ligands	[bmim]PF ₆			Fully immobilized transition metal complexes in hexafluorophosphate ionic liquids	[103]

9	Oxidation	Recycling procedure for Jacobsen's chiral Mn(III) epoxidation catalyst using ionic liquid	[bmim]PF ₆	7.5 ml	The pH of a solution of commercial household bleach is buffered to pH 11.3 with 0.05 M Na ₂ HPO ₄ and 1 M NaOH (a few drops) and then cooled to 0 °C. To 110 ml of this solution is added a precooled solution (0 °C) of 2,2-dimethylchromene (5.0 g, 31.3 mmol) and the catalyst (0.79 g, 1.25 mmol) in CH ₂ Cl ₂ (30 ml) and [bmim]BF ₄ (7.5 ml). The 2-phase system is stirred at 0 °C and the progress of reaction are monitored by TLC. After 2 h, the organic phase is separated and washed twice with water. The volatiles are concentrated in vacuum and the residue is stirred with hexane. After concentration of the upper hexane phase in vacuum, the residue is purified by GC on silica gel (deactivated with 1% NEt ₃ solution in ethyl acetate-hexane) with ethyl acetate-hexane (1:10) as eluent, to afford 4.74 g (86% yield) of the epoxide with 96 %ee. The brown oily ionic liquid phase (the lower phase) containing the catalyst is reused	Immobilization of catalyst, easy recycling of catalyst and no need to modify catalyst	[105]
10	Nucleophilic displacement reactions	Cyanide displacement of benzyl chloride	[bmim]PF ₆	In a 25 ml volumetric flask	At 40, 60 and 80 °C, in a 25 ml flask with benzyl chloride in the ionic liquid with 1 mol/l concentration, the amount of potassium cyanide was three times the stoichiometric amount of benzyl chloride. Before the introduction of benzyl chloride, the salt was stirred overnight in the liquid so that a uniform particle size was obtained and the salt would reach an equilibrium concentration	Making the PTC environmentally benign	[106]
11	Electrophilic nitration of aromatics	Aromatics nitration with nitration agents such as [NO ₂][BF ₄] systems	[emim] OTf/CF ₃ COO/NO ₃ /[HNEtPr ⁱ] ₂ [CF ₃ COO]/AlCl ₄ /Al ₂ Cl ₇	Around 500 mg	One example using [emim]PF ₆ : [emim]PF ₆ (623 mg, 2.43 mmol) and [NO ₂][BF ₄] (995 mg, 7.49 mmol) was mixed to formed a colorless oil. Adding toluene (3 ml) led to a vigorous reaction. After stirring overnight the mixture was extracted with ether. The ionic liquid phase was a yellow, highly viscous oil (with greenish precipitate)	Easy product isolation, recovery of the ionic liquid, no problems of neutralization of acids	[108]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
12	Radical reactions mediated by manganese(III) acetate	Cyclization of 1,3-dicarbonyl compounds and alkenes mediated by manganese acetate	[bmim]BF ₄ /PF ₆	2 cm ³	To a solution of [bmim]BF ₄ (2 cm ³) and dichloromethane (8 cm ³) containing cyclohexane-1,3-dione (0.10 g, 0.89 mmol) and α -methylstyrene (0.53 g, 2.63 mmol, 5 equiv.) was added manganese(III) acetate dihydrate (0.50 g, 1.88 mmol, 2.1 equiv.) under an atmosphere of N ₂ the mixture was heated overnight to form a yellow one. Dichloromethane (40 cm ³) was added and manganese(II) acetate was removed by filtration. The filtrate was then washed with water to remove the ionic liquid from the organic phase. The organic phase was then dried (MgSO ₄), evaporated and purified using column chromatography (silica) to give 2-methyl-2-phenyl-3,5,7,7-tetrahydro-2H-benzofuran-4-one (0.10 g, 50%) as an oil	Mild, experimental condition, high yield and easy recovery of manganese(II) acetate and ionic liquid	[109]
13	Carbonylation of aryl halides	Palladium-catalyzed carbonylation of aryl halides	[bmim]BF ₄ /PF ₆	2 ml	Example: under a nitrogen atmosphere, palladium acetate (3 mg, 0.5 mol%), triphenylphosphine (14 mg, 2 mol%) and [bmim]PF ₆ (2 ml) were added to an autoclave, and heated to 100 °C for 10 min. Bromobenzene (0.28 ml, 2.66 mmol), triethylamine (0.37 ml, 2.66 mmol) and methanol (0.54 ml, 13.3 mmol) were added to the autoclave after cooling to room temperature. The system was then pressurized with CO of 30 kg/cm ² and heated at 150 °C for 3 h. After that, the mixture was then taken out under N ₂ and evaporated and distillation under reduced pressure to give methyl benzoate and leave a residue of triethylammonium bromide and palladium species. The remaining mixture was used for a second run under the same conditions as the first one	Easy products separation and solvent–catalyst system recycling	[107]

14	Reduction of aldehydes	Reduction of aromatic and aliphatic aldehydes using trialkylboranes	[bmim]BF ₄ , [emim]BF ₄ /PF ₆	250 mg	At room temperature, benzaldehyde (106 mg, 1.00 mmol) and [emim]PF ₆ (250 mg) were placed in a 10 ml round-bottomed flask. Tributylborane (182 mg, 1.00 mmol) was added and the mixture stirred at 100 °C for 48 h. The product was extracted into ether (2 × 5 ml). The extracts were combined and dried over anhydrous MgSO ₄ . The solvent was removed under reduced pressure and then purified by silica gel chromatography to yield 102 mg (94%) of benzyl alcohol	Easy product separation and solvent recycling	[111]
15	Synthesis and reaction of zinc reagents	Reformatsky reaction and preparation of propargylic alcohols by zinc reagents	[Etdiazabicyclo-undecenium] [OTf], [bmim]BF ₄ , [bmim]PF ₆	1 g	At room temperature or 50–60 °C, bromodifluoroacetate (2 equiv.), benzaldehyde (1 equiv.) and zinc powder (2 equiv.) in 1 g ionic liquid, giving corresponding carbinol. The target product was extracted with commercially available diethyl ether	High yield and easy recycling of ionic liquids	[112]
16	Synthesis of the pharmaceutical Pravadoline	Sequence of nucleophilic displacement and Friedel–Crafts reactions	[bmim]PF ₆		At room temperature, with solid potassium hydroxide as the base, 2-methylindole and 1-(<i>N</i> -morpholino)-2-chloroethane hydrochloride reacted to give the 1-(2- <i>N</i> -morpholino)(ethyl)-2-methylindole followed by Friedel–Crafts reaction. The product was isolated by neutralizing with aqueous potassium carbonate solution and extraction of the product with toluene. The ionic liquid [bmim]PF ₆ was recovered and reused in the reactions after separation and drying under vacuum	High yield, no waste problem, easy recycling of ionic liquid	[113]
17	Sequential Claisen rearrangement and cyclization reactions	Sc(OTf) ₃ as Lewis catalyst	[EtDBU]OTf		At 200 °C, the reaction was carried out for 10 h, the catalyst and solvent can be reused after purifying under dynamic vacuum at 70–80 °C for 1 h	Reusable and stable catalyst and solvent	[114]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
18	Synthesis of CTV	Acid-catalyzed condensation of benzyl alcohol derivatives to form CTV	N ₆₄₄₄ Imide	2 ml	At 75–85 °C, the ionic liquid was stirred with 1 drop of H ₃ PO ₄ and liquid veratryl alcohol (1.035 g) resulting in a single liquid phase. Reaction was allowed to proceed for 4 h by which time all the monomer had been consumed. After cooling, methanol (15 ml) was added and product separated by filtration followed by washing with 5 ml of methanol. 822 mg (89%) of white crystalline product was collected and the methanol was removed under vacuum to recycle the ionic liquid. The ionic liquid was used five times	No use of large quantities of organic solvent, no strong dehydrating acids, high yield, easy recycling of ionic liquid	[115]
19	Cycloaddition of carbon dioxide to propylene oxide		[bmim]/[bpy]-Cl/BF ₄ /PF ₆	0.2–2.5 mmol	At room temperature, in a 90 cm ³ stainless autoclave, ionic liquid (0.2–2.5 mmol) and propylene oxide (100 mmol) were charged and the CO ₂ was introduced. The autoclave was heated up for 6 h. After cooling, the reaction mixture were analyzed with GC–MS	Excellent selectivity and ionic liquid recyclable	[116]
20	Wittig reactions	C=C bond formation	[bmim]BF ₄	2 ml	At 60 °C, a mixture of benzaldehyde (0.2 ml) and phosphorane (0.689 g) in 2 ml [bmim]BF ₄ was stirred for 2.5 h. The mixture was then extracted first with <i>Tbu</i> OMe (3 × 3 ml) and then with toluene (3 × 3 ml). The extracts were evaporated in vacuo. Filtration of the <i>tert</i> -BuOMe extract on a short SiO ₂ pad gave the first product and then Ph ₃ PO	Selective extraction of alkenes and Ph ₃ PO, reusable ionic liquids	[117]

21	Stille coupling	Cross-coupling catalyzed by palladium catalysts	[bmim]BF ₄	1 ml	To a flask under nitrogen were sequentially added 2-iodo-3methyl-2-cyclohexen-1-one (235.9 mg), copper(I) iodide (19.0 mg), triphenylarsine (31.0 mg) and bis-(benzotrile) palladium(II) chloride (19.0 mg). The mixture was dissolved in 1 ml [bmim]BF ₄ and tributylvinyltin (0.35 ml) was added. After stirred for 2 h, the reaction mixture was extracted with diethyl ether (10 × 10 ml). The organic layer were washed with saturated aqueous potassium fluoride (3 × 30 ml). The aqueous layer were combined and back-extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo. The resulting oily residue was purified by flash column chromatography to afford 3-methyl-2-vinylcyclohexenone (90.3 mg) as a pale yellow oil	Extensive recycling of solvents, no significant loss in activity and high selectivity	[118]
22	Preparation of heterocyclic compounds	One pot synthetic methods for preparation of heterocyclic compounds	8-Ethyl-1,8-diazabicyclo [5,4,0]-7-undecenium trifluoromethanesulfonate, 8-methyl-1,8-diazabicyclo [5,4,0]-7-undecenium trifluoromethanesulfonate	1.007 g	At room temperature, the mixture of benzaldehyde (318 mg) and ionic liquid (1.007 g), 2-aminobenzyl alcohol (309 mg) was stirred for 30 min, diethyl ether (10 × 10 ml) was added and the upper organic layer separated. The organic layer was dried over anhydrous MgSO ₄ , and the diethyl ether removed	Non-toxic ionic liquid solvents and fully recyclable	[119]
23	Lipase-catalyzed kinetic resolution of 1-phenylethanol		[bmim]PF ₆ /CF ₃ SO ₃ /(CF ₃ SO ₂) ₂ N/(CH ₃ O) ₂ SO ₂ , [4-MBP]BF ₄	4.4 ml	At 24 °C, the suspension of 1 mg of lipase and, 400 μl substrate solution in 4.4 ml ionic liquid, was incubated for 3 days in a thermomixer. The unconverted starting material was removed by vacuum distillation at 85 °C and 0.06 mbar. After cooling, the same amount of substrate was added again and the cycle repeated	Good activity, improved enantioselectivity and possibility of recycling	[122]

Table 5 (Continued)

Number	Reaction	Reaction description	Ionic liquid used	Scale	Brief details	Advantages	Reference
24	Alcoholysis, ammoniolysis and perhydrolysis catalyzed by <i>C. antarctica</i> lipase		[bmim]BF ₄ /PF ₆	0.5–1 ml	Typical alcoholysis: at 40 °C, the mixture of ethyl octanoate (10 mmol), alcohol (120 mmol) and lipase (25 mg) in ionic liquid (0.5 ml) was stirred	High reaction rate	[123]
25	Lipase-catalyzed transesterification	Transesterification of alcohol with vinyl acetate catalyzed by lipase	[emim]BF ₄ , [bmim]PF ₆	1 ml	At room temperature, a solution containing substrate (0.15 mmol), lipase (20 mg), and vinyl acetate (1.5–3 equiv.) in ionic liquid (1 ml) was stirred. After the reaction reached 10–50% completion, the enzymes were removed by filtration and the resulting solution was concentrated. The solution mixture was first extracted with ethyl ether and the ethereal phase was concentrated. The organic residues were subjected to silica gel chromatography to obtain unreacted substrate and acetylated product	High enantioselectivity	[124]

228 3.2. C–C and C–O cleavage reactions (see Table 4)

229 3.2.1. Catalytic cracking of poly(ethene) to give
230 light alkanes

231 The cracking of polyethylene is one of the most
232 important plastics recycling processes [47]. The com-
233 monly used methods include pyrolysis, catalytic crack-
234 ing with acidic materials and reactions in supercrit-
235 ical water. The wide range of products obtained is
236 a problem in each case. A new method using acidic
237 chloroaluminate(III) ionic liquids to crack polyethy-
238 lene has been developed [48]. The addition of acidic
239 co-catalysts such as [emim][HCl₂] (1 mol%) or con-
240 centrated sulfuric acid (2 mol%) is essential to pro-
241 vide a source of protons. Unlike the cracking reac-
242 tions using supercritical water or zeolites, the products
243 are mainly volatile alkanes (C₃–C₅) including propane
244 and 2-methylpropane. No alkenes are observed. It has
245 been shown that this method is quite selective toward
246 low molecular weight feedstocks. Another advantage
247 of this method is that the products are very easily sep-
248 arated from ionic liquids by solvent extraction or other
249 physical separation processes.

250 3.2.2. Acylative cleavage of cyclic and acyclic ethers

251 Although several methods for cleaving ethers are
252 available, a general reliable method to selectively
253 cleave ether linkages has not been reported [49].
254 Ionic liquids derived from [emim]I/AlCl₃ have been
255 used as solvent and Lewis acid catalyst for the acyla-
256 tive cleavage of a series of cyclic and acyclic ethers
257 such as tetrahydrofuran, 1,4-dimethyltetrahydrofuran,
258 tetrahydropyran, diethyl ether and diisopropyl ether
259 with excellent selectivities (see Fig. 3).

260 3.2.3. Dissolution of kerogen [18]

261 Kerogen is a cross-linked macromolecular system,
262 which resides in a type of sedimentary rock known
263 as oil shale. Liquefaction, gasification and even mod-
264 ification of oil shale are challenges for chemists and
265 engineers. Present methods for such processes include

266 pyrolysis, solvent extraction, direct hydrogenation and
267 the production of synthesis gas followed by the use of
268 Fischer–Tropsch technology. Ionic liquids [bmim]PF₆
269 and [bmim]Cl/AlCl₃ have been employed to treat oil
270 shale. Dissolution of kerogen has also been investi-
271 gated by heating it in acidic chloroaluminate(III) ionic
272 liquids for 1 min periods in a microwave oven.

273 3.2.4. Asymmetric ring opening reactions of
274 epoxides catalyzed by Cr(salen)

275 Asymmetric ring opening reactions of epoxides
276 with TMSN₃ catalyzed by a Cr(salen) complex has
277 been recognized as an attractive approach to the syn-
278 thesis of optically pure β-amino alcohols, which are
279 important structural elements in many biologically
280 active molecules as well as the starting point in the
281 design of many chiral ligands. A biphasic method
282 involving use of ionic liquids has been developed in
283 order to eliminate the drawback of the conventional
284 catalyst recycling procedure which involves the poten-
285 tially hazardous distillation of the neat liquid azides,
286 which may prove a limitation for large scale applica-
287 tions [50]. From the results of enantioselective ring
288 opening of *meso* epoxides and cyclopentene oxide,
289 it can be seen that without hazardous workup stages
290 such as distillation of the azide product, catalyst re-
291 cycling is quite simple. The catalytic activity and
292 enantioselectivity are found to be strongly dependent
293 on the nature of the anion in the ionic liquids.

294 In summary, studies on C–C cleavage reactions us-
295 ing ionic liquids are at a preliminary stage, but show a
296 promising perspective in laboratory and the chemical
297 industry.

298 3.3. C–C or C–heteroatom coupling reactions
299 (see Table 5)

300 3.3.1. Friedel–Crafts reaction

301 Friedel–Crafts alkylations and acylations are of
302 great commercial importance, and are also among
303 the earliest reported investigations using ionic liq-

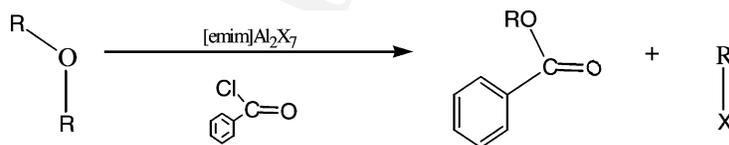


Fig. 3. Acylative ether cleavage in [emim]I–AlCl₃.

uids as Lewis acid catalysts [51]. The conventional catalyst in Friedel–Crafts reactions is AlCl_3 , which gives rise to disposal and by-product problems. The [emim]Cl– AlCl_3 ionic liquid system has been used in place of solid AlCl_3 . In this case, the ionic liquid acts not only as a catalyst but also as the solvent for the reaction. The main advantages are greatly enhanced reaction rates, high conversion and selectivity [51–57].

Recently, considerable attention has been focused on the catalytic use of rare earth(III) (RE) salts, especially, RE(III) trifluoromethanesulfonates [RE(OTf)₃] as water tolerant and recyclable Lewis acid catalysts in C–C coupling reactions [43]. Friedel–Crafts alkylation of aromatic compounds with alkenes using Sc(OTf)₃-ionic liquid systems has been developed giving the benefits of simple procedures, easy recovery and reuse of catalysts, contributing to development of environmentally benign and waste-free processes for this kind of reaction [58].

3.3.2. Diels–Alder reactions

The great usefulness of the Diels–Alder reaction lies in its high yield and high stereospecificity. When ionic liquids are used in the reaction significant rate enhancements, high yields and selectivities have been observed [59–62]. The processes are in principle “green”, but the use of organic solvents reduces the overall “greenness”. Further development is still required. Recently, ionic liquids acting as solvent or additives in scandium triflate-catalyzed Diels–Alder reactions have been investigated, giving facilitated catalyst recovery, accelerated reaction rate and improved selectivity [63].

One-pot aza-Diels–Alder reactions for the preparation of 6-aryl-5,6-dihydro-4-pyridones in ionic liquids have also been investigated [64]. The problems of organic solvent waste and Lewis acid waste can be dealt with in a new, low-waste and recyclable reaction system based on an ionic liquid as a low volatility reaction medium and an encapsulated metal triflate as a recoverable catalyst.

3.3.3. Dimerization

The Dimersol process developed in France by the IFP, is an industrial scale single-phase no-solvent system for the dimerization of propene and butene catalyzed by nickel complexes giving more valuable branched hexenes and octenes. The process is widely

used in 25 plants worldwide. The separation of products from the catalyst is difficult, however, which increases the operational costs and environmental impact. Chauvin et al. [45,65] have developed the Difasol process which employs ionic liquids. Furthermore, the use of acidic ionic liquids containing ethylaluminum dichloride in addition to aluminum trichloride ([bmim]Cl/ AlCl_3 /Et AlCl_2 = 1/1.2/0.25) makes it possible to use Ni(L)₂Cl₂ complexes (L = pyridine or phosphine) as catalyst precursors, which are easier to prepare and handle than the conventional catalysts. Propene is converted into isomeric hexenes with high activity at atmospheric pressure and temperatures from –15 to 5 °C. The products form an upper phase that can be easily separated by simple decantation. The pale yellow-orange catalyst remaining in the ionic liquid phase can then be reused several times. At 5 °C under atmospheric pressure, more than 250 kg of isohexenes per gram of nickel are produced, which is much greater than the amount obtained with organic solvent systems. Under the same conditions, butenes are converted into isooctenes with 97% selectivity, consisting of 56% 3-methylheptene, 38% 3,4-dimethylhexene, and 6% *n*-octene. The process can be retrofitted into existing Dimersol plants, giving improved yields, lower catalyst consumption and costs along with environmental benefits.

It has been shown that ionic liquids can be used in a “buffered” mode as solvent. The catalysts used are based on square planar Ni–O, O’ chelating acac systems. Since the catalyst was found to decompose in ionic liquids containing chloroethylaluminate, alkali metal chloride was added to buffer the acidity of ionic liquids [73,75].

3.3.4. Oligomerization and polymerization

Olefin oligomerization is conventionally catalyzed by AlCl_3 . The major disadvantage of using AlCl_3 is the resulting contamination problem. Acidic ionic liquids have been used as catalysts for this reaction [77]. It has been shown that the longer the alkyl chain of the 1-alkyl-3-methylimidazolium or *N*-alkylpyridinium cation, the higher the degree of oligomerization obtained. This enables the control of product distribution. The product forms a separate layer and can be easily removed from the system. It also reduces the amount of undesirable secondary reactions such as isomerization. Another advantage

lies in the reusability of the catalyst, which further reduces the costs and wastage from the process.

The first biphasic oligomerization of ethylene to higher α -olefins with nickel complexes has been investigated recently [74]. It has been found that the turnover frequencies can be correlated with polarity data obtained using solvatochromic dyes. It has also been shown that the hexafluorophosphate ionic liquids are good solvents for these reactions as a consequence of their polar and weak or non-coordinating properties.

Radical polymerization of methyl methacrylate (MMA) mediated by copper(I) in [bmim]PF₆ has also been investigated [76]. It has been demonstrated that the ionic liquid is an excellent solvent for Cu^I-*N*-propyl-2-pyridylmethanimine mediated living radical polymerization of MMA. Reactions are relatively fast, as has been observed with other polar/co-ordinating solvents. The polymer can be recovered essentially copper-free by a simple solvent wash. However, further work is required in order to optimize the process and to realize the potential to recycle the ionic liquid catalyst mixture.

3.3.5. Alkylation

The alkylation of isobutane with 2-butene to give branched *iso*-alkanes is a commercially important reaction. The target product is trimethylpentane, which can be converted to a methoxyether for use as a fuel additive to increase octane number. HF or H₂SO₄ is traditionally used as the catalyst, which is a typical example of a “non-green” process because of cooling and separation problems, high operating costs and safety aspects. Chauvin et al. [79] have investigated the reaction using [bmim]Cl/AlCl₃ ionic liquids as solvent. The main advantages arising from the use of the ionic liquid are high alkylate quality and simple product separation.

The alkylation of benzene with long chain alkenes or halogenated alkanes to produce linear alkylbenzenes (LAB) is also of commercial importance. The traditional catalyst is HF or AlCl₃ (catalyst/olefin mole ratio = 5–20). Acidic ionic liquids have been used as catalysts in a ratio as low as about 0.004 with very high conversion [80].

3.3.6. Allylation

Palladium(0)-catalyzed allylation of nucleophiles is a very useful reaction in organic synthesis. The ally-

lation of methylene compounds by 1,3-diphenylallyl acetate in [bmim]BF₄ has been investigated [87]. The reaction proceeds smoothly with the additional benefit of easy catalyst/solvent recycling. It has been shown that ionic liquids provide an ideal environment where stabilized ionic intermediates may be generated in situ. The process offers an attractive “greener” alternative to conventional processes where volatile organic solvents are frequently employed and catalyst reuse is difficult to implement.

Recently, enantioselective allylation reactions catalyzed by Pd(0)–ferrocenylphosphine ligand complexes in ionic liquids have been investigated, and the use of the homochiral ferrocenylphosphine ligands for the enantioselective Pd(0)-catalyzed allylation of dimethyl malonate (DMM) as well as the possibility of recycling the Pd⁰–ferrocenylphosphine ligand complexes in ionic solvents has been examined. Encouraging enantioselectivity and effective reuse of the catalysts has been demonstrated (Fig. 4) [89].

3.3.7. Heck reaction and Suzuki reaction

The vinylation of aryl halides catalyzed by palladium complexes, commonly called the Heck reaction, has received increasing attention because of its enormous synthetic potential for generating carbon–carbon bonds and its tolerance towards a wide range of functional groups [90]. However, the high consumption of the expensive palladium catalyst makes it a relatively impractical process on an industrial scale. Recycling the catalyst is therefore a key objective. *Trans*-di(μ -acetato)-bis[*o*-tolylphosphino]benzyl dipalladium(II) is an efficient catalyst for the Heck reaction of chlorobenzene with styrene. This reaction has been carried out in tetra-*n*-butylammonium bromide ionic liquid as solvent. A high activity has been reported. The products can be easily removed from the solution by distillation and the catalyst and solvent is then recycled [91].

Heck reactions of aryl halides with acrylates and styrene in [bmim]Br and [bmim]BF₄ ionic liquids as solvents have also been reported [93]. The reaction was found to occur more efficiently in [bmim]Br than in [bmim]BF₄. Further study revealed that [bmim]-2-ylidene (bmiy) complexes of palladium [PdBr(μ -Br)(bmiy)]₂ (**1**) and [PdBr₂(bmiy)₂] (**2**) could be isolated from the reaction with [bmim]Br but not with [bmim]BF₄. It has been suggested that

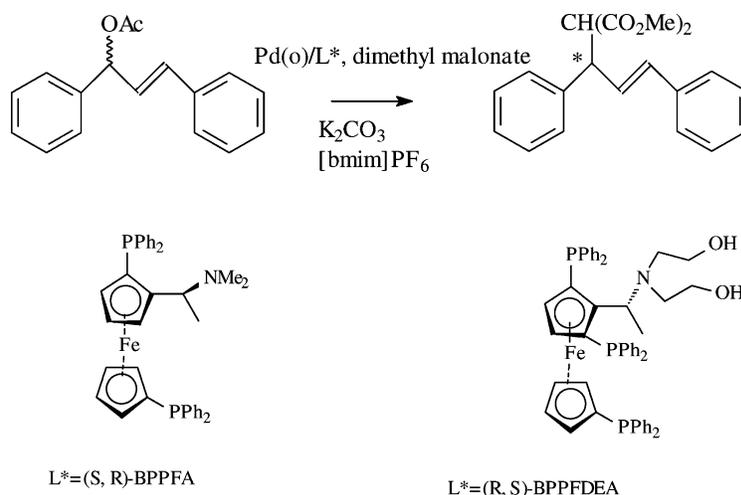


Fig. 4. Enantioselective allylation in ionic liquid.

490 the active precursor is complex **2** formed via the inter-
 491 mediate **1**. The origin of poor activity in [bmim]BF₄
 492 was proposed to be the transformation of **2** into a
 493 less active species in [bmim]BF₄. This study may be
 494 the first effort to probe into the mechanistic details
 495 of the effect of ionic liquid on reaction rate. More
 496 recently, palladium-catalyzed regioselective arylation
 497 of an electron-rich olefin by aryl halides has also
 498 been accomplished, using aryl iodides and bromides
 499 as arylating agents instead of the commonly used, but
 500 commercially unavailable and expensive, aryl triflates.
 501 The reaction proceeds with high efficiency and re-
 502 markable regioselectivity, leading almost exclusively
 503 to substitution by various aryl groups at the olefinic
 504 carbon α to the heteroatom of butyl vinyl ether [96].

505 Palladium (Pd[PPh₃]₄)-catalyzed Suzuki cross-
 506 coupling reactions of aryl halides with arylboronic
 507 acid have been conducted in the [bmim]BF₄ ionic
 508 liquid to afford biaryls, with the advantages of in-
 509 creased reactivity at reduced catalyst concentra-
 510 tion, no homo-coupled products, operation under
 511 aerobic conditions and no loss and decomposi-
 512 tion of palladium catalyst and repetitive catalytic
 513 runs [94].

514 3.3.8. Hydroformylation

515 Hydroformylation of olefins is another reac-
 516 tion of considerable industrial importance. An
 517 aqueous–organic biphasic hydroformylation system

518 catalyzed by water-soluble Rh catalysts has been
 519 commercialized. Unfortunately, the use of water as
 520 polar phase limits this process to C₂–C₅-olefins due
 521 to the low water solubility of higher olefins. As an
 522 alternative polar medium, a range of ionic liquids
 523 containing PF₆[−], SbF₆[−] and BF₄[−] have been em-
 524 ployed in an ionic liquid–organic biphasic system
 525 [45,97–101]. The solubility problem is thus over-
 526 come and the products are separated as an organic
 527 phase. The catalyst can also be reused. A small
 528 amount of catalyst leaching into the organic phase
 529 causes some loss in activity after each run how-
 530 ever. These problems have been improved recently
 531 by varying the ligand and the ions of ionic liquids
 532 [102,103]. From the results of 1-hexene hydroformy-
 533 lation catalyzed by rhodium in a biphasic system,
 534 it can be seen that the reaction rate and regioselec-
 535 tivity as well as the retention of the rhodium can
 536 be optimized by ensuring compatibility between the
 537 anions and cations of the ionic liquid and the mod-
 538 ified phosphite or phosphine ligands of the rhodium
 539 catalyst.

540 3.3.9. Nucleophilic displacement reactions

541 Nucleophilic displacement reactions are often car-
 542 ried out using phase-transfer catalysis (PTC) to faci-
 543 litate the reaction between the organic reactants and
 544 the inorganic ionic salts that provide the nucleophiles. The
 545 phase-transfer catalysts, often a tetraalkylammonium

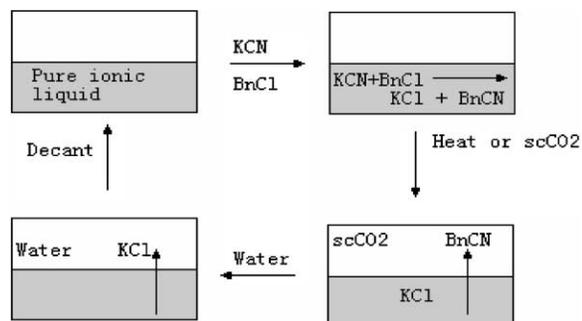


Fig. 5. Recyclable ionic liquid solvent system for nucleophilic substitution reactions.

546 salt, acts as a shuttle for the reactant anion between a
 547 polar phase that contains the salt and a non-polar phase
 548 that contains the organic reactant. This technique over-
 549 comes the problems of bringing the reactants into con-
 550 tact and, in addition, it provides some activation of the
 551 nucleophilic anion since it is much less tightly bound
 552 to a tetraalkylammonium cation than it would be to a
 553 metal cation. However, conventional PTC uses envi-
 554 ronmentally undesirable organic solvents like methy-
 555 lene chloride or *o*-dichlorobenzene. Catalyst separa-
 556 tion and recovery also represent significant challenges.
 557 Ionic liquids, because of their bulky organic cations,
 558 seem well suited for the type of reactions for which
 559 PTC is effective. A recyclable and catalytic ionic li-
 560 quid solvent system for nucleophilic substitution reac-
 561 tions has been developed (Fig. 5), demonstrating the
 562 viability of ionic liquids as a solvent for reactions be-
 563 tween organic compounds and inorganic salts [106].

564 3.3.10. Electrophilic nitration of aromatics

565 Electrophilic nitration of aromatics is a fundamental
 566 reaction of great industrial importance, whose prod-
 567 ucts are key organic intermediates or energetic materi-
 568 als. Although the mechanistic and synthetic aspects of
 569 nitration chemistry have been very thoroughly studied

570 over the years, there is continuing concern over en-
 571 vironmental aspects, disposal problems and regenera-
 572 tion of the used acids. An early study of catalysis of
 573 electrophilic aromatic substitution reactions in acidic
 574 [emim]chloroaluminate included examples of nitration
 575 with KNO_3 in particular [107]. More recently, a se-
 576 ries of ionic liquids of based on [emim] and [bmim]
 577 cations has been utilized as solvent for aromatic nitra-
 578 tion [108]. Counterion dependency of the NMR spec-
 579 tra of the ionic liquids is used to estimate the progress
 580 of counterion exchange (metathesis) reaction during
 581 nitration. It is found that nitration in ionic liquid is a
 582 useful alternative to classical nitration routes due to
 583 easier product isolation and the recovery of the ionic
 584 liquid solvent, and because it avoids problems associ-
 585 ated with neutralization of large quantities of strong
 586 acid.

587 3.3.11. Manganese(III) acetate mediated radical 588 reactions

589 Manganese(III) acetate is known to oxidize a vari-
 590 ety of carbonyl compounds to form radicals, which
 591 can undergo cyclization or intermolecular addition
 592 reactions to form radical adducts, which may be
 593 oxidized by a second equivalent of manganese(III)
 594 acetate (Fig. 6). These C–C coupling reactions are
 595 synthetically attractive because manganese(III) is in-
 596 expensive and, in contrast to related tributyltin hydride
 597 reactions, this oxidative method of radical generation
 598 leads to functionalized products. However, one signifi-
 599 cant drawback to the use of manganese(III) acetate
 600 is the harsh reaction conditions required because of
 601 its poor solubility in organic solvents. Acetic acid is
 602 invariably used which limits the range of substrates
 603 which can be employed, especially as many reactions
 604 require heating (often to $\geq 70^\circ\text{C}$). In addition, the use
 605 of acetic acid involves the separation and recovery
 606 of the manganese acetate at the end of the reactions.
 607 Radical cyclization reaction of 1,3-dicarbonyl com-
 608 pounds and alkenes mediated by manganese(III) ac-

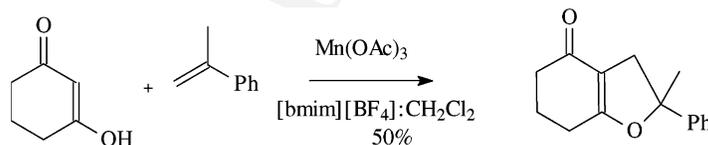


Fig. 6. Manganese(III) acetate mediated radical reaction in the presence of ionic liquid.

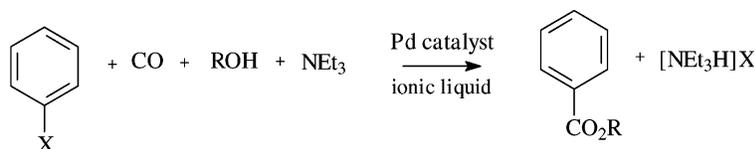


Fig. 7. Palladium-catalyzed carbonylation of aryl halides.

609 etate in the ionic liquids [bmim]BF₄ and [bmim]PF₆
 610 has been observed. The yields are often more than
 611 50% [108]. At the end of the reactions, the manganese
 612 acetate can be easily recovered (by precipitation) by
 613 addition of further organic solvent to the reaction
 614 mixture. After filtration, the manganese acetate was
 615 reacted with potassium permanganate to re-oxidize
 616 the manganese(II) back to manganese(III). The man-
 617 ganese(III) acetate can, therefore, easily be recycled
 618 although this does depend on the nature of ionic liquid.
 619 For example, ionic liquid [bmim]PF₆ makes it diffi-
 620 cult to the remove manganese byproducts. However,
 621 [bmim]BF₄ can be recovered on workup (in ≥95%
 622 yield) and reused without any detrimental effort on the
 623 product yields.

624 3.3.12. Palladium-catalyzed carbonylation of aryl 625 halides

626 Palladium-catalyzed carbonylation of aryl halides
 627 is a highly effective method for the synthesis of var-
 628 ious carbonyl compounds such as carboxylic acids,
 629 esters, amides, aldehydes and ketones. The separation
 630 of the products and the catalyst still is problematic,
 631 however, as in other homogeneous catalytic reactions.
 632 To circumvent this problem, palladium(0)-catalyzed
 633 single and double carbonylation of aryl halides in
 634 [bmim]BF₄ and [bmim]PF₆ has been investigated
 635 (Fig. 7) [110]. The results show that the palladium
 636 catalyst used in the ionic liquid could be recycled,
 637 after appropriate treatment such as distillation and
 638 extraction with ether of the products. The use of ionic
 639 liquid media significantly enhances the reaction rate
 of alkoxy carbonylation.

640 3.3.13. Reduction of aldehydes

641 The reduction of aldehydes by organoborane
 642 reagents is an important organic transformation. Tri-
 643 alkylboranes, most notably the pinanyl derivatives,
 644 have been found to be especially useful reducing
 645 reagents. However, reductions involving simple tri-
 646 alkylboranes generally require reaction temperatures
 647 in excess of approximately 150 °C. Ionic liquids like
 648 [bmim]BF₄ and [emim]PF₆ can be used in trialkyl-
 649 borane reductions of aromatic and aliphatic aldehydes
 650 with enhanced rate at low temperatures (even at room
 651 temperature) (Fig. 8) [111]. It is found that the organic
 652 products are easily removed from the ionic liquids
 653 via extraction and no decrease in reduction yields is
 654 found when the ionic solvent is reused.

655 3.3.14. Synthesis and reaction of zinc reagents 656 (Reformatsky reaction)

657 It is known that the preparation of Reformatsky
 658 reagents derived from ethyl bromodifluoroacetate in
 659 tetrahydrofuran is mediated by zinc. The same reaction
 660 has been carried out in ionic liquids with yields at least
 661 as good as those with conventional solvents (Fig. 9)
 662 [109]. The product extraction is straightforward and no
 663 volatile organic solvent problem is encountered. Syn-
 664 thesis and reaction of alkynyl zinc reagents has also
 665 been investigated.

666 3.3.15. Sequential reactions

667 Seddon's group has demonstrates sequential re-
 668 gioselective nucleophilic displacement reaction and
 669 Friedel–Crafts reactions to afford the pharmaceu-
 670 tical Pravadoline in the same ionic liquid, [bmim]PF₆

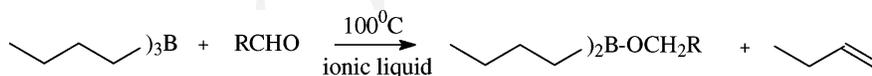


Fig. 8. Reduction of aldehydes using trialkylboranes in ionic liquids.

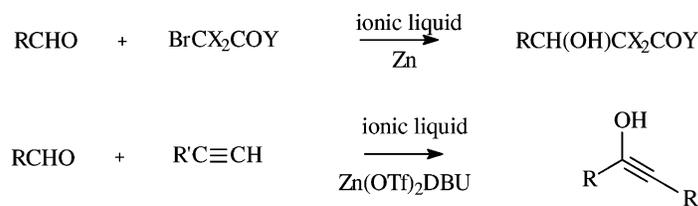


Fig. 9. The synthesis and reaction of zinc reagents in ionic liquids.

671 (Fig. 10) [113]. The Friedel–Crafts reaction was found
 672 to work without the need for Lewis acids and without
 673 all the associated waste aluminum disposal prob-
 674 lems of a conventional Friedel–Crafts reaction. It is
 675 thought to be the first high yield (94%) green route to
 676 a pharmaceutical in a ionic liquid avoiding the prob-
 677 lem of production of large quantities of waste found
 678 in traditional industrial pharmaceutical production.

679 Another Lewis acid-catalyzed sequential reaction
 680 involving a Claisen rearrangement followed by a cy-
 681 clization reaction in ionic liquids have also been re-
 682 ported (Fig. 11) [111]. It was found that the ionic
 683 liquid, 8-ethyl-1, 8-diazabicyclo[5,4,0]-7-undecenium
 684 trifluoromethanesulfonate ([EtDBU]OTf), is a good
 685 alternative reaction medium for sequential reactions
 which can be reused and be stable at high temperature.

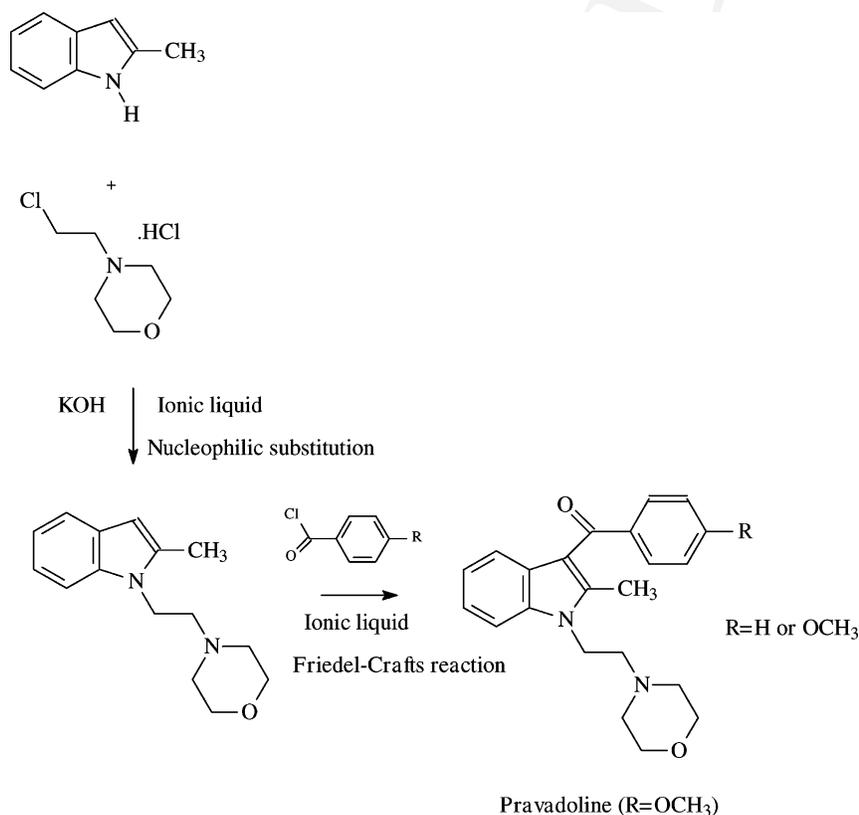


Fig. 10. Pharmaceutical preparation in an ionic liquid.

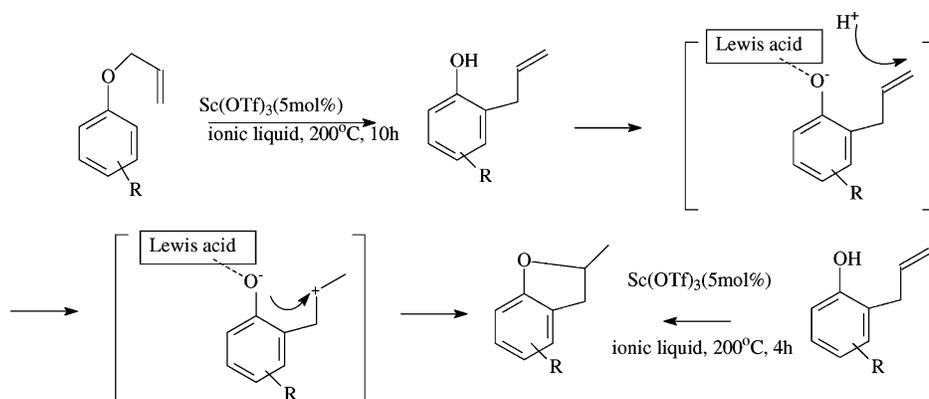


Fig. 11. Sequential reaction in ionic liquids.

686 3.3.16. Syntheses of cyclotrimeratrylene (CTV) and 687 tris-(O-allyl)CTV

688 Cyclic CTVs (Fig. 12) have been known for over
689 80 years but they are now receiving considerable at-
690 tention as supramolecular host compounds for various
691 species from low molar mass organic solvents through
692 to C_{60} . CTV are traditionally synthesized under harsh
693 dehydrating conditions and require the use of large
694 quantities of organic solvent in the reaction workup. It
695 has been demonstrated that the ionic liquid tributyl-
696 hexlammonium bis(trifluoromethylsulfonyl)amide
697 (N_{6444} Imide) provides a safe, non-volatile reaction
698 medium that is readily recycled [115]. The methodol-
699 ogy developed obviates the need for the use of large
700 quantities of organic solvent and strong dehydrating
701 acids yet provides a pure crystalline product in high
702 yields. Unlike most traditional synthetic routes to
703 CTV, extensive recrystallization or chromatographic
704 steps are avoided and the ionic liquid medium is
readily recovered.

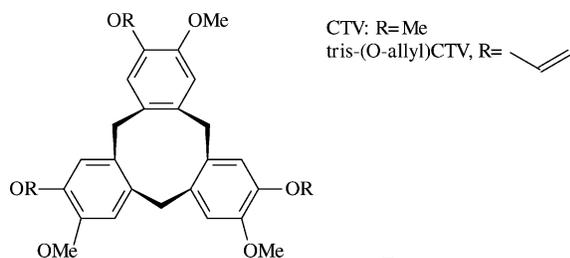


Fig. 12. CTV and tris-(O-allyl)CTV.

705 3.3.17. Cycloaddition of carbon dioxide to propylene 706 oxide catalyzed by ionic liquids

707 Five-membered cyclic carbonates are excellent
708 aprotic polar solvents and are used extensively as in-
709 termediates in the production of drugs and pesticides.
710 The formation of cyclic carbonates via cycloaddition
711 of carbon dioxide, which is one of the routes for
712 carbon dioxide chemical fixation, has received much
713 attention in regard to utilization of carbon resources
714 and the reduction of CO_2 pollution. However, when
715 organic and inorganic compounds such as metal
716 halides or MgO are used as catalysts, low reaction
717 rates and rigorous reaction condition remain a prob-
718 lem. Ionic liquids based on [bmim]⁺ and [bpy]⁺ have
719 been used as catalytic media for the cycloaddition
720 of carbon dioxide to propylene oxide [116]. It is re-
721 ported that the ionic liquid [bmim]BF₄ is the best
722 catalytic medium for the reaction, showing excellent
723 selectivity with relatively short reaction time. The re-
724 sulting product can be separated from the ionic liquid
725 by simple distillation, and the ionic liquid catalyst is
726 recyclable.

727 3.3.18. Wittig reactions

728 The Wittig reaction is amongst the most popular
729 methods for C=C bond formation, giving in most
730 cases good to excellent stereocontrol. The separation
731 of the alkene from the by-product (Ph_3PO) is a class-
732 ical problem, which is usually done by crystallization
733 and/or chromatography. It has been demonstrated that
734 [bmim]BF₄ can be used as a medium to perform
735 Wittig reactions using stabilized ylides allowing both

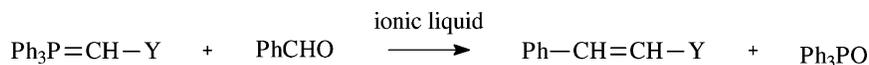


Fig. 13. Wittig reactions in ionic liquid.

736 easier separation of alkenes from Ph_3PO and also the
737 recycling of the solvent (Fig. 13) [117].

738 3.3.19. Stille coupling

739 The Stille coupling reaction has been one of the
740 most widely used steps in the preparation of a wide
741 variety of materials including polyenes, diaryls, and
742 aromatic carbonyl compounds. The main advantages
743 of the reaction stem from the air and moisture stable
744 coupling partner and the compatibility of the cou-
745 pling condition with a wide array of functional groups.
746 However, the one major limitation is the toxicity of
747 the organic reagents and byproducts. Moreover, like
748 all transition metal catalyzed cross-coupling reactions,
749 the catalyst itself has the problems of expense and the
750 need of expensive and/or toxic ligands. A series of
751 Stille coupling reactions in the ionic liquid $[\text{bmim}]\text{BF}_4$
752 has been successfully demonstrated (Fig. 14) [118].
753 The procedure permits extensive recycling of the sol-
754 vent and catalyst without significant loss in activity.
755 Furthermore, an interesting selectivity for aryl brom-
756 ides and aryl iodides was noted.

757 3.3.20. Preparation of heterocyclic compounds

758 One pot synthetic methods are one of the most
759 important synthetic reactions especially in the syn-

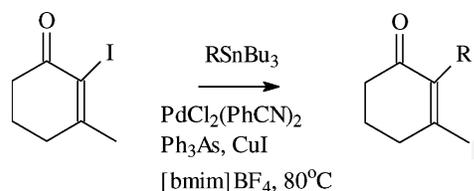


Fig. 14. The Stille coupling in ionic liquid.

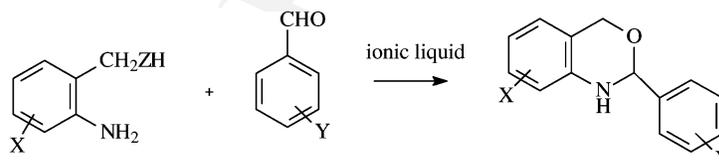


Fig. 15. Preparation of heterocyclic compounds in ionic liquids.

760 thesis of heterocycles, which often exhibit unique
761 physicochemical properties. Usually, the synthesis
762 of these heterocycles is carried out in polar organic
763 solvents such as THF, DMF or DMSO, and after
764 quenching with water, the products are extracted with
765 organic solvents. Therefore, these processes generate
766 considerable quantities of waste containing solvent
767 media and catalyst. A series of ionic liquid such as
768 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium triflu-
769 romethanesulfonate and 8-methyl-1,8-diazabicyclo
770 [5,4,0]-7-undecenium trifluoromethanesulfonate have
771 been developed and used as replacement for the more
772 expensive organic solvents in the one pot synthesis of
773 heterocycles (Fig. 15) [119]. These ionic liquids are
774 safe to use and are fully recyclable with no process
775 emissions.

776 3.3.21. Enzyme catalysis in ionic liquids

777 Today, a large number of biotransformations making
778 use of whole cells or isolated enzymes are employed
779 on the industrial and laboratory scale. Nevertheless,
780 there are still problems with substrate solubility, yield
781 or (enantio-)selectivity. Some progress has been made
782 by addition of organic solvent or high salt concentra-
783 tions or use of microemulsions or supercritical fluids.
784 Recent research has shown that it is possible to carry
785 out enzyme-catalyzed reactions and other types of bi-
786 transformations in ionic liquids.

787
788 3.3.21.1. Synthesis of Z-aspartame (Z = protecting
789 group). The first example of an enzymatic synthesis
790 in an ionic liquid was demonstrated by the synthesis of
791 Z-aspartame, a precursor to the artificial sweetener as-
792 partame, by the reaction of two amino acid derivatives,
793 carbobenzoxy-L-aspartate and L-phenylalanine methyl

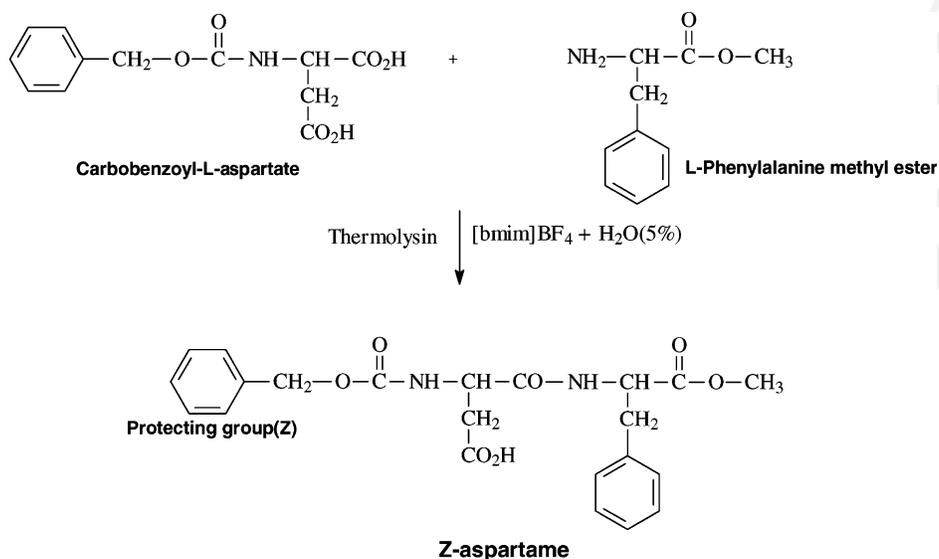


Fig. 16. Enzyme catalyzed synthesis of Z-aspartame in ionic liquid.

794 ester, catalyzed by thermolysin, a proteolytic enzyme
 795 (Fig. 16) [120]. The reaction was carried out using
 796 [bmim]BF₄ containing 5% by volume of water. The
 797 yield was 95%, which is similar to that reported for en-
 798 zymatic aspartame synthesis in organic solvents with
 799 low water content, with a competitive reaction rate.
 800 In addition, the enzyme, which normally requires im-
 801 mobilization, exhibited excellent stability in the ionic
 802 liquid.

803
 804 *3.3.21.2. Conversion of 1,3-dicyanobenzene to*
 805 *3-cyanobenzamide and 3-cyanobenzoic acid.* The
 806 biotransformation of highly polar substrates such as
 807 carbohydrates is difficult to carry out in common or-
 808 ganic solvents because of their sparing solubility. The
 809 first example of such a biotransformation in an ionic
 810 liquid system has been reported [121]. It shows that
 811 *Rhodococcus* R312, a whole-cell biocatalyst that fa-
 812 cilitates the transformation of nitriles to amides, could
 813 be used for the conversion of 1,3-dicyanobenzene to
 814 3-cyanobenzamide and 3-cyanobenzoic acid in the
 815 biphasic water-[bmim]PF₆ system. Unlike described
 816 in Section 3.3.21.1 above, the enzyme is not active
 817 in [bmim]PF₆, and the ionic liquid acts only as a
 818 reservoir for the substrates. The *Rhodococcus* R312
 819 remains in the aqueous phase, which is where the
 820 reaction takes place and the ionic liquid is used to dis-

821 solve concentrations of substrate above the aqueous
 822 solubility limit, which then partitions into the aque-
 823 ous phase. The results indicate improved catalytic
 824 stability compared with the use of organic solvents,
 825 and there is some evidence that ionic liquid may alter
 826 the selectivity of the transformation.

827
 828 *3.3.21.3. Kinetic resolution of 1-phenylethanol.*
 829 Lipase-catalyzed enantioselective reactions in pure
 830 ionic liquids such as [bmim]PF₆, [bmim]CF₃SO₃,
 831 and [bmim](CF₃SO₂)₂N has been reported (Fig. 17)
 832 [122]. As a model system, the kinetic resolution of
 833 rac-1-phenylethanol by transesterification with vinyl
 834 acetate was investigated. Lipases show good activity
 835 and, in some cases, improved enantioselectivity in the
 836 reaction. Another advantage is that the ionic liquids
 837 are not volatile and it is, therefore, possible to remove
 838 the products by distillation and repeat the catalytic
 839 cycle after addition of fresh substrate. The enzyme
 840 suspended in the ionic liquid could be reused three
 841 times with less than 10% loss of activity per cycle
 842 and the enantioselectivity was not influenced.

843
 844 *3.3.21.4. Alcoholysis, ammoniolysis and perhydroly-*
 845 *sis reactions catalyzed by Candida antarctica lipase.*
 846 The use of hydrolytic enzymes in anhydrous organic
 847 media has become a valuable addition to the syn-

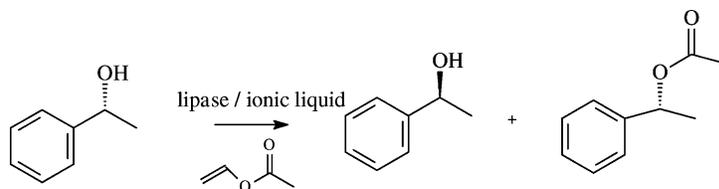


Fig. 17. Kinetic resolution of 1-phenylethanol catalyzed by enzyme in ionic liquid.

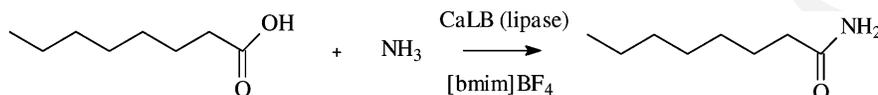


Fig. 18. Ammoniolysis reaction catalyzed by lipase in ionic liquid.

848 thetic repertoire. Reactions can be performed that are
 849 impossible in water, and the enzyme can even show
 850 enhanced thermostability. A serious drawback of con-
 851 ventional organic media is, however, the substantial
 852 reduction in reaction rate, which is mainly caused
 853 by altered partitioning of the reactant between the
 854 solvent and the active site. Also, the use of volatile
 855 organic solvents such as chlorinated hydrocarbons
 856 presents an environmental hazard. The ionic li-
 857 quids, [bmim]BF₄ and [bmim]PF₆ have been applied
 858 in a number of elementary reactions—alcoholysis,
 859 ammoniolysis (Fig. 18) and perhydrolysis [123].
 860 The reaction rates were comparable with, or better
 861 than, those observed in conventional organic reaction
 862 media.

863

864 **3.3.21.5. Lipase-catalyzed transesterifications in**
 865 **ionic liquids.** Transesterifications of alcohols in
 866 the presence of vinyl acetate in [emim]BF₄ and
 867 [bmim]PF₆ using *C. antarctica* lipase B (CALB,
 868 immobilized) and *Pseudomonas cepacia* lipase
 869 (PCL, native) as enzyme catalysts has been in-
 870 vestigated (Fig. 19) [124]. It was reported that
 871 lipases were up to 25 times more enantioselective
 872 in ionic liquids than in conventional organic
 873 solvents.

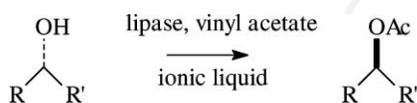


Fig. 19. Transesterification catalyzed by lipase in ionic liquid.

To sum up, C–C or C–heteroatom coupling reac- 874
 tions remain as the main area of research into catalytic 875
 application of ionic liquid as shown in a number of 876
 very recent publication. An increasing number of reac- 877
 tions are being tried out in ionic liquids [125–129]. 878

4. Potential and challenges 879

The solvent used in homogeneous catalysis plays 880
 a unique role in dissolving and stabilizing the reac- 881
 tant, ligand, and catalyst precursor, but necessarily 882
 must not react with the transition metal intermediates 883
 nor compete with the reactant for vacant coordination 884
 sites. In such a system, the catalytic center is often 885
 a rotationally highly free, three-dimensional complex 886
 having more than one site for coordination. Multi-site 887
 coordination is the most important characteristic of 888
 a homogeneous catalyst that distinguishes it from a 889
 heterogeneous catalyst. An important feature of homo- 890
 geneous systems is that each of the metallic centers 891
 is potentially catalytically active. Therefore, homoge- 892
 neous processes are highly efficient and highly spe- 893
 cific, chemo-, stereo-, regio-, and enantioselectivities 894
 can be attained. The disadvantage, however, is the need 895
 to separate solvent and catalyst from the product and 896
 unused reactants at the end of the reaction. 897

In heterogeneous catalysis, since the catalytic center 898
 is restricted within a hemispherical geometry by the 899
 surface, only a single site is available for reactant co- 900
 ordination. Therefore, the catalytic center in a hetero- 901
 geneous system is a restricted, two-dimensional one 902

903 providing only one site for coordination. In addition,
 904 only a part of the many metallic centers can be effec-
 905 tively utilized in the catalytic reaction. Hence, the low
 906 catalytic density, low TOF values and poor selectivi-
 907 ties often observed with heterogeneous catalysts can
 908 be easily understood.

909 Ionic liquids offer the opportunity of combining the
 910 advantages of both homogeneous and heterogeneous
 911 catalysis in one system. That is to say, immobiliza-
 912 tion of a catalyst (metal/oxide/complex) by support-
 913 ing it in an ionic liquid rather than on a surface may
 914 create highly free, three-dimensional centers as in a
 915 homogeneous catalyst but the catalytic reaction oc-
 916 curs at the interface between the ionic liquid (rather
 917 than a solid) and the reactants in either the gas or im-
 918 miscible liquid phase. Development of application of
 919 three-dimensional heterogeneous catalysis using ionic
 920 liquids as supports should present challenges for us
 921 over the next decade and beyond.

922 At the present time, several urgent questions regard-
 923 ing the fundamental aspects of ionic liquids need to be
 924 addressed. Among them, the physicochemical princi-
 925 ples of liquid properties and solubility of ionic liquids
 926 remains a frontline subject of ionic liquid research to-
 927 day. Meanwhile, the functionalization of ionic liquids
 928 ought to be carried out to make them capable of dis-
 929 solving metals or metal oxides. Furthermore, the co-
 930 ordination properties of ionic liquids remain to be re-
 931 vealed.

932 Uncited references

933 [39,104].

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