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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 Elsevier Science B.V. All rights reserved.

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 heterocylic 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 deplex 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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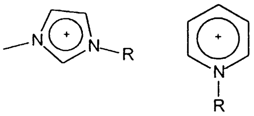
Table 1
Typical cation/anion combinations in ionic liquids[a]

Cations[a]	Anions	Coordination ability of anions
	$[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[CuCl_2]^-$, $[AlCl_4]^-$, $[AlBr_4]^-$, $[AlI_4]^-$, $[AlCl_3Et]^-$, $[NO_3]^-$, $[NO_2]^-$, $[SO_4]^{2-}$	Weak (neutral)
PR_4^+, SR_4^+, NR_4^+	$[Cu_2Cl_3]^-$, $[Cu_3Cl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$	None (acidic)

[a] R = alkyl.

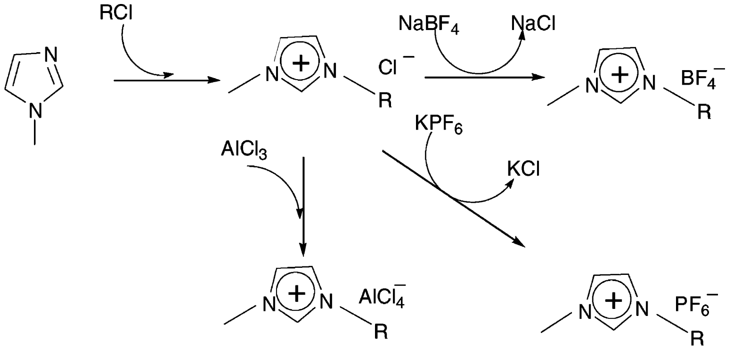


Fig. 1. Typical preparation routes for ionic liquids.

2. A wide range of materials including inorganic, organic and even polymeric materials are soluble in ionic liquids.
3. Excellent and variable Lewis/Brönsted acidity.
4. High polarity [21].
5. Negligible vapor pressure.
6. Potential to be reused and recycled.

Ionic liquid are generally thought to have another advantage in that they display a low coordination tendency, however, direct experimental evidence of this is still lacking, that is to say, the structure of the solute entities in ionic liquids is still unclear. Interconversion of coordinatively unsaturated–saturated species is a key feature in catalyst function, fundamental studies on the coordination behavior of ionic liquids with different materials such as metal clusters, oxides nanoparticles and coordination complexes are required in order to understand this area more clearly.

2. Current applications

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

More than 60% of products and more than 90% of processes worldwide rely on the rapidly expanding field of catalysis. High specificity and/or efficiency is the most important feature of “green” catalysis. Two concepts frequently discussed in “green” chemistry are atom economy and chemical specificity. Few of the many catalytic reactions can be atom economic. Furthermore, even for such reactions, in most cases it is hard to reach 100% conversion with 100% selectivity due to thermodynamic obstacles and/or the competition of parallel reactions. In order to measure the quality of a synthetic method, chemical specificity is more fundamental and important. High specificity, for example by accelerating the target reaction to reach equilibrium as fast as possible while eliminating or minimizing side reactions (high selectivity), or via

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	Chloroform	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
	0.60	149.87	Light brown	1.481	−95.87	316.34	r	r	s	s	i	i	s	s
[emim]Br/$AlCl_3$	0.50	162.21	Purplish black	1.575	13.61	272.51	r	r	s	i	i	i	s	i
	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
[emim]PF_6		256.13	Yellow	1.426	2.71	304.65	i	i	s	s	i	i	s	i
N-butylpyridine/$AlCl_3$	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
	0.60	148.67	Brownish yellow	1.497	18.11	260.24	r	r	s	i	i	i	s	s
$(CH_3)_3NHCl/2AlCl_3$	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 $AlCl_3$.
[c] s: soluble, i: insoluble, r: may react with each other.

reducing long synthetic routes to one or two steps (high efficiency), is usually our only choice. Using ionic liquids as replacement for organic solvents is one way to make a catalytic process "green", however, making a process highly specific is a more important concern from the view of "Green Chem.". As shown in this review ionic liquids, as a consequence of their unique properties, have a great potential to help in reaching these goals. However, the mechanistic role that ionic liquids play is still far from clear at present. The questions presented here will, it is to be hoped, stimulate the continuing growth of catalysis by ionic liquids.

Current applications of ionic liquids in catalysis as alternatives to conventional media are concentrated in two directions. One is to take the place of organic solvents due to their unique solvent properties and the other is to take the place of liquid acids due to their variable acidities. The former applications include dimerization reactions, Heck reactions and hydroformylation, while the latter includes alkylation reactions and Friedel–Crafts reactions. Many of these studies have significant commercial applications but fundamental studies of the relationship between the properties of ionic liquids and the improved performance compared with conventional solvents are still rare. For example, many studies have found that reaction rate, conversion and selectivity are enhanced to different degrees (see Tables 3–5), but the reason, i.e. why the liquids show higher efficiency/specificity in the reactions, is still an open question.

Improvement of current biphasic aqueous–organic systems by using ionic liquids in place of water has received significant recent attention. The disadvantage of traditional aqueous–organic systems is that the ligands have to be modified in order to give the catalyst the desired solubility in water [22–37], In addition, the poor solubility of some organic substrates in water giving rise to low reaction rates is another limitation. Water is a coordinating protic solvent with high polarity, i.e. water itself in many cases is rather reactive with organometallic catalysts. Ionic liquids do not suffer from these limitations. When used in place of water, ionic liquids can form ionic liquid–organic solvent systems without requiring any change or modification in either ligand or organic phase.

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

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

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

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

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

3.1.1. Hydrogenation

Many attempts have been made to develop biphasic processes for homogeneous hydrogenation catalyzed by transition metal complexes. In traditional aqueous–organic solvent system, modification of the ligands to introduce water-solubility is generally necessary but the cost is a great problem. $[RuCl_2\text{-}(S)\text{-}BINAP]_2\text{-}NEt_3$ as an asymmetric hydrogenation catalyst can be dissolved in the ionic liquid $[bmim]BF_4$ directly without any modification however and used in a biphasic system with isopropanol as the organic phase. Hydrogenated products Ibuprofen/Naproxen (2-acrylacrylic acids) have been obtained with high enantioselectivity (96 ee%). The products remain in the isopropanol phase and can be separated by simple decantation [39,41]. The recovered ionic liquid phase containing the catalyst can then be reused several times without any significant loss in catalytic activity or enantioselectivity.

Stereoselective hydrogenation of aromatic compounds in $[bmim]Cl\text{–}AlCl_3$ ionic liquid systems has also been investigated [42], showing that carbocyclic aromatic compounds are readily protonated [43].

Recently, supercritical CO_2 has been employed with ionic liquids to form ionic liquid/$scCO_2$ biphasic systems. By avoiding the use of organic solvent completely, the systems are the environmentally totally 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 redisgn, 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 biphase 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 of 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]
			[bmim]PF$_6$ SbF$_6$, BF$_4$ OTf [pmim]PF$_6$ [hmim]PF$_6$				
2	Diels–Alder reaction	Cycloaddition reaction catalyzed by acid catalyst	[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-naphtoquinoned 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-diazbicyclo [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-(trimethylilyl)oxybuta1,3-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 biphase 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 $[NiCl_2(P(I\text{–}Pr)_3)_2]$ 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 *n*-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 *n*-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_2TiCl_2 catalyst and $Al_2Me_3Cl_3$ (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]
		n-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]

		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]
4	Alkylation	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]
			[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]
			$Et_3NHCl/AlCl_3$	1.2 g of $AlCl_3$ and 0.42 g of Et_3NHCl	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_3NHCl (0.42 g) are then introduced. The desired alkylation reaction took place instantaneously	In situ formation of ionic liquid; no corrosion	[83]
5	Alkylation	Preparation of linear alkyl benzenes	Ionic liquid free of Lewis acidity Et_3NHCl/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]
			$Et_3NHCl/AlCl_3$	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_2CO_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 tetraallystannane (70.7 mg) are mixed in reactor and then stirred vigorously for 16 h. The mixture is extracted three times with Et_2O (10 ml). The organic extracts are combined and dried over anhydrous $MgSO_4$, The Et_2O 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, $Pd_2(dba)_3CHCl_3$ (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_2CO_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 an 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-*n*-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_2Cl_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*-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 *n*-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 triphenyphsphine 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 *N*, *N*-dialkylpyrrolidinium with BF_4^-, PF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$, and $N(CF_3SO_2)_2^-$	4 ml	At 80 °C, Rh(CO)$_2$(acac) 0.075 mmol, 1-hexene/Rh = 800, CO/H$_2$(molar ratio) = 1, P(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 guanidinum 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_2HPO_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_2Cl_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	Electrophlilic nitration of aromatics	Aromatics nitration with nitration agents such as $[NO_2][BF_4]$ systems	[emim] OTf/CF_3COO/NO_3/ $[HNEtPr^i{}_2][CF_3COO]$/ $AlCl_4$/Al_2Cl_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-2*H*-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. Bromobenzen (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-(*N*-morpholino)-2-chloroethane hydrochloride reacted to give the 1-(2-*N*-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_3PO_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 TbuOMe (3 × 3 ml) and then with toluene (3 × 3 ml). The extracts were evaporated in vacuo. Filtration of the *tert*-BuOMe extract on a short SiO_2 pad gave the first product and then Ph_3PO	Selective extraction of alkenes and Ph_3PO, 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-(benzonitrile) 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-diazbicyclo [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 ant 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_3SO_3/ $(CF_3SO_2)_2N$/$(CH_3O)_2SO_2$, [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 *C. antarctica* 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	Transesterificatio 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]

Table 6
Rh-catalyzed hydrogenation and isomerization of pent-1-ene[a]

Entry	Solvent	Conversion (%)	Yield (%)		TOF (min^{-1})[b]
		Pent-1-ene	Pentane	Pent-2-ene	
1[c]	Acetone	99	38	61	0.55
2	[bmim]SbF_6	96	83	13	2.54
3	[bmim]PF_6	97	56	41	1.72
4	[bmim]BF_4	10	5	5	0.15
5[d]	[bmim]Cl/CuCl	18	0	18 (98% *cis*)	0
6[e]	[bmim]PF_6	99	25	74	0.76

[a] Rh catalyst: 0.05 mmol; pent-1-ene: 18.4 mmol; solvent: 4 ml; $T = 30\,^{\circ}\mathrm{C}$; $p(H_2) = 0.1$ MPa; $t = 2$ h.
[b] Turnover frequency (TOF) defined as mole (pentane) per mole (Rh) per minute.
[c] Acetone: 10 ml; pent-1-ene: 9.2 mmol.
[d] Ionic liquid prepared by reacting 1.5 equiv. of CuCl with 1.0 equiv. of [bmim]Cl.
[e] Acetone(2 ml) was added.

Asymmetric hydrogenation of tiglic acid catalyzed by [Ru(O_2CMe)$_2$(*R*)-tolBINAP] in wet ionic liquid ([bmim]PF_6 with added water) gave 2-methylbutanoic acid with high enantioselectivity (92 %ee) and conversion (100%). It was found that at least for tiglic acid, there is no need to add an alcohol or other organic solvent, nor is there any need to prepare a fluorinated or water-soluble derivative of the catalyst. The products can be extracted from the ionic liquids by supercritical CO_2, with no concomitant extraction of ionic liquid or asymmetric catalyst. Furthermore, the ionic liquid/catalyst solution can be reused several times without significant loss of enantioselectivity or activity.

3.1.2. Isomerization

Isomerization of alkanes is one of the most important processes for producing reformulated gasoline. Studies in this area have left many questions unanswered. The isomerization of pent-1-ene to pent-2-ene has been reported by Chauvin et al. [45] when attempting the hydrogenation of pent-1-ene using the Osborn complex, $[Rh(nbd)(PPh_3)_2]^+[PF_6^-]$, as cationic catalyst precursor. Their results are listed in Table 6. It is interesting to note that no hydrogenation is observed when [bmim]Cl/CuCl was used as solvent. The product was *cis*-pent-2-ene with a selectivity of 98%, although the conversion was relatively low (18%).

Another result of interest reported by the same group is the olefin metathesis reaction (shown in Fig. 2) [46]. Transition metal complexes such as tungsten-based catalysts are the active catalysts for this reaction. $W(OAr)_2Cl_2$ complexes are quite soluble and remain in the [bmim]Cl/$AlCl_3$/$AlEtCl_2$ ionic liquid phase, and can subsequently be reused

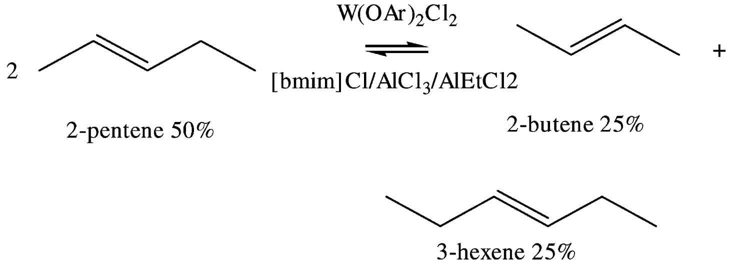


Fig. 2. Olefin metathesis.

several times after decantation of the hydrocarbon layer.

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

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

The cracking of polyethylene is one of the most important plastics recycling processes [47]. The commonly used methods include pyrolysis, catalytic cracking with acidic materials and reactions in supercritical water. The wide range of products obtained is a problem in each case. A new method using acidic chloroaluminate(III) ionic liquids to crack polyethylene has been developed [48]. The addition of acidic co-catalysts such as [emim][HCl_2] (1 mol%) or concentrated sulfuric acid (2 mol%) is essential to provide a source of protons. Unlike the cracking reactions using supercritical water or zeolites, the products are mainly volatile alkanes (C_3–C_5) including propane and 2-methylpropane. No alkenes are observed. It has been shown that this method is quite selective toward low molecular weight feedstocks. Another advantage of this method is that the products are very easily separated from ionic liquids by solvent extraction or other physical separation processes.

3.2.2. Acylative cleavage of cyclic and acyclic ethers

Although several methods for cleaving ethers are available, a general reliable method to selectively cleave ether linkages has not been reported [49]. Ionic liquids derived from [emim]I/$AlCl_3$ have been used as solvent and Lewis acid catalyst for the acylative cleavage of a series of cyclic and acyclic ethers such as tetrahydrofuran, 1,4-dimethyltetrahydrofuran, tetrahydropyran, diethyl ether and diisopropyl ether with excellent selectivities (see Fig. 3).

3.2.3. Dissolution of kerogen [18]

Kerogen is a cross-linked macromolecular system, which resides in a type of sedimentary rock known as oil shale. Liquefication, gasification and even modification of oil shale are challenges for chemists and engineers. Present methods for such processes include pyrolysis, solvent extraction, direct hydrogenation and the production of synthesis gas followed by the use of Fischer–Tropsch technology. Ionic liquids [bmim]PF_6 and [bmim]Cl/$AlCl_3$ have been employed to treat oil shale. Dissolution of kerogen has also been investigated by heating it in acidic chloroaluminate(III) ionic liquids for 1 min periods in a microwave oven.

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

Asymmetric ring opening reactions of epoxides with $TMSN_3$ catalyzed by a Cr(salen) complex has been recognized as an attractive approach to the synthesis of optically pure β-amino alcohols, which are important structural elements in many biologically active molecules as well as the starting point in the design of many chiral ligands. A biphasic method involving use of ionic liquids has been developed in order to eliminate the drawback of the conventional catalyst recycling procedure which involves the potentially hazardous distillation of the neat liquid azides, which may prove a limitation for large scale applications [50]. From the results of enantioselective ring opening of *meso* epoxides and cyclopentene oxide, it can be seen that without hazardous workup stages such as distillation of the azide product, catalyst recycling is quite simple. The catalytic activity and enantioselectivity are found to be strongly dependent on the nature of the anion in the ionic liquids.

In summary, studies on C–C cleavage reactions using ionic liquids are at a preliminary stage, but show a promising perspective in laboratory and the chemical industry.

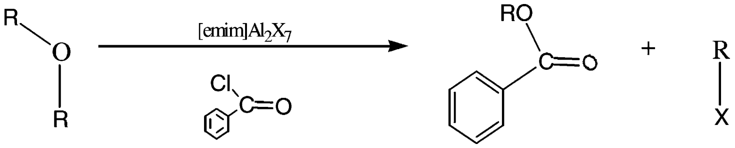


Fig. 3. Acylative ether cleavage in [emim]I–$AlCl_3$.

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

3.3.1. Friedel–Crafts reaction

Friedel–Crafts alkylations and acylations are of great commercial importance, and are also among the earliest reported investigations using ionic liquids 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 ($[bmim]Cl/AlCl_3/EtAlCl_2 = 1/1.2/0.25$) makes it possible to use $Ni(L)_2Cl_2$ 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 $5\,^{\circ}C$. 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 $5\,^{\circ}C$ 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]PF_6 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/coordinating 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 H_2SO_4 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/$AlCl_3$ 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 $AlCl_3$ (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 allylation of methylene compounds by 1,3-diphenylallyl acetate in [bmim]BF_4 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 Pd^0–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*-*o*-tolyphosphino]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]BF_4 ionic liquids as solvents have also been reported [93]. The reaction

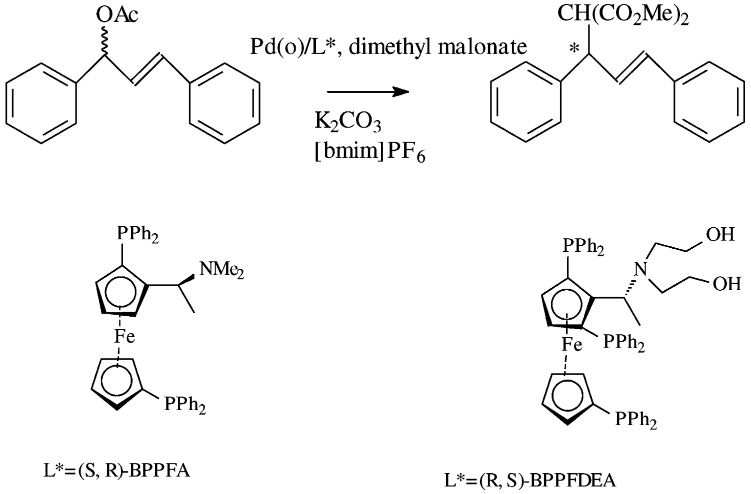


Fig. 4. Enantioselective allylation in ionic liquid.

was found to occur more efficiently in [bmim]Br than in [bmim]BF_4. Further study revealed that [bmim]-2-ylidene (bmiy) complexes of palladium $[PdBr(\mu\text{-}Br)(bmiy)]_2$ (**1**) and $[PdBr_2(bmiy)_2]$ (**2**) could be isolated from the reaction with [bmim]Br but not with [bmim]BF_4. It has been suggested that the active precursor is complex **2** formed via the intermediate **1**. The origin of poor activity in [bmim]BF_4 was proposed to be the transformation of **2** into a less active species in [bmim]BF_4. This study may be the first effort to probe into the mechanistic details of the effect of ionic liquid on reaction rate. More recently, palladium-catalyzed regioselective arylation of an electron-rich olefin by aryl halides has also been accomplished, using aryl iodides and bromides as arylating agents instead of the commonly used, but commercially unavailable and expensive, aryl triflates. The reaction proceeds with high efficiency and remarkable regioselectivity, leading almost exclusively to substitution by various aryl groups at the olefinic carbon α to the heteroatom of butyl vinyl ether [96].

Palladium ($Pd[PPh_3]_4$)-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acid have been conducted in the [bmim]BF_4 ionic liquid to afford biaryls, with the advantages of increased reactivity at reduced catalyst concentration, no homo-coupled products, operation under aerobic conditions and no loss and decomposition of palladium catalyst and repetitive catalytic runs [94].

3.3.8. Hydroformylation

Hydroformylation of olefins is another reaction of considerable industrial importance. An aqueous–organic biphasic hydroformylation system catalyzed by water-soluble Rh catalysts has been commercialized. Unfortunately, the use of water as polar phase limits this process to C_2–C_5-olefins due to the low water solubility of higher olefins. As an alternative polar medium, a range of ionic liquids containing PF_6^-, SbF_6^- and BF_4^- have been employed in an ionic liquid–organic biphasic system [45,97–101]. The solubility problem is thus overcome and the products are separated as an organic phase. The catalyst can also be reused. A small amount of catalyst leaching into the organic phase causes some loss in activity after each run however. These problems have been improved recently by varying the ligand and the ions of ionic liquids [102–104]. From the results of 1-hexene hydroformylation catalyzed by rhodium in a biphasic system, it can be seen that the reaction rate and regioselectivity as well as the retention of the rhodium can be optimized by ensuring compatability between the anions and cations of the ionic liquid and the modified phosphite or phosphine ligands of the rhodium catalyst.

3.3.9. Nucleophilic displacement reactions

Nucleophilic displacement reactions are often carried out using phase-transfer catalysis (PTC) to

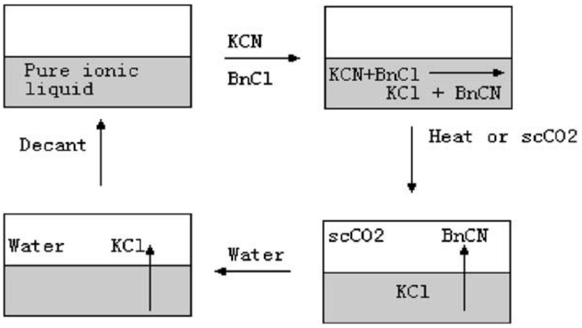


Fig. 5. Recyclable ionic liquid solvent system for nucleophilic substitution reactions.

facilitate the reaction between the organic reactants and the inorganic ionic salts that provide the nucleophiles. The phase-transfer catalysts, often a tetraalkylammonium salt, acts as a shuttle for the reactant anion between a polar phase that contains the salt and a non-polar phase that contains the organic reactant. This technique overcomes the problems of bringing the reactants into contact and, in addition, it provides some activation of the nucleophilic anion since it is much less tightly bound to a tetraalkylammonium cation than it would be to a metal cation. However, conventional PTC uses environmentally undesirable organic solvents like methylene chloride or *o*-dichlorobenzene. Catalyst separation and recovery also represent significant challenges. Ionic liquids, because of their bulky organic cations, seem well suited for the type of reactions for which PTC is effective. A recyclable and catalytic ionic liquid solvent system for nucleophilic substitution reactions has been developed (Fig. 5), demonstrating the viability of ionic liquids as a solvent for reactions between organic compounds and inorganic salts [106].

3.3.10. Electrophilic nitration of aromatics

Electrophilic nitration of aromatics is a fundamental reaction of great industrial importance, whose products are key organic intermediates or energetic materials. Although the mechanistic and synthetic aspects of nitration chemistry have been very thoroughly studied over the years, there is continuing concern over environmental aspects, disposal problems and regeneration of the used acids. An early study of catalysis of electrophilic aromatic substitution reactions in acidic [emim]chloroaluminate included examples of nitration with KNO_3 in particular [107]. More recently, a series of ionic liquids of based on [emim] and [bmim] cations has been utilized as solvent for aromatic nitration [108]. Counterion dependency of the NMR spectra of the ionic liquids is used to estimate the progress of counterion exchange (metathesis) reaction during nitration. It is found that nitration in ionic liquid is a useful alternative to classical nitration routes due to easier product isolation and the recovery of the ionic liquid solvent, and because it avoids problems associated with neutralization of large quantities of strong acid.

3.3.11. Manganese(III) acetate mediated radical reactions

Manganese(III) acetate is known to oxidize a variety of carbonyl compounds to form radicals, which can undergo cyclization or intermolecular addition reactions to form radical adducts, which may be oxidized by a second equivalent of manganese(III) acetate (Fig. 6). These C–C coupling reactions are synthetically attractive because manganese(III) is inexpensive and, in contrast to related tributyltin hydride reactions, this oxidative method of radical generation leads to functionalized products. However, one significant drawback to the use of manganese(III) acetate is the harsh reaction conditions required because of its poor solubility in organic solvents. Acetic acid is invariably used which limits the range of substrates which can be employed, especially as many reactions require heating (often to ≥70 °C). In addition, the use of acetic acid involves the separation and recovery of the manganese

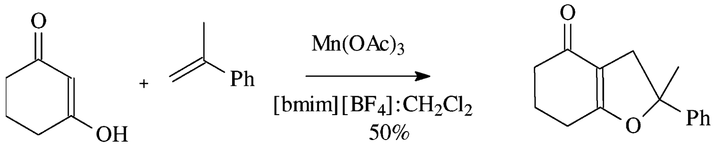


Fig. 6. Manganese(III) acetate mediated radical reaction in the presence of ionic liquid.

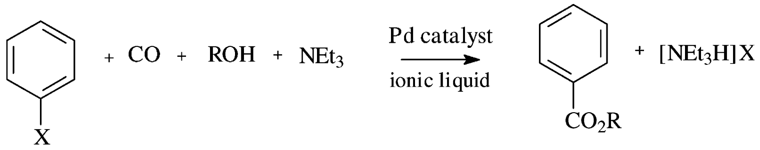


Fig. 7. Palladium-catalyzed carbonylation of aryl halides.

acetate at the end of the reactions. Radical cyclization reaction of 1,3-dicarbonyl compounds and alkenes mediated by manganese(III) acetate in the ionic liquids [bmim]BF_4 and [bmim]PF_6 has been observed. The yields are often more than 50% [108]. At the end of the reactions, the manganese acetate can be easily recovered (by precipitation) by addition of further organic solvent to the reaction mixture. After filtration, the manganese acetate was reacted with potassium permanganate to re-oxidize the manganese(II) back to manganese(III). The manganese(III) acetate can, therefore, easily be recycled although this does depend on the nature of ionic liquid. For example, ionic liquid [bmim]PF_6 makes it difficult to the remove manganese byproducts. However, [bmim]BF_4 can be recovered on workup (in $\geq$95% yield) and reused without any detrimental effort on the product yields.

3.3.12. Palladium-catalyzed carbonylation of aryl halides

Palladium-catalyzed carbonylation of aryl halides is a highly effective method for the synthesis of various carbonyl compounds such as carboxylic acids, esters, amides, aldehydes and ketones. The separation of the products and the catalyst still is problematic, however, as in other homogeneous catalytic reactions. To circumvent this problem, palladium(0)-catalyzed single and double carbonylation of aryl halides in [bmim]BF_4 and [bmim]PF_6 has been investigated (Fig. 7) [110]. The results show that the palladium catalyst used in the ionic liquid could be recycled, after appropriate treatment such as distillation and extraction with ether of the products. The use of ionic liquid media significantly enhances the reaction rate of alkoxylcarbonylation.

3.3.13. Reduction of aldehydes

The reduction of aldehydes by organoborane reagents is an important organic transformation. Trialkylboranes, most notably the pinanyl derivatives, have been found to be especially useful reducing reagents. However, reductions involving simple trialkylboranes generally require reaction temperatures in excess of approximately 150 °C. Ionic liquids like [bmim]BF_4 and [emim]PF_6 can be used in trialkylborane reductions of aromatic and aliphatic aldehydes with enhanced rate at low temperatures (even at room temperature) (Fig. 8) [111]. It is found that the organic products are easily removed from the ionic liquids via extraction and no decrease in reduction yields is found when the ionic solvent is reused.

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

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

3.3.15. Sequential reactions

Seddon's group has demonstrates sequential regioselective nucleophilic displacement reaction and Friedel–Crafts reactions to afford the pharmaceutical Pravadoline in the same ionic liquid, [bmim]PF_6 (Fig. 10) [113]. The Friedel–Crafts reaction was found to work without the need for Lewis acids and without

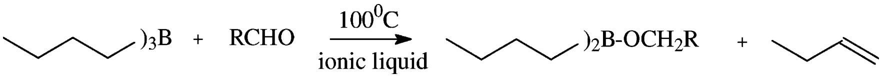


Fig. 8. Reduction of aldehydes using trialkylboraes in ionic liquids.

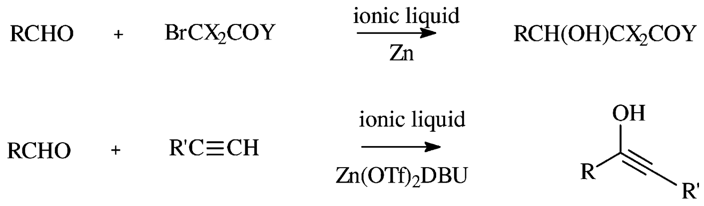


Fig. 9. The synthesis and reaction of zinc reagents in ionic liquids.

all the associated waste aluminum disposal problems of a conventional Friedel–Crafts reaction. It is thought to be the first high yield (94%) green route to a pharmaceutical in a ionic liquid avoiding the problem of production of large quantities of waste found in traditional industrial pharmaceutical production.

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

3.3.16. Syntheses of cyclotriveratrylene (CTV) and tris-(O-allyl)CTV

Cyclic CTVs (Fig. 12) have been known for over 80 years but they are now receiving considerable attention as supramolecular host compounds for various

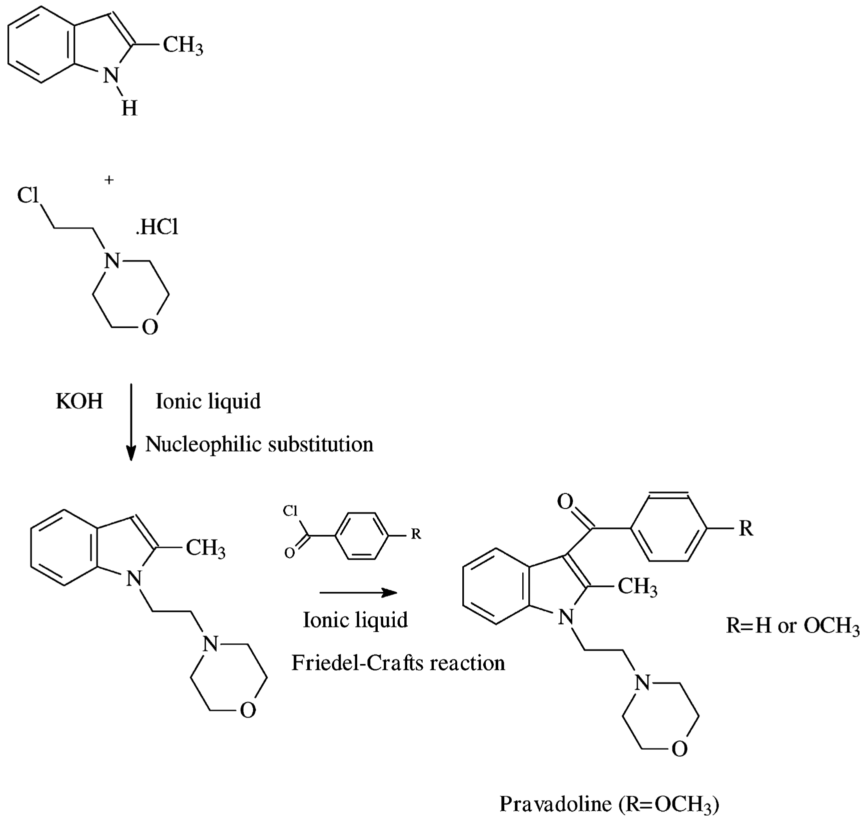


Fig. 10. Pharmaceutical preparation in an ionic liquid.

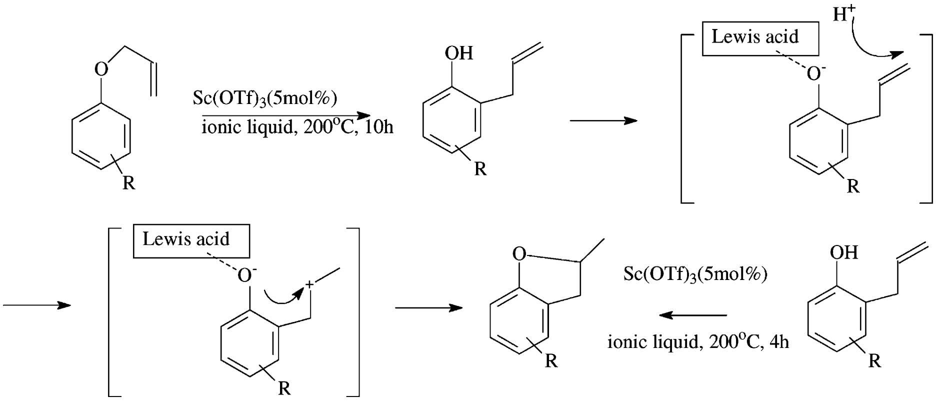


Fig. 11. Sequential reaction in ionic liquids.

species from low molar mass organic solvents through to C_{60}. CTV are traditionally synthesized under harsh dehydrating conditions and require the use of large quantities of organic solvent in the reaction workup. It has been demonstrated that the ionic liquid tributylhexlammonium bis(trifluoromethylsulfonyl)amide (N_{6444}Imide) provides a safe, non-volatile reaction medium that is readily recycled [115]. The methodology developed obviates the need for the use of large quantities of organic solvent and strong dehydrating acids yet provides a pure crystalline product in high yields. Unlike most traditional synthetic routes to CTV, extensive recrystallization or chromatographic steps are avoided and the ionic liquid medium is readily recovered.

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

Five-membered cyclic carbonates are excellent aprotic polar solvents and are used extensively as intermediates in the production of drugs and pesticides. The formation of cyclic carbonates via cycloaddition of carbon dioxide, which is one of the routes for carbon dioxide chemical fixation, has received much attention in regard to utilization of carbon resources and the reduction of CO_2 pollution. However, when organic and inorganic compounds such as metal halides or MgO are used as catalysts, low reaction rates and rigorous reaction condition remain a problem. Ionic liquids based on $[bmim]^+$ and $[bpy]^+$ have been used as catalytic media for the cycloaddition of carbon dioxide to propylene oxide [116]. It is reported that the ionic liquid $[bmim]BF_4$ is the best catalytic medium for the reaction, showing excellent selectivity with relatively short reaction time. The resulting product can be separated from the ionic liquid by simple distillation, and the ionic liquid catalyst is recyclable.

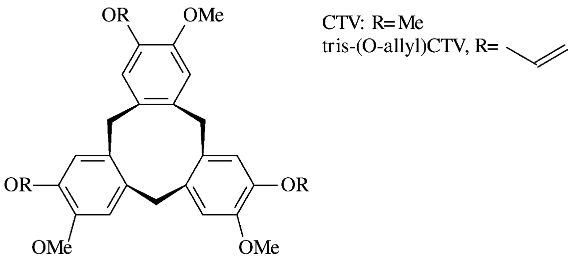


Fig. 12. CTV and tris-(*O*-allyl)CTV.

3.3.18. Wittig reactions

The Wittig reaction is amongst the most popular methods for C=C bond formation, giving in most cases good to excellent stereocontrol. The separation of the alkene from the by-product (Ph_3PO) is a classical problem, which is usually done by crystallization and/or chromatography. It has been demonstrated that $[bmim]BF_4$ can be used as a medium to perform Wittig reactions using stabilized ylides allowing both easier separation of alkenes from Ph_3PO and also the recycling of the solvent (Fig. 13) [117].

$$Ph_3P{=}CH{-}Y \quad + \quad PhCHO \xrightarrow{\text{ionic liquid}} Ph{-}CH{=}CH{-}Y \quad + \quad Ph_3PO$$

Fig. 13. Wittig reactions in ionic liquid.

3.3.19. *Stille coupling*

The Stille coupling reaction has been one of the most widely used steps in the preparation of a wide variety of materials including polyenes, diaryls, and aromatic carbonyl compounds. The main advantages of the reaction stem from the air and moisture stable coupling partner and the compatibility of the coupling condition with a wide array of functional groups. However, the one major limitation is the toxicity of the organic reagents and byproducts. Moreover, like all transition metal catalyzed cross-coupling reactions, the catalyst itself has the problems of expense and the need of expensive and/or toxic ligands. A series of Stille coupling reactions in the ionic liquid [bmim]BF_4 has been successfully demonstrated (Fig. 14) [118]. The procedure permits extensive recycling of the solvent and catalyst without significant loss in activity. Furthermore, an interesting selectivity for aryl bromides and aryl iodides was noted.

3.3.20. *Preparation of heterocyclic compounds*

One pot synthetic methods are one of the most important synthetic reactions especially in the synthesis of heterocycles, which often exhibit unique physicochemical properties. Usually, the synthesis of these heterocycles is carried out in polar organic solvents such as THF, DMF or DMSO, and after quenching with water, the products are extracted with organic solvents. Therefore, these processes generate considerable quantities of waste containing solvent media and catalyst. A serious of ionic liquid such as 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium trifluoromethanesulfonate and 8-methyl-1,8-diazabicyclo-[5,4,0]-7-undecenium trifluoromethanesulfonate have been developed and used as replacement for the more expensive organic solvents in the one pot synthesis of heterocycles (Fig. 15) [119]. These ionic liquids are safe to use and are fully recyclable with no process emissions.

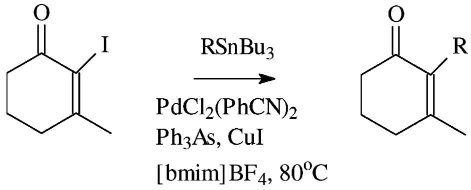


Fig. 14. The Stille coupling in ionic liquid.

3.3.21. *Enzyme catalysis in ionic liquids*

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

3.3.21.1. Synthesis of Z-aspartame (Z = protecting group). The first example of an enzymatic synthesis in an ionic liquid was demonstrated by the synthesis of Z-aspartame, a precursor to the artificial sweetener aspartame, by the reaction of two amino acid derivatives, carbobenzoxy-L-aspartate and L-phenylalanie methyl ester, catalyzed by thermolysin, a proteolytic enzyme

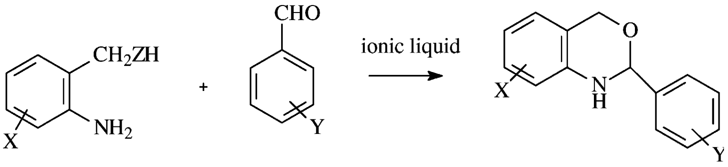


Fig. 15. Preparation of heterocyclic compounds in ionic liquids.

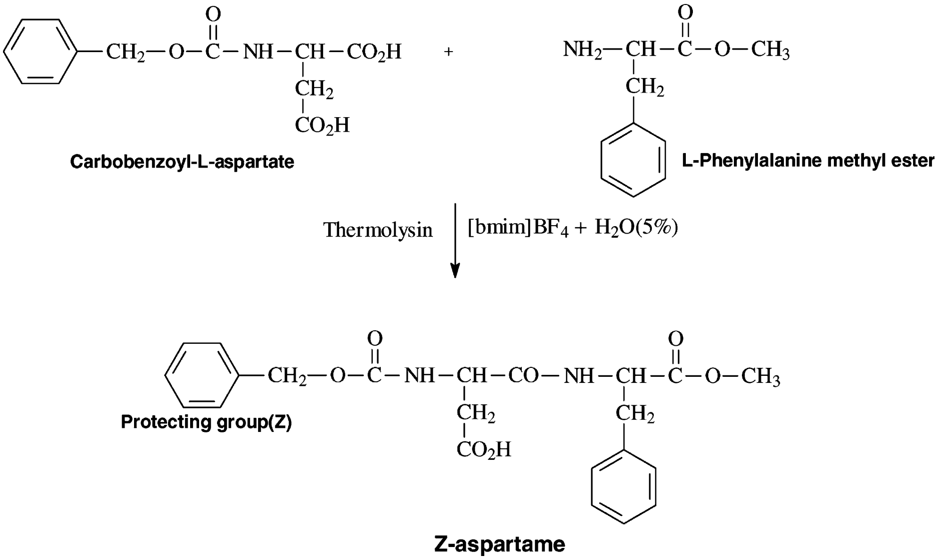


Fig. 16. Enzyme catalyzed synthesis of Z-aspartame in ionic liquid.

(Fig. 16) [120]. The reaction was carried out using [bmim]BF_4 containing 5% by volume of water. The yield was 95%, which is similar to that reported for enzymatic aspartame synthesis in organic solvents with low water content, with a competitive reaction rate. In addition, the enzyme, which normally requires immobilization, exhibited excellent stability in the ionic liquid.

3.3.21.2. Conversion of 1,3-dicyanobenzene to 3-cyanobenzamide and 3-cyanobenzoic acid. The biotransformation of highly polar substrates such as carbohydrates is difficult to carry out in common organic solvents because of their sparing solubility. The first example of such a biotransformation in an ionic liquid system has been reported [121]. It shows that *Rhodococcus* R312, a whole-cell biocatalyst that facilitates the transformation of nitriles to amides, could be used for the conversion of 1,3-dicyanobenzene to 3-cyanobenzamide and 3-cyanobenzoic acid in the biphasic water–[bmim]PF_6 system. Unlike described in Section 3.3.21.1 above, the enzyme is not active in [bmim]PF_6, and the ionic liquid acts only as a reservoir for the substrates. The *Rhodococcus* R312 remains in the aqueous phase, which is where the reaction takes place and the ionic liquid is used to dissolve concentrations of substrate above the aqueous solubility limit, which then partitions into the aqueous phase. The results indicate improved catalytic stability compared with the use of organic solvents, and there is some evidence that ionic liquid may alter the selectivity of the transformation.

3.3.21.3. Kinetic resolution of 1-phenylethanol. Lipase-catalyzed enantioselective reactions in pure ionic liquids such as [bmim]PF_6, [bmim]CF_3SO_3, and [bmim]$(CF_3SO_2)_2N$ has been reported (Fig. 17) [122]. As a model system, the kinetic resolution of rac-1-phenylethanol by transesterification with vinyl acetate was investigated. Lipases show good activity and, in some cases, improved enantioselectivity in the reaction. Another advantage is that the ionic liquids are not volatile and it is, therefore, possible to remove the products by distillation and repeat the catalytic cycle after addition of fresh substrate. The enzyme suspended in the ionic liquid could be reused three times with less than 10% loss of activity per cycle and the enantioselectivity was not influenced.

3.3.21.4. Alcoholysis, ammoniolysis and perhydrolysis reactions catalyzed by Candida antarctica lipase. The use of hydrolytic enzymes in anhydrous organic media has become a valuable addition to the synthetic repertoire. Reactions can be performed that are

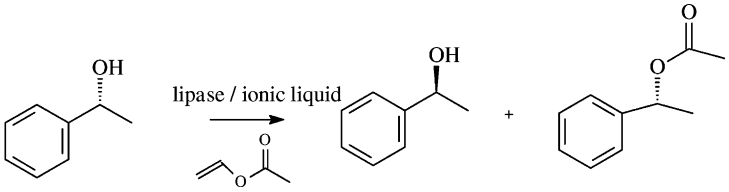


Fig. 17. Kinetic resolution of 1-phenylethanol catalyzed by enzyme in ionic liquid.

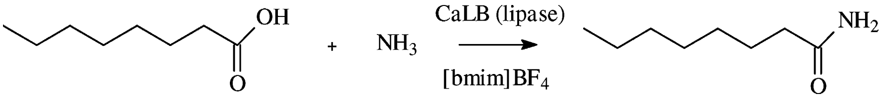


Fig. 18. Ammoniolysis reaction catalyzed by lipase in ionic liquid.

impossible in water, and the enzyme can even show enhanced thermostability. A serious drawback of conventional organic media is, however, the substantial reduction in reaction rate, which is mainly caused by altered partitioning of the reactant between the solvent and the active site. Also, the use of volatile organic solvents such as chlorinated hydrocarbons presents an environmental hazard. The ionic liquids, [bmim]BF_4 and [bmim]PF_6 have been applied in a number of elementary reactions—alcoholysis, ammoniolysis (Fig. 18) and perhydrolysis [123]. The reaction rates were comparable with, or better than, those observed in conventional organic reaction media.

3.3.21.5. Lipase-catalyzed transesterifications in ionic liquids. Transesterifications of alcohols in the presence of vinyl acetate in [emim]BF_4 and [bmim]-PF_6 using *C. antarctica* lipase B (CALB, immobilized) and *Pseudomonas cepacia* lipase (PCL, native) as enzyme catalysts has been investigated (Fig. 19) [124]. It was reported that lipases were up to 25 times more enantioselective in ionic liquids than in conventional organic solvents.

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

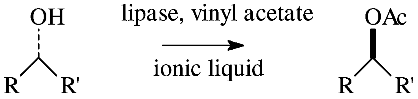


Fig. 19. Transesterification catalyzed by lipase in ionic liquid.

4. Potential and challenges

The solvent used in homogeneous catalysis plays a unique role in dissolving and stabilizing the reactant, ligand, and catalyst precursor, but necessarily must not react with the transition metal intermediates nor compete with the reactant for vacant coordination sites. In such a system, the catalytic center is often a rotationally highly free, three-dimensional complex having more than one site for coordination. Multi-site coordination is the most important characteristic of a homogeneous catalyst that distinguishes it from a heterogenous catalyst. An important feature of homogeneous systems is that each of the metallic centers is potentially catalytically active. Therefore, homogeneous processes are highly efficient and highly specific, chemo-, stereo-, regio-, and enantioselectivities can be attained. The disadvantage, however, is the need to separate solvent and catalyst from the product and unused reactants at the end of the reaction.

In heterogeneous catalysis, since the catalytic center is restricted within a hemispherical geometry by the surface, only a single site is available for reactant coordination. Therefore, the catalytic center in a heterogeneous system is a restricted, two-dimensional one providing only one site for coordination. In addition, only a part of the many metallic centers can be effectively utilized in the catalytic reaction. Hence, the low catalytic density, low TOF values and poor selectivities often observed with heterogeneous catalysts can be easily understood.

Ionic liquids offer the opportunity of combining the advantages of both homogeneous and heterogeneous catalysis in one system. That is to say, immobilization of a catalyst (metal/oxide/complex) by supporting it in an ionic liquid rather than on a surface may create highly free, three-dimensional centers as in a homogeneous catalyst but the catalytic reaction occurs at the interface between the ionic liquid (rather than a solid) and the reactants in either the gas or immiscible liquid phase. Development of application of three-dimensional heterogeneous catalysis using ionic liquids as supports should present challenges for us over the next decade and beyond.

At the present time, several urgent questions regarding the fundamental aspects of ionic liquids need to be addressed. Among them, the physicochemical principles of liquid properties and solubility of ionic liquids remains a frontline subject of ionic liquid research today. Meanwhile, the functionalization of ionic liquids ought to be carried out to make them capable of dissolving metals or metal oxides. Furthermore, the coordination properties of ionic liquids remain to be revealed.

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