

Catalysis in Ionic Liquids

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1. Introduction

Catalytic reactions in ionic liquids (ILs) have been examined for at least 20 years; for example, the first report of the use of an IL as a catalyst in Friedel–Crafts acylation was reported in 1986.¹ However, it is only in the past decade that there has been an explosion in their use in a wide range of catalytic and stoichiometric reactions as well as in many other applications, and this has led to a greater than exponential growth in the number of papers published. A number of good reviews cover the area of ILs in general, for example.^{2–9} Although they are often considered as green alternatives to volatile organic solvents, notably chlorinated hydrocarbons, their toxicity and biodegradability properties¹⁰ have not been fully determined and the manufacture of the ILs often contains a metathesis step which limits their green credentials to some extent. However, in both of these areas



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significant steps have been made in the understanding and creation of cleaner routes to the preparation of ILs.^{11,12} In addition, analytical methods for determination of the well-characterized materials have been developed.^{13–19} This is particularly important in catalysis where the impurity in the solvent can have a significant impact on the selectivity and activity. Furthermore, determination of the sensitivity of the system to impurities can significantly affect the economics of any process.

Besides their advantages with respect to environmental impact, a number of critical aspects of ILs make them an interesting medium in which to study chemical syntheses. The large number of cations and anions allow a wide range of physical and chemical characteristics to be achieved, including volatile²⁰ and involatile systems, and thus the terms “designer” and “task-specific” ILs have been developed.^{21,22} This allows not only control over processing of the reaction but also control over solvent–solute interactions. The latter is important, and the fact that these solvents are ionic and

highly structured, for example,^{23–28} can give rise to a distinct chemistry of their own compared with molecular solvent systems in both achiral and chiral processes.

In any process the steps following reaction are often at least as important for the overall environmental impact and economics. In this respect, ILs have been shown to have a significant advantage over conventional solvents for homogeneously catalyzed reactions. In these cases, the IL may be used in “biphasic catalysis”⁸ or the catalyst can be entrapped or “immobilized”, allowing extraction/distillation of the organic product and the IL/catalyst system reused. Recycling of the IL/catalysts in this way has been demonstrated in many examples and is vital given the high capital cost of the solvent. Similar considerations also exist for heterogeneous catalysts and biocatalysts. In particular, processes involving nanoparticulate catalysts and ILs have been particularly effective in screening the charged layer on the surface of the colloids, preventing aggregation and stabilizing the system.²⁹ By tuning the ILs’ composition, the stability, size, and solubility of the nanoparticles may all be tuned.³⁰

The same properties that make ILs effective solvents also make them interesting liquids for studies involving sonochemistry, acoustic cavitation, and sonoluminescence. Recent advances in using ultrasound to accelerate chemical reactions conducted in ILs have found them, in combination with catalysis, to be a versatile solution in several applications.³¹

The aim of this paper is to provide a state of the art review in the use of ILs’ solvents in catalyzed reactions. Given the large amount of studies on homogeneously versus heterogeneously catalyzed process as reported in ILs, the former papers will be used as illustrative examples only for the wide range of reactions studied. Furthermore, where appropriate, the use of ILs in biocatalytic and electrocatalyzed reactions has also been reviewed.

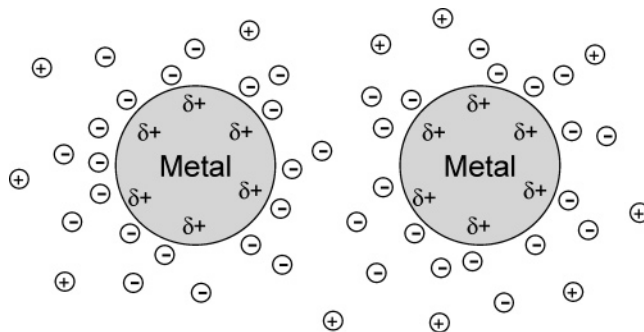
Within this review 1-alkyl-3-methyl imidazolium cations are denoted as $[C_n\text{mim}]^+$, 1-alkyl-2,3-dimethyl imidazolium cations are denoted as $[C_n\text{dmim}]^+$, 1-alkyl-3-alkyl’ imidazolium cations are denoted as $[C_nC_n'\text{mim}]^+$, *N*-alkylpyridinium cations are denoted as $[C_n\text{pyr}]^+$, 4-methyl-*N*-alkylpyridinium cations are denoted as $[C_n\text{mpyr}]^+$, *N*-alkyl, *N*-methyl pyrrolidinium cations are denoted as $[C_n\text{mpyr}]^+$, tetraalkylphosphonium cations are denoted as $[P_{m'm''n''n''}]^+$, and tetraalkylammonium cations are denoted as $[N_{m'm''n''n''}]^+$ where *n* represents the alkyl chain length attached to the N or P center. The anion bis(trifluoromethylsulfonyl)imide, i.e., $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, is denoted as $[\text{NTf}_2]^-$, and triflate is denoted as $[\text{OTf}]^-$.

2. Nanostabilized Catalysts in ILs

2.1. ILs as Solvents for Synthesis of Nanoparticles

Nanoparticle catalysts have attracted large interest because they exhibit a high surface to bulk metal ratio, which allows more efficient use in practice. This aspect is frequently accompanied by large enhancements in the activity and selectivity where they are used as catalysts.³² The recent achievements in this field allow control over the composition (including nanoalloys materials) and size.^{33–35} In spite of these advantages, nanocatalysts are kinetically unstable with respect to agglomeration to the bulk metal and therefore require stabilization. Therefore, to be used they need stabilization by either surface-ligating anions or other ligands

Scheme 1. Schematic Representation of Electrostatic Stabilization of Metal Colloid Particles



(Scheme 1). In this way it is possible to realize additional control, mostly on the solubility in an appropriate solvent and their isolation.³⁶ Combining different stabilizing effects may even improve the performance of nanoparticle catalysts. For example, Finke and co-workers^{37,38} showed that co-stabilization of rhodium nanoparticles with polyoxoanions and tetrabutylammonium cations leads to a high improvement of turnover frequency (TOF) for hydrogenation of olefins and arenes.

An important advantage of using ILs in such preparations is that they facilitate inorganic synthesis from highly polar starting materials under ambient conditions and under anhydrous or water-poor conditions. In this way, hydroxide or oxy-hydrate formation can be suppressed.

Several nanometallic catalysts have been shown to be activated after stabilization with ILs. Dupont et al.^{39,40} reported that iridium nanoparticles stabilized by the IL $[\text{C}_4\text{mim}][\text{PF}_6]$ showed a large increase in activity for the biphasic hydrogenation of various olefins and arenes under mild reaction conditions. These nanoparticles were obtained via rapid reduction of a $[\text{IrCl}(\text{cod})_2]$ (*cod* = 1,5-cyclooctadiene) complex in $[\text{C}_4\text{mim}][\text{PF}_6]$ with hydrogen at 75 °C. Structural characterization confirmed the colloidal properties of the particles (2–2.5 nm) and XRD the existence of iridium as Ir(0). Although the presence of water in the system causes decomposition of $[\text{C}_4\text{mim}][\text{PF}_6]$, no influence on the catalytic performance of the ionic media was observed.³⁹ Recently, this system has been examined by detailed kinetic modeling which indicated that the nanoparticles acted as a heterogeneous catalyst via a simple Langmuir adsorption mechanism.⁴¹ The IL is thought to limit diffusion of the nanoparticles and thus promote formation of small particles and limit their growth. A very similar procedure has also been applied to prepare rhodium⁴⁰ and ruthenium nanoparticles.⁴² Palladium⁴³ and platinum⁴⁴ nanoparticles with sizes of about 4.9 and 2.5 nm, respectively, were also obtained following the same protocol but using different precursors, i.e., $\text{Pd}(\text{acac})_2$ or $\text{Pt}_2(\text{dba})_3$ dissolved in $[\text{C}_4\text{mim}][\text{PF}_6]$ or $[\text{C}_4\text{mim}][\text{BF}_4]$.

Stabilization of gold (and platinum) nanoparticles by imidazolium derivatives has also been reported.^{45–47} Gold nanoparticles of ~5 nm were obtained by reduction of an aqueous solution of HAuCl_4 with an excess amount of NaBH_4 in the presence of 3.3’-[disulfanyl]bis(hexane-1,6-diyl)-bis(1-methyl-1*H*-imidazol-3-ium)dichloride. Formation of $[\text{BF}_4]^-$ - or $[\text{PF}_6]^-$ -based structures was simply achieved via an ionic exchange process. Significantly, gold nanoparticles of about 3.6 nm stabilized by a zwitterionic imidazolium sulfonate-terminated thiol (Figure 1) exhibit a remarkably high stability in aqueous solutions with high concentrations of electrolytes, ILs, and proteins.

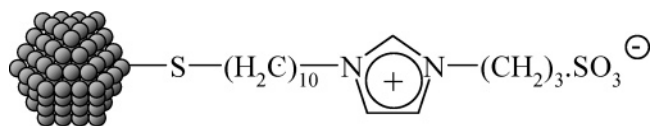


Figure 1. Schematic representation of the stabilization interaction between the zwitterionic imidazolium sulfonate-terminated thiol with a gold cluster. Reproduced by permission of The Royal Society of Chemistry.⁴⁷

Larger gold particles (48–49 nm) were also prepared by reduction of HAuCl_4 but using citrate as a reductant in $[\text{C}_4\text{mim}][\text{PF}_6]$.⁴⁸ However, to avoid precipitation of these larger particles, the presence of tetradecyltrimethylammonium bromide, as a cationic surfactant, was required. In order to avoid boric acid impurities in the resultant nanoparticles, clean reduction of HAuCl_4 with CO in $[\text{C}_4\text{mim}][\text{BF}_4]$ was investigated.⁴⁹ Water was found to be an important parameter in controlling the particle size which was found to increase as the concentration of water was raised. Furthermore, using *n*-hexane as a phase-transfer solution, the morphology of the gold nanoparticles into a ring structure could be achieved.

The capability of ILs to stabilize noble metal was also demonstrated for the extraction of gold and silver from ores.⁵⁰ Using $[\text{C}_4\text{mim}][\text{HSO}_4]$ as a solvent it was demonstrated that solubilized thiourea selectively complexed these elements, leading to stable structures.

Although imidazolium-based ILs have been widely demonstrated as a good stabilizing agent for nanoparticles, in some cases it is found that agglomeration still leads to a loss of activity, indicating that IL stabilization alone does have limitations. Adding other materials to ILs can combine different types of stabilizing effects, leading to more stable nanoparticles. It is important to note, however, that commonly used organic stabilizers, for example, 1,10-phenanthroline and poly(*N*-vinyl-2-pyrrolidone), generally have low solubility in ILs. In contrast, synthesis of ionic copolymers containing imidazolium IL-like units, which can act as soluble bifunctional costabilizers when dissolved in ILs, enhance the stability of the nanocatalysts. 1-Vinyl-3-alkyl imidazolium salts have been prepared from the *N*-alkylation of 1-vinylimidazole with the corresponding alkyl halides. The polymers were then synthesized by free-radical copolymerization of the 1-vinyl-3-alkyl imidazolium halide and *N*-vinyl-2-pyrrolidone using azo-bis-isobutyronitrile as the initiator in methanol. The resulting copolymers were highly soluble in 1-butyl-3-methylimidazolium ILs as well as in other highly polar organic solvents such as methanol. Rhodium nanoparticles were reported to be prepared and stabilized by hydrogen reduction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of the copolymers dissolved in $[\text{C}_4\text{mim}][\text{BF}_4]$ IL, resulting in a relatively narrow unimodal size distribution with a diameter of 2.9 ± 0.6 nm is observed.⁵¹

Another approach for the ILs' stabilization of reduced nanoparticles was proposed by Mevellec et al.⁵² Rhodium nanoparticles (~ 2.4 nm) were formed in an aqueous solution of *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium chloride. Using a metathesis step, the corresponding $[\text{NTf}_2]^-$ -based IL was formed, which separated and removed the nanoparticles from the water phase. The IL acted as a stabilizer and had to be diluted with $[\text{C}_4\text{mim}][\text{PF}_6]$ to enable the particles to be used as a catalyst.

Nanoparticles can also be formed during reactions using a homogeneous catalyst as the precursor. The first nanoparticles to be reported in ILs fall into this category, where in the Heck reaction $\text{Pd}(\text{OAc})_2$ was thermally decomposed in

the IL and shown to form highly stable 1–2 nm Pd clusters by EXAFS and TEM.^{53,54} Also, Heck or Suzuki and Stille coupling reactions carried out using $\text{Pd}(\text{OAc})_2$ treated with tetrabutylammonium acetate in tetrabutylammonium bromide led to fast formation of Pd nanoparticles of 2–6 nm in size, which were very active in these reactions.^{55–57} In the palladium nanoparticle-catalyzed Heck reaction in ILs, detailed TEM studies have shown that the role of the cluster may be to act as a reservoir.⁵⁸ The larger particles are thought to break up on oxidative addition of the phenyl iodide and, after the reaction, can either continue in the catalytic cycle or reaggregate. The palladium particles, reported therein, before reaction were ~ 2 nm, which is consistent with other TEM and EXAFS studies, but after reaction they were 6 nm. Other reactions, like the Sonogashira coupling, were reported to be catalyzed by Pd(0) nanoparticles of 10–14 nm using $[\text{C}_4\text{mim}][\text{BF}_4]$ as the solvent and ultrasound irradiation.⁵⁹

Although the IL is an efficient stabilizer in many cases, additional stabilization has been shown using PEG as a modifier.⁶⁰ Carbapalladacycle complexes also decompose in PEG upon reaction; the resulting Pd nanoparticles (2–5 nm) are stabilized by PEG acting as ligand. In this way, a reusable, homogeneous system in PEG has been developed that is able to catalyze the Suzuki and Sonogashira couplings. PVP-protected Pd nanoparticles have also been used for methoxycarbonylation of iodobenzene.⁶¹ Therein, imidazolium-based ILs inhibited reaction via formation of a carbene complex, whereas good activity was found in tetraalkylammonium- and *N*-alkylpyridinium-based ILs. Thiol-functionalized ILs have been utilized to promote formation of palladium nanowires. Uniform nanowires of 2–4 nm were formed, which were found to be active and recyclable for the Sonogashira coupling between phenylacetylene and phenyliodide in isopropyl alcohol.⁶²

Most reports using the combination of ILs with nanoparticles have concentrated on their morphology and catalytic activity. However, the mechanism by which the particles form and the IL stabilization effect have been much less examined. In conventional media, the stability of the colloids is explained according to the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory.^{63–65} Equally charged particle surfaces lead to Coulombic repulsion, i.e., the interaction potential decreases with particle surface distance. Following the DLVO theory the superposition with the permanently present van der Waals attraction can lead to a net interaction potential, which exhibits a local maximum. However, this theory can only explain the stabilization but not the additional activation of such particles. Using Ir(0) nanoparticles as a model, prepared via reduction of $[(1,5\text{-COD})\text{Ir}(\text{CH}_3\text{CN})_2]\text{BF}_4$ under H_2 in the presence of a proton sponge in acetone and predetermined but variable amounts of $[\text{C}_4\text{mim}][\text{NTf}_2]$, Starkey et al.⁶⁶ investigated formation of nanoparticles in a range of ILs using deuterium labeling and ^2H NMR, indicating that formation of *N*-heterocyclic carbenes from imidazolium-based ILs and subsequent ligation of the nanoparticles is important. This is consistent with other studies which have shown formation of the active catalytic carbene species in ILs.^{54,67} The carbene is thought to form via C–H oxidative addition at the acidic C(2) hydrogen on the imidazolium cation and clearly shows that the IL cannot be considered as an innocent solvent. Further evidence for the capability of ILs to form multiple hydrogen bonds has been reported by Mele et al.⁶⁸ Coupled with the results of Starkey et al.⁶⁶ a mechanism involving molecular recognition and

self-organization processes, i.e., close to that found in supramolecular chemistry, is likely.

Antonietti et al. considered that stabilization of the nanoparticles was due to the IL acting as a pure “universal” ligand.⁶⁹ The low interfacial tension of the solvent favors high nucleation rates and leads to small particles which undergo Ostwald ripening only weakly. The IL structure is important in this regard as it can easily incorporate many species due to the presence of hydrophobic regions and a high directional polarizability, which is oriented parallel or perpendicular to the dissolved species.

Alloying noble metals with group VIII elements is known to enhance the catalytic behavior and selectivity of the noble metals in various reactions.⁷⁰ However, this is conventionally achieved using high temperatures and not readily applicable to solution-phase chemistry due to the volatile nature of the solvent. Switching to a more thermally stable solvent, i.e. the IL, has allowed such nanoparticles to be formed. For example, nanorods, as well as nanoparticles with a range of Co_xPt_y compositions were synthesized in [C₄mim][NTf₂] and [C₂mim][NTf₂] using cetyltrimethylammonium bromide (CTAB) as the capping reagent.⁷¹ These materials were prepared from Pt(acac)₂ and Co(acac)₃ in dry [C₄mim][NTf₂] at 350 °C, leading to particles with an average diameter of 8 nm.

2.2. Active Complexes of Metal Compounds with ILs

Another approach considered for the synthesis of active catalysts in ILs is stabilization of the metal complexes by the IL.⁷² For example, in acetonitrile, palladium(II) chloride reacts with *N*-butyronitrile pyridinium chloride, [C₃CNpy]-Cl, **1**, leading to [C₃CNpy]₂[PdCl₄], **3** (Scheme 2). Addition of a further equivalent of PdCl₂ to **5** in dichloromethane resulted in formation of [PdCl₂(C₃CNpy)₂][PdCl₄], **4**, over a period of several days. Other *N*-butyronitrile pyridinium ILs, **2**, containing [PF₆]⁻, [BF₄]⁻, or [NTf₂]⁻ as counter anions led to formation of a different type of complexes, i.e., [Pd(C₃CNpy)₂Cl₂][PF₆]₂, **5**, [Pd(C₃CNpy)₂Cl₂][BF₄]₂, **6**, and [Pd(C₃CNpy)₂Cl₂][NTf₂]₂, **7**, respectively. All of these palladium complexes are air stable and do not decompose on washing with water or alcohols at room temperature, but they do decompose in water and alcohols over prolonged periods of time.

The structure of these complexes has been determined from single-crystal X-ray analysis. Figure 2 shows the structure of [C₃CNpy]₂[PdCl₄]. In this complex the [PdCl₄]₂⁻ anion is close to 15 hydrogen atoms belonging to 6 different cations with distances between 2.708 and 2.997 Å. Such hydrogen bonding explains to some degree their markedly higher melting points relative to those of the complexes containing other counter ions, for example, [BF₄]⁻.

Scheme 2. Synthesis of Palladium Complexes in ILs

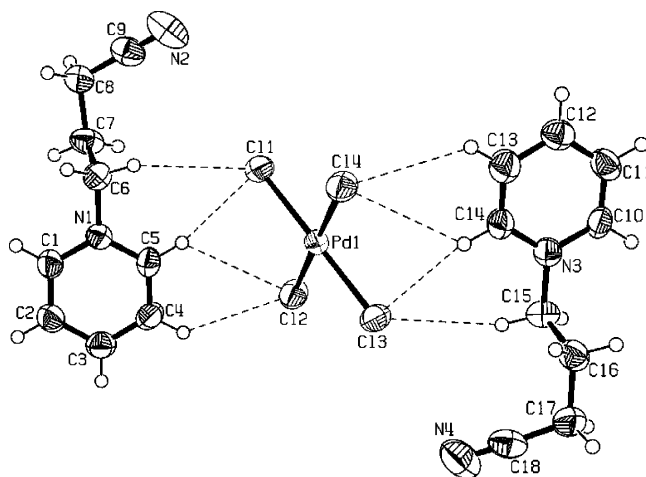
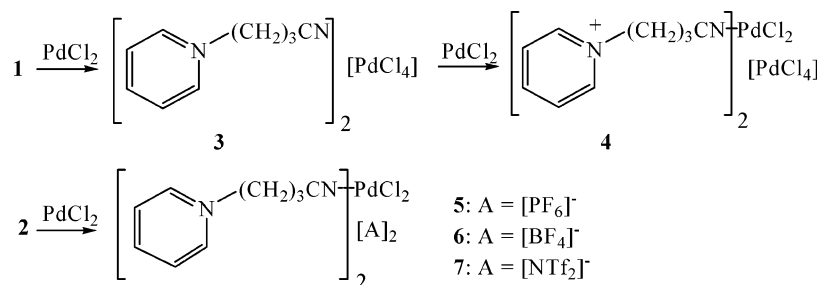


Figure 2. ORTEP representation of **5** showing some of the Cl–H interactions shorter than 3 Å; ellipsoids are drawn at the 50% probability level.⁷²

In the case of ILs as an immobilization media, ionic transition-metal catalysts are generally well retained during product separation, and many examples have been reported that illustrate their potential,⁷³ although quantitative data is not always available. However, with uncharged catalysts, leaching can be high and functionalized ligands may be required to prevent loss of the transition metal into the product phase.^{74,75}

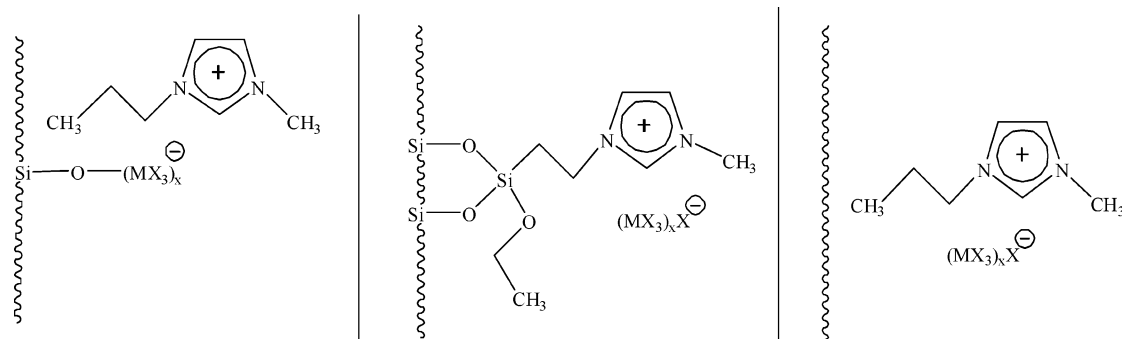
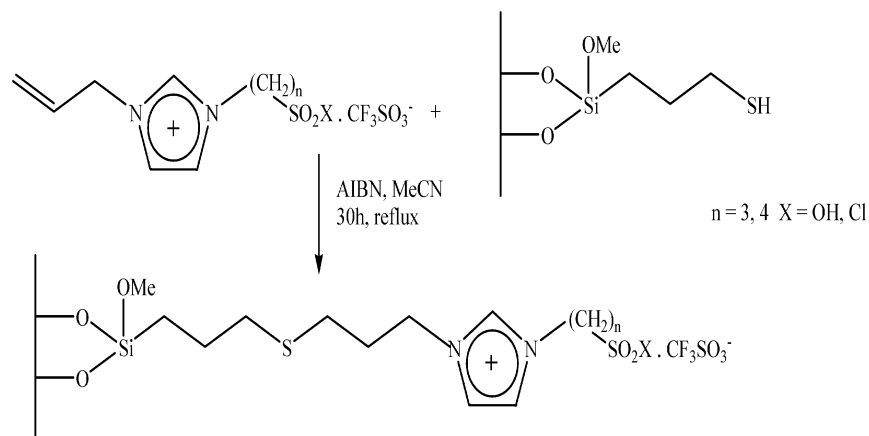
2.3. Supported IL-Stabilized Catalysts

Although ILs can, in many cases, be classed as involatile and therefore recovery of the IL from reactions is possible, this still requires liquid-phase processing. Heterogeneous systems offer significantly simpler workup via filtration/decantation of the solid material, and ILs have been supported on solids to allow for this possibility. A number of methods have been reported for preparation of solid-supported ILs.

Direct immobilization of IL on a solid support has been demonstrated using the routes shown in Scheme 3.⁷⁶ The choice of the chosen route depends on the combination of the support and IL, for example, the heterogeneity of the surface, hydrophilicity/hydrophobicity of the surface, surface area, pore width, and length of side chains of the inorganic cation.

This methodology has also been used to support Brønsted acid ILs via radical initiation using AIBN (Scheme 4). These IL-derived sulfonic acid silica-gel-supported catalysts have been used for a range of esterification and nitration reactions showing excellent recyclability and high activity.⁷⁷

The simplest method of preparing immobilized ILs is via incipient wetness impregnation.⁷⁶ Hölderich and co-workers

Scheme 3. Immobilization of the IL Anion, the IL Cation or as a Supported Liquid Phase**Scheme 4. Immobilization of ILs via Radical Initiation Using AIBN**

used this methodology to support chloroaluminate ILs on a range of oxide supports.^{78,79} The ILs are preformed and adsorbed onto dried supports. Although the supported IL was active on all supports used, the IL was found to destroy the pore structure of materials such as zeolites. Damage to the support was shown to be limited if an organic halide containing the cation of the desired IL was grafted onto the surface of the support before adding the metal halide, for example, AlCl_3 .⁷⁶ Incipient wetness has also been used to support analogous chloroferrate ILs on oxides and carbon, which showed good activity in a range of liquid-phase reactions. However, significant leaching of the IL was observed in the liquid-phase reactions limiting their use.⁸⁰ Attempts were also made to support chlorostannate ILs; however, due to their high viscosity, this was not practical.

Alternatively, a support material containing the cationic groups can be prepared using the sol-gel method. By adding 1-(triethoxysilylpropyl)-3-methylimidazolium chloride to a mixture of a silicon source and a template, mesoporous silica, which contains 1-propyl-3-methylimidazolium chloride groups bonded to surface silicon atoms, may be prepared. Addition of aluminum chloride leads to formation of ionic complexes.⁷⁶

Abelló et al. used the concept to support basic ILs. Choline hydroxide was supported on MgO and shown to be an efficient catalyst for the aldol reaction for a range of aldehyde and ketone substrates.⁸¹ In comparison with NaOH, choline hydroxide alone or MgO, the supported IL showed increased TOFs, although similar selectivities were found for all catalysts in general.

Mehnert and co-workers extended this methodology to support Rh(I) complexes for hydroformylation of hex-1-ene to heptanal in both IL and molecular solvents.⁸² Sasaki et al. used similar silyl-tethered ILs covalently bound to silica

to facilitate the immobilization of MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 , CuCl_2 and PdCl_2 for the Kharasch reaction between styrene and CCl_4 .⁸³ However, only the copper-based catalyst had significant activity and showed high selectivity toward the addition reaction over styrene oligomerization. Using EXAFS, the copper was shown to be present in the form of the $[\text{CuCl}_4]^{2-}$ anion. Epoxidation reactions have been performed using this technique employing the dinuclear peroxotungstate anion $[\{\text{W}(=\text{O})(\text{O}_2)_2(\text{H}_2\text{O})\}_2(\mu\text{-O})]^{2-}$ with H_2O_2 as the catalyst.⁸⁴ Using a range of olefin substrates, good yields were obtained in acetonitrile and comparable rates were found in the heterogenized anionic catalyst with the equivalent unsupported catalyst.

Stabilization of metal-nanoparticles is clearly demonstrated using ILs and can be used to support metals on supports. Using the fact that guanidine and guanidinium ions have the ability to form coordination complexes,⁸⁵ neutralization of 1,1,3,3-tetramethylguanidine and lactic acid has been used to provide a medium for Pd nanoparticles in solution and, subsequently, on high surface SBA-15 molecular sieve ($520 \text{ m}^2 \text{ g}^{-1}$).⁸⁶ Therein, the Pd nanoparticles (1–2 nm) were formed from $\text{Pd}(\text{OAc})_2$ in a THF/methanol solution, immobilized in the IL, and deposited on the support giving a coating of 20 wt % IL. Interestingly, the surface area of the support remained high after the IL treatment.

Immobilization of Ru nanoparticles using the same IL 1,1,3,3-tetramethylguanidinium cation on a montmorillonite clay⁸⁷ or on SBA-15 molecular sieve⁸⁸ has also been reported. In the case of Na-montmorillonite, the procedure consisted of treatment of the clay with an aqueous solution of the IL in order to exchange the Na cations with those of the IL and then exposure of the solid to an aqueous solution of RuCl_3 . However, many aspects concerning synthesis of the heterogeneous catalyst remain unclear including the nature of the

surface and whether the IL remains on the catalyst following preparation.

Mehnert et al. also demonstrated immobilization of a rhodium catalyst in $[C_4mim][PF_6]$ impregnated onto silica gel.⁸⁹ The catalyst was prepared by dissolving the IL–catalyst solution in acetone which was then used to impregnate the silica. Following evaporation of the acetone from the solid, an IL loading of 25 wt % was obtained with an average IL layer thickness of 6 Å. Figure 3 illustrates the confined IL phase containing the rhodium complex on the surface of a silica gel support material.

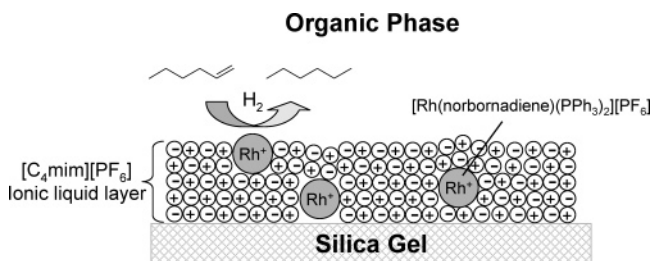


Figure 3. Confined IL phase containing the rhodium complex, $[Rh(\text{norbornadiene})(PPh_3)_2][PF_6]$, on the surface of a silica gel support material. Reproduced by permission of The Royal Society of Chemistry.⁸⁹

A similar procedure has also been reported for immobilization of a Pd catalyst on silica.^{90,91} A suspension of amorphous silica spheres was brought into contact with a solution of $Pd(OAc)_2$ in the IL and THF and the mixture evaporated to dryness, resulting in the immobilized catalyst on the support. Among the ILs tested, $[C_4mim][PF_6]$ was found support $Pd(OAc)_2$ most efficiently compared with $[C_4mim]Br$, $[C_4mim][NTf_2]$, or $[C_6mim][PF_6]$, for example. Electron X-ray microanalyses and atomic force microscopy confirmed that phosphorus, fluorine, and Pd were distributed on the surface of silica uniformly. These results, along with the dry character of the catalyst, suggested that the solution of $Pd(OAc)_2$ in an IL exists in the silica pores. In a similar manner, $Pd(PPh_3)_4$ and Pd black were immobilized, though Pd/C and $PdCl_2(PPh_3)_2$ could not be immobilized due to negligible solubility of the catalysts in the IL/THF mixture.

Incipient wetness techniques have been used to prepare $Pd(acac)_2$ dissolved in $[PF_6]^-$ ILs on activated carbon cloth for hydrogenation of citral in organic solvents using hydrogen.^{92,93} Although good activity was observed and the catalyst was recyclable, poor selectivity was achieved with citronellal and dihydrocitronellal found to be the primary products over a range of conditions and ILs used.

The concept of immobilization of palladium in a solid-supported IL has been developed by Karimi and Enders.⁹⁴ In this case, a palladium–carbene complex is formed on the surface of silica gel via a covalently bound IL. This supported palladium complex was then used for the Heck reaction, showing remarkable thermal stability, up to 280 °C, while retaining the activity.

The involatility of the IL has led to extension of homogeneous catalysts being used for gas-phase reactions. Both Hölderich and co-workers⁸⁰ and Wasserscheid, Fehrmann and co-workers^{95–97} used the idea of supported ILs to investigate gas-phase processes. For example, combining $[C_4mim][Rh(CO)_2I_2]$ with $[C_4mim]I$ supported on SiO_2 , a continuous, fixed-bed gas-phase carbonylation of methanol has been developed. High activity and selectivity were achieved, forming acetic acid and methyl acetate compared

with the byproduct dimethyl ether. A high ester to acid ratio was also found (~ 3.5).⁹⁵ Similarly, Yang et al. used a TPPTS–Rh complex $[TPPTS = \text{trisodium salt of tri}(m\text{-sulfophenyl})\text{phosphine}, P(m\text{-}C_6H_4SO_3Na)_3]$ derived supported IL using MCM-41 as the support for the liquid-phase hydroformylation of a range of alkenes.^{98,99} As with many of the supported ILs, good recyclability of the system was found.

2.4. ILs as Templates for Heterogeneous Catalysts

Since the work of Dai et al.¹⁰⁰ and Adams et al.¹⁰¹ utilizing the ILs as a template for formation of sol–gel and MCM materials, a number of “catalyst” supports have been formed using this approach. To form the MCM-41, 1,3-dialkylimidazolium bromides were dissolved in an aqueous solution and the silica was formed via a hydrothermal synthesis.¹⁰¹ Imidazolium hydroxides have also been used to form MCM-41, albeit the salt used in this case was not an IL.¹⁰² In the case of sol–gel formation, acid-catalyzed synthesis was employed using tetramethylorthosilicate as the precursor and $[C_2mim][NTf_2]$ as the template.¹⁰⁰ At room temperature and with a three-week curing time, a stable sol–gel was formed from which the IL could be extracted and reused (Figure 4). The technique is mild and does not require a supercritical fluid drying step, which can cause destruction of the sol–gel structure.

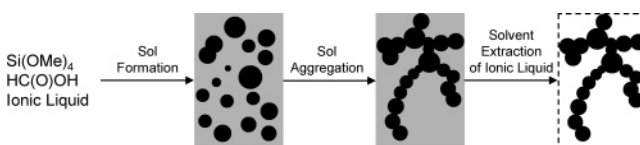
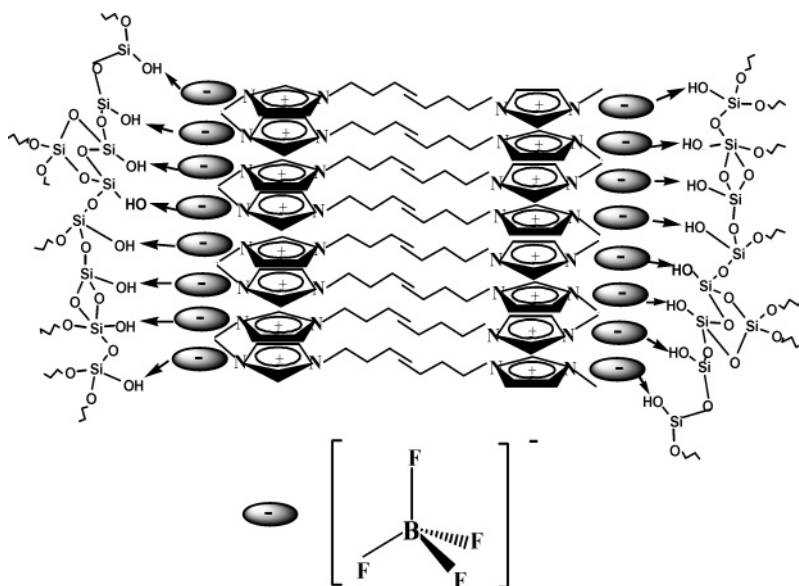


Figure 4. Mechanism for the aerogel formation in the IL. Reproduced by permission of The Royal Society of Chemistry.¹⁰⁰

ILs have also been shown to generate supports used in heterogeneous catalysis by sol–gel processing using water-lean reaction media.^{103–109} Zhou and Antonietti hydrolyzed titanium tetrachloride in $[C_4mim][BF_4]$ with less than stoichiometric water (water-poor conditions) using a low-temperature synthesis at 80 °C.¹⁰⁴ Therein, anatase powder consisting of 2–3-nm-sized particles and with surface areas of 554 m² g⁻¹ were prepared. Similar results were obtained by Yoo et al.^{106,108} using titanium tetraisopropoxide as the sol–gel precursor in $[C_4mim][PF_6]$. Furthermore, preparation of TiO_2 hollow microspheres has been reported by Nakashima and Kimizuka in ILs by means of an “interfacial” sol–gel reaction.¹⁰³ Commonly, the synthesis route in conventional molecular solvents leads to amorphous titania at a much reduced rate compared with the crystalline form produced via the IL method. Importantly, anatase is formed in the IL route, and it is in this form that the oxide exhibits the catalytic properties, e.g., in photocatalysis.¹¹⁰

Monolithic mesoporous silica with wormhole framework silica were similarly prepared using $[C_4mim][BF_4]$ as the template, and tetramethyl orthosilicate was used as the sol–gel precursor via a nanocasting technique.¹⁰⁵ On the basis of the molecular structure and properties of $[C_4mim][BF_4]$, Zhou et al. proposed a so-called hydrogen-bond– π – π stack mechanism to justify the self-assembly of IL in the reaction system for formation of the wormlike mesopore.¹⁰⁵ According to this mechanism (Scheme 4), both the hydrogen bond formed between the $[BF_4]^-$ and silano group of silica gel and the π – π stack interaction of the neighboring

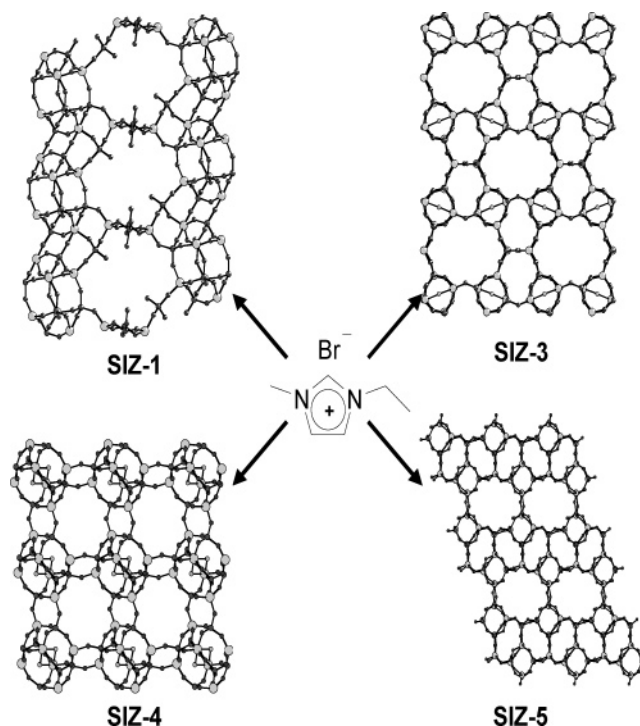
Scheme 5. Schematic Illustration of the Proposed Hydrogen-Bond-co- π - π Stack Mechanism¹⁰⁵

imidazolium rings play crucial roles in formation of the wormhole framework of mesoporous silica.

The structure of the solvent and supramolecular effects become important when reactions are conducted with higher concentrations of inorganic reactant, and this leads to a range of material characteristics. The nature of the anion is also important. In the case of formation of mesoporous silica, Zhou et al.¹⁰⁵ proposed that the $[\text{BF}_4]^-$ anion interacted with the silanol groups forming hydrogen bonds, inducing an oriented arrangement of the anion along the pore walls and structuring the cations forming the arrangement illustrated in Scheme 5.

Other evidence for the template effect of ILs in the synthesis of well-defined textured silica materials has been shown using the sol-gel nanocasting technique with a range of $[\text{C}_n\text{mim}]\text{Cl}$ for $n = 10, 14, 16, 18$.¹⁰⁶ Formation of the well-ordered, lamellar super-micropores was considered to result from the particular spatial aggregation of the IL molecules. Due to the increase in lamellar spacing with increasing alkyl chain length,¹¹¹ an expansion in the pore from 1.2 to 1.5 nm was observed. The stability of these pores was maintained after the IL was removed, and this was attributed to formation of pillars or touching undulations between the neighboring lamellar layers.

Similarly, Dai et al. used 1,3-dialkylimidazolium bromide salts to study formation of periodic mesoporous organosilica materials via a bis(triethoxysilyl)ethane precursor.¹¹² Control of the morphology of these materials has been further investigated using halide-based imidazolium salts with both alkyl and ether side-chain functionalities.¹¹³ Therein, the structure of the micelles and, therefore, the pore structure as well as the particle morphology were strongly influenced by the nature and length of the imidazolium side chain. For example, by increasing the alkyl chain length from C_{14} to $\text{C}_{16}/\text{C}_{18}$ in $[\text{C}_n\text{mim}]\text{Br}$, the materials changed from spheres to ellipsoids and rods, respectively, and by replacing the C_{14} chain with a $\text{C}_{14}-\text{O}-\text{CH}_2$ chain, tubular-shaped particles were synthesized. Cetyltrimethyl phosphonium bromide IL has also been used as a template to form MCM-41.¹¹⁴ The subsequent material had some hydrothermal stability, albeit temporary. Mesoporous silica films may be prepared using long-chain $[\text{C}_n\text{mpyr}]\text{Br}$ salts as templates.¹¹⁵ The films were

Scheme 6. Different Aluminophosphate Zeotype Frameworks Obtained Using $[\text{C}_2\text{mim}]\text{Br}^a$ 

^a Adapted by permission from Macmillan Publishers Ltd: *Nature* **2004**, 430, 1012 (<http://www.nature.com>), Copyright 2004.¹¹⁶

formed on silicon substrates and, using deep ultraviolet calcination as opposed to thermal treatment, led to a strong silica matrix with maintenance of the hexagonal pore structure with limited contraction.

Morris and co-workers demonstrated the potential of using ILs as both solvents and templates for formation of new zeolitic materials (Scheme 6).¹¹⁶ Using $[\text{C}_2\text{mim}]\text{Br}$ four different aluminophosphate zeotype frameworks were formed which were related to the synthesis conditions used. In each case the synthesis was performed at 150 °C; however, by changing the ratio of aluminum and phosphorus precursor as well as the presence of added water and HF, the hydrogen-bonded network was changed which altered the structure of

the zeolite formed, giving rise to SIZ-1, SIZ-3, SIZ-4, and SIZ-5 materials. Similarly, using a eutectic of choline chloride and urea, zeolites could be formed.

Using a similar IL-mediated sol–gel synthesis route, it is possible to prepare supported palladium on silica catalysts.¹¹⁷ The catalyst was prepared in one step by forming Pd colloids in situ on dissolution of palladium acetate in [C₄mim][NTf₂] in the presence of triphenyl phosphine. This mixture was incubated with (EtO)₄Si and formic acid over a short gelation time, and the final material was obtained after refluxing the solid in acetonitrile to remove the IL. Similarly, Ru/SiO₂ catalysts have been synthesized from [C₁₆mim][RuCl₆].¹¹⁸ In this case, the mesoporous silica is formed around the ruthenium nanoparticles.

2.5. Stabilization of IL Emulsions by Nanoparticles

The combination of three generic solvent types which are mutually immiscible, such as water, oil, and IL, gives rise to a range of possible simple and multiple emulsion types. A high degree of stabilization of these emulsions was found to occur using fumed silica nanoparticles for a range of hydrophobic and hydrophilic ILs.¹¹⁹ Since silica is one of the most common supports in heterogeneous catalysis, this may provide some practical advantages. Currently, many applications of ILs as solvents for chemical reactions involve two-phase systems enabling extractive separation of reactant, product, and catalyst species. Therefore, simple or multiple emulsions, with high surface areas enabling fast mass transfer, are likely to bring significant advantages. Dilution of the expensive ILs with water to form aqueous dispersions of IL “nanoreactor” drops allows increased surface area between the two phases as well as giving cost benefits.

3. Hydrogenations in ILs

Several features of ILs make them as useful in hydrogenation catalysis. The solubility of H₂ in ILs is one of the properties that can control such reactions. Measurements using high-pressure ¹H NMR spectroscopy provided solubility data which allowed comparison of different solvents.¹²⁰ In general, the solubility of hydrogen in ILs is very low compared with molecular organic solvents but has similar solubility compared with water. Interestingly, despite the low solubility, essentially no difference in the rate of benzene reduction was found using [H₄Ru₄(η⁶-C₆H₆)₄][BF₄]₂ as the catalyst in ILs and molecular solvents. This is in part due to the higher solubility of hydrogen in the substrate compared with the IL, and thus, the hydrogen solubility in the neat IL has less influence on the reaction rate. In the ideal biphasic process, the ratio of substrate to catalyst immobilization solvent should be high to decrease the effect of mass transfer, which often limits such reactions.

The low solubility of hydrogen can be offset by the environment provided by the IL. In some cases, the ILs are non-nucleophilic and have an inert environment that can increase the stability of the catalysts.¹²¹ However, the rule is not general. For homogeneous catalysts there are many cases in which some catalysts behave better in molecular solvents than in ILs. For example, Dyson and co-workers reported that the ruthenium clusters [Ru₃(CO)_{12-x}(tpptn)_x] (x = 1–3) and [H₄Ru₄(CO)₁₁(tpptn)] (where tpptn = P(*m*-C₆H₄SO₃Na)₃) and the cubane [Ru₄(η⁶-C₆H₆)₄(OH)₄]⁴⁺ catalyze the hydrogenation of a range of alkenes and arenes more

efficiently in water than in ILs.^{122,123} In these cases, the active catalyst is generated in situ under reaction conditions. Therein, the water reacts with the clusters, generating the active catalyst. This process cannot occur in dry ILs and may not occur even if the IL is wet due to the strong hydrogen bonding between water and the IL.

The importance of water has been clearly demonstrated by Rossi et al.¹²⁴ RuO₂–hydrate dissolved in [C₄mim][PF₆], [C₄mim][BF₄], and [C₄mim][OTf] promotes hydrogenation of hex-1-ene under mild reaction conditions but only if the water of hydration is maintained with the dried sample being almost inactive in the ILs. This observation is of particular interest since the poisoning tests with Hg and CS₂ demonstrated that the active species is Ru(0), generated in situ, and not the oxide. Some differences in rate were observed between the ILs used, thus showing the importance of the anion, commonly thought to control the chemistry in general. However, a comparison of the IL-mediated rates with those obtained under solvent-free conditions showed much lower TOFs in the ionic environment. These differences were attributed to the existence of the mass-transfer limitations.

The solubility of the active catalysts in ILs is a very important parameter. Numerous reports indicated that attachment of imidazolium salts to achiral or chiral Rh and Ru catalysts increased the preferential solubility of the catalysts in the IL. This enables high concentrations to be used and also limits leaching of the catalyst from the IL during workup. Hence, in many cases the imidazolium-modified catalysts were successfully reused without significant loss of catalytic efficiency.^{75,74,125–128}

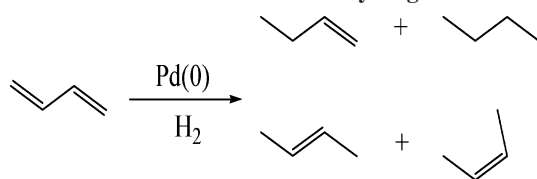
3.1. Hydrogenation on IL-Stabilized Nanoparticles

Due to their stabilization of nanoparticles, ILs have provided an important media in which to perform nanoparticle-catalyzed hydrogenations. The IL may be tailored to have an influence on the stabilization, size, and solubility of the catalyst, factors which play a role in catalysis. However, ILs cannot be considered as innocent as shown by Starkey et al.⁶⁶ For example, at high temperatures, imidazolium-based materials readily produce metal-*N*-heterocyclic carbene complexes from nanoparticles upon deprotonation. In these cases, the carbene ligands can be bound to the nanoparticle surface or form mononuclear mono- or biscarbene complexes.³⁰

3.1.1. Hydrogenation of 1,3-Butadiene

Hydrogenation of 1,3-butadiene was found to be highly selective to but-1-ene using Pd nanoparticles in [C₄mim][BF₄] forming >3 times more but-1-ene than but-2-ene (Scheme 7).⁴³ This selectivity was found to depend on whether the IL was present as well as the anion employed. Changing from [BF₄][−] to [PF₆][−] resulted in formation of high concentrations of butane. The selectivity was assigned to the different solubility of 1,3-butadiene and but-1-ene. However, there are several other factors which can also affect the

Scheme 7. Reaction Products in the Hydrogenation



selectivity; for example, the adsorption of IL of the nanoparticles will influence reaction rates, isomerization of but-1-ene to but-2-ene, and solubility of hydrogen.

3.1.2. Hydrogenation of Alkenes and Arenes

Phenanthroline ligand-protected palladium nanoparticles in $[\text{C}_4\text{mim}][\text{PF}_6]$ have been shown to be very active and selective for hydrogenation of C_6 -olefins (hex-1-ene, cyclohexene, cyclohexadiene) at low temperature and low pressure of hydrogen.¹²⁹ Interestingly, although cyclohexene was reduced, when 1,3-cyclohexadiene was used as a substrate, complete selectivity forming cyclohexene was found. The high selectivity was attributed to the higher adsorption strength of the diene compared with the monoene on the Pd metal. These nanoparticles not only showed very high activity but were also reusable for hydrogenation of olefins under mild reaction conditions. In this case the ligand prevented aggregation of the palladium nanoparticles.

Palladium nanoparticles, prepared from a mixture of $[\text{N}_{4444}]\text{Br}$, $n\text{Bu}_3\text{N}$, and PdCl_2 or $\text{Pd}(\text{OAc})_2$ have also been reported to be catalytically active for the chemoselective hydrogenation of carbon-carbon double bonds in the presence of benzyloxy groups in $[\text{C}_4\text{mim}][\text{PF}_6]$.¹³⁰ Under these conditions, selective reduction of $\text{C}=\text{C}$ bonds was found for both benzyl propenoate to benzyl propanoate as well as β -substituted, β -unsaturated esters. In contrast, cleavage of the benzyloxy group was observed when benzyl benzoate and benzyl *o*-fluorobenzoate were reacted. Both hydrogenation of the double bond and hydrogenolysis of the O -benzyl bond were observed from cinnamyl or geranyl benzyl ethers and from alkenyl benzyl ethers. In most cases the reactions were complete within 20 h; however, for hydrogenation of the benzyl ether of 9-decenol to decyl benzyl ether, 40 h was required. Using this method 1-benzyloxy-2-allylbenzene was also found to undergo selective hydrogenation to 1-benzyloxy-2-propylbenzene.

Ru nanoparticles stabilized in $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}][\text{OTf}]$ have been used for selective hydrogenation of alkenes and benzene under mild reaction conditions.⁴² On examination of the ternary phase diagram (benzene/cyclohexene/ $[\text{C}_4\text{mim}][\text{PF}_6]$) a maximum of 1 wt % cyclohexene was soluble in the IL and then only with 4% benzene also present in the ionic phase. This solubility difference enabled extraction of cyclohexene during benzene hydrogenation. However, despite extraction, the selectivity was limited to 39% and then only obtainable at very low benzene conversion. Although, this selectivity/yield is too low for technical applications, it represents a rare example of partial hydrogenation of benzene by soluble transition-metal nanoparticles.

Ir and Rh nanoparticles have also been tested in $[\text{C}_4\text{mim}][\text{PF}_6]$ for arene hydrogenation under mild reaction conditions.^{39,40} In the case of iridium, the TOFs obtained were very high and the recovered nanoparticles were able to be used several times without any significant loss in catalytic activity. In contrast, the recovered Rh nanoparticles showed significant agglomeration into large particles with an associated loss of catalytic activity. Hydrogenation of arenes containing functional groups, such as methoxy in anisole, was also achievable using iridium nanoparticles. However, in addition, hydrogenolysis of the $\text{C}-\text{O}$ bond was found, which is also found in conventional supported metal catalysis, suggesting that a similar mechanism occurs in each case.

The activity/selectivity of the nanoparticles is highly dependent on the preparation method. For example, $[\text{NTf}_2]^-$ -

stabilized rhodium nanoparticles synthesized in an aqueous solution of *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)-ammonium chloride before being transferred into $[\text{C}_4\text{mim}][\text{PF}_6]$ have been reported to hydrogenate styrene in the biphasic media to ethylbenzene with no hydrogenation of the aromatic ring.⁵² No visible agglomeration of the particles was observed, and the Rh(0) suspension could be reused without loss of activity. In contrast, Rh nanoparticles stabilized in poly[(*N*-vinyl-2-pyrrolidone)-co-(1-vinyl-3-alkylimidazolium halide)] copolymers were found to be highly active in hydrogenation of benzene in $[\text{C}_4\text{mim}][\text{PF}_6]$.⁵¹

3.1.3. Hydrogenation of Ketones

Fonseca et al. have shown that acetone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, cyclopentanone, and benzaldehyde can be hydrogenated to the corresponding alcohols with high TOFs using iridium nanoparticles stabilized by $[\text{C}_4\text{mim}][\text{PF}_6]$.¹³¹ The catalyst was prepared by reduction of $[\text{Ir}(\text{cod})\text{Cl}]_2$ in the IL and found to be a recyclable catalytic system under either solventless or biphasic conditions.

3.2. Homogeneous Catalytic Hydrogenation in ILs

The first reported hydrogenation catalysts used in ILs were based on rhodium complexes such as $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RhCl}(\text{PPh}_3)_3$, and $[\text{Rh}(\text{cod})_2][\text{BF}_4]$ or $[\text{C}_4\text{mim}]_3[\text{Co}(\text{CN})_5]$ in $[\text{C}_4\text{mim}][\text{BF}_4]$. These were tested in hydrogenation of hex-1-ene, cyclohexene, and butadiene, resulting in moderate activities and selectivities.^{132,133} More recent developments have led to the investigation of complex cluster-IL systems designed specifically for the reaction of interest. This is particularly important in reactions where ligand dissociation from the precatalysts is a prerequisite to form a homogeneous active species. In these cases, successful transfer of the reaction from molecular solvents into ILs may be problematic without a degree of understanding.¹³⁴ For example, the Noyori-type precatalysts for hydrogenation and transfer hydrogenation of ketones are among the complexes which require such ligand dissociation but in order for the catalyst to be effective in the IL the precatalyst must be redesigned to aid this process. In this case, the catalyst must have a labile ligand which has a high degree of affinity for the IL to aid formation of the catalytically active species. Furthermore, the IL can be modified to aid this process by, for example, addition of a cosolvent which enhances the solvation of the dissociated ligand, such as water.

The Ru-cluster $[\text{H}_4\text{Ru}_4(\eta\text{-C}_6\text{H}_6)_4]^{2+}$ is a catalyst precursor used to hydrogenate aromatic compounds under biphasic conditions.¹³⁵⁻¹³⁷ The real catalyst is formed in the reaction medium under hydrogen atmosphere, $[\text{H}_6\text{Ru}_4(\eta\text{-C}_6\text{H}_6)_4]^{2+}$, and was found to hydrogenate arenes (benzene, toluene, cumene) in $[\text{C}_4\text{mim}][\text{BF}_4]$ with slightly higher TOFs than aqueous-organic systems.¹³⁸ Reaction of the triply bridged chloro dimer $[(\eta^6\text{-}p\text{-cymene})_2\text{-Ru}_2(\mu\text{-Cl})_3][\text{PF}_6]$ with 1,1,1-tris(diphenylphosphinomethyl)ethane in the presence of ammonium hexafluorophosphate in methanol affords $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-TRIPHOS})\text{Cl}][\text{PF}_6]$, which in $[\text{C}_4\text{mim}][\text{BF}_4]$ under biphasic conditions has proven to be a highly active arene hydrogenation catalyst.¹³⁹ However, this cluster is essentially inactive toward arenes with alkene substituents such as styrene and 1,3-divinylbenzene, whereas the turnover for the hydrogenation of allylbenzene to allylcyclohexane is considerably higher than expected. Interestingly, in this system aromatic ring hydrogenation is preferred over vinyl reduction in propenylbenzene. Steines et al. showed that the

Cp*-ruthenium complex $[\text{Cp}^*\text{Ru}(\eta^4\text{-CH}_3\text{-CH=CH-CH=CH-COOH})(\text{CF}_3\text{SO}_3)]$, when immobilized in $[\text{C}_4\text{mim}][\text{PF}_6]$ for biphasic homogeneous hydrogenation of sorbic acid, efficiently enables the stereoselective hydrogenation leading to formation of *cis*-3-hexenoic acid.¹⁴⁰ Compared with other biphasic systems, the IL-mediated hydrogenation proceeded with enhanced activity and selectivities of up to 90%.

Other clusters have also been evaluated as catalysts/precatalysts for the biphasic hydrogenation of styrene in $[\text{C}_4\text{mim}][\text{BF}_4]$ including $[\text{HFe}(\text{CO})_{11}]^-$, $[\text{HWOs}_3(\text{CO})_{14}]^-$, $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$, and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$.¹⁴¹ $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ was found to be the most active cluster and also showed the highest selectivity for the hydrogenation of styrene to ethylbenzene. The IL has multiple roles including enhancing the catalyst activity, stabilization of the catalyst, and providing regioselective control. For example, by changing the IL to $[\text{C}_8\text{mpyr}][\text{BF}_4]$, a single-phase reaction medium was formed which, using $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$, resulted in the highest TOF for all the ILs studied. Furthermore, as found for Ru nanoparticles, $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ was found to selectively reduce cyclohexadiene to cyclohexene in ILs, whereas in molecular solvents poor regioselectivity was achieved. This is thought to be associated with the biphasic nature of the reaction which, due to the higher solubility of the diene compared with the monoene in the IL, results in preferential hydrogenation.¹⁴¹

Biphasic IL-organic processes have many advantages over single-phase reactions, in particular, ease of separation of the product while maintaining the catalyst in the IL. However, the reactions occur at the boundary between the two liquids, and therefore, mass-transfer issues are often found. In an analogous manner to fluorinated biphasic catalysis, Dyson et al. developed an IL-water catalyst system that undergoes a temperature-controlled and reversible two-phase-single-phase transition.¹⁴² At room temperature $[\text{C}_8\text{mim}][\text{BF}_4]$ is immiscible with water; however, on heating to 80 °C, a single phase is formed. Using this system and $[\text{Rh}(\eta\text{-C}_7\text{H}_8)(\text{PPh}_3)_2][\text{BF}_4]$ as the catalyst, butyne-1,4 diol was hydrogenated. The reaction led to a mixture of but-2-ene-1,4-diol and butane-1,4-diol. Interestingly, the catalyst was also found to be active in the hydrogenation of C=C bonds, resulting in formation of succinic acid in the hydrogenation of maleic acid. This methodology enables the catalyst to be recycled while increasing the mass-transfer characteristics of the system.

Dyson and co-workers also reported the nitrile derivatization of ILs in order to further increase the catalyst stabilization and retention on product separation. The catalyst $[\text{Pd}(\text{NCC}_3\text{mim})_2\text{Cl}_2][\text{BF}_4]_2$ was formed on dissolution of PdCl_2 in $[\text{C}_3\text{CNmim}][\text{BF}_4]$ and used for hydrogenation of 1,3-cyclohexadiene under biphasic conditions.¹⁴³ Although both cyclohexene and cyclohexane were formed, cyclohexene was formed with a selectivity of 97%, again thought to be due to the higher solubility of the diene as compared with the monoene in the IL. In this system, the catalyst is part of the IL and, therefore, not easily lost during extraction of the product.

In all homogeneously catalyzed reactions the main challenge is to prevent loss of catalyst on workup. In many IL processes solvent extraction is employed as thermal degradation of the catalyst may occur on using distillation. However, despite the predominantly good retention of the catalyst by the IL, some leaching nearly always occurs. Use of scCO_2 as an extractant would be advantageous in this respect due

to the low solubility of the catalysts employed and IL. Liu et al. examined the use of scCO_2 extraction on the $[\text{C}_4\text{mim}][\text{PF}_6]$ -mediated hydrogenation of dec-1-ene and cyclohexene using a Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$.¹⁴⁴ For facile hydrogenations, no activity advantages were found using the scCO_2 biphasic media compared with using hexane, for example. The protocol of using the supercritical fluid as the extractant was demonstrated and enabled the catalyst/IL system to be recycled four times with no loss in activity. Therein, hydrogenation of carbon dioxide in the presence of dialkylamines to produce *N,N*-dialkylformamides was also performed using this protocol employing a scCO_2 -insoluble $\text{RuCl}_2(\text{dppe})_2$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) catalyst. These reactions involve ionic carbamate intermediates since dialkylamines react with CO_2 reversibly to form dialkylammonium dialkylcarbamates. In the scCO_2/IL system the catalyst and carbamate are both soluble in the IL phase. Carbamate was completely converted to dialkylformamides using 55 bar of hydrogen under a total pressure of 276 bar. This system showed a lower reactivity than that reported by Kröcher et al.;¹⁴⁵ however, in general, the selectivity was found to be higher for amines using the scCO_2/IL biphasic system.

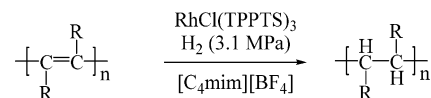
3.3. Hydrogenation of Functionalized ILs

As well as solvents, ILs have been used as substrates for hydrogenation employing Pd complexes of ILs as catalysts.¹⁴⁶ Hydrogenation of allyl-functionalized imidazolium bromide and the corresponding $[\text{BF}_4]^-$ salt did not occur in the neat IL with Wilkinson's catalyst. This was thought to be due to inhibition of the catalyst by the bromide present as an anion or an impurity from the metathesis reaction to form the $[\text{BF}_4]^-$ salt. This has been shown by many studies; however, on dilution of the $[\text{BF}_4]^-$ -based IL with methanol, hydrogenation to $[\text{C}_4\text{mim}][\text{BF}_4]$ occurred at 60 °C and 100 bar of H_2 .⁷³

3.3.1. Selective Hydrogenation of Polymers

Direct modification of unsaturated polymers, such as polybutadiene, and rubbers, such as nitrile-butadiene rubber or styrene-butadiene rubber, by catalytic hydrogenation is of great interest to the chemical industry. The ability to control the extent of hydrogenation allows fine-tuning of the physical, mechanical, and chemical properties of these materials in order to meet a specific function.¹⁴⁷ Hydrogenation of the vinyl group was shown to occur with $\text{RhCl}(\text{TPPTS})_3$ as catalyst in $[\text{C}_4\text{mim}][\text{BF}_4]$ (Scheme 8).

Scheme 8. Reduction of Unsaturated Polymers in $[\text{C}_4\text{mim}][\text{BF}_4]$

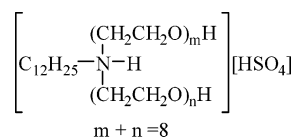


In the biphasic system toluene/ $[\text{C}_4\text{mim}][\text{BF}_4]$ the activity of the catalyst was found to follow the order of the mass of the hydrogenated polymer. Addition of water was found to increase the reaction rate, whereas no enhancement was observed on incorporation of functional groups on the polymer. Biphasic hydrogenation of poly(acrylonitrile-butadiene) rubbers in ILs has also been reported to be catalyzed by $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ dissolved in $[\text{C}_4\text{mim}][\text{BF}_4]$ or a mixture of 1,3-dialkylimidazolium tetrafluoroborate ILs.¹⁴⁸ In all ILs similar hydrogenation was achieved,

suggesting that viscosity and melting point do not affect the applicability of these ILs, at least for reactions that have to be performed at temperatures much higher than the melting point.

Polystyrene-*b*-polybutadiene-*b*-polystyrene block copolymers have been hydrogenated with Ru/TPPTS or Ru/TPPTS/TPP (TPP = triphenylphosphine) as catalysts in a polyether-modified ammonium salt IL (Scheme 9).¹⁴⁹ Under optimized conditions, the hydrogenation degree of the polybutadiene segments of the polymer was 89% with no additional hydrogenation of aromatic groups. As found with many hydrogenations, the IL-immobilized catalyst was recovered simply by phase separation and recycled without significant changes in the catalytic activity.

Scheme 9. Structure of the Polyether-Modified Ammonium IL



3.4. Asymmetric Hydrogenations

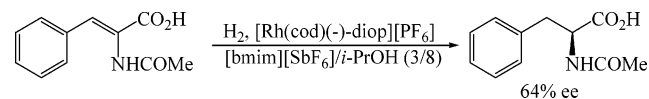
Catalytic asymmetric hydrogenation has been established as one of the most efficient strategies for the synthesis of optically active molecules.^{150,151} The reactivity and enantioselectivity (ee) of a transition-metal-based asymmetric catalyst are highly sensitive to the conformational, steric, and electronic properties of the chiral ligand. Under these circumstances, the ionic environment of the ILs may be expected to exhibit a certain influence; therefore, a number of studies devoted to the investigation of comparative asymmetric hydrogenations in molecular and IL solvents have been reported.

3.4.1. Enantioselective Hydrogenation

3.4.1.1. Enantioselective Hydrogenation of C=C Bonds.

Chauvin et al. were among the first to investigate enantioselective metal-catalyzed reactions in ILs.⁷³ Therein, the enantioselective hydrogenation of α -acetamidocinnamic acid using $[\text{Rh}(\text{cod})\{(-)\text{-diop}\}][\text{PF}_6]$ catalyst in the biphasic system $[\text{C}_4\text{mim}][\text{SbF}_6]/i\text{-PrOH}$ was found to yield (*S*)-*N*-acetylphenylalanine in 64% ee (Scheme 10).

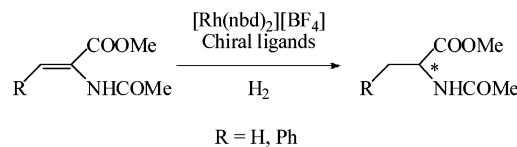
Scheme 10. Enantioselective Hydrogenation of α -Acetamidocinnamic Acid Using $[\text{Rh}(\text{cod})\{(-)\text{-diop}\}][\text{PF}_6]$ Catalyst in $[\text{C}_4\text{mim}][\text{SbF}_6]/i\text{-PrOH}$



Hydrogenations of enamide compounds to optically active α -amino acid derivatives in $[\text{C}_4\text{mim}][\text{PF}_6]-i\text{-PrOH}$ using Rh-MeDuPHOS¹⁵² or in $[\text{C}_4\text{mim}][\text{PF}_6]/[\text{C}_4\text{mim}][\text{BF}_4]$ -alcohol/water using Rh-EtDuPHOS or Ru-BINAP,¹⁵³ either as biphasic or monophasic systems, were found to occur with high enantioselectivity. Therein, the products were easily extracted from the IL, allowing recycling of the catalyst/IL system. In contrast, using a similar system, the enantioselective hydrogenation of methyl α -benzamido cinnamate occurred with very low conversion in $[\text{C}_4\text{mim}][\text{BF}_4]$ using a range of catalysts. However, in $[\text{C}_2\text{mim}][\text{OTf}]$, Rh-EtDuPHOS gave 95% conversion and 89% ee.¹⁵⁴ Comparing the behavior of $[\text{Rh}(\text{NBD})_2][\text{BF}_4]$ catalysts in alcoholic

solvents and ILs for enantioselective hydrogenation of the same enamides showed little difference in selectivity and ee; however, the reaction rate in the ILs was smaller (Scheme 11).¹⁵⁵

Scheme 11. Enantioselective Hydrogenation of Enamides



Addition of water to ILs or alcohol/IL mixtures has been shown to result in an increase in both ee and reaction rate. This is exemplified in the use of “wet ILs” for Ru-catalyzed enantioselective hydrogenation of tiglic acid, where, under optimized conditions, wet $[\text{C}_4\text{mim}][\text{PF}_6]$ in the presence of (*R*)-toBINAP was found to give the highest ee’s (92%) with 100% conversion.¹⁵⁶ A similarly beneficial effect of water in this reaction was also reported by Wolfson et al.¹⁵⁷ Therein, the role of water was thought to influence the mixing of the phases.

The need for optimized systems to perform a fair comparison is of particular importance in enantioselective reactions as many variables such as hydrogen concentration in the liquid phase and ligand type can affect the reaction rate and the ee. Jessop et al. have shown this clearly comparing IL and molecular solvent mediated enantioselective hydrogenation of tiglic and atropic acid using Ru-BINAP catalysts.¹⁵⁸ Tiglic acid is known to require low concentrations of hydrogen to give high enantioselectivity, and $[\text{C}_2\text{mim}][\text{NTf}_2]$ was shown to have an optimized ee of 95% compared with only 88% in methanol. In contrast, the optimized ee for atropic acid was 87% in $[\text{C}_4\text{mim}][\text{PF}_6]$ -methanol but 92% in pure methanol, and very poor ee’s in the pure ILs were reported. Pugin et al. showed that in the hydrogenation of enamides all ferrocene-based ligands led to better ee’s and/or activities in wet ILs than in methanol, while the ligands bppm, prophos, and me-duphos, shown in Figure 5, resulted in inferior results.¹⁵⁵ The superiority of the wet ILs system compared with the IL/isopropyl alcohol one was explained by the difference in solubility of the catalysts. In general, the dissolved catalyst concentration was found to be much lower in water than in alcohols if ligands without highly polar or charged groups were used.

The higher ee’s observed with many ligands (Figure 5) in wet ILs compared with organic solvents also raises the question of whether the effect may be due to a different hydrogen concentration in wet ILs or solvent effects such as solvation of the catalyst and reactants. The hydrogen concentration depends on factors such as hydrogen solubility in the solvent, applied hydrogen pressure, and mixing.¹⁵⁵ Hydrogen also has a lower solubility in ILs than in organic solvents. Accordingly, all hydrogenations that were performed in alcohols are faster than those in pure ILs. The effect of the hydrogen concentration has also been reported in the asymmetric reduction of (*Z*)- α -acetamido cinnamic acid catalyzed by $(-)$ -1,2-bis((2*R*,5*R*)-2,5-diethylphospholano)benzene(cyclo-octadiene) rhodium(I) trifluoromethanesulfonate dissolved in *i*-propanol, $[\text{C}_4\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}][\text{PF}_6]$. Therein, increasing pressure in $[\text{C}_4\text{mim}][\text{PF}_6]$ was found to dramatically increase the enantioselectivity as well as the conversion; however, optimization of the enantioselectivity was determined by the concentration of the

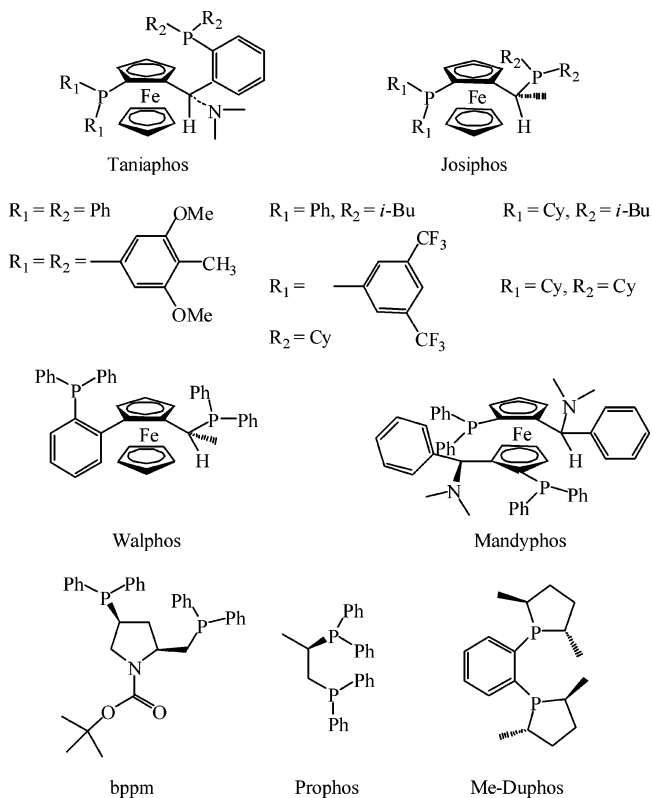


Figure 5. Ligands used in the Rh-catalyzed hydrogenation of enamides in ILs.

dissolved hydrogen and not by the pressure, with equivalent ee's found at 100 bar in [C₄mim][PF₆] but only 50 bar in [C₄mim][BF₄].¹⁵⁹

It is interesting to note that in the results obtained by Pugin et al. generally the ee's tend to be lower at 10 bar than at 1 bar and that the decrease is less marked in wet ILs than in organic solvents.¹⁵⁵ This effect was most pronounced with ligand Josiphos (having 1-alkyl-3,5-bis-trifluoromethylbenzene as substituents), where differences in ee's of 13% in methanol and 7% in wet IL were observed. Although lower hydrogen availability may be responsible for this effect, it could also be caused by a change in the solvation of the reactants in the wet ILs.

Asymmetric hydrogenation of ethenamine has also been reported. IL-grafted chiral Rh complexes of a 1,4-bisphosphine ligand, having two 1,2-dimethylimidazolium salt tags closely resembling the IL reaction medium, have been tested in asymmetric hydrogenation of *N*-acetylphenylethenamine in an IL.¹⁶⁰ The reaction occurred with total conversion and ee's higher than 95%. However, the catalytic efficiency of the Rh complex dropped significantly after two reaction cycles.

3.4.1.2. Enantioselective Hydrogenation of C=O Bonds.

In contrast to C=C bond reduction, ketones do not easily undergo homogeneous hydrogenation in the presence of simple transition-metal catalysts; however, by increasing the electron density on the rhodium center by using ligands based on fully alkylated bidentate diphosphanes, efficient C=O hydrogenation has been observed.^{161–163} An alternative catalyst was prepared in situ from a rhodacarborane catalyst precursor with the suicide alkene ligand [closo-1,3- $\{\mu$ -(η^2 -3-CH₂=CHCH₂CH₂)₂}-3-H-3-PPh₃-3,1,2-RhC₂B₉H₁₀] treated with [C₈mim][BF₄], [C₄mim][PF₆], or *N*-butylpyridinium 1-carbadodecaborate. Introduction of the molecular asym-

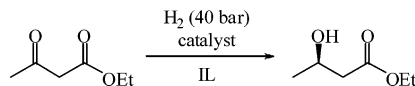
metry in the catalytic hydrogenation was achieved by complexation of the rhodium center with the optically active (*R*)-BINAP ligand.¹⁶⁴ Use of the rhodacarborane catalyst precursor in the hydrogenation of aromatic ketones in ILs provided both a new route to the corresponding alcohols as well as the opportunity to include optically active phosphanes in the rhodacarborane catalyst system as structural components. This modified catalyst promoted the asymmetric hydrogenation of prochiral ketones under mild conditions. Both acetophenone and ethyl benzoylformate were hydrogenated to form (*R*)-phenylethanol and ethyl (*R*)-mandelate, respectively, in quantitative yields and with >97% ee. In comparison, use of THF instead of the ILs led to a reduction in the yield/TOF and ee. Furthermore, replacement of rhodacarborane catalyst precursor with [Rh(cod)Cl]₂ caused a significant decrease in performance in both reactions examined.

[RuCl₂(TPPTS)₂]-(*1S,2S*)-DPENDS (DPENDS = 1,2-diphenyl-1,2-ethylenediamine sulfonate disodium)-KOH catalyst was examined for the asymmetric hydrogenation of aromatic ketones in a series of hydrophilic ILs [C_{*n*}mim][*p*-CH₃C₆H₄SO₃] (*n* = 2, 4, 8, 12). An ee of 85% was obtained in the asymmetric hydrogenation of acetophenone; however, using 2-fluoroacetophenone, 2-chloroacetophenone, 2-bromoacetophenone, 2-(trifluoromethyl)acetophenone, 4-(trifluoromethyl)acetophenone, 2-methoxyacetophenone, and 4-methoxyacetophenone led to only moderate ee's.¹⁶⁵

Polar phosphonic-acid-derived Ru(BINAP)(DPEN)Cl₂ (DPEN = (*R,R*)-1,2-diphenyl-ethylenediamine) systems have also been used for asymmetric hydrogenation of aromatic ketones in [C₄mim][BF₄], [C₄mim][PF₆], and [C₃dmim][NTf₂] leading to high ee's. The catalysts dissolved in the IL were recycled and reused with no appreciable leaching of Ru into the chiral alcohol products.¹⁶⁶

Asymmetric hydrogenation of diketones in ILs has been reported by several groups. Hydrogenation of ethyl acetoacetate with the ammonium salt of 4,4'- and 5,5'-Ru-diamBINAP in ILs based on 1,3-dialkylimidazolium, *N*-alkylpyridinium, and tetralkylphosphonium cations occurred with moderate ee's (Scheme 12).¹⁶⁷ However, reduced ee's

Scheme 12. Enantioselective Hydrogenation of Ethyl Acetoacetate



were found in the IL compared with when the reaction was performed in water as a biphasic reaction. The IL allowed the catalyst to be recycled with an increase in ee with recycle number. Interestingly, addition of 10% water to [C₄mim][PF₆] reduced the ee from 75% to 13%.

Asymmetric hydrogenation of β -aryl ketoesters, using Ru modified by 4,4'-substituted BINAP derivatives, has been carried out in both methanol and the monophasic mixture of [C₄mim][BF₄] and methanol.¹⁶⁸ In general, the differences in ee obtained in the IL/methanol mixture compared with results in methanol were very small and the IL only played a role to aid the recycle of the catalyst.¹⁶⁹

The enantioselective hydrogenation of β -alkyl ketoesters and β -aryl ketoesters has been reported by Lam et al. with the β -alkyl ketoesters showing higher rates of reaction in ILs.¹⁷⁰ In ILs the hydrogenation of these substrates lead to very high ee's and conversions using BINAP or chiral dipyriddyphosphine ligand-modified Ru catalysts. However,

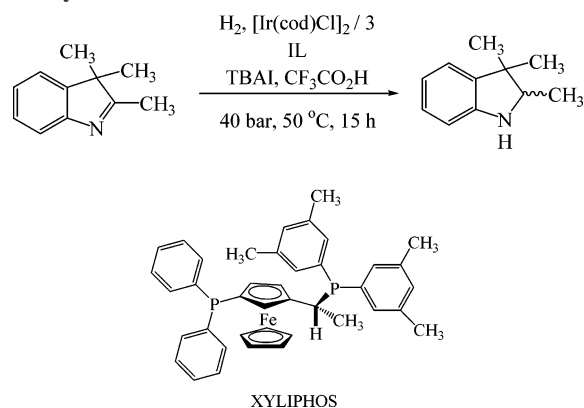
incorporation of halides (Cl, F) in the alkyl substituents generates electronegative groups which cause a dramatic decrease in ee. Under these conditions the effect of the IL anion becomes very important. For CF_3 substituents, the ee was only 21% in the presence of $[\text{PF}_6]^-$ compared with 50% in the $[\text{BF}_4]^-$ -based IL. However, replacing the alkyl with a halide in ethyl 4-chloro-3-oxobutyrate, typical Ru–BINAP catalysts in $[\text{N}_{2222}]\text{Br}$, $[\text{C}_4\text{mim}][\text{PF}_6]$, or $[\text{C}_4\text{mim}][\text{OTf}]$ all showed similar ee's.

Asymmetric hydrogenation of α -keto esters in ILs was also reported using Ru–BINAP as a catalyst. Again, the enantioselectivity was found to be strongly dependent on the anion of the IL used. For example, for hydrogenation of methyl pyruvate, 81% ee was obtained in $[\text{C}_4\text{mim}][\text{BF}_4]$ while only 55% enantioselectivity was obtained in $[\text{C}_4\text{mim}][\text{PF}_6]$.¹⁷⁰ It was notable that the chiral dipyridylphosphine ligand showed better performance than BINAP in the IL, which may be related to the dipyridyl backbone. Using this ligand, reduction of other α -keto esters was achieved with a range of enantioselectivities dependent on the substrate used. Low enantioselectivities and conversions were observed in the hydrogenation of ketopantolactone in both $[\text{BF}_4]^-$ - and $[\text{PF}_6]^-$ -based ILs. Moderate enantioselectivities but low conversions were obtained with ethyl 2-oxo-4-phenylbutyrate. High ee's but again low conversions were attained in the hydrogenation of methyl benzoylformate, and low conversions and enantioselectivities were found for ethyl benzoylformate.

3.4.1.3. Enantioselective Hydrogenation of C=N Bonds.

Enantioselective hydrogenation of trimethylindolenine in ILs was reported to occur with iridium catalysts modified with XYLIPOS as the ligand (Scheme 13).¹⁷² These experiments

Scheme 13. Enantioselective Hydrogenation of Trimethylindolenine in ILs

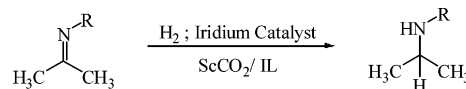


were carried out in ILs having 1,3-dialkylimidazolium and *N,N*-dialkylpyrrolidinium cations in combination with either a short (butyl) or a long (decyl) alkyl substituent and either $[\text{BF}_4]^-$ or $[\text{NTf}_2]^-$ anions. In comparison with reactions carried out in toluene, the time to reach 100% conversion was reduced from 23 h to less than 15 h in $[\text{C}_{10}\text{mim}][\text{BF}_4]$ with no loss of selectivity and 94% conversion after only 8 h in $[\text{C}_{10}\text{mpy}][\text{NTf}_2]$. In the ILs >80% ee was achieved which was comparable with the best results obtained in molecular solvents.¹⁷² Hydrogenation of trimethylindolenine indicated that the viscosity of the ILs was limiting due to poor gas to liquid mass transfer. To reduce this effect, the ionic media required slightly higher reaction temperatures. In addition, the presence of trace amounts of oxygen has been shown to affect the reaction significantly in molecular

solvents. Interestingly, the IL-mediated reaction was found to be less sensitive toward oxygen, which may also be due to the higher viscosity.¹⁷³

Enantioselective imine hydrogenation has also been performed using a combination of IL and scCO_2 with a phosphano-dihydrooxazole iridium catalyst (Scheme 14).^{174,175}

Scheme 14. Enantioselective Imine Hydrogenation in ScCO_2/IL Mixtures

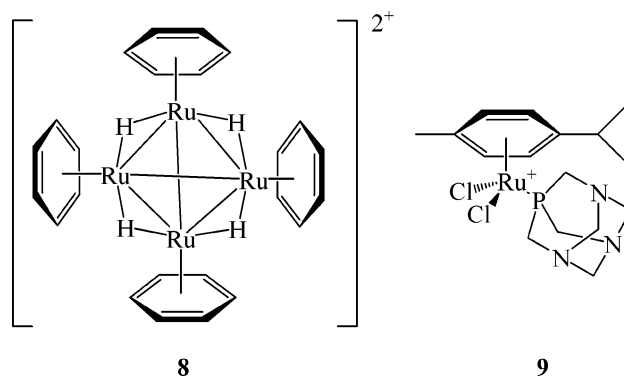


The combination of solvents was reported to make the system even more effective, exploiting the molecular interaction of the stationary IL phase with the catalyst and the mass-transfer properties of the mobile CO_2 phase. The presence of CO_2 was found to be not only beneficial but, in certain cases, mandatory for efficient hydrogenation in the IL. As for many other examples, the choice of the anion of the IL was found to strongly influence the selectivity of the catalyst with ee's varying from 30% in $[\text{C}_4\text{mim}][\text{BF}_4]$ to 78% in $[\text{C}_2\text{mim}][\text{BARF}]$, assuming no influence of the alkyl chain of the imidazolium cation. The increase in the ee was attributed to the decreasing coordination ability of the anion.

3.5. Role of the ILs Purity in Hydrogenation Reactions

For many catalyzed processes in ILs, the purity of the solvent can have a significant influence on the outcome of the reaction including reaction rate and selectivity. This has been illustrated for the hydrogenation of benzene and other arene substrates under biphasic conditions using Ru complexes **8** and **9** (Scheme 15).¹⁷⁶ In general, chloride-free ILs gave a higher turnover frequency than chloride-contaminated IL with water as a solvent showing intermediate behavior. On recycling, the catalysts in the three solvents showed approximately constant turnover frequencies, which may indicate the effect of chloride is not cumulative.

Scheme 15. Ru Complexes Used for the Hydrogenation of Benzene and Other Arene Substrates under Biphasic Conditions



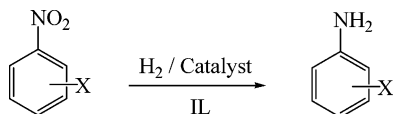
3.6. Hydrogenation via Heterogeneous Catalysis in ILs

Heterogeneously catalyzed hydrogenation reactions in ILs were among the first to combine solids and the IL. Carlin et al. immobilized palladium on carbon in an IL copolymer membrane for gas-phase (propene) hydrogenation. Heterogeneous catalysts have also been suspended in ILs for

selective hydrogenation reactions. Selective hydrogenation of α,β -unsaturated aldehydes (cinnamaldehyde to hydrocinnamaldehyde and citral to citronellal) has been performed in a wide range of hydrophilic and hydrophobic ILs.¹⁷⁷ For carbon-supported palladium catalysts, the selectivity for reduction of the conjugated C=C bond was improved using ILs as solvents compared with conventional molecular organic solvents, albeit at the expense of lower reaction rates. Furthermore, in this system the catalyst was easily recycled without the need to isolate or filter the catalyst and could be used without further treatment. Some deactivation due to pore blocking was found on the first recycle, but thereafter the activity remained constant. In these reactions, the anion strongly influenced the selectivity with $[\text{NTf}_2]^-$ -based ILs allowing reduction of both the C=C and the C=O double bonds, while $[\text{BF}_4]^-$ -based ILs showed excellent C=C selectivity. The mechanism by which the IL enhances the selectivity was thought to be due to an increased IL-carbonyl interaction which adjusts the adsorption geometry of the aldehyde by weakening the interaction of the carbonyl with the surface of the catalyst, thus favoring the π_{CC} or di- σ_{CC} interactions as opposed to the η^4 adsorption.

Xu et al. also demonstrated that 5 wt % Pt/C, 5 wt % Pd/C, and Raney nickel catalysts can be used for hydrogenation of halonitrobenzenes to the corresponding haloanilines in $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ 1,3-dialkylimidazolium-based ILs (Scheme 16).¹⁷⁸ Although 100% conversion of the halo-

Scheme 16. Hydrogenation of Halonitrobenzenes to Haloanilines



nitrobenzenes was obtained, decreased rates were observed in the ILs compared with methanol. This was attributed to mass-transfer effects associated with the higher viscosity of the IL compared with methanol. However, increased selectivity was found in the ILs compared with methanol with respect to dehalogenated products. Therein, <1.3% dehalogenation was obtained in ILs, in contrast, to up to 20.2% dehalogenation in methanol using Raney Ni. This behavior was attributed to either a decrease in the chemisorption of the haloanilines due to increased solvation by the ILs compared with methanol or simply a lower dehalogenation reaction rate.

Hydroamination of a range of aldehydes has been shown to proceed efficiently in $[\text{C}_4\text{mpyr}]^+[\text{NTf}_2]^-$, $[\text{C}_4\text{mim}]^+[\text{NTf}_2]^-$, and $[\text{C}_4\text{mim}]^+[\text{BF}_4]^-$ using supported palladium catalysts as well as PdCl_2 using 2,6-dimethylmorpholine, piperidine, and morpholine as the amination reagents.¹⁷⁹ Slower rates were observed in the IL compared with molecular solvents with the exception of those in water which inhibited the reaction. Thus, for efficient recycle, the catalyst/IL system had to be dried to maintain catalytic activity.

In order to disentangle the various mass-transfer limitations in three-phase reactions and thus understand the lower rates of reaction in the IL compared with molecular solvents, hydrogenation of phenylacetylene to styrene in heptane and $[\text{C}_4\text{mim}]^+[\text{NTf}_2]^-$ was examined in detail by Hardacre et al.¹⁸⁰ By comparing the kinetics of the palladium on calcium-carbonate-catalyzed reaction in a stirred tank reactor and a rotating disc reactor (Figure 6), the reaction rate in the IL

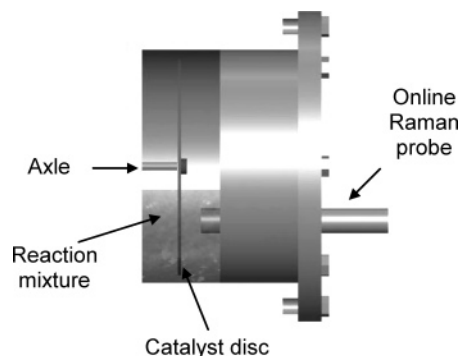


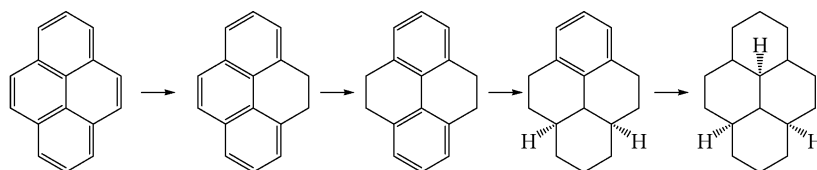
Figure 6. Schematic of the rotating disc reactor used for the selective hydrogenation of phenylacetylene. Reprinted from Hardacre, C.; Mullan, E. A.; Rooney, D. W.; Thompson, J. M.; Yablonsky, G. S. *Chem. Eng. Sci.* **2006**, *61*, 6995 with permission from Elsevier.¹⁸⁰

was found to be limited by the mass transfer of dissolved hydrogen.

Most other forms of using ILs and solids for hydrogenations have concentrated on the stabilization of nanoparticles or heterogenization of complexes on solids. For example, Huang et al. immobilized palladium nanoparticles on a mesoporous SBA-15 molecular sieve (pore size 6.7 nm) using ILs, leading to a very active and selective heterogeneous catalyst for solvent-free hydrogenation of hex-1-ene, cyclohexene, and cyclohexadiene.⁸⁶ Therein, the TOF was enhanced at least 10 times on comparison with analogous tests under homogeneous conditions, and for hydrogenation of 1,3-cyclohexadiene, cyclohexene was the only identified hydrogenated product. The high TOF can be associated with the high accessibility of Pd in these catalysts. No leaching or catalyst deactivation has been observed during the recycle experiments, and the nanoparticle size was invariant. Similarly, Ru nanoparticles supported on SBA-15 in 1,1,3,3-tetramethylguanidinium lactate were tested in hydrogenation of benzene.⁸⁸ This Ru catalyst was found to hydrogenate benzene to cyclohexane even at mild conditions (20 °C, 1.0 MPa). Although the activity was comparable to $[\eta^6\text{-C}_6\text{Me}_6)_2\text{-Ru}_3(\mu_3\text{-O})(\mu_2\text{-H})_3][\text{BF}_4]$ in ILs, the selectivity of the heterogeneous catalyst was found to be low with no formation of cyclohexene observed. Montmorillonite has also been used to immobilize Ru nanoparticles in 1,1,3,3-tetramethylguanidinium trifluoroacetate.⁸⁷ Comparison of this catalyst with homogeneous Ru-cluster-based catalysts, such as $[(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_3(\mu_3\text{-O})(\mu_2\text{-H})_3][\text{BF}_4]$ or $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_3\text{-H})_4]\text{Cl}_2$, for hydrogenation of benzene showed comparable TOFs with the $[\text{BF}_4]^-$ -based cluster and much higher TOFs than chloride-based catalyst. This is unusual as TOFs associated to homogeneous catalysts are, in general, superior to those associated to heterogeneous systems.

A silica-supported rhodium precatalyst dissolved in $[\text{C}_4\text{mim}]^+[\text{PF}_6]^-$ was also shown to be active for hydrogenation of hex-1-ene, cyclohexene, and 2,3-dimethyl-2-butene in a Robinson–Mahoney reactor.⁸⁹ In general, the catalyst evaluation showed enhanced activity for the supported IL system in comparison to the homogeneous and biphasic reaction system. The enhanced activity of the rhodium complex in an IL phase was explained as being due to the absence of any coordinating solvent.⁷³ Some limitations were observed, including a reduced reactivity for hydrogenation of cyclohexene as well as a decrease in activity on increasing the chain length from hex-1-ene to dodec-1-ene.

Scheme 17. Hydrogenation of Pyrene in ILs



Marr and co-workers examined the use of an IL to form a solid support as well as immobilize the catalyst. Using palladium nanoparticles supported in $[C_4mim][NTf_2]$ as the template for an aerogel structure, a Pd/SiO₂ catalyst was formed which showed excellent activity and selectivity for the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde with little 3-phenylpropanol forming.¹¹⁷ This methodology has also been used for entrapment of $[RhCl(PPh_3)_3]$ in an aerogel prepared by an IL route for hydrogenation of styrene.¹⁸¹ This catalyst proved to be 5 times more active than the $[RhCl(PPh_3)_3]$ entrapped in silica prepared by a more conventional sol-gel route, keeping the selectivity to ethylbenzene. The enhanced performance was related to the stabilizing effect of IL.

$Pd(acac)_2$ has been supported on an active carbon cloth using Aliquat 336 hexafluorophosphate ($[A336][PF_6]$), $[C_4mim][PF_6]$, and $[C_4mim][BF_4]$ for the selective hydrogenation of citral.^{92,93} Following reaction, the palladium is found to be in a reduced state by XPS. The reactions, performed in hexane, showed a range of products, and the overall product profile was influenced by the IL which was used to immobilize the palladium.

Polymer-supported ILs-immobilized nanoparticles represent another further category of heterogeneous catalysts investigated in hydrogenation reactions.¹⁸² Platinum, palladium, and rhodium nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) and immobilized in $[C_4mim][PF_6]$ have been reported to be effective for olefin and arene hydrogenations. Hex-1-ene, dodec-1-ene, cyclohexene, and benzene were hydrogenated with TOFs comparable to those obtained in homogeneous conditions. For Pt nanoparticles, the TOFs were comparable with or better than those of nanoparticles prepared by reduction of $Pt_2(bis\text{-}dibenzylidene\text{ acetone})_3$ and immobilized in $[C_4mim][PF_6]$.⁴⁴ Under the same reaction conditions, the palladium nanoparticles showed a higher TOF for hydrogenation of cyclohexene than equivalent palladium nanoparticles stabilized by 1,10-phenanthroline and immobilized in $[C_4mim][PF_6]$.¹⁸³

In another attempt to heterogenize both the IL and active catalysts, $[C_4mim][PF_6]$ and either Wilkinson's catalyst or Ru-BINAP were entrapped in a poly(diallyldimethylammonium chloride)-based support.¹⁸⁴ These systems showed little leaching of the catalyst or IL in liquid-phase hydrogenation of 2-cyclohexen-1-one and 1,3-cyclooctadiene and for the Ru-BINAP system asymmetric hydrogenation of methyl acetoacetate. Comparison with the equivalent IL/organic solvent biphasic system showed an increased TOF with similar chemo- and stereoselectivities.

3.7. Biocatalysis in ILs for Reduction of Organic Molecules

ILs also offer advantages over organic solvents for certain classes of biotransformations using isolated enzymes and whole cells, although there has been significantly less reported on the latter.¹⁸⁵ Howarth et al.¹⁸⁶ used yeast to mediate ketone reductions in $[C_4mim][PF_6]$ and found that

the response to the IL varied considerably with substrate structure. Lenourry et al.¹⁸⁵ compared the reaction of the biocatalyst, *Sporomusa termitida*, for reduction of the C=C double bonds in a range of enoates and nitroalkenes in $[C_4mim][PF_6]$ with a standard two-liquid-phase reaction system containing an organic solvent as a benchmark. The results suggested that this system may even have potential for asymmetric hydrogenation of C=C double bonds. However, the initial reduction rate in the IL was 20% lower than the initial rate in tetradecane, and the overall yield was 7% lower.

3.8. Hydrogen-Transfer Reactions in ILs

As well as conventional hydrogenation reactions, hydrogen-transfer processes have been reported in both first- and second-generation ILs. The partial reduction of anthracene and pyrene was achieved using the IL $[C_2mim][HCl_2]$ as a proton source (Scheme 17).¹⁸⁷ For complete reduction to the alicyclic products, anhydrous HCl gas was found to be the most effective proton source. In the reduction of pyrene, a single diastereomer was formed. Hydrogenation of 9,10-dimethylanthracene occurred only at the inner cycle, forming the cis and trans isomers in a 6:1 ratio.

Other studies to generate catalysts from metal chlorides in the Lewis-acidic chloroaluminate IL $[N\text{-}octyl\text{-}3\text{-}picolinium]Cl-AlCl_3$ have also been reported for hydrogenation of benzene.¹⁸⁸ In comparison with the poor activity shown by $ZrCl_4$, $NiCl_2$, $CrCl_3$, $CoCl_2$, and $SmCl_3$, both $PdCl_2$ and K_2PtCl_4 were found to show significant reactivity with K_2PtCl_4 giving almost quantitative conversion to cyclohexane.

ILs have recently been reported as suitable solvents for the palladium(II)-catalyzed homogeneous transfer hydrogenation of α,β -unsaturated carboxylic acids using sodium or triethylammonium formate as the hydrogenating agent.¹⁸⁹ Again, the chemical reactivity is governed by the anion used in which a 99% yield was observed using $[BF_4]^-$ as the anion while only 2% was found using $[PF_6]^-$.

Catalytic asymmetric transfer hydrogenation has become a useful tool to obtain optically active secondary alcohols from carbonyl compounds and is an interesting alternative to hydrogenation with molecular hydrogen.¹⁹⁰ The hydrogen donors most commonly used for ketones are propan-2-ol, generally used with a base, and formic acid, generally used as an azeotrope with triethylamine. The latter is important as hydrogenation is accompanied by evolution of CO₂, which prevents the reverse oxidation reaction. Berthold et al. described a microwave-assisted reduction in ILs under transfer hydrogenation conditions with an achiral palladium catalyst and formate salts.¹⁹¹ Since then, asymmetric transfer hydrogenation has been shown to be successful in ILs. Geldbach and Dyson¹⁹² reported the asymmetric transfer hydrogenation of acetophenone with 2-propanol/KOH in $[C_4dmim][PF_6]$ by use of modified arene-Ru(II) complexes with Noyori's chiral *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine giving ee's up to 98% with conversions between 80% and 95%.¹⁹³ Although the IL enabled the

recycle of the catalyst, a reduction in conversion was observed. However, on changing to a formic acid/triethylamine emulsion, the recyclability of the catalyst was improved, particularly if the IL system was washed with water, leading to >99% ee and ≤96% yield over five reactions. Kawasaki et al.¹⁹⁴ selected two types of chiral catalysts for the recyclable asymmetric transfer hydrogenation of ketones with the azeotrope in ILs. As well as a catalyst similar to that employed by Geldbach and Dyson,¹⁹² a Ru(II) complex of an amino amide derived from proline in the presence of [RuCl₂(cymene)]₂ was studied. The results of the asymmetric transfer hydrogenation of a range of acetophenone derivatives using the azeotropic mixture of formic acid and triethylamine confirmed the results of Geldbach and Dyson, indicating that the best combination was the chiral benzene–Ru complex of Noyori¹⁹³ and [C₄mim][PF₆]. Interestingly, no improvement in ee for acetophenone was found comparing solventless conditions, i.e., using the azeotrope as the solvent, and [C₄mim][PF₆] or [C₄mim][BF₄]; however, a decrease in the conversion from 60% to 53% or 15%, respectively, was observed.

Introduction of the imidazolium moiety to the chloroalkoxy derivative of Noyori's ligand¹⁹³ enhanced the stability of this catalyst¹⁹⁴ as compared with the results of Geldbach and Dyson.¹⁹²

4. Catalytic Oxidation in ILs

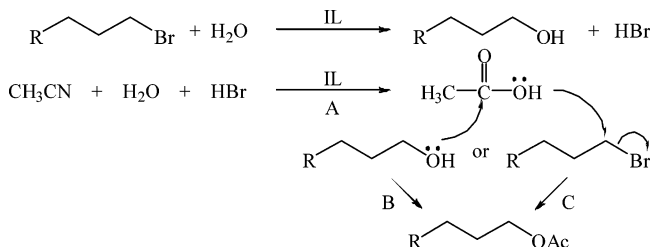
Oxidation reactions have been widely studied in ILs,¹⁹⁵ and in many cases, the solvent cannot be considered inert as the formation and stability of radical species can be strongly affected by the presence of an ionic environment. Pulse radiolysis studies have demonstrated this elegantly by examining the rate constants for several reduction and oxidation reactions in a range of ILs.¹⁹⁶ Furthermore, ILs have been shown to be ideal media for the simultaneous generation of radical cations and anions.¹⁹⁷ For example, in *N*-alkylpyridinium-based ILs solvated electrons can react with the pyridinium moiety to produce a pyridinyl radical, which, in turn, can transfer an electron to an acceptor. Therein, the rate constant for reduction of duroquinone by the benzophenone ketyl radical in [N₁₄₄₄][NTf₂] was found to be much lower than that measured in water due to the high viscosity of the IL.

ILs have commonly been quoted as possible “green” replacements for organic solvents mainly due to their nonmeasurable vapor pressure, which is only one criterion for a clean solvent. Commonly for organic pollutants in aqueous streams, oxidation is used to remediate the water. In this regard, but of significant interest for oxidation reactions in ILs, use of three common advanced oxidation processes (UV, UV/H₂O₂, and UV/TiO₂) has been used to analyze the degradation of 1,3-dialkylimidazolium ILs in aqueous solution.¹⁹⁸ Over a range of [C_{*n*}mim]Cl and [C_{*n*}mim][BF₄] ILs as well as [C₂C₂im][BF₄], the latter was found to be most stable in the photodegradation systems. Elongating the 3-methyl substituent of an imidazolium IL by one CH₂ group significantly decreases the degradability compared with the case of a methyl group substituted directly at the quaternary nitrogen. For –CH₃, the C–H bonds are much more polarized and, therefore, easier to break than the same system separated with a CH₂ group. Interestingly, in many cases, the ILs were much more stable with respect to oxidation than the methylimidazole standard.

4.1. ILs as a Media for Organic Oxidations

ILs have been used as a solvent for hydrogen peroxide oxidation processes, for example, for cycloaddition of CO₂ to epoxides,^{199–201} oxidation of 4-alkyl and 4-aryl-1,4-dihydropyridines to the corresponding pyridine,²⁰² as well as nucleophilic hydroxylation of alkyl halides and mesylates using water.²⁰³ In the latter case, selective hydroxylation of 2-(3-bromopropyl)naphthalene to 2-(3-hydroxypropyl)naphthalene was found with >90% yield using water/[C₄mim][BF₄] or water/[C₄mim][OTf] solvent with either 1,4-dioxane or acetone cosolvent. Scheme 18 illustrates a possible

Scheme 18. Reaction Mechanism for Formation of Acetoxypropyl naphthalene



A: hydrolysis of CH₃CN to acetic acid
 B: esterification of alcohol and acetic acid
 C: nucleophilic displacement of bromoalkane to acetoxyalkane

mechanism for formation of acetoxyalkane via two different reaction paths: esterification of alcohol via hydroxylation or nucleophilic acetoxylation of bromoalkane. Only the esterification reaction proceeded quantitatively, which lead to the conclusion that formation of acetoxyalkane resulted from esterification of the alcohol by acetic acid generated from hydrolysis of CH₃CN under acidic catalytic conditions via hydroxylation of bromoalkane. The oxidant has also been tethered to the IL. For example, Wang et al.²⁰⁴ synthesized an IL containing a carboxy group which can be used in organic oxidative synthesis after oxidizing it to a peracid. This IL was found to be particularly active using hydrogen sulfate as the counterion in order to increase its acidity. Using this system, carbonyl compounds were obtained from the oxidation of chain olefins and 1,2-cycloalkandiol from cycloalkenes.

In addition, a range of oxidation reagents has been supported by ILs. For example, 1-(4-diacetoxyiodobenzyl)-3-methylimidazolium tetrafluoroborate (Figure 7) was re-

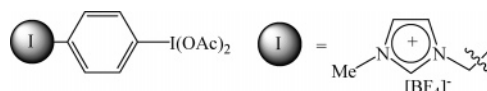


Figure 7. Schematic of 1-(4-diacetoxyiodobenzyl)-3-methylimidazolium tetrafluoroborate.

ported as an effective reagent in the selective oxidation of alcohols and *N*-alkyl-*N'*-arylthioureas;^{205,206} *o*-iodoxybenzoic acid in a solution of [C₄mim]Cl and water has been shown to result in excellent yields of the corresponding carbonyl compounds,^{207,208} and oxidation of alcohols to the corresponding carbonyl compounds occurred with Dess–Martin-periodinane supported in [C₄mim][PF₆] and [C₄mim][BF₄]²⁰⁹ or with chloroperbenzoic acid [C₄mim][BF₄] for formation of esters/lactones.²¹⁰

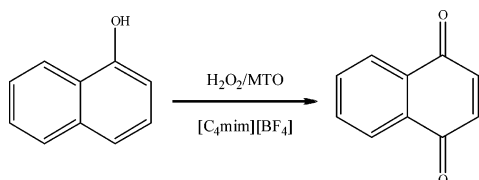
Efficient oxidation of various primary and secondary benzylic alcohols to the corresponding carbonyl compounds has also been achieved with other self-oxidation supported reagents, for example, *N*-bromosuccinimide and 2,6-lutidine

in $[\text{C}_4\text{mim}][\text{BF}_4]$,²¹¹ potassium permanganate,²¹² manganese dioxide,^{213,214} *N*-hydroxyphthalimide, and 3-pyridinylmethyl-*N*-hydroxyphthalimide. Using these reagents, better performance was found in the IL than in the conventional organic solvents for the aerobic oxidation of *N*-alkylamides to imides.²¹⁵

Cerium(IV) ammonium nitrate has been used in $[\text{C}_4\text{mim}][\text{BF}_4]$ to mediate oxidative radical C–C bond-forming coupling reactions between 1,3-dicarbonyls and α -methylstyrene.²¹⁶ The combination of bismuth(III)nitrate pentahydrate and a range of ILs, including tetrabutyl ammonium fluoride, has been found to be effective for oxidation of benzyl halides to form aldehydes.²¹⁷ Using this approach, Khodaei et al. demonstrated that a one-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones from benzyl halides was possible with yields up to 90%.

Methyltrioxorhenium(VII) (MTO) has been used in a range of ILs in conjunction with H_2O_2 for epoxidation of alkenes,^{218–220} oxidation of aromatic aldehydes/ketones to phenols,²²¹ and oxidation of phenol/methoxybenzene derivatives to benzoquinones (Scheme 19).²²² These reactions were

Scheme 19. Oxidation of 1-Naphthol to 1,4-Naphthoquinone Using a Hydrogen Peroxide/Methyltrioxorhenium System in $[\text{C}_4\text{mim}][\text{BF}_4]$



found to be highly efficient; for example, the benzoquinones were formed in good yields in $[\text{C}_4\text{mim}][\text{BF}_4]$ even in the case of the methoxybenzene derivatives. Moreover, after extraction of the products, the IL solution still showed catalytic activity.

The Baeyer–Villiger oxidation of cyclic ketones was achieved using the same methyltrioxorhenium/hydrogen peroxide system in $[\text{C}_4\text{mim}][\text{BF}_4]$.²²³ This oxidative methodology was tested on the methylated flavanones naringenin and hesperetin and showed that the catalytic system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ in IL is more efficient than CH_3ReO_3 supported on poly(4-vinylpyridine) polymers/ H_2O_2 in *tert*-butyl alcohol.

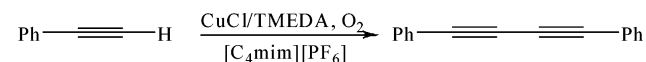
Cyclic hexaalkylguanidinium hexafluorophosphate with sodium hypochlorite as the oxidant has also been used for selective oxidation of a series of substituted benzyl alcohols. In this reaction, the room-temperature IL acts as both phase-transfer catalyst and solvent.²²⁴ ILs incorporating the oxidant in its structure have also been reported, for example, selenium-containing anions $[\text{SeO}_2(\text{OR}')^-]$ ($\text{R}' = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CF}_3, \text{C}_6\text{H}_5$)²²⁵ and liquid salts of Cr and Mo.²²⁶

4.2. Homogeneous Catalytic Oxidation in ILs

4.2.1. Glaser Oxidative Coupling

Terminal alkynes have been shown to undergo oxidative coupling in the presence of the CuCl –tetramethylethylenediamine catalytic system in $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$ under aerobic conditions to produce 1,3-diynes in excellent yields under mild conditions (Scheme 20). Therein, the

Scheme 20. Oxidative Coupling of Terminal Alkynes

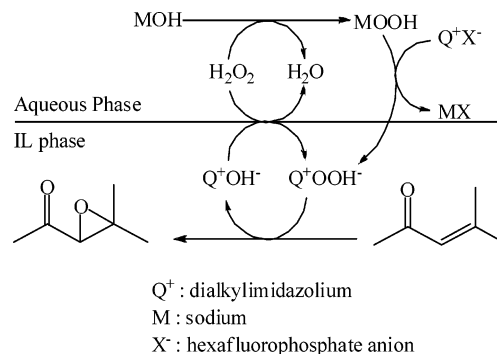


alkynes showed enhanced activity/conversion in ILs compared with methanol. For formation of 1,4-diphenyl-1,3-butadiyne 95% yield was obtained in $[\text{C}_4\text{mim}][\text{PF}_6]$ in 4.5 h compared with a 75% yield in 12 h in methanol.²²⁷

4.2.2. Epoxidation

Epoxidation reactions have been studied extensively in ILs. For example, Bortolini reported the quantitative epoxidation of electrophilic alkenes in both $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ using aqueous basic solutions of hydrogen peroxide as oxidant and NaOH as basic catalyst. Despite the differences in hydrophilicity of the ILs, similar yields were found.²²⁸ Epoxidation of electron-deficient, α,β -unsaturated carbonyl compounds in IL/water biphasic system using basic catalysis, Na_2CO_3 , NaHCO_3 , or NaOH , with hydrogen peroxide as an oxidant at room temperature has also been reported to occur with very high selectivities.²²⁹ A mass-transfer model was proposed for the epoxidation of α,β -unsaturated carbonyl compounds in the IL/ H_2O biphasic system, suggesting that, as in traditional organic solvent/ H_2O biphasic system, transport of OOH^- from the aqueous phase to IL initiates the cycle followed by the reverse transport of OH^- (Scheme 21). Importantly, transport of the cation of the IL is vital for the process to occur.

Scheme 21. Mass-Transfer Model of Epoxidation of Mesityl Oxide in the $[\text{C}_4\text{mim}][\text{PF}_6]/\text{H}_2\text{O}$ Biphasic System

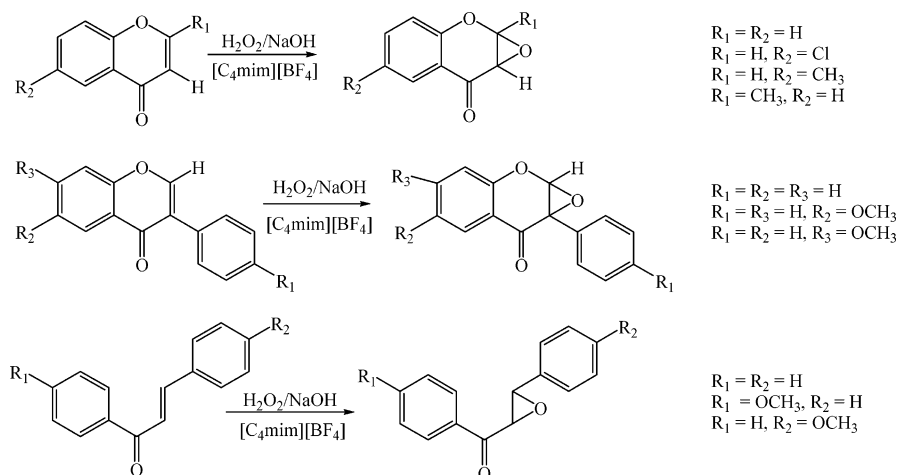


A similar system has been described by Bernini et al. for epoxidation of chromone, isoflavone, and chalcone derivatives using $[\text{C}_4\text{mim}][\text{BF}_4]$ as the solvent and alkaline hydrogen peroxide as oxidant (Scheme 22).²³⁰ All reactions proceed in good yields and faster than in conventional solvents with no evidence of products derived from the opening of the epoxide ring.

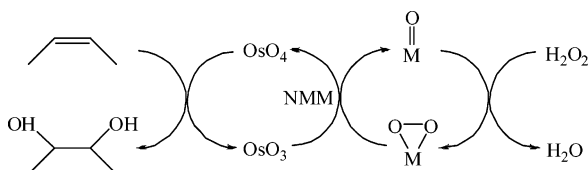
Development of epoxidation reactions in ILs is one of the few examples of the use of microchannel reactor technology using this media. Epoxidation of alkenes has been examined in a microreactor using electro-osmotic flow to pump the liquid.²³¹ Epoxidation of cyclohexene was performed using hydrogen peroxide in the presence of manganese(II) and copper(II) complexes of Schiff and reduced Schiff bases as catalysts and $[\text{C}_4\text{mim}][\text{BF}_4]$ as the IL. Although a comparison of the microfluidic system showed increased reactivity compared with a conventional batch reactor, the epoxide selectivity was low with 2-cyclohexen-1-ol being the major product.

4.2.3. Hydrocarbons to Other Oxygenated Compounds

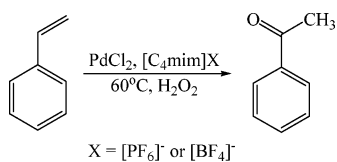
A range of hydrocarbons has been oxidized selectively to oxygenates using IL-mediated reactions. Using $[\text{C}_4\text{mim}][\text{PF}_6]$ to immobilize a bimetallic catalytic system consisting of

Scheme 22. Epoxidation of Chromone, Isoflavone, and Chalcone Derivatives Using [C₄mim][BF₄] as the Solvent and Alkaline Hydrogen Peroxide as the Oxidant


osmium tetroxide as the substrate-selective catalyst and VO(acac)₂ or MeReO₃ as cocatalyst, the dihydroxylation of alkenes in the presence of H₂O₂ occurred in high yield.²³² However, on addition of *N*-methylmorpholine (NMM), significantly higher activities were observed with the modifier increasing the electron-transfer process. The mechanism of the coupled bimetallic catalytic system as shown in Scheme 23 does not involve the IL, which only acts as a solvent in this case.

Scheme 23. Coupled Bimetallic Catalytic System for Dihydroxylation of Olefins Immobilized in an IL


In contrast, for the palladium-catalyzed Wacker H₂O₂ oxidation of styrene to acetophenone (Scheme 24), the [C_{*n*}mim]⁺-based ILs are thought to be cocatalysts.²³³ The reaction was performed in a closed reactor under a pressure of carbon dioxide or nitrogen to reduce the partial pressure of oxygen, which is responsible for the generation of benzaldehyde and benzoic acid, thus promoting the hydrogen peroxide oxidation pathway leading to an increased yield of acetophenone. The enhanced yield in the presence of the IL is thought to involve formation of an oxaziridinium ion-type intermediate involving an imidazolium cation. In addition, the imidazolium cation activates the H₂O₂ which, in turn, reoxidizes palladium(0) to palladium(II) to complete the reaction cycle.

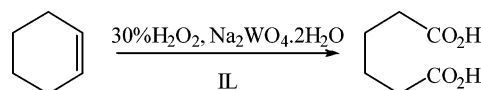
Scheme 24. Wacker Oxidation of Styrene to Acetophenone


Direct hydroxylation of benzene with hydrogen peroxide to form phenol has attracted much attention and been extensively investigated in molecular solvents.²³⁴ One of the challenges in selective oxidation reactions is to prevent overoxidation of the substrate as the desired intermediary

product is often more reactive than the original reactant. In order to overcome this problem, biphasic reactions can be performed whereby the phenol is removed from the reaction medium. Using equimolar amounts of benzene and hydrogen peroxide without organic solvent, the biphasic hydroxylation of benzene to phenol using H₂O₂ mediated by a separate IL phase has been reported. High conversions and selectivity were achieved using metal dodecanesulfonate salts such as ferric tri(dodecanesulfonate) as the catalyst.²³⁵

Manganese(III) porphyrin catalysts in combination with iodobenzene diacetate have been demonstrated for the oxidation of alkanes and alkenes in the presence of [C₄mim]-[PF₆].^{236,237} In the pure IL, oxidation of tetralin resulted in ketone formation with high conversion and yield; however, in a mixture with organic solvents (dichloromethane, acetonitrile, or 1,2-dichloroethane) alcohol products were also formed. In this mixed solvent system cyclohexane, cyclooctane, adamantane, and tetralin were oxidized with high ratios of alcohol to ketone. Furthermore, under the same conditions oxidation of alkenes (styrene, α -methylstyrene, cyclooctene, 1-decene, or 1,2-dihydronaphthalene) resulted in formation of the corresponding epoxides.²³⁸

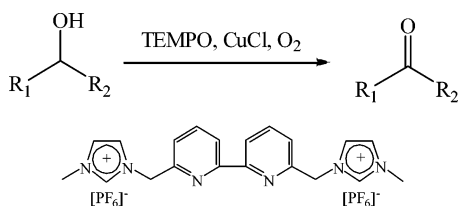
Direct catalytic oxidation of cyclohexene to adipic acid with hydrogen peroxide catalyzed by Na₂WO₄·2H₂O and acidic ILs has also been performed with excellent yields and selectivities with the catalyst easily reused (Scheme 25).²³⁹ Therein, only ILs with strongly acidic anions such as hydrogen sulfate or tosylate provided high conversions and selectivities.

Scheme 25. Direct Catalytic Oxidation of Cyclohexene to Adipic Acid

4.2.4. Alcohols to Carbonyl and Carbonyl to Carboxylate Compounds

Selective oxidation of alcohols to the corresponding aldehydes or ketones in an oxygen atmosphere has been studied using the TEMPO–CuCl system. In [C₄mim][PF₆], aerobic oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones was achieved without overoxidation to the corresponding carboxylic acids.²⁴⁰ The

catalytic activity of a TEMPO 2,2,6,6-tetramethylpiperidine-1-oxyl derivative radical bearing an IL-type appendage has also been examined for oxidation of the same group of alcohols under IL–aqueous biphasic conditions in the presence of NaOCl and KBr. Similar results were obtained under these conditions to the single-phase medium with the functionalized IL easily recycled and reused without loss of activity and selectivity.²⁴¹ In order to increase the recyclability of the catalyst, ILs have also been modified by incorporating a tethered 2,2'-bipyridine ligand which can complex with CuCl during the TEMPO-catalyzed oxidation reaction, thus immobilizing it more efficiently (Scheme 26).²⁴²

Scheme 26. Oxidation of Alcohols in ILs Incorporating a Tethered 2,2'-Bipyridine Ligand



Using a similar approach, aerobic oxidation of primary alcohols to aldehydes has been reported to be catalyzed by the three-component system acetamido–TEMPO/Cu(ClO₄)₂/DMAP and TEMPO/HBr/H₂O₂ in [C₄mpyr][PF₆]. Again, the reaction showed excellent yields to the corresponding carbonyl compounds.^{243,244}

The ruthenium catalyst tetrapropylammonium perruthenate has been used as a mild and selective catalyst for oxidation of alcohols to aldehydes and ketones in conjunction with either *N*-methylmorpholine-*N'*-oxide or molecular oxygen as oxidant in two different catalytic systems in a range of [C₄mim]⁺-based ILs.²⁴⁵ As is commonly observed in oxidations, benzylic alcohols showed a faster rate of reaction and higher yields compared with aliphatic alcohols even after extended reaction times.

Oxidation of benzyl alcohol to benzaldehyde has also been investigated using Pd(OAc)₂ dissolved in a range of 1,3-dialkylimidazolium-based ILs with oxygen as the oxidant. As found with many palladium salts, dissolution requires heating which thermally decomposes the palladium salt resulting in formation of palladium metal.⁵³ Although better TOFs were observed in the IL compared with in dimethyl sulfoxide, the catalyst is likely to be different in each case.²⁴⁶ Where chloride was present in the IL, the selectivity to benzaldehyde dropped with formation of dibenzyl ether. Addition of water was found to increase the amount of benzoic acid formed; however, as shown in many reactions, the influence of water is much weaker in ILs than would normally be expected. Oxidation of toluene and ethylbenzene was also demonstrated but with very low yields.

The aerobic oxidations of aliphatic and aromatic alcohols into the corresponding aldehydes and ketones have also been efficiently performed with several ruthenium catalysts in various ammonium salts under low oxygen pressure and without any cocatalyst.²⁴⁷

Aerobic oxidation of 2,3,6-trimethylphenol to trimethyl-1,4-benzoquinone and 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone with high yield using copper(II) chloride as catalyst has been demonstrated using a solvent mixture of [C₄mim]Cl and *n*-butanol.^{248,249} Little influence of the cation was found on either the catalytic activity or selectivity, with

the major advantage of the system being that catalytic amounts of copper(II) chloride may be used. In this case an oxotetracuprate [Cu₄(μ₄-O)Cl₁₀]⁴⁻ complex was isolated as the active species.

Chhikara et al. have recently shown that the complex salt [C₄mim]₃[PO₄(W(O)(O₂)₂)₄] dissolved in [C₄mim][BF₄] is highly active for oxidation of alcohols using hydrogen peroxide.²⁵⁰ Secondary alcohols were converted using this system to their respective ketones in good to excellent yields. Whilst oxidation of primary alcohols did result in the corresponding aldehydes and carboxylic acids, this occurred with slower reaction rates. Using a similar approach, selective oxidation of benzylic and secondary alcohols with hydrogen peroxide has also been shown to be catalyzed using [C₄mim]₃[PO₄(W(O)(O₂)₂)₄].²⁵¹

Several aromatic aldehydes have been oxidized to the corresponding carboxylic acids using the catalyst [Ni(acyl)₂] and oxygen at atmospheric pressure as the oxidant in [C₄mim][PF₆].²⁵² However, in this case the carboxylic acid yields were smaller than those found in molecular solvents.²⁵³

4.2.5. Oxidation of C=NOH Bonds

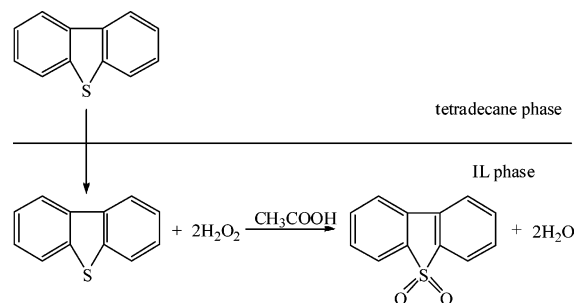
Water-soluble iron(III) porphyrins and phosphotungstic acid are effective catalysts for the H₂O₂-mediated oxidation of the C=NOH bond in *N*-hydroxyarginine and other oximes in [C₄mim][BF₄].²⁵⁴ In this case, the ionic environment was thought to stabilize the reactive intermediate in a similar manner as found for manganese(III) porphyrins-catalyzed oxygenation reactions.²⁵⁵

4.2.6. Oxidation of Thiols

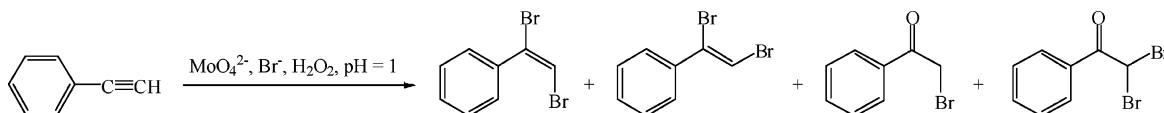
Coupling of thiols to disulfides at room temperature using oxygen has been shown to be catalyzed by cobalt(II) phthalocyanines dissolved in [C₄mim][BF₄].²⁵⁶ As in many other cases, catalyst solubility, recycling, and easy product isolation represent the main advantages of using ILs.

Of greater commercial importance is the oxidation reaction of thiols to sulfones, for example, in the removal of sulfur-containing compounds from light oils. Using a combination of chemical oxidation and solvent extraction with [C₄mim]-[PF₆] and [C₄mim][BF₄], a one-pot process has been reported by Lo et al.²⁵⁷ Therein, the sulfur-containing compounds were extracted into the IL and oxidized using H₂O₂ and acetic acid as the catalyst, forming the corresponding sulfones (Scheme 27). The IL acts as both the extraction medium for the organosulfur compounds as well as the oxidation solvent. The process is controlled by the anion with the yields using [PF₆]⁻ found to be greater than those found in the presence of [BF₄]⁻.

Scheme 27. Oxidation of Thiols to Sulfones in Biphasic Tetradecane–IL Conditions



Scheme 28. Mo(VI)-Catalyzed Oxybromination of Phenylacetylene with Hydrogen Peroxide and KBr



4.2.7. Oxybromination

Oxybromination of phenylacetylene has been shown to be catalyzed by molybdenum(VI) with hydrogen peroxide as oxidant and potassium bromide as source of bromine in a two-phase water/solvent system, where solvent was either dichloromethane or an IL (Scheme 28).²⁵⁸ Using [C₄mim][PF₆] or [C₄mim][NTf₂], increased yields and reaction rates were observed compared with DCM with complete conversion of the substrate forming, importantly, α -bromoacetophenone and α,α -dibromoacetophenone as the major products. Similarly, oxybromination of styrene has been performed using vanadium(V) as catalyst.²⁵⁹ A range of ILs was studied with the anion found to control the reaction selectivity. The selectivity is thought to be associated with the structure of the IL, allowing an initially high concentration of the active species to form in the IL phase. The reaction between the bromiranium species, formed upon reaction of the vanadium-bound hypobromite intermediate and the substrate, with a vanadium-coordinated molecule of water to form the bromohydrin is enhanced by slow diffusion in the IL leading to the higher reaction rates and selectivity.

Bromination of substituted alkenes has been reported to occur in [C₄mim][CCl₃COO], [C₄mim][CF₃COO], and [C₂mim][BF₄] involving oxidation of NaBr by hydrogen peroxide in the presence of H₂SO₄ with no other catalyst.²⁶⁰ Although thermodynamically powerful, H₂O₂ is kinetically a slow oxidant for the halide salts and halogenations must typically be catalyzed for halogenation reactions to occur on a useful time scale. Yields of between 70% and 95% were obtained for a range of alkenes and alkynes; however, if [C₂mim][BF₄] is used, Ph-OMe bonds are cleaved. Furthermore, the reactions in the ILs showed high stereoselectivities with, for internal alkenes, erythro–threo ratios (trans–cis addition products) larger than 99:1.

4.3. Homogeneous Asymmetric Catalytic Oxidation in ILs

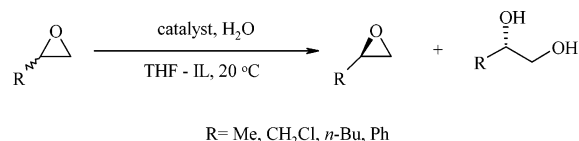
Although less extensively studied than asymmetric hydrogenation, asymmetric oxidations have also been performed in ILs. For example, the Sharpless catalytic asymmetric dihydroxylation of olefins, which represents a route for the synthesis of a wide range of enantiomerically pure vicinal diols, has been demonstrated in water/IL or water/IL/*tert*-butyl alcohol solvent mixtures.^{261,262} By immobilizing the osmium complex catalyst in the IL phase, a series of alkenes (hex-1-ene, styrene, β -methyl-*trans*-styrene, methylcyclohexene, 1,2-diphenylethene, 1,2-dibutylethene) was oxidized selectively (ee > 80%) and high yields obtained using either a biphasic [C₄mim][PF₆]/water or monophasic [C₄mim][PF₆]/water/*tert*-butyl alcohol solvent. This methodology has been extended to the use of scCO₂ in the separation process, thus eliminating the need for organic solvents either in the reaction or during the workup process. The final diol was isolated without any contamination with osmium.²⁶³ Asymmetric dihydroxylation of methyl *trans*-cinnamate leading to *N*-benzoyl-(2*R*,3*S*)-3-phenylisoserine, an important unit of the C-13 side chain of the taxol

(paclitaxel) family for antitumor activity, has also been reported to occur with very high yields and ee's (90–97%) using the equivalent system with a range of [PF₆][−], [BF₄][−], and [NTf₂][−]-based 1,3-dialkylimidazolium-based ILs.²⁶⁴ Asymmetric dihydroxylation of alkenes using *N*-methylmorpholine oxide as a co-oxidant with osmium tetroxide and a combination of an IL and a bis-cinchona alkaloid also showed good catalyst recyclability and selectivity for *trans*-stilbene, styrene, β -methyl-*trans*-styrene, and methyl *trans*-cinnamate.²⁶⁵ Importantly, overoxidation of the diols, commonly found in molecular solvents, was not observed in the presence of the IL.

4.4. ILs in Kinetic Resolution Reactions

Hydrolytic kinetic resolution of racemic epoxides, using Jacobsen's complex ((salen)Co(III)(OAc)) as a catalyst, is one of the most practical approaches toward the preparation of enantiopure terminal epoxides.²⁶⁶ In the presence of 1,3-dialkylimidazolium-based [PF₆][−] and [NTf₂][−] ILs, the chiral Co(III)(salen) complex catalyzed the hydrolytic kinetic resolution of racemic epoxides and diols with ee's between 85% and 100% (Scheme 29). Importantly, the IL allowed

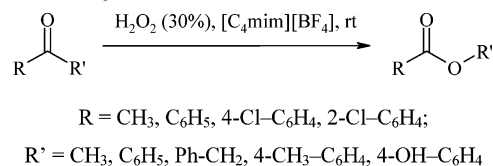
Scheme 29. Hydrolytic Kinetic Resolution of Racemic Epoxides



the Co(II)(salen) complex to be oxidized without acetic acid to form the active Co(III)(salen) complex during reaction. In addition, the Co(III) state was stable with respect to reduction, enabling the reuse of the catalyst without a reoxidation process.²⁶⁷ Interestingly, the catalytic activity of the recovered IL phase increased upon reuse, which was thought to be due to an increase in the concentration of catalytically active Co(III) complex.

4.5. Heterogeneous Catalytic Oxidation in ILs

A range of heterogeneously catalyzed oxidations has been performed in ILs. For example, a Sn- β molecular sieve has been shown to catalyze the Baeyer–Villiger oxidation of aryl ketones to esters in IL at room temperature (Scheme 30).²⁶⁸ The reaction occurred with high yields for a variety of aryl ketones with 30% aqueous hydrogen peroxide in [C₄mim][BF₄]. Therein, the active species was thought to

Scheme 30. Baeyer–Villiger Oxidation of Aryl Ketones to Esters Using Sn- β Molecular Sieve as the Catalyst

be the tetrahedral Sn- β framework and not SnO₂ occluded in the material.

Heterogeneous catalytic oxidation of a series of thioethers (2-thiomethylpyrimidine, 2-thiomethyl-4,6-dimethyl-pyrimidine, 2-thiobenzylpyrimidine, 2-thiobenzyl-4,6-dimethylpyrimidine, thioanisole, and *n*-heptyl methyl sulfide) has been studied extensively in a wide range of ILs using MCM-41- and UVM-type mesoporous catalysts containing Ti or Ti and Ge.²⁶⁹ The oxidations were carried out using anhydrous hydrogen peroxide or the urea–hydrogen peroxide adduct and showed that ILs are very effective solvents, achieving greater reactivity and selectivity than reactions performed in dioxane. The effects of halide and acid impurities on the reactions were also investigated. This study highlighted the importance of how the IL is prepared and whether acid or salt metathesis was used. Even with trace concentrations of acid, the reaction rate was found to increase substantially. Therefore, to investigate the IL effect, salt metathesis for the triflate-based ILs was used. Although the catalyst was able to be recycled, some titanium leaching was observed in the ILs; however, this was greatly reduced compared with a pure organic media. Other heterogeneous catalysts also proved to be effective for oxidation of these substrates. Ta₂O₅–SiO₂ catalysts prepared by a sol–gel method using tetraethyl orthosilicate and tantalum(V) ethoxide as the sources of silicon and tantalum and two families of quaternary ammonium salts [N_{111n}]⁺Br[−] (*n* = 14, 16, 18) and [N_{nnnn}]⁺Br[−] (*n* = 10, 12, 16, 18) as surfactants were found to be effective for the selective sulfoxidation of 4,6-dimethyl-2-thiomethylpyrimidine using peroxide as an oxidizing agent in a range of ILs.²⁷⁰ Remarkably, these catalysts exhibited excellent stability against leaching in IL. Almost no leaching was also found for Ti-SBA-15 and UL-TS-1 catalysts for the same reaction.²⁷¹ For the Ta₂O₅–SiO₂ sol–gel catalysts, some correlations were found between the Kamlet–Taft parametrization of the IL and conversion of sulfide to sulfone.²⁷² Therein, conversion was found to increase with the solvent parameters α , the hydrogen-bond-donor ability, but decrease with π^* , dipolarity/polarizability, and β , the hydrogen-bond-accepting ability. Interestingly, the molecular solvents examined showed a similar trend. For these reactions, the IL cation is thought to hydrogen bond to the surface of the catalyst, thus activating the peroxide (Figure 8).

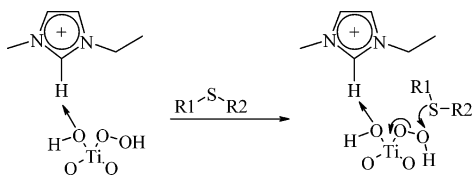


Figure 8. Schematic illustrating the mechanism by which the IL cation activates peroxide during oxidation of thioethers.

To date, although there have been many reports of reactions in ILs, the chemical engineering data concerning mass transport has been limited. As found with 3-phase hydrogenation reactions,^{177,179,180} although it was possible to oxidize cinnamylalcohol selectively using a Pd/Al₂O₃ catalyst in [C₄mim][NTf₂], a decrease in activity was observed compared with toluene.²⁷³ Again, using the combination of a stirred tank reactor and a rotating disc reactor (Figure 6), the mass-transfer limitations in this reaction were studied in detail and the loss in rate was ascribed to pore diffusion limitation in the IL compared with toluene.

Polymer-supported active species represents another category of heterogeneous catalysts tested in oxidation reactions in ILs. For example, complexation of the polymer carriers with copper(II) acetate leads to the heterogenized catalysts with immobilized copper.²⁷⁴ Their catalytic activity was measured in the model oxidation reaction of hydroquinone to *p*-benzoquinone using hydrogen peroxide. The catalysts were tested in the presence of [C₄mim][BF₄] leading to superior selectivities as compared with molecular solvents. A range of variables such as the ion-exchange groups after sorption, Cu(II) loading, method of modification, and IL concentration were reported to influence the activity of the system.

4.6. Electrochemical Oxidation in ILs

The superoxide ion (O₂^{•−}) has been studied extensively due to its use as a highly active oxidation species. Al Nashef et al.²⁷⁵ have shown that this radical can be easily generated electrochemically from oxygen dissolved [C₄mim][PF₆] at atmospheric pressure. Under these conditions a range of electrochemical oxidations has been performed in ILs. Under an oxygen atmosphere, phenol and 4-*tert*-butyl-phenol in [C₂mim][NTf₂] and [C₄mpyrr][NTf₂] have been shown to be converted to the corresponding phenyl triflate molecule.²⁷⁶ This was found to occur on formation of O₂^{2−} dianions, which triggered transformation of the phenol to phenolate and then to the phenoxyl radical. The phenoxyl radical then reacts with the [NTf₂][−] anion of the IL. Electro-oxidation of benzyl alcohol has also been conducted in an IL/supercritical CO₂ two-phase system using an undivided cell with a Pt working electrode.²⁷⁷ Using [C₄mim][BF₄] and [C₄mim][PF₆], it was found that benzyl alcohol could be selectively oxidized to benzaldehyde with the aldehyde selectivity highest when the pressure of CO₂ was lower than ~9.3 MPa. This observation was attributed to an optimization of the solubility difference between the reactants and products.

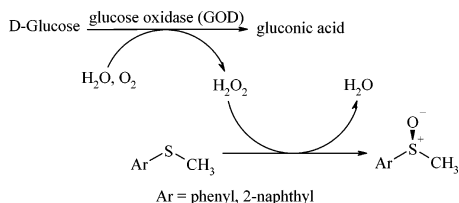
Electro-oxidation of bromide in acetonitrile and [C₄mim][NTf₂] using a platinum electrode has also been examined.²⁷⁸ Therein, formation of tribromide was reported via electro-oxidation of bromide to bromine followed by chemical reaction of bromine with bromide. The reactivity of electrogenerated bromine with cyclohexene showed two different products in acetonitrile and [C₄mim][NTf₂].²⁷⁹ Bromination of the substrate in the IL yielded *trans*-1,2-dibromocyclohexane, while in acetonitrile, *trans*-1-(*N*-acetylamino)-2-bromocyclohexane was formed as the major product.

The electrochemical oxidation of anisole, mesitylene, naphthalene, and anthracene has been performed in a wide range of ILs with formation of anodic dimerization products.²⁸⁰ Under similar conditions, using 1,2-dimethoxybenzene as the substrate, polyveratrole was formed in which the morphology was dependent on the IL used in the electrolysis. Electrooxidative polymerization of aromatic compounds such as pyrrole, thiophene, and aniline has also been carried out using a Pt electrode in [C₂mim][OTf].²⁸¹ Again, the IL was able to control the morphological structure of the polypyrrole film formed on the anode and improve the electrochemical capacity and conductivity. Although rates of polymerization were found to increase in the IL for pyrrole and thiophene, the polymerization rate of aniline was found to decrease compared with molecular solvents.

4.7. Biooxidation in ILs

There is strong evidence showing that hydrophilic, functionalized ILs can effectively act as solvents for both chemical and biological homogeneous catalysts for oxidation reactions. For example, Sheldon and co-workers reported the epoxidation of cyclohexene in IL with a peracid formed through perhydrolysis carried out by *Candida antarctica* lipase.²⁸² The high stability of oxidase and peroxidase as catalysts in ILs under reaction conditions has also been demonstrated for the chemo- and stereoselective oxidation of sulfides.²⁸³ In this case, both the substrate of glucose oxidase (glucose) and peroxidase (sulfide) are soluble in [C₄mim][PF₆], and the biphasic reaction, in the presence of water, occurred with a stereoselectivity similar to that obtained in water (Scheme 31). This methodology was of

Scheme 31. Enzymatic Chemo- and Stereoselective Oxidation of Sulfides

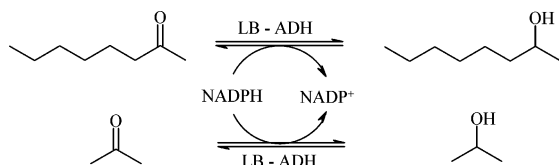


particular interest for water-insoluble molecules, e.g., methyl-2-naphthyl sulfide which was oxidized with an ee of 92%. In water the proteins induce formation of an emulsion with the organic product making separation difficult; this does not occur in the presence of the IL.

The oxidation has also been demonstrated by chloroperoxidase from *Caldariomyces fumago*, which catalyzes the stereoselective oxidation of 1,2-dihydronaphthalene to (1*R*,2*R*)-(+)-dihydroxytetrahydronaphthalene in homogeneous citrate buffer/[C₁mim][MeSO₄] or [C₄mim][MeSO₄] mixtures using *tert*-butyl hydroperoxide as the oxidant.²⁸⁴ The enzyme was found to tolerate up to 30 vol % while maintaining the enzyme activity for 24 h. In comparison, for nonionic organic solvents such as *tert*-butyl alcohol or acetone, the activity dropped after 3 h.

Biphasic systems containing [C₄mim][NTf₂] and a buffer have also shown higher activity for the enantioselective reduction of 2-octanone, catalyzed by an alcohol dehydrogenase from *Lactobacillus brevis*, compared with the analogous system using methyl *tert*-butyl ether.²⁸⁵ This is thought to be due to the difference in the partition coefficient in the two solvent systems (Scheme 32).

Scheme 32. Enantioselective Reduction of 2-Octanone, Catalyzed by an Alcohol Dehydrogenase from *Lactobacillus brevis*



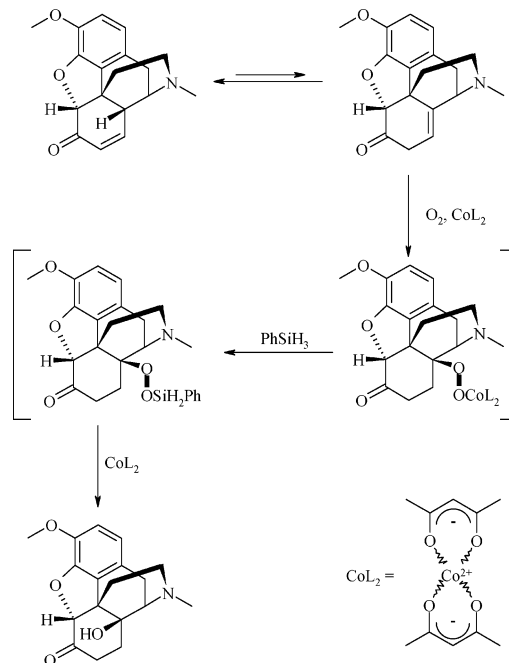
The tolerance of oxidative enzymes to IL is high for many systems. For example, laccase *C* from *Trametes* sp. and horseradish and soybean peroxidases have been shown to be active in the presence of between several volume percent to almost 100% IL.²⁸⁶ Therein, oxidation of syringaldazine catalyzed by laccase *C* from *Trametes* sp. was found not to

require the presence of mediators using the ILs; however, as found with organic solvents, the catalytic activity of the enzymes was decreased by either adding a water-miscible IL, e.g., [C₄mpyr][BF₄], or suspending the enzyme in a water-immiscible IL, e.g., [C₄mim][PF₆]. In contrast, for oxidation of anthracene, catalyzed by laccase *C*, in the presence of mediators, replacement of *tert*-butyl alcohol with [C₄mpyr][BF₄] increased the yield of the oxidation product severalfold. A significant enhancement of the activity, as well as providing excellent thermal stability of horseradish peroxidase, was reported following its immobilization in a [C₄mim][BF₄]-based sol-gel matrix.²⁸⁷

The presence of an IL has also been shown to be of benefit by reducing the activity of water. By addition of [C₁mim][MeSO₄], the β -galactosidase from *Bacillus circulans* catalyzed synthesis of *N*-acetylglucosamine from lactose and *N*-acetyllactosamine in a transglycosylation reaction is improved by reducing the hydrolysis of product, resulting in a doubling of the yield.²⁸⁸

Chemo-enzymatic processes have been achieved using ILs. For example, in [C₄mim][PF₆], Walker and Bruce demonstrated the conversion of codeine to oxycodone using a combination of morphine dehydrogenase and its associated nicotinamide cofactor, which forms neopinone followed by use of bis(acetylacetonato)cobalt (II) catalysis, for the subsequent hydration of the double bond (Scheme 33).²⁸⁹ Unfortunately, the biological component is inhibited by the chemical catalyst, thus preventing this occurring under one-pot conditions.

Scheme 33. Conversion of Codeine to Oxycodone Using a Combination of Morphine Dehydrogenase and Its Associated Nicotinamide Cofactor



The ability of hemin, microperoxidase-11, and cytochrome *c* to oxidize 2-methoxyphenol (guaiacol) has been investigated in [C₄mim][NTf₂], [C₄mim][PF₆], and [C₈mim][PF₆].²⁹⁰ All three biocatalysts displayed peroxidase activity when activated by an electron acceptor; *tert*-butyl hydroperoxide for hemin and hydrogen peroxide for microperoxidase-11 and cytochrome *c*. However, some differences were found between these protoporphyrins. Hemin required the addition

of a coordinating base, pyridine or *N*-methylimidazole, to produce an active complex, while cytochrome *c* did not require exogenous ligands for activity in IL, although their addition increased peroxidase activity. Hemin and microperoxidase-11 showed markedly higher activities in the IL compared to molecular solvents, while the cytochrome *c* activity was comparable for both solvents types.

5. Acid–Base-Catalyzed Reactions in ILs

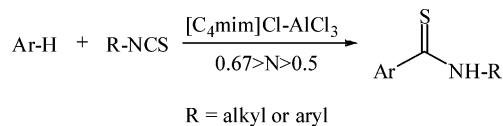
5.1. Acid-Catalyzed C–C and C–X Bond-Forming Reactions

Friedel–Crafts processes were among the first reactions to be studied using ILs and have been shown to be particularly effective in the first-generation ILs based on the chloroaluminate anion.¹ Boon et al. reported the alkylation and acylation of benzene with a range of alkylhalides and acetylchloride in [C₂mim]Cl–AlCl₃ mixtures at room temperature. Reaction was only observed where the melt became Lewis acidic, i.e., in excess AlCl₃, and multiple alkylation products were observed. Using an analogous system, Adams et al. showed that excellent regioselectivities could be obtained by employing the [C₂mim]Cl–AlCl₃ IL for the reaction of acetyl chloride with toluene, chlorobenzene, and anisole.²⁹¹ This has continued with both the common Lewis acid anions ([Al₂Cl₇][−], [Al₃Cl₁₀][−]) being employed as well as protic anions such as [HX₂][−], [XH(AIX₄)][−], and [XH(Al₂X₇)][−]. Xiao et al. have shown that by judicious choice of the halide, X, and the type of anion employed, a range of selectivities between alkane cracking, alkene polymerization, and Friedel–Crafts alkylation of aromatics with alkenes can be effected.²⁹² For example, using [Al₂Cl₇][−], alkanes may be cracked but react slowly but alkenes polymerize rapidly. In contrast, use of a protic anion such as [HCl(Al₂Cl₇)][−] results in much increased activity toward alkane cracking and alkenes polymerization. Protic ammonium salts combined with AlCl₃ have also been reported for the alkylation of α -methyl-naphthalene using long-chain olefins and compared directly with zeolites, AlCl₃ and FeCl₃.^{293,294} Rapid reaction was found for the [EtNH₃]Cl–AlCl₃ using excess AlCl₃ equivalent to that found using AlCl₃ in cyclohexene at 353 K; in both cases between 90% and 100% selectivity for monoalkylation was observed. Although good conversion was also achieved using zeolites, much higher temperatures were required. Similarly, alkylation of benzene with 1-dodecene has been performed using [C₇mim]X–AlCl₃ binary ILs (X = Cl, Br, I).²⁹⁵ Interestingly, by changing X, the Lewis acidity of the [Al₂Cl₆X][−] was varied, and with X = Br, the best catalytic performance was found.

A wide range of substrates has been examined using chloroaluminate-catalyzed Friedel–Crafts reactions. For example, aryl keto acids have been prepared using [C₄mim]Cl–AlCl₃-catalyzed acylation and arylation of aromatic substrates using cyclic acid anhydrides with good yields with the exception of nitrobenzene.²⁹⁶ Friedel–Crafts reactions using chloroaluminate ILs have also been performed between PCl₃ and benzene to form dichlorophenylphosphine.^{297–299} The binary ILs, [Et₃NH]Cl–AlCl₃, [N₄₄₄₄]Br–AlCl₃, and [C₄pyr]Cl–AlCl₃, gave yields of the desired product up to 68% depending on the binary mixture chosen and the ratio of PCl₃ to benzene employed, which may be compared with yields of 25% using AlCl₃ in the conventional process. After extraction with petroleum ether, the IL could be reused albeit with a small drop in yield. Coupling of aromatics and

isothiocyanates has also been reported using [C₄mim]Cl–AlCl₃ with 2 mol equiv of the IL to the reactants found to be optimum for the process (Scheme 34).³⁰⁰

Scheme 34. Lewis-Acid-catalyzed Coupling of Aromatics and Isothiocyanates



As well as chloroaluminate-based ILs, use of strong Lewis acids dissolved in second-generation ILs has been reported for Friedel–Crafts acylation reactions. In *N*-alkylpyridinium-based ILs, acylation of a range of aromatics using acetic anhydride has been observed with both FeCl₃ and AlCl₃³⁰¹ as well as alkylation of benzene with alkylhalides.³⁰² For both alkylation and acylation reactions, [BF₄][−] and [CF₃COO][−]-based ILs were found to be effective with the latter, in general, showing higher conversions. Surprisingly, some reaction was found between acetic anhydride and benzene, toluene, and bromobenzene even in the absence of the Lewis acid as well as between benzene and 1-chlorobutane/1-bromopropane. The reactions were run biphasically, and it was shown that the IL and FeCl₃–IL system could be recycled without loss in activity for the reaction between acetic anhydride and benzene or benzene and 1-chlorobutane. Baleizão et al. compared haloaluminate ILs with AlCl₃ dissolved in [C₅mim][BF₄] and [C₅mim][PF₆] for dealkylation of methyl dehydroabietate and acylation of methyl dehydroabietate with acetyl chloride.³⁰³ In these reactions, although the binary ILs showed good activity, dissolution of AlCl₃ in the non-halide based ionic liquids only showed significant activity with a large excess of the Lewis acid dissolved in [C₅mim][BF₄]. No reaction was observed on dissolving AlCl₃ in [C₅mim][PF₆].

Binary ILs have also been synthesized using FeCl₃,³⁰⁴ InCl₃,^{305,306} and ZnCl₂³⁰⁷ as the Lewis acid. Using [C₄mim]Cl–ZnCl₂ as the IL and catalyst, the Friedländer condensation between amino aromatic ketones and dicarbonyls was performed at room temperature with yields above 60%. This methodology was also extended to formation of quinones from furan derivatives. Unlike many chloroaluminate systems, these ILs were reusable.

In the case of [C₄mim]Cl–InCl₃ and InCl₃ dissolved in [C₄mim][NTf₂], a range of activated and deactivated aromatic substrates was found to be acylated with anhydride or acid chloride reagents showing higher activity compared with InCl₃ dissolved in the reagents or 1,2-dichloroethane.³⁰⁵ Therein, the IL is hydrolytically stable and could be dissolved in water to allow separation from the reaction mixture and reuse on dehydration. A small decrease in activity was observed on recycle, which was thought to be associated with mechanical losses on work up. For [C₄mim]Cl–ZnCl₂ the reaction was extracted with diethyl ether and reused without further purification and with only a small loss in yield on the second and third reactions.

Transition-metal/rare earth metal triflates and bis(trifluoromethylsulfonyl)imides have been used extensively for carbon–carbon bond-forming reactions in ILs. For example, Gordon and Ritchie have shown that Sc(OTf)₃ is a highly efficient catalyst for the allylation of 2-methoxyhexanone and benzoin methyl ether using tetraallyltin system.³⁰⁸ In this case, the catalyst increased the rate of reaction and also improved the stereoselectivity. M(OTf)_x (M = Sc, In, Hf, Y, Yb, Lu)

dissolved in $[\text{C}_4\text{mim}][\text{SbF}_6]$ have been used to catalyze the alkenylation of a range of arenes with alkynes, for example, benzene by 1-phenyl-1-propyne, at 85 °C.³⁰⁹ In the latter reaction, yields above 80% were obtained in 1–24 h depending on the catalyst. For comparison, using $\text{Sc}(\text{OTf})_3$ in the presence of the IL resulted in 91% yield in 4 h, whereas only 27% yield was found in 96 h in the absence of solvent. A wide range of other metal triflate salts, for example, $\text{Ag}(\text{OTf})$, $\text{Cu}(\text{OTf})_2$, and $\text{Zn}(\text{OTf})_2$, were also reported but showed much lower activity. Decantation of the products allowed the catalyst/IL mixture to be readily recycled. Using this approach, acylation of 1-methylpyrrole with acid anhydrides or acylchlorides has been reported using $\text{Yb}(\text{OTf})_3$ in $[\text{C}_4\text{pyr}][\text{BF}_4]$.³¹⁰ Similar yields were found in the IL compared with CH_3NO_2 or CH_2Cl_2 , albeit with increased reaction rates. $\text{Zn}(\text{NTf}_2)_2$ and $\text{Co}(\text{NTf}_2)_2$ have been shown to be active for the acylation of chlorobenzene with benzoyl chloride and *m*-xylene with benzoic acid in $[\text{C}_4\text{mim}][\text{NTf}_2]$ with the cobalt salt showing the higher activity.³¹¹ A comparison of the acylation of toluene with benzoyl chloride in the presence or absence of $[\text{C}_2\text{mim}][\text{NTf}_2]$ showed that reaction rates increased dramatically when the IL was used in combination with $\text{Co}(\text{NTf}_2)_2$ or $\text{Ni}(\text{NTf}_2)_2$.

Anjaiah et al. reported the use of $\text{Yb}(\text{OTf})_3$ for the carbon–Ferrier rearrangement of triacetyl glucal with allyl silanes, propargyl silane, and silyl enoethers in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{NTf}_2]$.³¹² In both ILs, the corresponding C-glycosides were formed with reasonable yields and stereoselectivities typically above 95%. Similarly, $\text{Yb}(\text{OTf})_3$ has been used in $[\text{C}_4\text{mim}][\text{PF}_6]$ to react carbonyl groups with 2-mercaptoethanol to prepare 1,3-oxathiolanes.³¹³ For a wide range of carbonyl compounds, yields between 72% and 98% were achieved at room temperature.

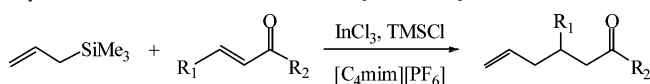
Bismuth salts and oxides have also been used for Friedel–Crafts acylation reactions in ILs.³¹⁴ An increase in conversion was observed on dissolving Bi_2O_3 and $\text{Bi}(\text{OTf})_3$ in a $[\text{NTf}_2]^-$ -based IL compared with the solventless reaction for the reaction of anisole and toluene with benzoyl chloride at 80 and 150 °C, respectively. Interestingly, good conversion was only obtained in $[\text{NTf}_2]^-$ - and $[\text{PF}_6]^-$ -based ILs with little reaction found in ILs with either $[\text{OTf}]^-$ or $[\text{BF}_4]^-$.

Despite the extensive use of these salts as catalyst, the exact nature of the catalytic species has not been studied in detail in many cases. However, the detailed kinetics of the $\text{In}(\text{OTf})_3$ -, $\text{Sc}(\text{OTf})_3$ -, and $\text{Al}(\text{OTf})_3$ -catalyzed acylation of anisole with benzoic anhydride in $[\text{C}_4\text{mim}][\text{NTf}_2]$ has been reported by Goodrich et al.³¹⁵ Using a combination of kinetic modeling and NMR it was shown that the reaction is consistent with a ligand-exchange reaction between the metal salt, benzoic anhydride, and the IL, resulting in formation of a free acid which acts as the catalyst.

5.1.1. Sakurai Reaction

Several α,β -unsaturated ketones underwent the Sakurai reaction with allyltrimethylsilane in the presence of InCl_3 using $[\text{C}_4\text{mim}][\text{PF}_6]$ or $[\text{C}_4\text{mim}][\text{BF}_4]$ as the solvent (Scheme 35).³¹⁶ InCl_3 was a more effective catalyst in either of these two ILs than in the normal solvent of choice, CH_2Cl_2 .

Scheme 35. Sakurai Coupling Reaction between α,β -Unsaturated Ketones with Allyltrimethylsilane

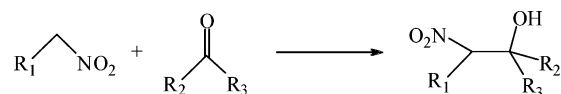


However, the choice of IL had little influence on yields of the δ,ϵ -unsaturated ketone product.

5.1.2. Henry Reaction

Henry reactions can be accelerated in chloroaluminate ILs.³¹⁷ The chloroaluminates with higher compositions of organic species of the chloroaluminates prove to be more efficient rate promoters than the ones with lower organic species in catalyzing Henry reactions, involving both aliphatic and aromatic carbonyl compounds. The exact IL used was found to influence the yields obtained with $[\text{C}_2\text{mim}]\text{Cl} \geq [\text{C}_4\text{pyr}]\text{Cl} \geq [\text{C}_4\text{mpyr}]\text{Cl} \geq [\text{C}_4\text{mim}]\text{Cl}$. The 1,1,3,3-tetramethyl guanidine (trifluoroacetate and lactate)-based IL was also reported as a recyclable catalyst for Henry reactions to produce 2-nitroalcohols (Scheme 36).³¹⁸ The catalyst can be applied to both aromatic and aliphatic aldehydes.

Scheme 36. Henry Reaction to Produce 2-Nitroalcohols



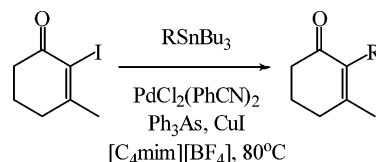
5.1.3. Carbonyl Allylation of Aldehydes and Ketones

In $[\text{C}_4\text{mim}][\text{BF}_4]$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ acts as an efficient catalyst for carbonyl allylation.³¹⁹ By applying IL, the need for the presence of a second cation or ultrasonic radiation, typically associated with the SnCl_2 -mediated allylation reaction, was avoided. Furthermore, ketones, which are less reactive than aldehydes, were found to be allylated in high yields with this system. Due to the strong electron-donating effect, allylation of anisaldehyde failed. *n*-Butanal also exhibited low activity due to the electron-donating effect of the aliphatic chain.

5.1.4. Stille Coupling

The Stille coupling reaction has been performed in $[\text{C}_4\text{mim}][\text{BF}_4]$ using bis(benzonitrile)palladium(II) chloride, triphenylarsine, and copper(I) iodide as the catalyst system (Scheme 37).³²⁰ Using this solvent for the reaction of

Scheme 37. Stille Coupling Reaction between α -Iodoenone and Vinyltributyltin



α -iodoenone and vinyltributyltin afforded results comparable with those obtained using NMP as the solvent. Better results were obtained in the coupling of α -iodoenone with phenyltributyltin. Both α - and β -iodocyclohexenones afforded the Stille coupling products in generally good yield. Extraction of the product with diethyl ether led to an IL layer that could be recycled several times with only a slight loss in activity.

5.2. Sulfonylation Reactions of Aromatics

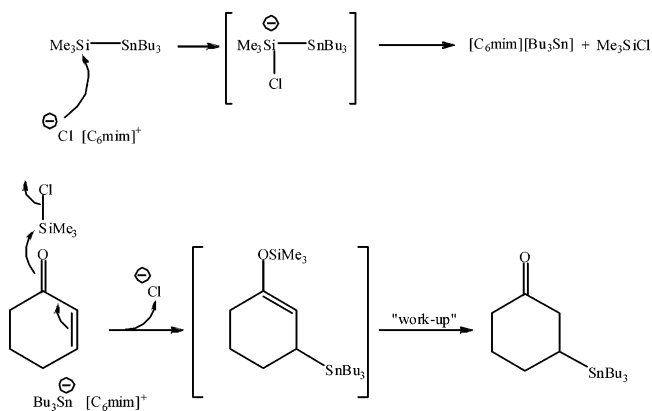
Sulfonylation reactions of aromatics has been reported using $[\text{C}_4\text{mim}]\text{Cl}-\text{FeCl}_3$ with FeCl_3 in excess at room temperature with excellent yields with the exception of nitrobenzene where no reaction was observed. Both *p*-toluene

sulfonyl chloride and benzene sulfonyl chloride were effective as sulfonylation reagents. In contrast, for the alkylation of α -methylnaphthalene, binary $[\text{EtNH}_3]\text{Cl}-\text{FeCl}_3$ - and $[\text{EtNH}_3]\text{Cl}-\text{ZnCl}_2$ -based ILs showed little reaction.

5.3. Silylstannations of α,β -Unsaturated Carbonyl Compounds

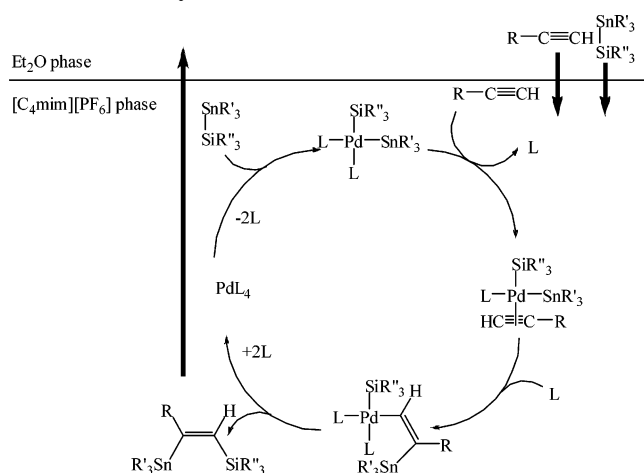
The tributylstannyl anion, Bu_3Sn^- , can be generated in 1,3-dialkylimidazolium-based ILs from $\text{Me}_3\text{SiSnBu}_3$ and reacted with α,β -unsaturated carbonyl compounds (cyclohex-2-en-1-one, cyclopent-2-en-1-one, *trans*-4-phenyl-3-buten-2-one) to afford 3-tributylstannylated products in good yields (Scheme 38).³²¹ As shown in many reactions, the choice of

Scheme 38. Transformation of α,β -Unsaturated Carbonyl Compounds into 3-Tributylstannylated Products



cation and anion is found to affect the yields obtained. Lower yields of 3-tributylstannylcyclohexanone were obtained using $[\text{C}_4\text{mim}][\text{BF}_4]$ compared with $[\text{C}_4\text{mim}]\text{Cl}$ even after extended reaction times and use of elevated temperatures. Optimum results for the silylstannation of cyclohex-2-en-1-one were found using $[\text{C}_6\text{mim}]\text{Cl}$. In contrast, the reaction of less active molecules, such as terminal alkynes, required the presence of an additional catalyst.³²² Tetrakis(triphenylphosphine)-palladium(0) $\text{Pd}(\text{PPh}_3)_4$ was found to catalyze addition of silylstannanes $\text{Bu}_3\text{SnSiMe}_3$ and $\text{Bu}_3\text{SnSiMe}_2\text{Ph}$ to terminal alkynes in both $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ giving excellent yields of the 1-trialkylsilyl-2-tributylstannyl-1Z-alkenes as a regio- and stereoselective product. Similar

Scheme 39. Reaction Mechanism for $\text{Pd}(\text{PPh}_3)_4$ -Catalyzed Addition of Silylstannanes $\text{Bu}_3\text{SnSiMe}_3$ and $\text{Bu}_3\text{SnSiMe}_2\text{Ph}$ to Terminal Alkynes in the ILs



reaction times were found in the IL compared with those reported in tetrahydrofuran (Scheme 39). The reaction mechanism was supported by theoretical studies using ab initio Hartree–Fock calculations.

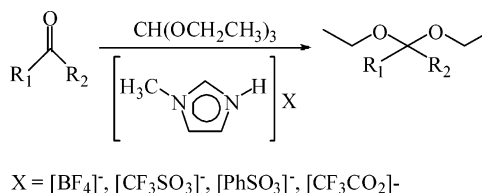
5.4. Debromination of 2-Bromoketones

$[\text{C}_4\text{mim}][\text{Co}(\text{CO})_4]$ in combination with sodium hydroxide is an active system found to catalyze the debromination of 2-bromo-2'-acetonaphthone and 2-bromoacetophenone to their corresponding ketones.³²³

5.5. Protection of Carbonyls to Acetals and Ketals

Protection of carbonyls as acetals (or ketals) is one of the most important reactions in organic chemistry. Although a lot of conventional catalysts including acidic catalysts have been reported for the protection of carbonyls as dimethyl acetals, many of these procedures are associated with one or more disadvantages such as toxic and expensive catalysts, poor chemoselectivity and yield, and loss of catalyst.³²⁴ Recent work demonstrated that a series of Brønsted-acidic ILs can be used as efficient catalysts for protection of various carbonyl compounds at room temperature (Scheme 40).³²⁵

Scheme 40. Brønsted-Acidic ILs Catalyzed Protection of Carbonyls



This process occurs with good isolated yields and simple workup and allows for the recyclability of the catalyst. A similar approach has been proposed using *N*-methylimidazolium tetrafluoroborate as the IL.³²⁶

5.6. Deprotection

Deprotection of 1,1-diacetates using a catalytic amount of InBr_3 immobilized in $[\text{C}_4\text{mim}][\text{PF}_6]$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $[\text{C}_4\text{mim}][\text{BF}_4]$ results in the corresponding parent aldehydes in excellent yields.^{327,328} Various functional groups were found to be reacted under these conditions including molecules containing acid-sensitive or oxidizable groups such as methoxy, benzyloxy, methylenedioxy, nitro, chloro, and double bonds. Furthermore, the phenolic acetate function also remained unaffected. Acetals such as 1,1-ethylenedioxy-1-phenylmethane and 1,1-dimethoxy-1-phenylmethane could also be converted to their corresponding carbonyl compounds.

5.7. Ligand Substitution Reactions: Fluorination Reactions

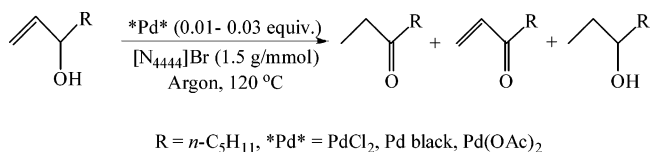
Fluorination reactions are important and often require harsh conditions or fluorinating agents. Amigues et al. have shown that fluorine–chlorine halogen exchange was surprisingly rapid in dry $[\text{C}_4\text{mim}][\text{BF}_4]$, and after only 2 h, a significant conversion of PCl_3 to PF_3 was observed with no hydrolysis products detected.³²⁹ Nucleophilic trifluoromethylation reactions with organic halides have been shown to occur in ether-functionalized $[\text{NTf}_2]^-$ -based ILs using trifluoromethyl-

(trimethyl)silane. These reactions were catalyzed using CuI with KF resulting in yields between 27% and 98% which were dependent on the substrate and catalyst system used.³³⁰ Interestingly, the use of [C₄mim][PF₆], glyme, or acetonitrile resulted in no yield even after 24 h. In addition, Kim and Shreeve demonstrated that Ph₃P and CsF could be used as catalysts in these ILs with trifluoromethyl(trimethyl)silane for the trifluoromethylation of aldehyde, ketone, enone, and lactam. Chiral α,β -epoxy carbinol compounds have also been converted to the corresponding chiral monofluoro-methylated α,β -epoxy compounds via fluorination with 2,2-difluoro-1,3-dimethylimidazolidine in [C₄mim][PF₆] by Kitazume et al.³³¹

5.8. Isomerization

The palladium-catalyzed process for the conversion of allylic alcohols to ketones has been reported in [N₄₄₄₄]Br (Scheme 41).³³² In comparison with DMF, the IL solvent

Scheme 41. Palladium-Catalyzed Isomerization of Allylic Alcohols to Ketones



showed, in general, much higher selectivities toward the saturated ketone in the case of 1-octen-3-ol. However, the selectivity obtained was strongly dependent on the allylic alcohol chosen; for example, terminal olefins showed high selectivity, whereas this is reduced significantly with β -substitution. Interestingly, when comparing PdCl₂, Pd(OAc)₂, and palladium black as the catalyst, similar results were found in each case, with only a small drop in conversion for the latter. This is consistent with evidence from Heck^{53,54} and oxidation²⁴⁶ reactions performed with similar catalysts that the palladium salt decomposes on dissolution forming palladium nanoparticles.

Corma et al. also employed palladium-based catalysts for the cycloisomerization of 2,2-diallylmalonates in 1,3-dialkylimidazolium-based ILs.³³³ In toluene using PdCl₂(PhCN)₂ as the catalyst, both acyclic and cyclic products are observed. In comparison, in [C₄mim][PF₆], 93% selectivity towards the corresponding cyclopentene, where the endocyclic C=C double bond is tetrasubstituted, is found. Similar selectivities were also found for PdCl₂ and PdBr₂ as the catalyst and showed higher TOFs compared with PdCl₂(PhCN)₂. The TOF was further increased by addition of AgPF₆ to the reaction mixture with little change in the selectivity. This additive is thought to replace the chloride in PdCl₂ with [PF₆]⁻ by forming AgCl, which increases the hardness of the palladium center, increasing the TOF.

An extensive study of the isomerization of 2-methyl-3-butenitrile into 3-pentenitrile using nickel–phosphine catalysts has been investigated under biphasic IL–organic solvent conditions by Vallée et al.³³⁴ In 1,3-dialkylimidazolium-based ILs the presence of the C(2) proton was found to reduce the conversion of 2-methyl-3-butenitrile substantially, possibly due to formation of a Ni–carbene complex. In contrast, excellent conversions were obtained using a methyl capping group. A similar trend was also observed in the selectivity of the process toward 3-pentenitrile. The conversion and selectivity were found to be sensitive toward the ligand employed in the reaction. For

example, the number of ionic groups attached to a phosphorus center was examined and found to decrease the conversion significantly as the charge increased. Using a biphasic reaction medium with heptane as the organic phase it was possible to immobilize the catalyst and allow good recycle of the system.

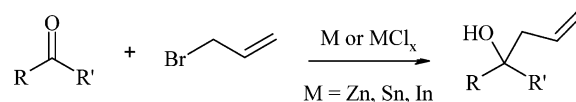
5.9. Acid-Catalyzed Reactions in ILs Using Heterogeneous Catalysts

Recently, there has been significant interest in the possibility of using solid acid catalysts in ILs for C–C bond-forming reactions. Kadtare et al. have shown that zeolites can catalyze Friedel–Crafts acylation reactions in ILs.³³⁵ However, a more detailed study of the mechanism of the reaction showed that while the activity in the ILs was higher than that found in molecular solvents, this was subject to a strong deactivation with time in a continuous flow process.³³⁶ Hardacre et al. clearly demonstrated that the zeolite was acting as a catalyst precursor whereby cation exchange from the IL with the surface protons of the zeolite formed a homogeneous acid in solution. The acid was responsible for the catalysis, in particular in ILs based on [NTf₂]⁻. The activity of the zeolite could be recovered by recalcination of the solid, removing the exchanged organic cation and regenerating the proton sites. A similar ion-exchange mechanism has also been proposed by Shen et al.³³⁷ Using H₃PW₁₂O₄₀ supported on MCM-41, an increase in conversion was found for the alkylation of phenol using ILs compared with hexane. In both cases it cannot be ruled out that some heterogeneous activity contributes, but there does not appear to be a significant contribution from the solid acid.

Prins cyclization reactions between aldehydes and homoallylic alcohols were also demonstrated using zeolites and Amberlyst-15 ion-exchange resin in [C₄mim][PF₆].³³⁸ High yields of tetrahydropyrans were formed, and the IL–acid catalyst system was recyclable. In this case, the recycled IL in the absence of the catalyst was not examined, and therefore, it was not possible to ascertain whether the same mechanism as shown for zeolites and H₃PW₁₂O₄₀ was taking place. Interestingly, the yields decreased with recycle as well as in the presence of water, both of which were consistent with the exchange mechanism.

Metals, in particular In, Sn, and Zn, have been shown to mediate the allylation of ketones and aldehydes using allyl halides in [C₂mim][BF₄] and [C₄mim][BF₄] (Scheme 42).³³⁹

Scheme 42. Metal-Mediated Allylation of Ketones and Aldehydes in ILs

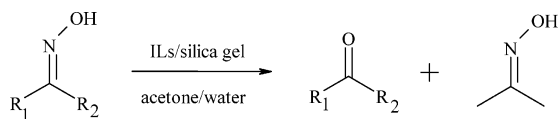


The metal is thought to form the organometallic complex in solution, and this is the reactive intermediate. In general, no advantage of the IL system is observed over the molecular solvent system; however, interestingly, substoichiometric quantities of indium may be used for the reaction.

5.10. Deoxygenation

Acid-functionalized ILs using acetoxy and octylic acid groups physically confined into the silica gel were tested in deoxygenation of oximes (Scheme 43).³⁴⁰ One hundred percent conversions and selectivities were achieved when *p*-methoxy

Scheme 43. Deoxygenation of Oximes over Silica Gel Confined ILs



benzaloxime and *p*-nitro benzaloxime were used as substrates only in the presence of water. In contrast, significantly lower activity was observed using acetophenone oxime as the substrate. This was attributed to the steric hindrance of acetophenone oxime. Similarly, when acetone oxime was used as the reactant, no reaction occurred, which explains the observation that acetone oxime was produced on conversion of other oxime substrates. This result suggested that formation of acetone oxime may be an important step in the deoxygenation reactions.

5.11. Acid-Catalyzed Reactions with Task-Specific ILs

Davis and co-workers pioneered the area of task-specific ILs,²² and this concept has been utilized in acid-catalyzed reactions, in particular in the form of Brønsted-acidic ILs where an acid group is tethered to the anion or cation. Forbes and Weaver used a phosphonium-tethered sulfonic acid tosylate IL to perform the esterification of acetic acid to ethyl acetate.³⁴¹ Yields >80% were achieved, but this was significantly modulated by the amount of water present in the system as well as the acetic acid to ethanol ratio. The yield was optimized where the water:IL ratio was 7:1, and an equimolar amount of acid and alcohol was used. Similarly, Sahoo et al. tethered sulfonic acid groups onto imidazolium and phosphonium ILs and further modified their Brønsted acidity using *p*-toluenesulfonate and trifluoroacetate anions.³⁴² Using these ILs, the Mannich reaction between acetophenone, aniline, and benzaldehyde has been performed showing excellent yields and recyclability. Recently, Olah et al. have shown that it is possible to support HF by reaction of amines and polymer containing amines forming amine-(HF)_{*n*}-based salts as liquids or as a solid.³⁴³ With formation of a salt, the volatility of the HF was reduced, allowing it to be handled more easily. The material formed was used for the alkylation of isobutane with isobutene or but-2-ene alkylation and showed high activity and, in the case of the polymer supported material, good recycle over four reactions. Some change in the selectivity was reported on recycle, which was attributed to small amounts of leaching of HF from the catalyst.

5.12. Base-Catalyzed Reactions

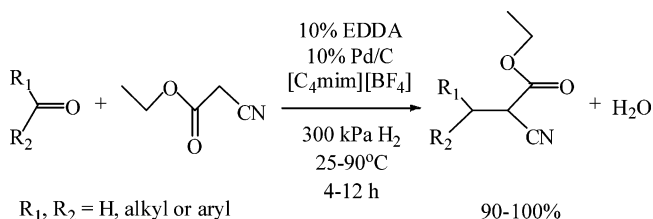
Base-catalyzed processes have been much less studied in ILs compared with acid-catalyzed reactions, in particular those employing solid base catalysts. Hydrotalcite supported in [BF₄]⁻ and [PF₆]⁻ ILs has been used for Knoevenagel and nitro reactions.³⁴⁴ Khan et al. reported that high yields were obtained for both reactions; however, it should be noted that the ILs catalyzed the Knoevenagel reactions in the absence of the catalyst. KF on alumina has also been supported in [C₄mim][BF₄] and [C₄mim]Br and used for the base-catalyzed heterocyclization of diamines using bromoacetyl bromide to form a range of 1,4-benzothiazines.³⁴⁵ Good yields and recycle were obtained using this system.

The Lewis basicity of the IL may also be used to catalyze reactions. MacFarlane et al. examined a range of ILs using acid–base indicators so as to categorize their acidity.²⁰ Using acetylation of alcohols as the probe reaction, the Lewis basicity of dicyanamide and acetate was demonstrated, whereas in [NTf₂]⁻ no reaction was found, in agreement with the indicator studies.

Knoevenagel and Claisen–Schmidt reactions have also been performed using alkali-metal hydroxides as the catalyst in ILs.³⁴⁶ Using an ethanolic solution of NaOH or KOH in [C₄mim][PF₆], both the Knoevenagel reaction between benzaldehyde and malononitrile and the Claisen–Schmidt reaction of acetophenone with benzaldehyde were performed with good conversions and selectivity. In the case of reacting 2-hydroxyacetophenone with benzaldehyde, some subsequent cyclization of the product to the flavanone was also observed. In each case, the IL was recycled at least three times; however, much of the base used in the reaction disappears and is thought to react with the acidic proton at the C(2) position on the imidazolium ring. The self-aldol condensation of propanal and crossed aldol condensation of propanal with 2-methylpent-2-enal in a range of ILs, including [C₄mim]-[PF₆] and [C₆mim][BF₄], at 80–100 °C has been reported by Mehnert et al.³⁴⁷ in which NaOH was used as the base in the form of solid particles. Increased yields of oligomers >C₉ were found compared with molecular solvents.

Ethylenediammonium diacetate has also been employed for the Knoevenagel reaction in [C₄mim][BF₄].³⁴⁸ In this case, the objective was to perform a one-pot process whereby the condensation reaction was carried out in the presence of a heterogeneous catalyst under hydrogen so as to reduce C=C in the condensate product (Scheme 44). This was effective

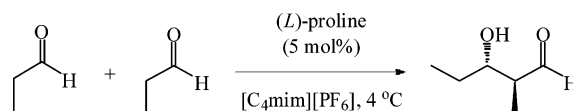
Scheme 44. One-Pot Knoevenagel/reduction Process with Ethylenediammonium Diacetate in [C₄mim][BF₄]



for a range of aromatic aldehydes and ketones as well as methylene compounds such as ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate. Use of dimethylammonium dimethylcarbamate has been reported (as a distillable, ionic medium) for similar aldol condensations by Kreher et al.³⁴⁹ For the reaction of benzaldehyde with propanal, yields of 61% after 25 h at 50 °C were obtained.

Amine bases have been immobilized in ILs to perform aldol and Henry reactions. For example, asymmetric aldol condensations have been shown using propanone and a range of aromatic and aliphatic aldehydes to have ee's up to 89% at high conversion with L-proline (Scheme 45).^{350–353} Little loss in activity or ee was observed on recycle of the catalyst/IL system. In addition, the aldol reaction of acetone derivatives with aldehydes resulted in optically active fluorinated

Scheme 45. Asymmetric Self-Aldol Condensation of Propanal



α,β -epoxy carbonyl compounds using [C₂mim][OTf] and proline.³⁵⁴ Davey et al. demonstrated that amines in ILs can reduce formation of self-aldol condensation products, increasing the selectivity for the cross-aldol reaction.³⁵⁵ Using ILs based on [NTf₂]⁻ and [FAP]⁻ and piperidine as the catalyst, the aldol condensation of 4-*tert*-butylbenzaldehyde and propanal to form 3-(4-*tert*-butyl-phenyl)-2-methyl-propanal was shown to have significantly higher selectivities at high conversions of the 4-*tert*-butylbenzaldehyde compared with either the industrial process using NaOH or using piperidine in molecular solvents. The higher selectivities in the IL system appear to be related to formation of an insoluble iminium species which reduces the concentration of free catalyst available for reaction and prevents catalysis of the self-aldol condensation. β -Nitroalknols have also been prepared from ketones and aldehydes by reaction with nitroalkanes in [C₂mim][BF₄] and [C₄mim][BF₄] using DBU as the catalyst.³⁵⁶ High rates of reaction were observed in both ILs for all reactant combinations with the exception of the reaction of cyclopentanone with nitromethane, where good yields were found in [C₂mim][BF₄], and yet no reaction was observed in [C₄mim][BF₄].

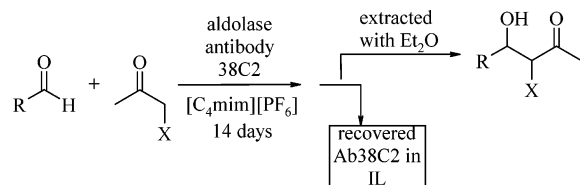
Amines may also be tethered to the IL and used in molecular solvents. Cai et al. have shown that task-specific ILs may be formed by alkylating methyl imidazole with 2-bromoethylamine hydrobromide, forming a tethered primary amine.³⁵⁷ In both the [BF₄]⁻ and [PF₆]⁻-based ILs, Knoevenagel reactions between a range of aromatic aldehydes with ethylcyanoacetate and malononitrile in water are efficiently performed. Therein, the IL was easily recycled from the products and reused. Silica-supported amine catalysts have been used in [C₄mim][PF₆] for the self-aldol condensation of *n*-decanal.³⁵⁸ *N*-Methyl-3-aminopropylated tethered on silica showed excellent recyclability and was found to be more active in the IL than previously tested molecular solvents.

Base-catalyzed *N*-alkylation reactions have been shown in ILs using K₂CO₃ and Cs₂CO₃.³⁵⁹ Using pyrrole or indole as the nucleophile and a range of alkylating agents such as alkyl halides and sulfonates as the electrophiles, good yields are obtained in a mixture of acetonitrile and [C₄mim][BF₄]. The advantage of this method is the ease of workup and lack of a strong base requirement.

5.13. Enzymatic Catalyzed Aldol Reactions in ILs

The aldol reaction catalyzed by aldolase antibody 38C2 in an IL [C₄mim][PF₆] is another way to produce fluorinated compounds.³⁵⁴ Thus, aldol reaction of hydroxyacetone with 4- or 3-(trifluoromethyl)benzaldehyde occurs smoothly in this system with recovery of the antibody. The reaction produced the 3,4-dihydroxy-4-{4- or 3-(trifluoromethyl)-phenyl}butan-2-one (Scheme 46). However, acetone, methyl ethyl ketone, methoxyacetone, fluoroacetone, and chloroacetone were reported to be inactive in this system. Moreover, in the case

Scheme 46. Aldol Reaction Catalyzed by Aldolase Antibody 38C2 in an IL



of aliphatic and/or α,β -unsaturated aldehydes, the aldol reaction did not proceed.

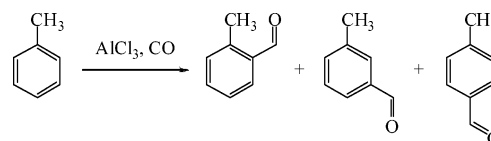
6. Carbonylation and Hydroformylation

6.1. Carbonylation

6.1.1. Carbonylation of Aromatic Hydrocarbons via Homogeneous Catalysis

Carbonylation of toluene is a reaction known to require highly acidic catalyst systems to obtain any conversion. It was initially reported by Knifton³⁶⁰ and Saleh³⁶¹ using first-generation 1,3-dialkylimidazolium and *N*-alkylpyridinium chloroaluminate ILs (Scheme 47). As also occurs in halide-

Scheme 47. Carbonylation of Toluene Using AlCl₃ in ILs



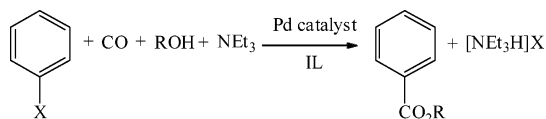
based ILs, AlCl₃ has been shown to be soluble in [NTf₂]⁻-based systems and used for carbonylation of toluene.³⁶² The overall solubility of AlCl₃ is strongly dependent on the cation employed with most [cation][NTf₂]-AlCl₃ mixtures found to exhibit temperature-dependent monophasic-biphasic behavior. In the carbonylation of toluene using *N*-alkylpyridinium [NTf₂]⁻ based ILs, yields of toluene aldehyde between 10% and 30% were found but with high selectivities (~85%). A maximum yield was obtained using [C₂pyr]⁺ as the cation, and this was attributed to the need to balance the solubility for toluene and CO in the catalyst layer.

Other chloroaluminate ILs have also been investigated in this reaction.³⁶³ Using a range of Lewis-acidic chloroaluminate ILs based upon a 2:1 ratio of AlCl₃ and [C_{*n*}mim]Cl (*n* = 2, 4, 6, 8, 12 or where C_{*n*} is replaced by benzyl), toluene carbonylation at room temperature was performed with HCl (3 atm) and CO (8 atm).³⁶⁴ A gradual decrease in the activity for the toluene carbonylation reaction was found with increasing alkyl chain length. Therein, the role of HCl was examined in the reaction using semiempirical methods. In particular, formation of HCl adduct with the IL correlates with the activity of the system. In the IL, the Al³⁺ species interact with HCl gas to form highly acidic protons and chloroaluminate species, which allows the dissolution/reaction of CO to occur even at relatively low pressures with rapid formation of aldehyde.

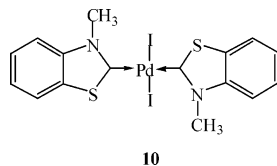
6.1.2. Carbonylation of Aryl Halides and Terminal Alkynes via Homogeneous Catalysis

α,β -Acetylenic ketones are useful intermediates for the synthesis of a variety of important heterocyclic and biologically active compounds.³⁶⁵ Using PdCl₂(PPh₃)₂ as the catalyst in [C₄mim][PF₆], good yields of α,β -acetylenic ketones were observed from the coupling of phenyl iodides and terminal alkynes in the presence of CO.³⁶⁶ In contrast, when performed in [C₄mim][NTf₂], the selectivity was poor due to competition with the Sonogashira coupling reaction.

Palladium catalysts, such as [PdCl₂(PPh₃)₂], have also been shown to catalyze the carbonylation of aryl halides with alcohols and water in the presence of NEt₃ in [C₄mim][PF₆], [C₄mim][BF₄], and Aliquat 336 to form benzoate derivatives (Scheme 48).^{367,368} The rate enhancement effect found in the

Scheme 48. Carbonylation of Aryl Halides with Alcohols and Water in the Presence of Net_3 in ILs

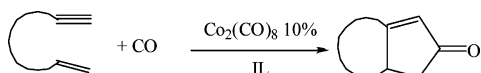
ILs was thought to be due to stabilization of an ionic or polar transition state, for example, an acylpalladium species, which subsequently is attacked by the hydroxyl anionic species or water/alcohol. Calò et al. used carbene-based palladium catalysts, **10** (Scheme 49), for analogous reactions in the IL,

Scheme 49. Carbene-Based Palladium Catalyst for the Methoxycarbonylation Reaction

tetrabutylammonium bromide.³⁶⁹ Although high yields were found for carbonylation products with a range of aryl halides (iodobenzene, bromobenzene, *p*-bromoacetophenone) for the less reactive aryl halides, such as bromobenzene, the presence of triphenylphosphine was required for efficient methoxycarbonylation. The main advantage of using the IL as the solvent was to protect and heterogenize the catalyst.

6.1.3. Pauson–Khand Reaction

The ILs $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$ have been shown to allow the $\text{Co}_2(\text{CO})_8$ -catalyzed intramolecular and intermolecular Pauson–Khand annelation (Scheme 50).³⁷⁰ In this

Scheme 50. Intramolecular Pauson–Khand Annelation Catalyzed by $\text{Co}_2(\text{CO})_8$ in ILs

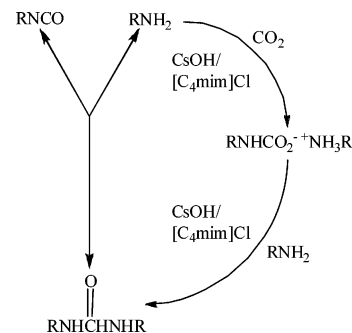
case, a pressure of CO of at least 10 bar was required with diethyl allyl propargyl malonates showing quantitative conversion in the corresponding cyclopentenones. In contrast, using heteroatom-tethered enynes, lower yields for the cyclocarbonylation products were observed, and in the case of the reaction of phenyl acetylene with norbornene, moderate yields were obtained. Interestingly, on replacement of the C(2) proton with a methyl group, lower yields were obtained.

6.1.4. Carbonylation of Alcohols via Homogeneous Catalysis

Jiang et al. reported that dimethyl carbonate formed by the oxidative carbonylation of methanol with PdCl_2 as a catalyst is highly selective in $[\text{C}_4\text{mim}][\text{PF}_6]$.³⁷¹ Therein, supercritical carbon dioxide was used to extract the products from the IL. Similarly, carbonylation of terminal 3-alkyn-1-ols and 1-alkyn-4-ols has been found to be catalyzed by $\text{Pd}(\text{OAc})_2$ in combination with the ligand 2-(diphenylphosphino)pyridine in $[\text{C}_4\text{mim}]^+$ -based ILs. Consorti et al. showed that quantitative and selective formation of *exo*- α -methylene γ - and δ -lactones was observed with the lactones distillable from the IL catalyst system to allow further reactions to be performed.³⁷²

6.1.5. Carbonylation of Amines and Nitrobenzene via Homogeneous Catalysis

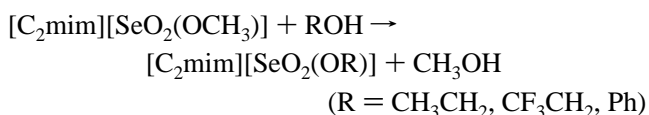
Symmetric urea derivatives have been synthesized in good yield from amines using CO_2 as the carbonyl source in the presence of a range of 1,3-dialkylimidazolium-based ILs and CsOH as a strong base (Scheme 51).^{373,374} Using the IL there

Scheme 51. Carbonylation of Amines Using CO_2 as the Carbonyl Source in the Presence of a Range of 1,3-Dialkylimidazolium-Based ILs and CsOH 

is no need for an additional dehydrating agent; however, the yields obtained were strongly dependent on the choice of anion with $[\text{PF}_6]^-$ -based ILs showing particularly poor reactions. Little influence of the cation was found. The *N,N'*-disubstituted urea derivatives could then easily be converted into the corresponding carbamates, and the carbamates can be thermally decomposed to form isocyanates.

ILs can also mediate the oxidative carbonylation of amines (aniline and cyclohexyl amine) to give the corresponding carbamates or ureas using a palladium-(1,10-phenanthroline)²⁺ complex catalyst without any additional organic solvent.³⁷⁵ Although $\text{Pd}(\text{phen})\text{Cl}_2$ was insoluble in water or methanol, addition to a solution of the catalyst in either $[\text{C}_4\text{mim}][\text{BF}_4]$ or $[\text{C}_4\text{mim}][\text{PF}_6]$ did not result in precipitation. In this study, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, Cl^- , and $[\text{FeCl}_4]^-$ anions were examined using aniline as the substrate. Again, $[\text{PF}_6]^-$ inhibited the reactions; however, this was probably due to decomposition of the anion found after the reaction. The reductive carbonylation of nitrobenzene to the corresponding carbamate has also been performed using $\text{Pd}(\text{phen})\text{Cl}_2$ catalyst in a wide range of 1,3-dialkylimidazolium ILs, including those where the alkyl chain is functionalized with a carboxylic and sulfonic acid groups.³⁷⁶ In the acidic ILs, high catalytic activity was observed with the carboxylic-acid-based ILs showing higher activity than those based on sulfonic acid. Surprisingly, in comparison with similar reactions, the ILs based on hexafluorophosphate showed higher activity than those based on tetrafluoroborate.

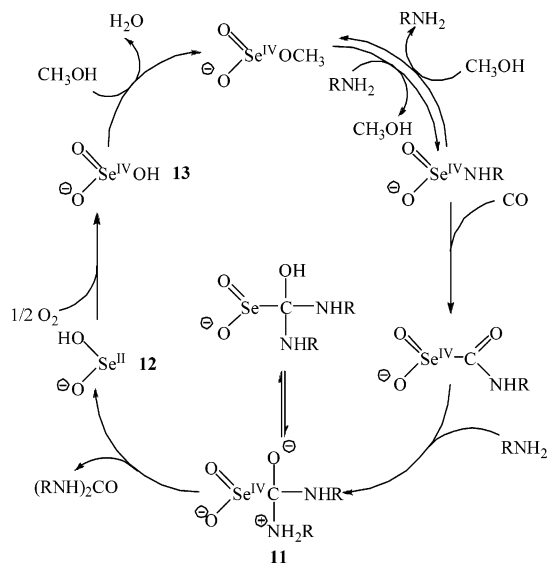
The alkali-metal-containing selenium compound $[\text{KSeO}_2(\text{OCH}_3)]$ has been shown to react with $[\text{C}_n\text{mim}]\text{Cl}$ ($n = 1, 2, 4$) leading to 1,3-dialkylimidazolium-based ILs with anions containing selenium.²²⁵ Other ILs were also formed on reaction of the $[\text{SeO}_2(\text{OCH}_3)]^-$ anions with a range of alcohols



These ILs were also found to be highly active for carbonylation of aniline to form phenyl carbamate and diphenylurea, even at temperatures as low as 40 °C. Similarly, phospho-

nium methylselenites, $[P_{2222}][SeO_2(OCH_3)]$ and $[P_{4444}][SeO_2(OCH_3)]$, have been formed and showed high activity for this reaction.³⁷⁷ The selenium anion is thought to be strongly involved in the catalytic cycle, where the methoxy group is displaced by the amido group and subsequently reacts with a CO, generating a selenium carbamoyl complex. Urea is formed by the additional reaction of another amine with the carbonyl carbon (Scheme 52). On the basis of cyclic

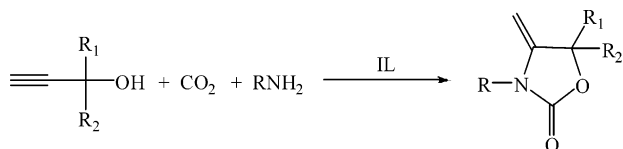
Scheme 52. Carbonylation of Aniline to Phenyl Carbamate and Diphenylurea with Phosphonium Methylselenites



voltammetry results, the imidazolium cation is believed to interact electronically with the anionic selenium species, resulting in the high activity observed by facilitating the redox mechanism ($11^{IV} \rightarrow 12^{II} \rightarrow 13^{IV}$).

The carbonylation of amines with propargylic alcohol using CO_2 as carbonyl source to yield *N*-substituted 4-methylene-2-oxazolidinones has been observed in 1,3-dialkylimidazolium ILs. The corresponding 4-methylene oxazolidinones were formed in high yields under mild conditions with the exception of using aromatic amines as a substrate due to their low nucleophilicity (Scheme 53).³⁷⁸ Again, using $[PF_6]^-$ as the anion resulted in poorer yields than the corresponding IL based on $[BF_4]^-$ due to the instability of the hexafluorophosphate anion. Interestingly, higher yields were obtained as the alkyl chain length of the $[C_n\text{mim}]^+$ cation increased.

Scheme 53. Carbonylation of Amines with Propargylic Alcohol Using CO_2

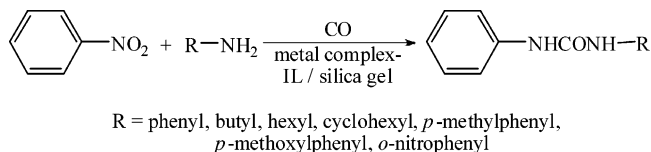


6.2. Carbonylation via Heterogeneous Catalysis

6.2.1. Carbonylation of Amines and Nitrobenzene

Carbonylation reactions of amines to symmetrical diphenylureas and of amines and nitrobenzene to afford the corresponding ureas have been reported to occur using silica-gel-confined ILs containing a metal complex as a heterogeneous catalyst in the absence of oxygen (Scheme 54).³⁷⁹ High catalytic activity was observed and attributed to the

Scheme 54. Carbonylation without Molecular Oxygen of Amines and Nitrobenzene



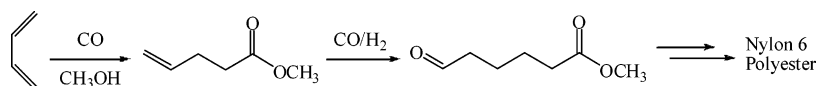
effect of the high concentration of IL containing a metal complex due to confinement into the nanopores or cavities of the silica gel matrix. $[C_{10}\text{mim}][BF_4]$ and $[C_2\text{mim}][BF_4]$ combined with $HRu(PPh_3)_2Cl_2$, $Rh(PPh_3)_3Cl$, $Pd(PPh_3)_2Cl_2$, and $Co(PPh_3)_3Cl_2$ were confined in silica gel. Using the Co and Ru complexes, low TOFs were found compared with catalysts based on Rh and Pd in $[C_{10}\text{mim}][BF_4]$. In contrast, using $[C_2\text{mim}][BF_4]$, poor activity was found for all catalysts.

6.3. Hydroformylation

One of the first reactions performed in ILs employed biphasic conditions for the Rh-catalyzed hydroformylation of long-chain olefins. Commonly, using water as the solvent, the olefins which can be utilized are limited to ethyl–pentyl chain lengths due to solubility issues.^{73,380,381} The biphasic hydroformylation of pent-1-ene in $[C_4\text{mim}][PF_6]$ and $[C_4\text{mim}][BF_4]$ with $Rh(\text{acac})(CO)_2$ as well as with cationic ligands showed excellent results.^{75,125} Furthermore, Keim et al. demonstrated that this system may be extended to the hydroformylation of methyl-3-pentenoate (Scheme 55).³⁸² In this case, the regioselectivity of the reaction is approximately maintained over the reaction and may be controlled by the choice of ligand.

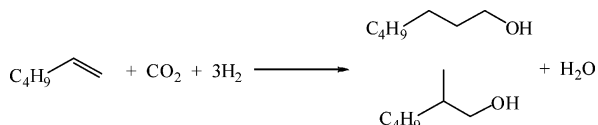
The IL also results in a significant enhancement of the catalyst's lifetime and productivity. For example, using oct-1-ene as the substrate with $[C_4\text{mim}][PF_6]$ and a catalyst formed in situ on mixing $Rh(CO)_2\text{acac}$ with two equivalents of *N*-quaternization cationic phosphines, with peripheral 1-imidazolium groups, a TOF of a 32 mol of oct-1-ene mol^{-1} of Rh h^{-1} was found.³⁸³ Hydroformylation of oct-1-ene using Rh was also reported to be catalyzed by electron-poor phosphine-substituted cobaltocenium salts as ligands in the presence of ILs.¹²⁵ Therein, 1,1'-bis(diphenylphosphino)cobaltocenium hexafluorophosphate was found to be particularly active in $[C_4\text{mim}][PF_6]$ and also gave high selectivity for the *n*-product with no detectable catalyst leaching into the product phase. Platinum complexes may also be used in an analogous manner, for example, *cis*- $[Pt(PPh_3)_2Cl(SnCl_3)]$ and *cis*- $[Pt(PPh_3)_2(SnCl_3)_2]$, resulting from the catalyst precursor *cis*- $[Pt(PPh_3)_2Cl_2]$ in the presence of $SnCl_2$.³⁸⁴ The activity has been shown to be high in 1,3-dialkylimidazolium-based ILs where the $[C_4\text{mim}]^+$ cation is thought to bind strongly the chloride, thus activating the catalyst, as shown by density functional theory calculations.

The biphasic hydroformylation of lower volatility alkenes, such as dodec-1-ene, has been shown in an IL–supercritical CO_2 system under continuous flow.³⁸⁵ As in organic–IL biphasic systems, the IL retains the catalyst while the supercritical phase contains the substrate and gaseous reagents as well as acts as an extractant phase for the product. In this case, the choice of ligand for the rhodium complex was critical for efficient reaction, and it was demonstrated that, for example, sodium salts of sulfonated phosphines were insufficiently soluble in the ILs to obtain acceptable rates. However, by replacing the sodium by a cation similar to that derived from the IL, this allowed good solubility and activity

Scheme 55. Biphasic Hydroformylation of Methyl-3-pentenoate in [C₄mim][PF₆] and [C₄mim][BF₄] with Rh(acac)(CO)₂

to be achieved. Furthermore, the choice of IL was important with [C₈mim][NTf₂] showing the highest TOF at 500 h⁻¹.

Hydroformylation of hex-1-ene using carbon dioxide as carbonyl carbon source has also been achieved resulting in the chemoselective formation of heptanols using a ruthenium complex employed in a biphasic 1,3-dialkylimidazolium chloride–toluene system (Scheme 56).³⁸⁶ The high concen-

Scheme 56. Hydroformylation of Hex-1-ene Using Carbon Dioxide

tration of chloride is reported to be the cause of the chemoselectivity forming alcohols in favor of hydroformylation compared with the conventional systems used. For the biphasic system to be effective, the choice of IL and organic cosolvent is important. The conversion of hex-1-ene was found to increase following the order cyclohexane < Et₂O < THF < toluene. This was attributed to the increased miscibility of the cosolvent with [C₄mim]Cl. Furthermore, with increasing alkyl chain length, the reactivity of the alkene was also found to increase, again due to the increased alkene solubility. However, in the case of [C₈mim]Cl, where a single phase was formed, decreased chemoselectivity was found.

6.4. Hydroformylation via Heterogeneous Catalysis

Recently, several authors used supported ionic-liquid-phase catalyst systems for Rh-catalyzed olefin hydroformylation.^{82,97,387,388} In these systems the catalysts are composed of a transition-metal complex dissolved in a thin film of the IL, which is held on a porous solid with high surface area by physisorption, tethering, or covalent anchoring. Wasserscheid et al.³⁸⁷ and Mehnert et al.⁸² used this system for the liquid-phase hydroformylation of oct-1-ene and hex-1-ene, respectively, employing [C₄mim][PF₆] and [C₄mim][BF₄]. Although high activities were found, with linear to branched ratios up to 2.5, metal leaching was found which was comparable to conventional biphasic reactions. Yang et al. used TPPTS–Rh complex in an MCM-41-supported IL for the liquid-phase hydroformylation of hex-1-ene, oct-1-ene, dec-1-ene, and dodec-1-ene.⁹⁸ Again, linear products were formed in preference to the branched aldehyde with the highest ratio being 3.8 found for hexane.

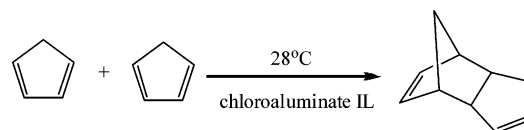
Fehrmann and Wasserscheid and co-workers^{97,387,388} used the supported IL phase concept to examine the continuous gas-phase hydroformylation of propene using [Rh(acac)(CO)₂] with bisphosphine sulfoxantphos ligand as the catalyst dissolved in [C₄mim][C₈H₁₇OSO₃]. High degrees of linearity in the aldehyde were observed up to 96%. These catalysts were tested for long-term stability and showed no appreciable decrease in selectivity over a 200 h period. In addition, although a drop in activity was observed, this could be recovered by pumping the catalyst system for a short period of time to remove the high boiling point products retained on the catalyst.

7. Dimerization

Oligomerization of olefins under biphasic conditions using chloroaluminate ILs of the type [cation]Cl/AlCl₃/AlEtCl₂ as catalyst solvent for Ni complexes ([Ni(MeCN)₆][BF₄]₂) was first reported by Chauvin et al.^{389–392} When dissolved in the Lewis-acidic chloroaluminate ILs, the Ni catalyst exhibited an enhanced catalytic activity. Sato et al. showed that to obtain the desired catalyst formulation, i.e., 1 equiv of phosphine per nickel atom, 1 equiv of complexes [NiCl₂(P(*i*-Pr)₃)₂] and [NiCl₂(pyridine)₂] was needed to be dissolved in the IL in the presence of tetramethylbenzene.³⁹³ For dimerization of butene, the distribution of butene dimers was independent of addition of phosphine ligands. Moreover, the product mixture was independent of feedstock with both but-1-ene and but-2-ene yielding the same dimer distribution. (cod)Ni(hfacac) has also been employed as a catalyst in a range of chloroaluminate ILs.^{394,395} By introducing the acidic IL with weak organic bases, a significant enhancement of catalyst activity was obtained with a high linear selectivity of dimer product over that observed in toluene. Ethene dimerization and oligomerization was shown using nickel(II) complexes dissolved in a [C₄mim]Cl/AlCl₃/AlEtCl₂ system in the presence of aromatic solvents.³⁹⁶ By switching from NiF₂ and NiCl₂(PCy₃)₂ as the catalyst, which produced dimers and trimers, to [Ni(MeCN)₆][BF₄]₂, selectivity toward but-1-ene was achieved at 83%.

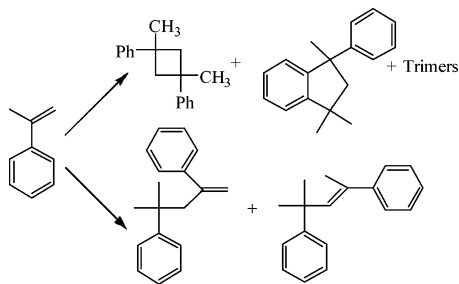
Nickel(II) heterocyclic carbene complexes of the formula NiI₂(carbene)₂ (carbene = 3-methyl-1-propylimidazolin-2-ylidene, 1-butyl-3-methylimidazolin-2-ylidene, 1-isopropyl-3-methylimidazolin-2-ylidene, 1,3-diisopropylimidazolin-2-ylidene) represent other catalysts investigated in the dimerization of but-1-ene and propene in 1,3-dialkylimidazolium-based chloroaluminate IL.³⁹⁷ These complexes showed high activity in the IL compared with in toluene and higher activity than NiCl₂(PCy₃)₂ in the IL for but-1-ene dimerization. This is thought to be due to the higher stability of the complex in the IL compared with in toluene.

Dimerization of 1,3-cyclopentadiene has also been studied in the 1,3-dialkylimidazolium- and *N*-alkylpyridinium-based chloroaluminate ILs (Scheme 57). As expected, with increas-

Scheme 57. Dimerization of 1,3-Cyclopentadiene in the 1,3-Dialkylimidazolium- and *N*-Alkylpyridinium-Based Chloroaluminate ILs

ing AlCl₃ concentration, the rate increased due to the ILs' higher Lewis acidity. A higher rate of dimerization was also found with the ILs based on [C₂mim]Cl compared with those based on [C₄pyr]Cl.³⁹⁸

In addition to chloroaluminate ILs, ILs based upon FeCl₃ have been shown to efficiently catalyze the dimerization of α -methylstyrene (Scheme 58).³⁹⁹ One hundred percent conversion was achieved in 5 min using Et₃NHCl–2AlCl₃, Et₃NHCl–2FeCl₃, [C₄mim]Br–2AlCl₃, and [C₄mim]Br–2FeCl₃; however, in all but Et₃NHCl–2AlCl₃ significant

Scheme 58. Product Distribution for Dimerization of α -Methylstyrene


trimer formation was observed. In the latter, 97% selectivity toward the dimer 1,1,3-trimethyl-3-phenylindane was found. On addition of a polar solvent such as tertiary amyl alcohol or tertiary butanol, the substrate was mainly converted to unsaturated dimers 4-methyl-2,4-diphenyl-1-pentene and 4-methyl-2,4-diphenyl-2-pentene, although the reaction rate became much lower. No reaction was observed using $\text{Et}_3\text{NHCl}-2\text{ZnCl}_2$ and $\text{Et}_3\text{NHCl}-2\text{CuCl}_2$.

As an alternative to the chloroaluminate ILs, sulfonic-acid-functionalized ILs have been investigated for oligomerization of a range of olefins.⁴⁰⁰ Therein, branched olefin products were formed with high conversions and selectivity. As with the biphasic chloroaluminate system, the IL used in this case could be recycled.

Ni complexes have also been examined in second-generation ILs for oligomerization of ethene. Using a combination of $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 4, 6, 8, 10$) and the cationic Ni complex $(\eta^3\text{-methyllyl})[\text{bis}(\text{diphenylphosphino})\text{methane}-\text{monoxide}-\kappa^2\text{-P,O}]\text{nickel(II)hexafluoroantimonate}$ $[(\text{mall})\text{Ni}(\text{dppmO})][\text{SbF}_6]$ conversion of ethene to higher α -olefins was found under biphasic conditions.^{401,402} Interestingly, the exact composition of the IL was critical in determining the reaction outcome; for example, high activity was only observed for water and chloride-free systems and with each cation used some tuning of the product distribution was enabled, although no clear dependence on chain length was observed. With increasing chain length, the catalytic activity of $[(\text{mall})\text{Ni}(\text{dppmO})][\text{SbF}_6]$ was found to decrease. This is thought to be due to the higher solubility of the oligomerization products as the lipophilicity increased which in turn raised the internal higher olefins' concentration in solution, known to poison cationic Ni complexes. Overall, ethene oligomerization showed higher reactivity and selectivity than in conventional solvents with the TOF being

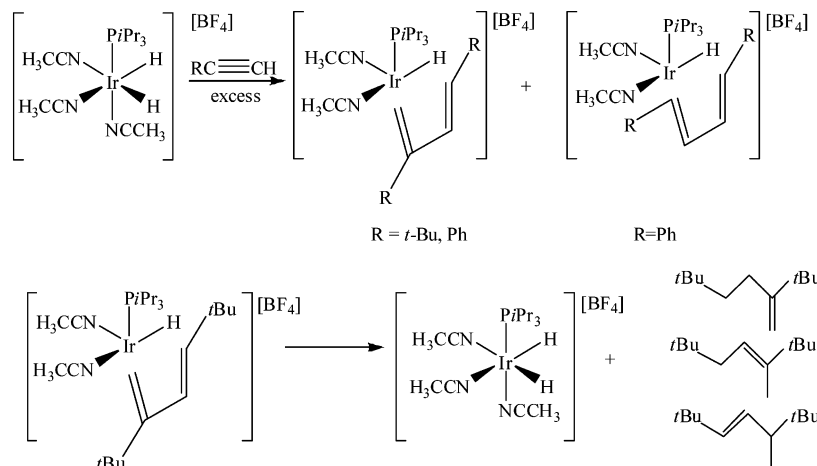
correlated with polarity data determined using solvatochromic dyes.

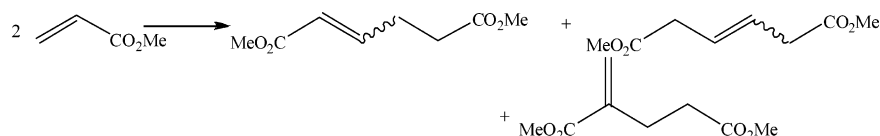
Second-generation ILs have also been used for dimerization of butadiene using Pd complexes, where a significant rate enhancement was obtained by exchanging THF with $[\text{C}_4\text{mim}][\text{BF}_4]$.⁴⁰³ One hundred percent selectivity toward 1,3,6-octatriene was obtained using palladium dichloride, acetate, and acetylacetonate in the presence of triphenylphosphine, which was dissolved in $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{PF}_6]$, and $[\text{C}_4\text{mim}][\text{OTf}]$ using butadiene.⁴⁰³

Alkyne oligomerization has been studied under biphasic toluene- $[\text{C}_4\text{mim}][\text{BF}_4]$ conditions using $[\text{Ir}(\text{H})_2(\text{NCCH}_3)_3(\text{P-}i\text{Pr}_3)][\text{BF}_4]$ as the catalyst precursor (Scheme 59).⁴⁰⁴ With an excess of terminal alkynes such as $t\text{-BuC}\equiv\text{CH}$ and $\text{PhC}\equiv\text{CH}$, the complex transforms into $[\text{Ir}(\eta^4\text{-(R)}_2\text{C}_4\text{H}_4)(\text{NCCH}_3)_2(\text{P-}i\text{Pr}_3)][\text{BF}_4]$ ($\text{R} = t\text{-Bu, Ph}$) with a range of 1,3- and 1,4-disubstituted butadiene isomers depending on R. The complex formed reacted with hydrogen to restore the initial catalyst and resulted in dimerization in the case of $t\text{-BuC}\equiv\text{CH}$, while $\text{PhC}\equiv\text{CH}$ produced styrene and ethylbenzene as major products.

ILs may be formed by neutralization of 1-alkylimidazoles with Brønsted acids resulting in halogen-free salts. In one of the rare examples of their use in catalysis, Picquet et al. examined their use in the dimerization of methyl acrylate and ring-closing metathesis.^{405,406} Therein, diethyl ether containing a phosphine ligand was used as the solvent in which to produce the Brønsted-acidic IL, which resulted in formation of protonated ethers and phosphines, such as $[\text{Et}_2\text{OH}][\text{BF}_4]$ and $[\text{HPBu}_3][\text{BF}_4]$. Thus, the reaction mixture employed contained a catalyst, for example, $\text{Pd}(\text{acac})_2$, in a mixture of $[\text{HPBu}_3][\text{BF}_4]$ and $[\text{Et}_2\text{OH}][\text{BF}_4]$ as the IL (Scheme 60). Using this system the TOF for dimerization of methyl acrylate was strongly dependent on the nature of the cation and the presence of chloride, the latter causing a drop in TOF. For example, use of HBF_4 -protonated butylimidazole resulted in a monophasic system and moderate TOFs with 98% selectivity toward linear dimers. In contrast, using methylimidazole as the IL source resulted in a biphasic system, thus leading to lower TOFs due to poorer mass-transfer control. A similar system using $[\text{C}_4\text{mim}][\text{BF}_4]$ was also found to be active in a continuous, biphasic system.⁴⁰⁷

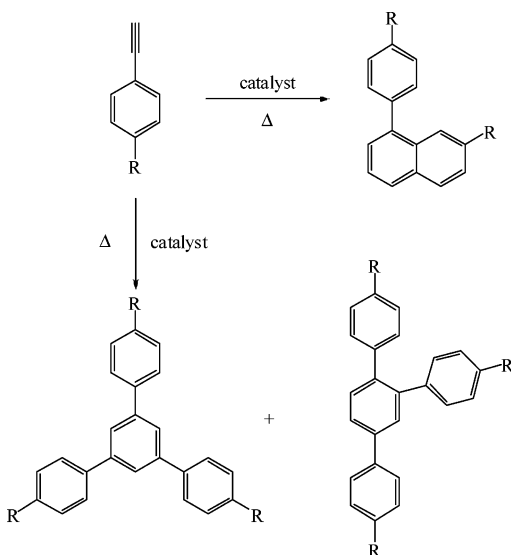
Furthermore, cationic ruthenium allenylidene complexes such as $[\text{Ru}(\text{=C=C=CPh}_2)(p\text{-cymene})(\text{PCy}_3)\text{Cl}][\text{PF}_6]$ have been shown to catalyze this reaction in HBF_4 -protonated

Scheme 59. Alkyne Oligomerization under Biphasic Toluene- $[\text{C}_4\text{mim}][\text{BF}_4]$ Conditions Using $[\text{Ir}(\text{H})_2(\text{NCCH}_3)_3(\text{P-}i\text{Pr}_3)][\text{BF}_4]$


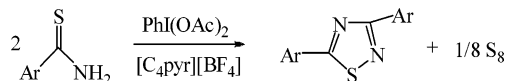
Scheme 60. Dimerization of Methyl Acrylate Using Pd(acac)₂ in a Mixture of [HPBu₃][BF₄] and [Et₂OH][BF₄][HPBu₃][BF₄] and [Et₂OH][BF₄].

butylimidazole.⁴⁰⁵ By replacing the [PF₆]⁻-based complex with [OTf]⁻, a dramatic increase in activity and selectivity was observed as well as outperforming reactions in toluene- or [C₄mim]⁺-based ILs. A further increase in activity was observed on changing the IL anion to triflate with no loss of selectivity.

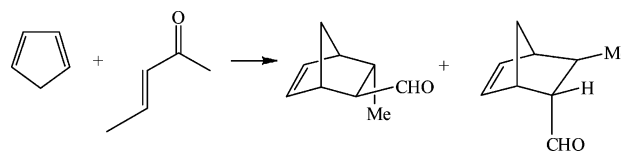
1,3-Butadiene cyclodimerization has been reported to be catalyzed by iron complexes, prepared in situ by reduction of [Fe(NO)₂Cl]₂ with metallic zinc, diethylaluminum chloride, or *n*-butyllithium dissolved in [C₄mim][BF₄] or [C₄mim][PF₆].⁴⁰⁸ In [C₄mim][PF₆], 4-vinyl-1-cyclohexene was formed with 100% selectivity and very high TOF. Under similar reaction conditions, isoprene led quantitatively to a mixture of cyclic dimers 2-methyl-4-(1-methylethenyl)cyclohexene, 1-methyl-4-(1-methylethenyl)cyclohexene, 2,4-dimethyl-4-vinylcyclohexene, and 1,4-dimethyl-4-vinylcyclohexene. Cyclo-oligomerization of arylolefines may also be catalyzed by ruthenium(II) porphyrins in [C₄mim][PF₆] and [C₈mim][PF₆] (Scheme 61).⁴⁰⁹

Scheme 61. Cyclooligomerization of Arylolefines Catalyzed by Ruthenium(II) Porphyrins

Dullius et al. reported that hydrodimerization of 1,3-butadiene may be catalyzed using [(η³-C₄H₇)Pd-μ-Cl]₂, [(η³-C₄H₇)Pd(1,5-cyclooctadiene)][BF₄], palladium acetate, and [C₄mim]₂[PdCl₄] dissolved in [C₄mim][BF₄], forming the dimer 1,3,6-octatriene and telomer octa-2,7-dien-1-ol predominantly.⁴¹⁰ Optimizing the conditions led to a telomer selectivity of 94% using [C₄mim]₂[PdCl₄]. Interestingly, the TOF observed for these reactions was significantly increased by introducing an atmosphere of carbon dioxide. Oxidative dimerization of thioamides may also be performed using the IL [C₄pyr][BF₄] using phenyliodine(III) diacetate, allowing formation of 3,5-diaryl-1,2,4-thiadiazoles (Scheme 62).⁴¹¹

Scheme 62. Oxidative Dimerization of Thioamides in [C₄pyr][BF₄]**7.1. Diels–Alder Reactions**

Aqueous solutions used as reaction solvents may affect dramatically some Diels–Alder reaction rate constants and stereoselectivities. This rate enhancement has been attributed to the “hydrophobic effect” resulting in aggregation of nonpolar reactants in water and a gain in free energy.⁴¹² In many cases, when an IL is used, the reaction rate is further enhanced; for example, reaction of cyclopentadiene with methylvinyl ketone is faster in [BF₄]⁻-based ILs than in water or organic solvents.⁴¹³ Moreover, the 1,3-dialkylimidazolium salts can be used as additives for reaction of crotonaldehyde with cyclopentadiene (Scheme 63).⁴¹⁴ Binary mixtures of

Scheme 63. Diels–Alder Reaction of Crotonaldehyde with Cyclopentadiene

choline chloride and ZnCl₂/SnCl₂ (1:2) have also been reported as efficient Lewis-acid catalysts for a range of Diels–Alder reactions.⁴¹⁵ High endo:exo ratios were observed as well as high yields. In this case the products could be decanted from the IL and the catalyst system reused.

Few asymmetric Diels–Alder reactions performed in ILs have been reported to date. Meracz and Oh observed an ee of 96% for the Diels–Alder reaction of oxazolidinone and cyclopentadiene at room temperature using a rigid copper bisoxazoline-based chiral Lewis acid with a yield of 65% in [C₄C₄im][BF₄]. This was compared with dichloromethane, which showed only 76% ee with a yield of only 4%.⁴¹⁶ Doherty et al. also reported that ILs can increase the ee and yield for the reaction between oxazolidinones and cyclopentadiene using platinum complexes of BINAP as well as conformationally flexible NUPHOS-type diphosphines.⁴¹⁷ Significant enhancements in the enantioselectivity (Δee ≈ 20%) as well as reaction rate were achieved in ILs compared with the organic media even when the IL was in biphasic conditions with diethyl ether in a volume ratio of 1:10 (IL:ether). In addition, the IL allowed the catalyst to be recycled in air without hydrolysis or oxidation of the phosphine ligand.

8. Polymerization

In addition to oligomerization reactions, a wide range of catalytic polymerizations have been performed in ILs.^{418,419}

8.1. Radical Polymerization in ILs

Carlin and co-workers found the combination of TiCl_4 and AlEtCl_2 in AlCl_3 – $[\text{C}_2\text{mim}]\text{Cl}$ to be catalytically active for ethylene polymerization.⁴²⁰ This was further improved using Cp_2TiCl_2 instead of TiCl_4 , where higher yields of polyethylene were achieved.⁴²¹

Second-generation ILs have also been used as solvents for free-radical polymerization and transition-metal-mediated living free-radical polymerization.^{422,423} Controlled radical polymerization may be achieved by atom-transfer radical polymerization—the process which is based on transition-metal-catalyzed reversible activation and deactivation of growing macromolecules.⁴²⁴ Carmichael et al. reported the first example of transition-metal-mediated living-radical polymerization of methyl methacrylate in $[\text{C}_4\text{mim}][\text{PF}_6]$ using copper(I)-mediated living radical polymerization. Therein, the rate of reaction was enhanced and a narrow polydispersity of polymers was obtained.⁴²⁵ The system was particularly active on addition of a 1 mol equiv of *N*-propyl-2-pyridylmethanimine to a deoxygenated suspension of $\text{Cu}(\text{I})\text{Br}$. By washing the polymer with solvent, it was possible to make the product copper free. Similarly, $[\text{C}_4\text{mim}][\text{PF}_6]$ was found to accelerate the rate of propagation of methyl methacrylate in free-radical polymerization.⁴²⁶

The effect of $[\text{C}_4\text{mim}][\text{PF}_6]$ on the living radical polymerization of methyl methacrylate initiated with arenosulfonyl chlorides and $\text{Cu}_2\text{O}/2,2'$ -bipyridine as the catalyst was also investigated by Percec et al.⁴²⁷ Using the IL dramatically accelerated the living-radical polymerization with an initiation efficiency of 100% maintained during the polymerization and eliminating the induction period of this catalyst. The resulting poly(methyl methacrylate) had a molecular weight distribution of 1.1 and perfect bifunctional chain ends. From kinetic analysis the propagation rate was found to be first order in the IL concentration, indicating that the IL participates in the reaction mechanism. Compared with conventional processes, the IL system allowed a significant reduction of the catalyst concentration and decrease in polymerization temperature from 80 to 22 °C to be achieved. A similar rate increase was not observed for the same living-radical polymerization catalyzed by CuCl/bpy .

Rhodium in the form of (diene) $\text{Rh}(\text{acac})$ and [(diene)- $\text{RhCl}]_2$ has been used in polymerization in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{pyr}][\text{BF}_4]$.⁴²⁸ Using catalysts based on either 1,5-cyclooctadiene or norbornadiene, the phenylacetylene polymerization in the presence of triethylamine as cocatalyst led to high yields of poly(phenylacetylene) with molecular weights in the range between 55 000 and 200 000 Da and a high 95–100% cis selectivity.

The clean synthesis of block copolymers of butyl acrylate has also been achieved using atom-transfer radical polymerization.^{429–431}

Free-radical polymerization of methyl methacrylate and styrene using the organic initiators azo-bis-isobutyronitrile and benzoyl peroxide in $[\text{C}_4\text{mim}][\text{PF}_6]$ has been shown to form polymers with molecular weights up to 1000 higher than the analogous reactions in benzene.^{423,432} In a similar manner, free-radical copolymerization of styrene and methyl methacrylate has also been reported by Zhang et al.⁴³³

In many polymerization reactions the cation of the IL has been shown to have a significant influence as found for dimerization reactions. Ma et al. have shown that by increasing the alkyl chain length on imidazolium-based IL-mediated reverse atom-transfer radical polymerization of

methyl methacrylate, employing 2,2-azo-bis-isobutyronitrile/ $\text{CuCl}_2/\text{bipyridine}$ as the initiating system, the polymerization was more controlled.⁴³⁴ This was attributed to the higher solubility of the polymethyl methacrylate in $[\text{C}_{12}\text{mim}][\text{BF}_4]$ compared with $[\text{C}_4\text{mim}][\text{BF}_4]$. A more systematic study has recently been reported for the free-radical polymerization of model monomer *n*-butyl methacrylate.⁴³⁵ Using 1,3-dialkylimidazolium, *N*-alkylpyridinium, and tetraalkylammonium salts, the properties of the ILs were varied by changing the cation alkyl chain length as well as by varying the anion. A comparison with analogous polymerizations in toluene and bulk showed that the solvents had little effect on the tacticity of the polymer; however, the molecular weight and degree of polymerization were highly sensitive to the choice of the solvent. Much higher degrees of polymerization were found in the IL compared with reactions in toluene and, in some cases, during bulk polymerization. Interestingly, although 1,3-dialkylimidazolium-based ILs resulted in an increase in the degree of polymerization with increasing viscosity on replacing the C(2) proton with a methyl group, a viscosity-independent degree of polymerization was observed. In general, the 1,3-dialkylimidazolium-based ILs showed a higher degree of polymerization compared with *N*-alkylpyridinium and tetraalkylammonium salts. Furthermore, the glass-transition temperatures and thermal stabilities were also higher for polymers synthesized in the ILs compared with those formed in toluene.

Formation of polymer electrolytes with high ionic conductivity has been examined using the in situ free-radical polymerization of compatible vinyl monomers in $[\text{C}_2\text{mim}][\text{NTf}_2]$.⁴³⁶ On polymerization of methyl methacrylate in IL in the presence of a cross-linker, self-standing, flexible, and transparent films were formed known as “ion gels”. With increasing mole fraction of IL, the glass-transition temperature of the polymers was lowered and the systems behaved as a simple binary system of polymer and IL.

Electrosynthesis of polymers in ILs is relatively common, in particular, polyaniline. In this case, highly electrostable polymers have been synthesized in $[\text{C}_4\text{mim}][\text{BF}_4]$ which may undergo multiple (>1 000 000) redox cycles without degradation.⁴³⁷ Polypyrrole- and poly(*N*-methylpyrrole)-conductive films have also been prepared via electrosynthesis from the corresponding monomers using $[\text{C}_4\text{mim}][\text{PF}_6]$ as the electrolyte.⁴³⁸ Polymerization of benzene electrochemically in ILs to prepare poly(*p*-phenylene) has been demonstrated in chloroaluminate-based ILs.^{439–442} Therein, the polymerization potential was only slightly modified by the melt acidity or in the presence of protons. The latter act as superacids in these acidic melts, and this invariance indicates that benzene only weakly interacts with either the chloroaluminate anion or the protons.

8.2. Charge-Transfer Polymerization

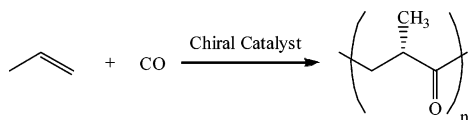
Vijayaraghavan and MacFarlane have shown that charge-transfer polymerization of methyl methacrylate could be achieved in a range of hydrophobic and hydrophilic ILs at room temperature.⁴⁴³ In this case lower temperatures are required than conventional free-radical polymerization and low molecular weight polymers are formed. In the IL, the yield of polymer was found to be dependent on addition of a free-radical quencher such as hydroquinone and the concentration of the amine additive.

8.3. Radical Polymerization Using Chiral ILs and/or Chiral Ligands

Polymerization of methyl acrylate in a chiral IL 1-(*R*-(+)-2'-methylbutyl)-3-methylimidazolium hexafluorophosphate—an analogue of [C₄mim][PF₆] containing a chiral substituent at the imidazolium ring—has been reported by Biedron and Kubisa.⁴⁴⁴ In an achiral environment, radical polymerization of methyl acrylate led to atactic polymers; however, using the chiral IL the isotactic (mm) fraction increased.

Stereoselective copolymerization of propene and carbon monoxide using chiral ligands, such as (2*S*,3*S*)-DIOP and (*R*)-P-Phos, has also been demonstrated in [C₄mim][PF₆], [C₆mim][PF₆], and [C₈mim][PF₆] (Scheme 64).⁴⁴⁵ Using

Scheme 64. Stereoselective Copolymerization of Propene and Carbon Monoxide



(2*S*,3*S*)-DIOP in [C₄mim][PF₆], the Pd-catalyzed copolymerization of propene and CO resulted in regioregular polyketones with the product polymer showing 61% stereoregularity. By optimizing the catalyst/ligand/IL combination, an optical rotation of +15.9° and polydispersity of 1.2 for the polyketone was achieved using (*R*)-P-Phos and [C₆mim][PF₆].

8.4. Biphasic Radical Polymerization

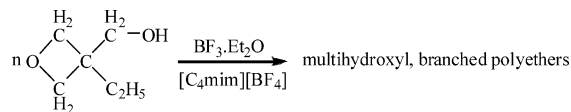
ILs have recently been used as solvents for biphasic atom-transfer radical polymerization to facilitate separation of the products from the catalysts.⁴⁴⁶ CuBr/*N,N,N',N'*-tetraethyldiethylenetriamine was tethered to a butylimidazolium-based [BF₄]⁻ IL which formed a biphasic mixture with methyl methacrylate and toluene. Employing this IL catalyst allowed a large reduction in the amount of IL required. Even with only 5 wt % compared with the organic solvent, polymerization of methyl methacrylate at 60 °C resulted in polymers with low polydispersity and was well controlled. Although the catalyst could be recycled, without regeneration, the activity was low due to oxidation of Cu⁺ to Cu²⁺. However, on reduction with copper metal, the activity was restored.

8.5. Ionic Polymerization

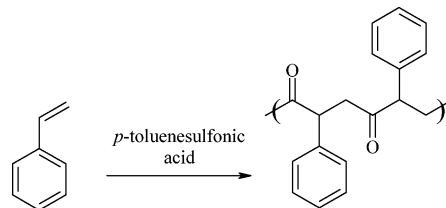
Cationic polymerization of styrene has been carried out in [C₄mpyr][NTf₂] using strong Brønsted-acid catalysts.⁴⁴⁷ A comparison of the use of bis(oxalato)boric acid with the Lewis acid, AlCl₃, showed that with the Brønsted acid lower molecular weights and low polydispersities were obtained. Interestingly, higher molecular weights were found than expected based on complete dissociation of the acid, indicating that the acid may be only partially dissociated. For the cationic ring-opening polymerization of 3-ethyl-3-hydroxymethyloxetane, [C₄mim][BF₄] has been shown to lead to almost quantitative formation of multihydroxyl, branched polyethers (Scheme 65).⁴⁴⁸ In this system the molecular weights of the polymers obtained were similar to those found in bulk polymerization or in molecular solvents.

Alkene copolymerization with CO has been shown to be catalyzed using palladium complexes in a range of *N*-alkylpyridinium-, 1,3-dialkylimidazolium-, tetraalkylammonium-, and tetraalkylphosphonium-based [NTf₂]⁻ ILs (Scheme

Scheme 65. Cationic Ring-Opening Polymerization of 3-Ethyl-3-hydroxymethyloxetane



Scheme 66. Alkene Copolymerization with CO with Palladium Complexes in a Range of *N*-Alkylpyridinium-, 1,3-Dialkylimidazolium-, Tetraalkylammonium-, and Tetraalkylphosphonium-Based [NTf₂]⁻ ILs



66).^{449,450} Improved yields and increased molecular weights were found compared with polymerizations run in methanol. Catalyst leaching was found to be small; however, this was dependent on the IL used; for example, in [C_{*n*}pyr][NTf₂] ILs, for *n* = 8, 10, and 18, significant palladium incorporation into the polymer was found.

8.6. Oxidative Polymerization

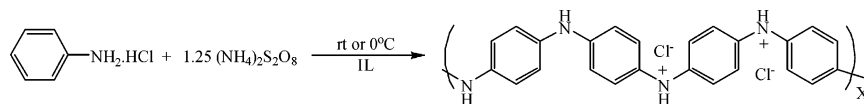
Oxidative polymerization of benzene to form poly(*p*-phenylene) has been demonstrated in chloroaluminate ILs based on [C₄pyr]Cl catalyzed by CuCl₂.⁴⁵¹ In this process the benzene molecules react with CuCl₂, and thus, polymerization only proceeded when the number of moles of benzene was greater than the oxidative agent. Organo-soluble polyaniline has also been prepared using oxidative coupling polymerization of anilium chloride with ammonium persulfate in 2-hydroxyethyl ammonium formate, resulting a polyaniline salt (Scheme 67).⁴⁵²

9. Heck Reaction

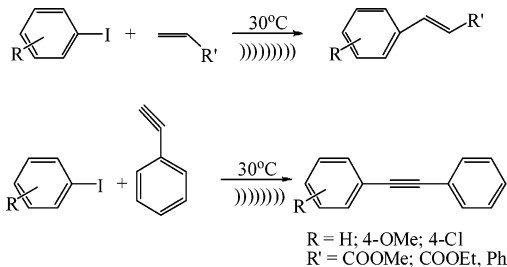
The Heck reaction is among one of the most widely studied reactions and has been reviewed at length.^{453–456} ILs have been used extensively for Heck coupling reactions of a wide range of substrates using both homogeneous and heterogeneous catalysts and found to be an excellent solvent system in terms of recyclability, yield, and control over selectivity as initially demonstrated for aryl halides and olefins using palladium catalysts by Carmichael et al.⁴⁵⁷

9.1. Homogeneous Catalysis

Although many Heck reactions use dissolved metal complexes salts normally based on palladium, whether the reactions in ILs are truly homogeneously catalyzed or activated by metal colloids is under debate. Nanoparticles of palladium have been shown by a number of studies in ILs both under conventional thermal and ultrasonic heating.^{53,54,58,458} For example, using in situ EXAFS, palladium clusters of 0.8–1.6 nm diameter have been found to be the main species present during the Heck reaction of aryl halides with alkylacrylate compounds in a range of [PF₆]⁻, [BF₄]⁻, and [NTf₂]⁻ ILs using Pd(OAc)₂.⁵³ This transformation correlated well with the activity of the system with the presence of chloride not only reducing the rate of formation of nanoparticles but also the rate of reaction. Similarly, under

Scheme 67. Oxidative Coupling Polymerization of Anilium Chloride with Ammonium Persulfate in 2-Hydroxyethyl Ammonium Formate

ultrasonic activation, nanoparticles were observed in $[C_4C_4im]-Br$ and $[C_4C_4im][BF_4]$.⁵⁴ In this case, formation of the *trans* Heck coupling products was found in yields between 73–87%; however, under similar conditions, i.e., 30 °C and ultrasound, no reaction was observed in dimethylformamide and *N*-methyl-2-pyrrolidinone (Scheme 68).

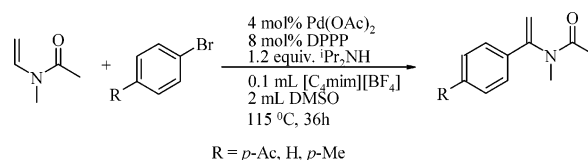
Scheme 68. Heck Coupling under Ultrasonic Activation

A range of phosphine ligands, ammonium salts, and phosphonium halides have been shown to accelerate the Heck reactions, and in particular, use of carbene palladium complexes have been studied in detail.^{459,460} The ability of ILs, for example, 1,3-dialkylimidazolium-based systems, to form carbene species has been demonstrated, and thus, use of ILs for the Heck reaction may be considered as a noninnocent solvent.^{461,462}

A wide range of Pd(0) and Pd(II) catalysts have been shown to be active for the Heck reaction in ILs including palladacycles based on *trans*-di(*m*-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II), 1,3-dimesitylimidazol-2-ylidene-palladium(0)–(η^2, η^2)-1,1,3,3-tetramethyl-1,3-divinyl disiloxane, and (1,3-dimesitylimidazol-2-ylidene)-(naphthoquinone)palladium(0).⁴⁶³ Phosphine-free systems have also been reported as effective Heck catalysts in ILs, for example, Pd(II) complexes with bisimidazole ligands as well as PdCl₂.⁴⁶⁴ The latter were found to catalyze the reaction of chlorobenzene and styrene forming stilbene in high yield.⁴⁶² This is particularly important industrially due to the use of chloroarenes. In this reaction, ILs, such as $[N_{4444}]Br$ and $[N_{4444}][OAc]$, showed significantly improved activity and stability of the catalyst system used compared with a range of polar molecular solvents with and without the presence of activators including $[PPh_4]Cl$ or $[AsPh_4]Cl$.⁴⁶² However, to achieve the high yields, dried and degassed ILs were necessary. Other haloarenes were also found to react such as deactivated *p*-bromoanisole; again, $[N_{4444}]^+$ based ILs were found to be more active compared with 1,3-dialkylimidazolium and tetraalkylphosphonium ILs.

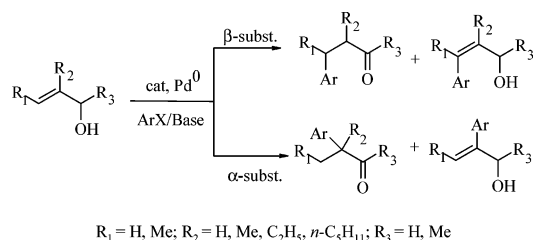
Brønsted-acid ILs based on guanidine and acetic acid have also been shown to be highly active for palladium-catalyzed Heck reactions.⁴⁶⁵ The IL acts as a solvent as well as a base, and high yields/TON were found in the reaction of bromobenzene and styrene using both Pd(OAc)₂ and PdCl₂. In this case, formation of the IL by reaction with acetic acid resulted in an active species, whereas reaction of the amine with HPF₆ formed an inactive IL. In the latter case, decomposition of the catalyst and formation of palladium black was observed.

The choice of anion in many Heck reactions is critical in governing the activity. In particular, the presence of halide ions has been shown to increase reaction rates and increase catalyst stability with iodide showing the greatest improvement over bromide and then chloride.^{466,467} In situ NMR has been used to study the effect of the anion.⁶⁷ For the Heck arylation of electron-rich olefins with aryl halides, α selectivity > 99% was observed in $[C_4mim][BF_4]$ using Pd(OAc)₂ with good yields compared with up to 75% in organic solvents (Scheme 69). However, using $[C_4mim]Br$ the rate

Scheme 69. Heck Arylation of Electron-Rich Olefins with Aryl Halides

of reaction was increased over $[C_4mim][BF_4]$ with the effect being attributed to the in situ formation of 1-butyl-3-methylimidazol-2-ylidene (bmiy) complexes of palladium $[PdBr(\mu-Br)(bmiy)]_2$ and $[PdBr_2(bmiy)_2]$ only observed in the bromide-based system.^{468,469} Interestingly, the high α selectivity may also be achieved using $[C_4mim][BF_4]$ as an additive in DMSO; however, this effect is strongly dependent on the choice of IL.⁴⁷⁰ Although the ionic pathway to form the α product is promoted by the IL, this is not the only effect, hydrogen-bonding interactions also are important, and thus the selectivity is modulated by the choice of both anion and cation. Using the $[C_4mim][BF_4]$ –DMSO solvent mixture, enamides were also found to undergo similar regioselective arylation.

Regioselective Heck coupling of aryl bromides with allylic alcohols have also been shown to be catalyzed by Pd(OAc)₂, PdCl₂, and *trans*-bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)diiodopalladium(II) in a range of tetraalkylammonium- and 1,3-dialkylimidazolium-based ILs (Scheme 70).^{179,471–474} Using these catalysts the β -arylated carbonyl

Scheme 70. Regioselective Heck Coupling of Aryl Bromides with Allylic Alcohols

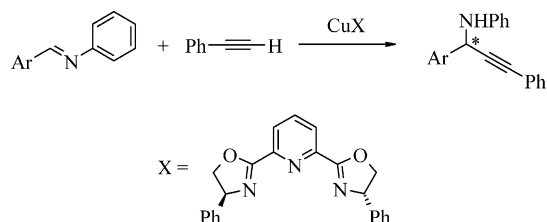
compound was formed predominantly using both aryl bromides and iodides. As compared with *N*-methylpyrrolidinone or under solventless conditions, the activity in the IL media was higher. From kinetic analysis of the reaction, an induction period was observed in the case of the stabilized *trans*-bis(2,3-dihydro-3-methylbenzothiazole-2-ylidene)diiodopalladium(II) catalyst, which indicated that this may be

a catalyst precursor and that nanoparticles may be responsible for the catalysis. The highest rates of reaction were found in the $[\text{NTf}_2]^-$ -based IL compared with the halide-based system, indicating that mass transfer may be important and the rate can be increased by reducing the viscosity of the IL.⁴⁷⁵

Highly regioselective Heck reactions of heteroaryl halides with electron-rich olefins in IL have also been reported for reactions of the heteroaryl halides, halopyridines, bromoquinoline, and bromothiophenes with the electron-rich olefins vinyl ethers and allylic alcohol.⁴⁷⁶ Using 1,3-bis(diphenylphosphino)propane as the ligand with $\text{Pd}(\text{OAc})_2$, the linear selectivity reported by Calò et al.^{471–473} and Forsyth et al.⁴⁷⁴ using allylic alcohols could be completely switched to a branched selectivity in $[\text{C}_4\text{mim}][\text{BF}_4]$. In contrast, in molecular solvents a mixture of regioisomers was observed using this catalyst/ligand system.

The related reaction of alkynes and imines may be performed enantioselectively using the in situ formed copper(I)-bis(oxazoline) complex in $[\text{C}_4\text{mim}][\text{NTf}_2]$.⁴⁷⁷ A range of substrates was found to give ee's between 84% and 99% with yields > 74% with excellent recyclability over six reactions. Interestingly, while changing the cation from $[\text{C}_4\text{mim}]^+$ to $[\text{C}_4\text{dmim}]^+$ to $[\text{C}_8\text{mim}]^+$, resulting in similar yields for the reaction of *N*-benzylidene-aniline with phenylacetylene, a decrease in enantioselectivity was observed showing that a balance of both the lipophilicity and hydrogen-bonding donor ability of the cation is required for high enantioselectivity (Scheme 71). In contrast, the type of anion was found to have little effect on the ee, but using $[\text{BF}_4]^-$ compared with either $[\text{PF}_6]^-$ or $[\text{NTf}_2]^-$ resulted in a significant reduction in yield.

Scheme 71. Reaction of *N*-Benzylidene-Aniline with Phenylacetylene

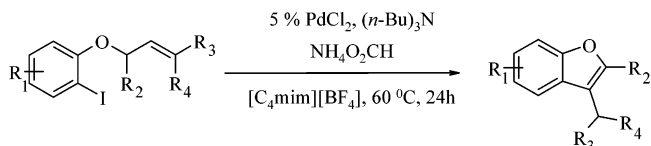


Although it is thought that the complex between $\text{Cu}(\text{OTf})_2$ and pybox forms in situ, this has not been confirmed and $\text{Cu}(0)$ may be the active catalyst. This hypothesis has been demonstrated using the copper nanoparticles to catalyze the Suzuki coupling of *p*-iodotoluene in DMF ⁴⁷⁸ as well as, more recently, copper colloids, derived from the reaction of iodobenzene with copper bronze, catalyzing the Heck coupling between aryl iodides/bromides with acrylates in the mixed IL $[\text{N}_{4444}]\text{Br}/[\text{N}_{4444}][\text{OAc}]$.⁴⁷⁹

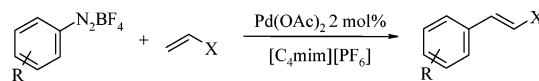
Intramolecular Heck reactions in $[\text{C}_4\text{mim}][\text{BF}_4]$ have also been reported using PdCl_2 as the catalyst.⁴⁸⁰ Therein, the intramolecular Heck reaction of *ortho*-iodo benzyl allyl ethers to substituted benzofurans was observed with reasonable yields at 60 °C (Scheme 72).

As well as aryl halides and triflates, diazonium salts may be used for the Heck reaction (Scheme 73). Kabalka et al. have shown that $\text{Pd}(\text{OAc})_2$ may be used for the reaction of olefins with substituted tetrafluoroborate arene diazonium salts in $[\text{C}_4\text{mim}][\text{PF}_6]$ with excellent yields using methyl acrylate or methyl acetonitrile at room temperature and 50 °C.⁴⁸¹ In contrast, vinyl ethers and vinyl esters showed no

Scheme 72. Intramolecular Heck Reaction of *ortho*-Iodo Benzyl Allyl Ethers to Substituted Benzofurans



Scheme 73. Heck Reaction with Diazonium Salts



reactivity, and styrenes formed dimer products. Furthermore, in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}]\text{Br}$, little yield was also found.

As found in many IL-mediated processes, microwave irradiation has been shown to be very effective for PdCl_2 - and $\text{Pd}(\text{OAc})_2$ -catalyzed Heck reactions in $[\text{C}_4\text{mim}][\text{PF}_6]$. Using these systems coupling of bromo and iodo arenes with butyl acrylate was reported to occur in 45 min or less.⁴⁸² This concept has been extended to use a continuous micro-flow system using $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ with a palladium carbene catalyst for the reaction of iodobenzene with butyl acrylate. In this system, although both ILs were effective, the lower viscosity of the $[\text{C}_4\text{mim}][\text{NTf}_2]$ enabled more efficient flow in the reactor.⁴⁸³

9.2. Heterogeneous Catalysis

Although there have been many studies examining the role of dissolved palladium species in ILs for the Heck reaction, use of traditional heterogeneous catalysts in ILs has not been studied to the same extent. The solid catalysts, for example, Pd/C , allow the catalyst to be simply recovered by filtration and have been shown to be effective for a number of activated haloarenes in ILs.^{482,484–486} Pd/C has been used to react iodo and bromo arenes with and without microwave irradiation in $[\text{C}_8\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$. However, little reaction was observed with chloroarenes unless microwave irradiation was used. Although the system is shown to be recyclable, both catalyst and IL were recycled together. Similarly, $\text{Pd}(0)$ and $\text{Pd}(\text{II})$ supported on silica have been reported for iodoarene Heck reactions in $[\text{C}_4\text{mim}][\text{PF}_6]$.⁴⁸⁶ The $\text{Pd}(\text{II})$ -supported catalysts were found to be highly active in the IL compared with DMF ; however, an induction period was observed which was thought to be due to the transformation from $\text{Pd}(\text{II})$ to $\text{Pd}(0)$. Significant leaching of Pd into the liquid phase was observed and found to be much higher in the IL than in DMF . Fifty percent of the palladium supported on the oxide was found in the IL after 1 h. More recently, Forsyth et al. have shown clearly that palladium leaching from the Pd/C catalysts is high enough for the catalysis to be considered as homogeneously catalyzed rather than heterogeneously catalyzed.⁴⁷⁴ Furthermore, much lower leaching is found in the absence of reagents, which indicates that it is the reaction which causes the dissolution and not the presence of the IL or amine. This is understandable given that the proposed mechanism of the Heck reaction involves oxidative addition of the haloarene to the $\text{Pd}(0)$ center, forming an ionic species which can then dissolve in the IL. The induction periods seen in many of the heterogeneously catalyzed reactions are thus due to the dissolution rate of palladium into solution.

Aerogels containing palladium metal nanoparticles have also been prepared using an IL-mediated route and tested

for activity toward Heck C–C coupling reactions.¹¹⁷ Using this catalyst the Heck reaction of butyl acrylate with iodobenzene was performed in DMF and showed quantitative conversion, forming *trans*-butyl cinnamate as the primary product after 2 h.

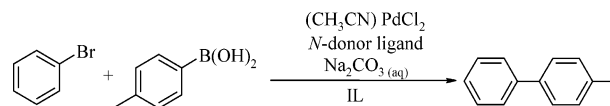
Carbon-supported palladium has also been shown to be effective in catalyzing the direct coupling of electron-deficient haloarenes, the Ullmann coupling reaction, using Aliquat 336 as the IL.⁴⁸⁷ In the presence of aqueous KOH and the IL, 100% selectivity for the coupling of phenyl iodide was achieved in the presence of 5% Pd/C and ethyl acrylate. However, depending on the base utilized and whether the system was multiphase or not, a range of selectivity was achieved, for example, NEt₃ favored the Heck coupling whereas KOH led to the Ullmann product. Interestingly, under solventless conditions a 1:1 product selectivity was observed. No recycle data was given, and therefore, although the IL led to an increase in reaction rate, it is not possible to ascertain whether the reaction was homogeneously or heterogeneously catalyzed.

Heterogeneous Heck catalysts have been reported to be stable with respect to leaching in ILs. For example, immobilization of Pd(OAc)₂ in silica gel pores with the aid of the [C₄mim][PF₆] has been found to be active for the Heck reaction in *n*-dodecane at 150 °C, giving an average of 95% and TON 68 000.⁹⁰ By grafting with silane coupling reagents, Pd(OAc)₂ was also immobilized on each of the reversed phase silica gels using the same IL and shown to catalyze the Heck reaction of aryl halides with cyclohexyl acrylate in water without a phosphines ligand with high yields and excellent recyclability for six reactions.⁹¹ The basic support, Mg–Al-layered double hydroxides, has been reported to stabilize palladium nanoparticles in the Heck coupling of chloroarenes and olefins.⁴⁸⁸ Using styrene and butylacrylate, the Heck reaction with chloroarenes was performed in [N₄₄₄₄]Br under conventional thermal and microwave heating. This system showed a higher activity over a range of other supported catalysts, including Pd/C, Pd/SiO₂, Pd/Al₂O₃, and resin-supported [PdCl₄]²⁻. Some leaching of the palladium was found; however, this solubilized species was not found to be active. Similarly, this catalytic system was found to be effective for Suzuki-, Sonogashira-, and Stille-type coupling reactions. PEG-supported 3-methylimidazolium chloride has also been shown to be an efficient recyclable medium for the Pd-catalyzed Heck reaction of aryl bromides and aryl chlorides.⁴⁸⁹ The combination of PEG-supported 3-methylimidazolium chloride with Pd(OAc)₂ provides a ligandless catalytic system for such reactions.

10. Suzuki Cross-Coupling

Palladium-catalyzed cross-coupling reactions represent another alternative for formation of C–C bonds and have also been studied in detail using ILs. Palladium(II) imidazole complexes have been used as catalyst precursors for the Suzuki coupling reactions in ILs leading to an air-stable catalyst system.^{490,491} However, to obtain a good reaction, preactivation of the catalyst was needed in the IL prior to reaction by reacting the catalyst precursor [(CH₃CN)PdCl₂] with a range of *N*-coordinating ligands, including alkyl-imidazoles, giving an active system for reaction of bromobenzene and tolylboronic acid (Scheme 74). A wide range of ILs was examined with only [C₄mim]Cl and [C₄mim][MeSO₃] showing no reaction. Furthermore, the stability of

Scheme 74. Suzuki Cross-Coupling of Bromobenzene and Tolylboronic Acid



the catalyst in the ILs was strongly dependent on the choice of ligand employed as well as the IL anion and cation.^{491,492}

The *N*-heterocyclic carbene Pd(II) complex {[Pd(Me)(3-mesityl-1-(pyrazolylmethylene)imidazolium)]chloride} was also reported to exhibit high activity for Suzuki and Heck coupling reactions [C₄mim][PF₆].⁴⁹³ Using a butylimidazole-tethered [C₄C₄im]⁺-based IL which could coordinate to PdCl₂ dissolved in the system afforded the same results.^{494,495}

Biphasic IL–water or toluene systems have also been shown to act as a good reaction medium for Suzuki and Heck couplings.⁴⁹⁶ In this case two alkylpiperidinium tetrafluoroborate melts were used in conjunction with PdCl₂, giving comparable activity with phosphine-stabilized phosphine palladium catalysts.

10.1. Heterogeneous Catalysis

Fewer studies have been reported using heterogeneous catalysts for the Suzuki–Miyaura cross-coupling reaction in ILs. Corma et al. have shown that a butylimidazolium-tethered oxime carbapalladacycle bromide catalyst could be prepared and dissolved in [C₄mim][PF₆].⁴⁹⁷ However, the activity of this catalyst–IL system was poor with yields below 30%; however, when adsorbed onto a high surface area Al/MCM-41 aluminosilicate, high yields were found for a range of substrates in DMF and toluene promoted by [NBu₄]Br. Although the catalyst could be recycled and the conversion maintained over three reactions, active palladium was found in solution and estimated to be responsible for 30% of the conversion observed.

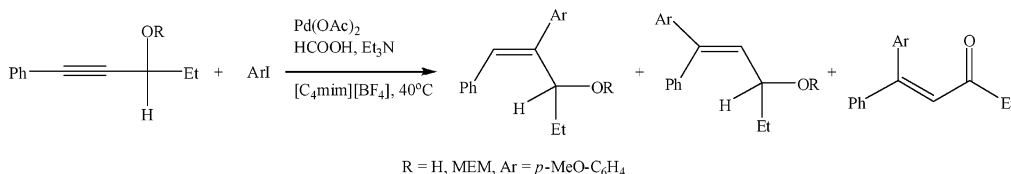
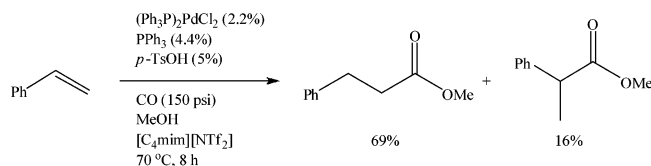
11. Other Reactions

11.1. Hydroarylation

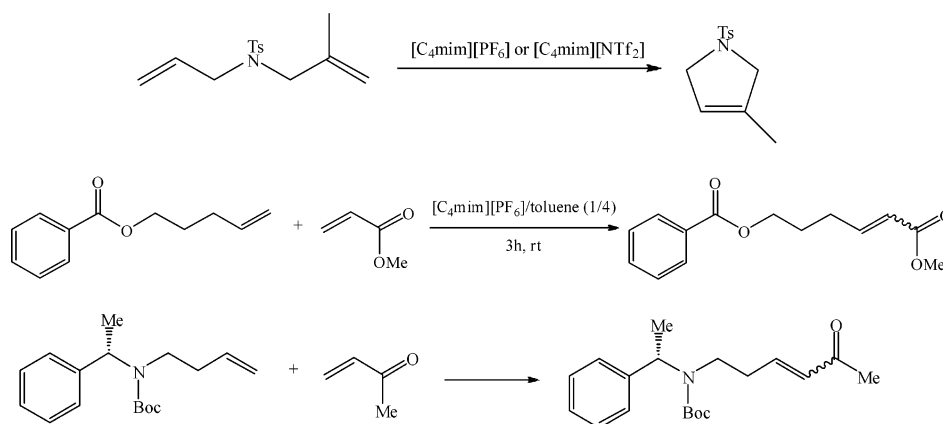
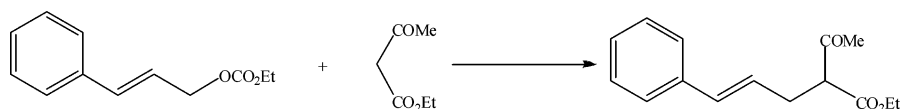
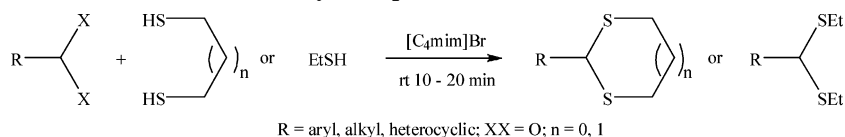
Pd(OAc)₂ has been shown to catalyze the hydroarylation of propargylic alcohols with aryl iodides in the presence of HCOOH and Et₃N in [C₄mim][BF₄] (Scheme 75).⁴⁹⁸ Therein, the reaction showed good stereoselectivity with the IL process resulting in better regioselective control than found in molecular solvents.

11.2. Hydroesterification

Klingshirn et al. used a wide range of ILs for the [(Ph₃P)₂PdCl₂]-catalyzed hydroesterification of styrene with CO and methanol giving high selectivity for linear over branched esters products (Scheme 76).⁴⁹⁹ The high linear selectivity was found to be independent of the reaction conditions and indicated that the IL mediated the cationic reaction mechanism. Some variation was observed on changing the anion of the IL. In the case of chloride, strong coordination of the anion led to a decrease in both selectivity and activity. Although higher yields and selectivity were found for [EtSO₄]⁻-based ILs compared with [PF₆]⁻ and [NTf₂]⁻ anions, no clear correlation was found with corresponding Kamlet–Taft parametrization.

Scheme 75. Hydroarylation of Propargylic Alcohols with Aryl Iodides in the Presence of HCOOH and Et₃N in [C₄mim][BF₄]**Scheme 76. Hydroesterification of Styrene with CO and Methanol****11.3. Ring-Closing Metathesis of Di-, Tri-, and Tetrasubstituted Dienes**

The ring-closing metathesis of di-, tri- and tetrasubstituted diene and enyne substrates has been demonstrated using Grubbs and Hoveyda–Grubbs ruthenium carbene complex bearing an IL tag in mixed solvent systems containing [C₄mim][PF₆] and CH₂Cl₂ or toluene.^{500–502} Buijsman et al. showed that Grubbs catalyst could be used dissolved in pure [C₄mim][PF₆], but a significant decrease in conversion was found on the second recycle.⁵⁰³ Although in many cases the IL protects the catalyst and enables reuse, when the catalyst is modified with the IL tag the recyclability is improved significantly.⁵⁰⁴ Similarly, imidazolium-tagged ruthenium catalysts have also been reported to perform di- or trisubstituted diene metathesis including substrates containing oxygen in [C₄mim][PF₆] and [C₄mim][NTf₂] (Scheme 77).⁵⁰⁵

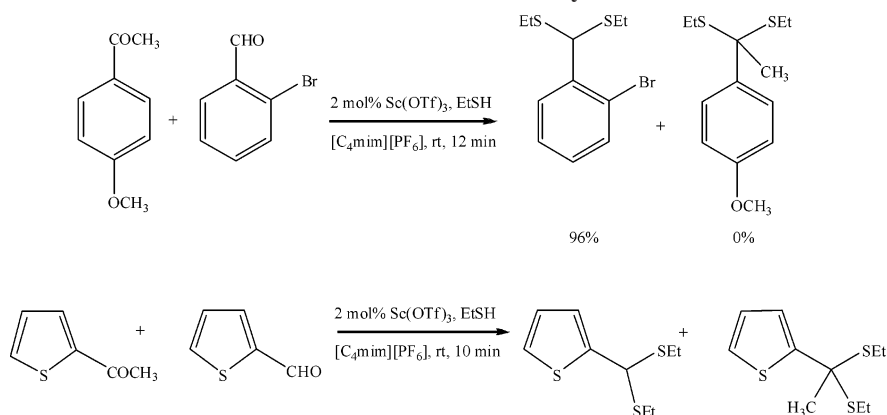
Scheme 77. Ring-Closing Metathesis of a Variety of Di- or Trisubstituted Dienes**Scheme 78. Trost–Tsuji C–C Coupling between Ethyl Cinnamyl Carbonate and Ethyl Acetoacetate****Scheme 79. IL-Mediated Thioacetalization of Carbonyl Compounds****11.4. Trost–Tsuji C–C Coupling**

De Bellefon et al. have shown that PdCl₂, dissolved in [C₄mim]Cl in the presence of triphenylphosphine trisulfonate, is highly effective for the Trost–Tsuji C–C coupling between ethyl cinnamyl carbonate and ethyl acetoacetate (Scheme 78). Use of the IL increased the solubility of the reactants compared with the corresponding aqueous system resulting in increased reaction rates and also prevented conversion of the carbonate into cinnamyl alcohol.⁵⁰⁶ Nucleophilic substitution of acetate groups in allylic compounds with a range of ester-derived nucleophiles has been shown with Pd(OAc)₂ in the presence of a phosphine ligand and base in [C₄mim][BF₄]. In this case, good yields were achieved and the catalyst could be recycled with no requirement to form the carbanion nucleophile separately.⁵⁰⁷

11.5. Thioacetalization of Carbonyl Compounds

Both Lewis-acid-catalyzed and IL-mediated thioacetalization of carbonyl compounds have been reported.⁵⁰⁸ In the absence of a catalyst, [C₄mim]Br has been shown to mediate the thioacetalization of activated and weakly activated aromatic aldehydes as well as heterocyclic and aliphatic aldehydes and acid-sensitive substrates such as furfural without formation of any side products (Scheme 79). However, reaction with aromatic ketones did not result in the corresponding thioacetals, whereas cyclohexanone formed

Scheme 80. Thioacetalization and Transthioacetalization of Aromatic Aldehydes

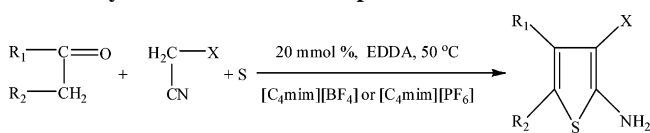


the thioacetal in almost quantitative yield. This difference in reactivity was attributed to the higher electron density around the carbonyl carbon of an aromatic ketone, making it less susceptible to nucleophilic attack. Thioacetalized and transthioacetalized products of aromatic and aliphatic aldehydes have also been prepared using $\text{Sc}(\text{OTf})_3$ dissolved in $[\text{C}_n\text{-mim}]^+$ -based $[\text{PF}_6]^-$ and $[\text{BF}_4]^-$ ILs (Scheme 80).⁵⁰⁹

11.6. Gewald Synthesis

2-Aminothiophenes derivatives are important intermediates in the manufacture of pharmaceuticals, dyes, and conducting polymers, for example, and may be prepared in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ using ethylenediammonium diacetate as a catalyst for the Gewald reaction.⁵¹⁰ Significant rate enhancements and improvements in the yield were observed under these conditions compared with molecular solvents. This is not surprising given that the Knoevenagel condensation is a key step in the Gewald reaction and ethylenediammonium diacetate in $[\text{C}_4\text{mim}][\text{PF}_6]$ has been shown previously to catalyze the reaction of aldehydes and ketones with methylene compounds (Scheme 81).⁵¹¹

Scheme 81. Ethylenediammonium-Diacetate-Catalyzed Gewald Synthesis of 2-Aminothiophenes

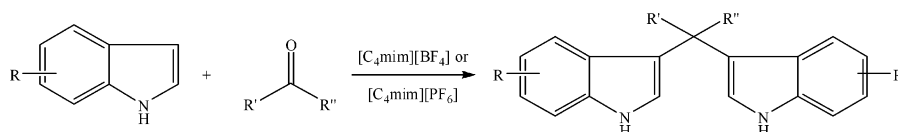


11.7. Reactions of Carbonyl Compounds

11.7.1. Reactions with Indoles

$[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$ have been used to prepare bis-indolylmethanes via the electrophilic substitution reaction of indoles with aldehydes and ketones (Scheme 82).⁵¹² Both aromatic and aliphatic aldehydes as well as cyclic ketones resulted in good yields with rates dependent on the substrate employed. In a similar manner, the microwave-activated synthesis of tetrahydro- β -carboline-diketopiperazines in $[\text{PF}_6]^-$ -based ILs has been performed.⁵¹³

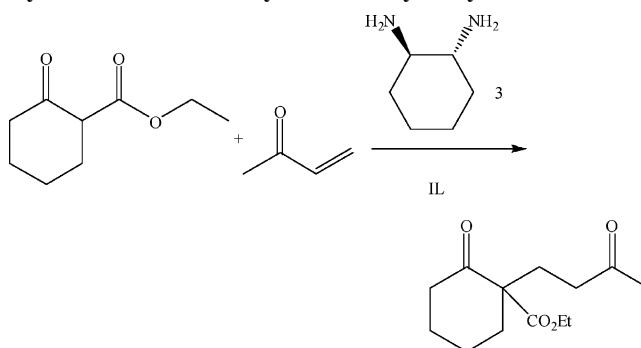
Scheme 82. Preparation of Bis-indolylmethanes through Electrophilic Substitution Reactions of Indoles with Aldehydes and Ketones in ILs



11.7.2. Michael Additions

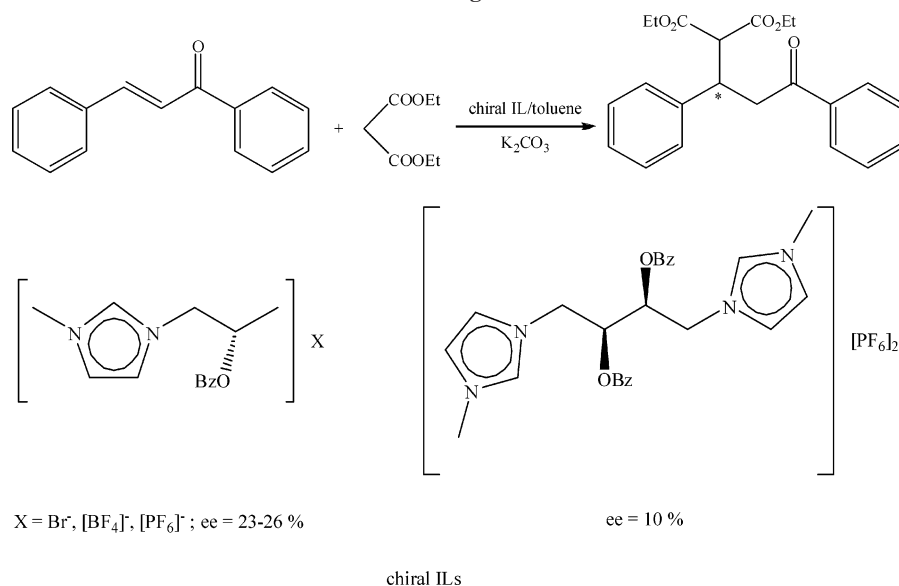
A wide range of Michael additions and related reactions have been performed in ILs. For example, in $[\text{C}_4\text{mim}][\text{BF}_4]$, both $\text{Ni}(\text{acac})_2$ for the conversion of acetylacetone to methylvinylketone^{514,515} and $\text{Cu}(\text{OTf})_2$ for a range of addition reactions have been used as catalysts and show higher rates of reaction compared with molecular solvents or under solventless conditions. Enantioselective Michael addition reactions have also been performed in $[\text{BF}_4]^-$ -based ILs using (*R,R*)-*trans*-1,2-diaminocyclohexane as the chiral auxiliary.⁵¹⁶ In this case ee's up to 91% were found for conversion of ethyl cyclohexanone-2-carboxylate to methyl vinyl ketone with good yields even when catalytic amounts of diamine were employed (Scheme 83). Changing the cation from $[\text{C}_4\text{mim}]^+$ to $[\text{C}_4\text{dmim}]^+$ to $[\text{C}_4\text{pyr}]^+$ caused the yield to drop and was attributed to the change in the IL ability to solvate water.

Scheme 83. Conversion of Ethyl Cyclohexanone-2-carboxylate to Methyl Vinyl Ketone

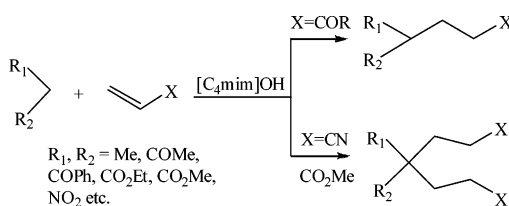


Enantioselective Michael additions of malonates to form enones has been examined using chiral functionalized imidazolium salts with Br^- , $[\text{BF}_4]^-$, and $[\text{PF}_6]^-$ anions (Scheme 84).⁵¹⁷ With toluene as a cosolvent, some chiral induction was achieved with yields of >90% and ee's between 23% and 26%. Using a dication chiral IL reduced the ee to 10%.

Scheme 84. Enantioselective Michael Addition of Malonates Using Chiral Functionalized Imidazolium Salts



Incorporation of hydroxide as the anion using [C₄mim]⁺ allows the IL to be employed as the catalyst and solvent for a wide range of Michael addition reagents. Although the Michael addition to α,β -unsaturated ketones gave the expected monoaddition product, in the case of the reaction of 1,3-dicarbonyl compounds with α,β -unsaturated esters and nitriles, bis-addition was found in the IL (Scheme 85).⁵¹⁸

Scheme 85. Reaction of 1,3-Dicarbonyl Compounds with α,β -Unsaturated Esters and Nitriles

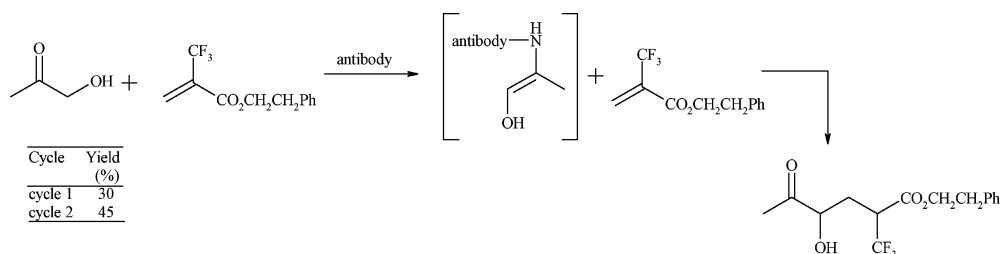
The biocatalyzed Michael reaction for the reaction of fluoromethylated imines with hydroxyacetone has also been performed using aldolase 38C2 in [C₂mim][OTf].³⁵⁴ For the reaction between hydroxyacetone and 2-(phenyl)-ethyl-2-

(trifluoromethyl)acrylate 30% yield of the Michael adduct was formed after 14 days and 45% yield was found on recycle (Scheme 86).

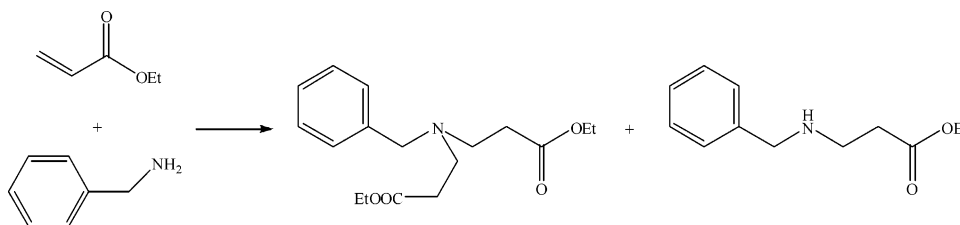
Aza-Michael addition reactions between benzylamine and ethyl acrylate have also been reported to give high yields using a wide range of tetraalkylammonium halide ILs as catalysts in water (Scheme 87).⁵¹⁹ In contrast, aromatic amines, such as aniline, gave poor results. Furthermore, [C₄mim][BF₄] could also be employed in this manner for the aza-Michael reaction of a variety of aliphatic amines and α,β -unsaturated compounds as well as the aza-Michael reaction with N₃⁻ addition to α,β -unsaturated carbonyl compounds in the presence of acetic acid.⁵²⁰ Cu(acac)₂ dissolved in [C₄mim][PF₆] and [C₄mim][BF₄] has been found to catalyze the aza-Michael reaction of amines and nitriles with α,β -unsaturated carbonyl compounds forming the corresponding β -amino carbonyl compounds and nitriles with high yields.⁵²¹

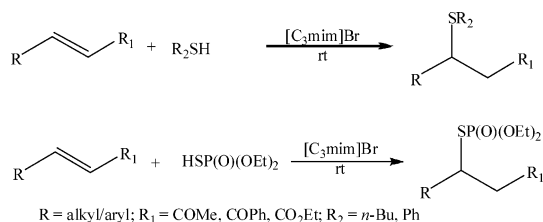
As observed in water, bromide, in this case in the form of [C₃mim]Br, has been shown to catalyze the Michael addition of thiols and diethyl dithiophosphate to a range of conjugated alkenes (Scheme 88).⁵²² Although good yields were obtained

Scheme 86. Biocatalyzed Michael Reaction of Fluoromethylated Imines with Hydroxyacetone



Scheme 87. Aza-Michael Addition Reactions between Benzylamine and Ethyl Acrylate

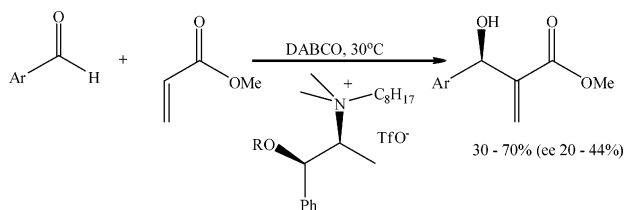


Scheme 88. Michael Addition of Thiols and Diethyl Dithiophosphate to Conjugated Alkenes

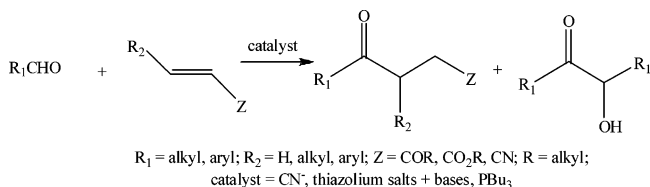
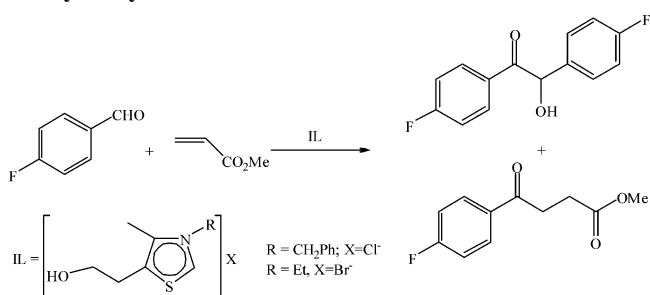
in many cases, steric hindrance at the β position of the alkene resulted in a loss of activity.

11.7.3. Baylis–Hillman Reaction

The Baylis–Hillman reaction is a useful C–C bond-forming reaction and has been shown to be catalyzed by DABCO for the reaction between methyl acrylate and a range of aldehydes.⁵²³ In this case the choice of cation was found to be critical with only [C₄dmm][PF₆] reaction showing. In contrast in [C₄mim][PF₆], the IL was found to react with the aldehyde in the presence of base.⁵²⁴ The reaction may also be performed using the chiral IL *N*-ocetyl(-)-*N*-dimethyl-ephedrinium triflate (Scheme 89).⁵²⁵ Therein, reaction of benzaldehyde and methyl acrylate led to formation of the alkoxyester with up to 44% ee.

Scheme 89. Baylis–Hillman Reaction of Benzaldehyde and Methyl Acrylate**11.7.4. Stetter Reaction**

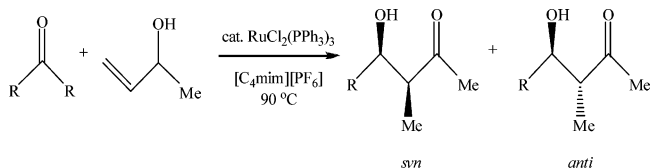
The Stetter reaction to prepare 1,4-dicarbonyls has been reported in [C₄mim][BF₄], [C₄mim][PF₆], and [C₄mim][NTf₂] ILs by Anjaiah et al. (Scheme 90).⁵²⁶ For a range of aldehydes and olefins, both showed that both thiazolium salts

Scheme 90. Stetter Reaction**Scheme 91. Condensation of *p*-Fluorobenzaldehyde with Methyl Acrylate**

and Et₃N could be employed as catalysts in the ILs giving good yields of the 1,4-adducts (Scheme 91).

11.7.5. Cross-Coupling between Aldehydes and Allylic Alcohols

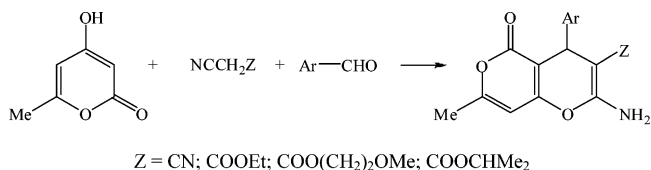
As well as base-catalyzed aldol reactions, RuCl₂(PPh₃)₃ has been shown to catalyze the aldol condensation between allylic alcohols and aldehydes in [C₄mim][PF₆], even those with low reactivity such as 2-naphthaldehyde or *p*-anisaldehyde (Scheme 92).⁵²⁷ Interestingly, in the IL the electron-

Scheme 92. Condensation between Allylic Alcohols and Aldehydes in [C₄mim][PF₆]

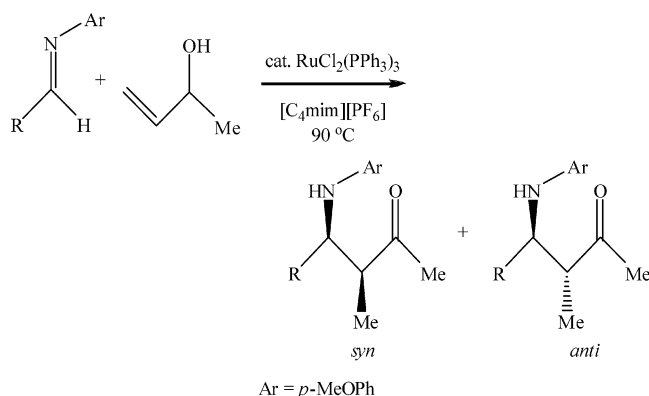
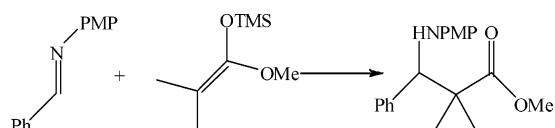
deficient aldehydes showed the highest activity which is the opposite trend to that found in molecular solvents, including water. This was attributed to the increased solvation by the IL of the more polarized electron-deficient aldehydes. In contrast, neither aromatic nor aliphatic ketones gave good yields under these conditions.

11.7.6. Cross-Condensation of Carbonyl Compounds with Derivatives of Cyanoacetic Acid

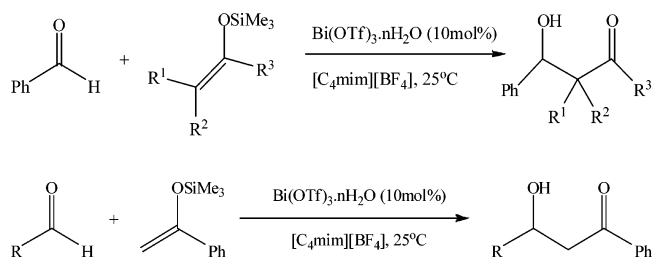
The three-component reaction of 4-hydroxy-6-methylpyran-2(2*H*)-one with cyanoacetic acid derivatives and carbonyl compounds has also been shown to occur in [C₄mim][PF₆] to form substituted 2-amino-7-methyl-5-oxo-4,5-dihydropyrano[4,3-*b*]pyrans (Scheme 93).⁵²⁸ In the presence of Et₃N, higher yields were found in the IL compared with using ethanol.

Scheme 93. Three-Component Reaction of 4-Hydroxy-6-methylpyran-2(2*H*)-one with Cyanoacetic Acid Derivatives and Carbonyl Compounds in [C₄mim][PF₆]**11.7.7. Mannich-type Reaction**

In a similar manner to the aldol reaction, the reaction between allylic alcohols and imines can be catalyzed by RuCl₂(PPh₃)₃ in [C₄mim][PF₆] (Scheme 94).⁵²⁷ The corresponding reaction in water was found to form the aldol product due to hydrolysis of the imine; however, in the IL only Mannich products were obtained with increased yields over molecular solvent systems. Akiyama et al. have also shown that the Mannich reaction of silyl enolates with imines may be performed in [C₄mim][OTf] and [C₂mim][OTf] in the presence or absence of base, indicating that residual acid is not the catalyst but the triflate anion (Scheme 95).⁵²⁹

Scheme 94. Mannich Reaction**Scheme 95. Mannich Reaction of Silyl Enolates with Ald-imines****11.7.8. Mukaiyama Aldol Reaction**

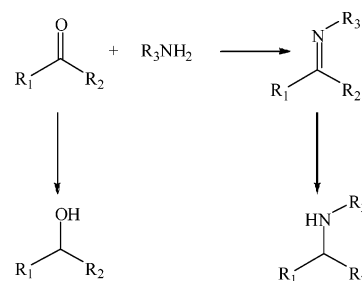
IL-mediated-uncatalyzed and Lewis-acid-catalyzed Mukaiyama aldol reactions show good reactivity for the coupling of trimethylsilane derivatives with aldehydes (Scheme 96). For example, the reaction between nonyl aldehyde and

Scheme 96. Mukaiyama Aldol Reactions for Coupling of Trimethylsilane Derivatives

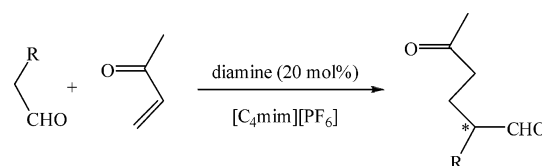
1-methoxy-2-methyl-1-trimethyl-silyloxypropene was performed in $[C_n\text{mim}]^+$ based ILs containing Cl^- , $[\text{BF}_4]^-$, and $[\text{PF}_6]^-$ anions. A combination of long alkyl chain cations with chloride was found to result in the highest yield of the aldol product.⁵³⁰ In $[\text{C}_4\text{mim}][\text{BF}_4]$, $\text{Bi}(\text{OTf})_3$ catalyzed the formation of a range of β -hydroxy ketones and esters with aldehydes; however, substitution of the aldehyde with a ketone resulted in no reaction for the reaction of acetophenone with (1-phenylvinyl)oxy)trimethylsilane.⁵³¹ Using this method, thioesters were also prepared, although in this case poor syn/anti selectivity was observed.

11.7.9. Reductive Amination of Carbonyl Compounds with Amines

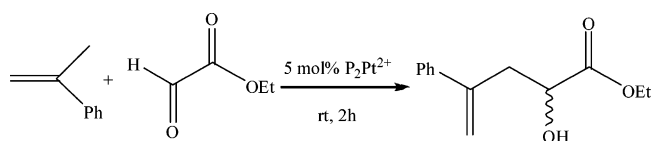
Direct reductive amination of carbonyl compounds with amines has been achieved using the cationic homogeneous iridium catalyst, $[\text{Ir}(\text{cod})_2][\text{BF}_4]$, without any other ligands and gaseous hydrogen (Scheme 97).⁵³² As a reaction medium, $[\text{C}_4\text{mim}][\text{BF}_4]$ was found to be superior to the other organic solvents. While the cation exhibited a small effect, the counteranion of the IL has been found to exert a significant influence on the selectivity with tetrafluoroborate found to give the best selectivities. This effect was attributed to a compatibility of the IL anion with that in the catalyst.

Scheme 97. Reductive Amination of Carbonyl Compounds with Amines**11.7.10. 1,4-Conjugate Addition of Unmodified Aldehyde**

The 1,4-conjugate addition of aldehydes to 3-buten-2-one may be performed using diamines derived from L-proline in $[\text{C}_4\text{mim}][\text{PF}_6]$ and was found to show higher activity than reactions catalyzed by other amines (Scheme 98). Using these conditions up to 59% ee of (2*S*)-5-keto-aldehyde was obtained with the largest ee found with increasing bulkiness of the diamine used.⁵³³

Scheme 98. 1,4-Conjugate Addition of Aldehydes to 3-Buten-2-one**11.7.11. Carbonyl–Ene Reaction**

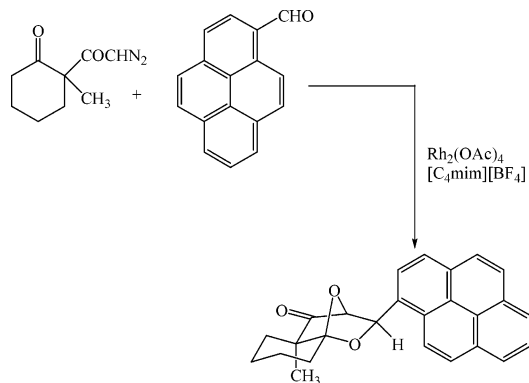
The enantioselective carbonyl–ene reaction is demanding; however, using enantiopure Lewis acid complexes of conformationally flexible acyclic and monocyclic NUPHOS diphosphines, δ - and λ - $[(\text{NUPHOS})\text{Pt}(\text{OTf})_2]$ have been shown to act as efficient catalysts for the reaction between various unsymmetrical 1,1'-disubstituted alkenes and phenylglyoxal or ethyl glyoxylate in a range of ILs (Scheme 99).⁵³⁴

Scheme 99. Carbonyl–Ene Reactions of α -Methylstyrene and Ethyl Glyoxylate

Therein, up to 95% ee's and 90% yields were obtained depending on the substrate used. In all cases, the enantioselectivities in the ILs were at least comparable to those obtained in dichloromethane. As shown for similarly catalyzed Diels–Alder reactions in ILs,⁴¹⁷ racemization of the catalyst was found in dichloromethane whereas little racemization was observed in the IL leading to the greater ee's observed.

11.7.12. Tandem Cyclization–1,3-Dipolar Cycloaddition Reaction of α -Diazo Ketones

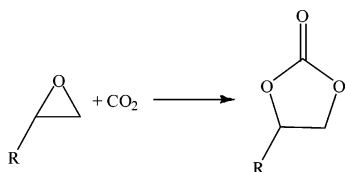
Synthesis of oxa- and dioxo-bridged polycyclic systems using the cyclization–cycloaddition reaction of transient five- or six-membered-ring carbonyl ylides with α -diazo ketones has been catalyzed by Rh(II) and Cu(II) salts dissolved in

Scheme 100. Rhodium(II)-Catalyzed Tandem Reaction of α -Diazo Ketone and an Aldehyde in $[\text{C}_4\text{mim}][\text{BF}_4]$


$[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_1\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}][\text{PF}_6]$ (Scheme 100).⁵³⁵ The reaction was found to proceed with high stereoselectivity in all ILs and molecular solvents. However, in the case of $[\text{C}_4\text{mim}][\text{BF}_4]$, a significant increase in the yield of the cycloaddition product was also observed compared with organic solvents. Higher yields were obtained using the rhodium-based catalysts compared with the copper system. The ILs based on $[\text{BF}_4]^-$ rather than $[\text{PF}_6]^-$ also lead to increased yields. Albeit a small difference, greater yields were observed in the ILs compared with in dichloromethane.

11.7.13. CO_2 Cycloaddition to Epoxide

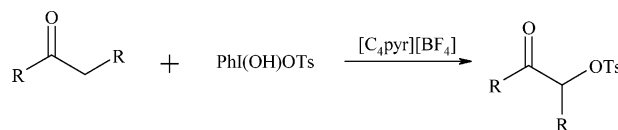
This subject was recently reviewed by Sun et al. extensively and demonstrates the applicability of ILs for CO_2 fixation to produce cyclic carbonates (Scheme 101).⁵³⁶ Peng

Scheme 101. CO_2 Cycloaddition to Epoxide


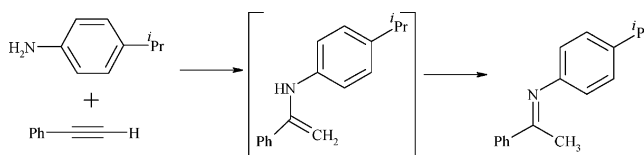
et al. have shown that addition of CO_2 to propylene oxide may be mediated by 1,3-diacylimidazolium and *N*-alkylpyridinium-based ILs based on Cl^- , $[\text{BF}_4]^-$, and $[\text{PF}_6]^-$ with $[\text{C}_4\text{mim}][\text{BF}_4]$ showing the best reactivity.⁵³⁷ In comparison with aliphatic epoxides, aromatic compounds are less active in this reaction but may be performed in $[\text{N}_{4444}]\text{Br}$ and $[\text{N}_{4444}]\text{I}$.^{536,538–540} At atmospheric pressure, styrene oxide and glycidyl methacrylate oxirane, the latter susceptible toward polymerization, have been reacted with CO_2 in the $[\text{N}_{4444}]^+$ melts with the iodide anion showing higher activity than bromide due to its decreased nucleophilicity. By reacting halide-based ILs, for example, $[\text{C}_4\text{mim}]\text{Cl}$ and $[\text{C}_4\text{mim}]\text{Br}$, with Lewis acids, such as zinc halides, the activity of the IL and Lewis acid are improved for this reaction. Formation of $[\text{ZnX}_2\text{Y}_2]^{2-}$ ($\text{X}, \text{Y} = \text{Cl}$ or Br) was found to catalyze the cycloaddition of CO_2 to propylene oxide. Kim et al. demonstrated that anions containing a higher proportion of bromide were more reactive, which supports the fact that the nucleophilicity of the halide is important.⁵⁴¹ A similar effect of metal halides has also been observed for styrene oxide with the activity determined by the ionization potential and ionic radius of the metal cations used.⁵⁴² In addition, chromium salen has been observed to catalyze the reaction of CO_2 with styrene oxide in $[\text{C}_4\text{mim}][\text{PF}_6]$.⁵⁴³

11.7.14. α -Tosyloxylation of Ketones

Tosylation using HTIB of a range of ketones has been performed in $[\text{C}_4\text{pyr}][\text{BF}_4]$ resulting in good yields of the α -tosylated compound (Scheme 102).⁵⁴⁴

Scheme 102. α -Tosyloxylation of Ketones

11.8. Heterogeneous Catalysis
11.8.1. Hydroamination Reactions

Heterogeneous catalysts obtained by the deposition of metal complexes $[\text{Rh}(\text{DPPF})(\text{NOR})][\text{ClO}_4]$, $[\text{Pd}(\text{DPPF})][\text{OTf}]_2$, $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)][\text{OTf}]_2$, and $\text{Zn}(\text{OTf})_2$ on the diatomic earth support from $[\text{C}_2\text{mim}][\text{OTf}]$, using a shock-frozen and freeze-drying technique, were tested for catalytic activity on addition of 4-isopropylaniline to phenylacetylene (Scheme 103).⁵⁴⁵ The reaction yields the enamine (4-isopropylphenyl)-

Scheme 103. Addition of 4-Isopropylaniline to Phenylacetylene


(1-phenyl-vinyl)-amine which isomerizes in situ to the corresponding imine (4-isopropyl-phenyl)-(1-phenylethylidene)-amine. The product was formed according to approximate second-order kinetics. For the supported $[\text{Rh}(\text{DPPF})(\text{NOR})][\text{ClO}_4]$, $[\text{Pd}(\text{DPPF})][\text{OTf}]_2$, and $\text{Zn}(\text{OTf})_2$ catalysts the rate of reaction was significantly higher than in the corresponding homogeneous catalysis. In contrast, for $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)][\text{OTf}]_2$ the catalytic activity was higher for the homogeneous catalyst. This was explained by a strong complexation of the copper(I) center by the IL which competes with coordination of the substrate. In the case of the homogeneous catalysis, the most pronounced side reaction was oligomerization of phenylacetylene. Under similar reaction conditions, the performance of the two-phase system was intermediate between the catalysis using homogeneous and supported catalysts.

12. Conclusions

As is clear from this review, catalysis in ILs is hugely varied and in many cases the IL enables more efficient reactions to take place compared with molecular solvents. It is necessary to optimize both reactions to enable a true comparison to be made. Large increases in reactivity and selectivity have been achieved using this medium for homogeneously catalyzed reactions, and in some cases, reactions have been demonstrated to only work in the ionic environment and not in the molecular solvents. While similar remarks can also be attributed to heterogeneously catalyzed reactions, the depth of study has not yet been achieved for trends to be easily identified. However, it is clear that there is a large potential using the combination of ILs and solid catalysts in both liquid-phase and gas-phase reactions. The latter shows the versatility of ILs in stabilizing homogeneous

catalysts and enables good mass transport of gas reagents using thin films of the IL. Much more research needs to be performed in this area to explore the scope of IL–solid interactions in terms of chemical reactivity and selectivity. To date, an understanding as to how ILs affect surface reactions and the mass transport phenomena within such systems is limited. This is particularly important in solid-catalyzed processes, and further research needs to address this issue.

13. Acknowledgment

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