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Hydrogenation in Ionic Liquids

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1. Introduction

One of the principal present-day challenges facing the field of transition metal catalysis is the efficient recycling and reuse of catalysts and ligands. The use of ILs is rapidly advancing in this discipline. Due to their tunable physico-chemical properties, which differ markedly from those of conventional organic and aqueous media, ILs can provide a means of catalyst immobilization. The non-nucleophilic and weakly co-ordinating nature of many classes of ionic liquid provides an inert reaction medium that can extend the lifetime of a catalyst. Recyclability of the catalyst system is a key attribute of IL media and it is this enhancement of catalyst performance that is driving research in this field. Low-polarity compounds, for example diethyl ether and *n*-hexane, are poorly soluble in common ILs, providing a suitable accompanying solvent for biphasic catalysis. The positive aspects of homogeneous and heterogeneous catalysis are combined using a biphasic system, in which the catalyst resides in the IL, but the substrates/products are retained in the alternate phase. Thus, the biphasic system provides a cost-effective way to successfully separate the desired product by simple decantation, leaving the catalyst immobilised in the IL and ready for reuse. Product isolation is often simplified even in monophasic catalysis if the substrate is soluble in the IL medium, but the product can be separated by simple extraction or distillation, due to the low vapour pressure of the IL. The reduced polarity of the hydrogenated products in comparison with the substrate can also be exploited for separation from the IL/catalyst phase. Increasing the difference in polarity between the IL and the hydrogenated product can also render the product insoluble in the IL, thus allowing facile decantation of the product from the IL, leaving the IL/catalyst phase ready for the next reaction.

Research into catalytic hydrogenations in ILs began in 1995 with the almost simultaneous work of Chauvin[1] and Dupont.[2] Since then this field has been extended from conventional hydrogenation using transition metal catalysts to transfer hydrogenation and the effect of nanoparticles on hydrogenation reactions in ILs. Supported ionic liquid catalysis (SILC) is also a relatively new field. Using this method, the added benefit of selectivity provided by the homogeneous catalyst can be combined with the attributes of heterogeneous biphasic catalysis. The homogeneous catalyst is, in effect, immobilised on a heterogeneous support. One of the first investigations in this area was carried out by Mehnert *et al.*[3] in 2002, with a flurry of papers ensuing from 2007-2009.

It is intended that this chapter should cover recent progress in hydrogenation reactions carried out in ILs. Wasserscheid and Schulz[4] contributed a chapter in 'The Handbook of Homogeneous Hydrogenation' covering homogeneous hydrogenation in ILs which covers

advances up to 2005. More recent summaries of hydrogenation in ILs can be found in 'Ionic Liquids in Synthesis' as part of the chapter on Transition Metal Catalysis in Ionic Liquids[5] and within several reviews covering the wider area of IL catalysis.[6, 7, 8] Moreover, outside the scope of this chapter is the concept of tailored ILs used in hydrogenation reactions, which was covered in 2008 by Sebesta *et al.*[9] For each hydrogenation reaction reviewed in this chapter, the catalyst and IL are noted, together with the genre of substrate. Particular consideration is paid to conversion and turnover numbers obtained using ILs as alternatives to commonly used volatile organic solvents. A section describing kinetic and thermodynamic studies of reactions in ILs is also presented. ILs are not always the preferred choice of solvent, and cases where the IL was found to be less effective than a conventional molecular solvent are included.
Throughout this chapter abbreviations used are as follows:
[emim]: 1-ethyl-3-methylimidazolium, [bmim]: 1-*n*-butyl-3-methylimidazolium, [omim]: 1-*n*-octyl-3-methylimidazolium, [dmim]: 1-*n*-decyl-3-methylimidazolium, [dodecylmim]: 1-*n*-dodecyl-3-methylimidazolium, [bdmim]: 1-*n*-butyl-2,3-dimethylimidazolium, [TEA]: tetraethylammonium, [TBA]: tetrabutylammonium, [mbpy]: 4-methyl-*N*-butyl-pyridinium, [DAMI]: 1,3-di(*N*,*N*-dimethylaminoethyl)-2-methylimidazolium, [C_8Py]: *N*-octylpyridinium, [BMPL]: *N*-butyl-*N*-methylpyrrolidinium, [B3MPYR]: *n*-butyl-3-methylpyridinium, [bmmim]: 1-*n*-butyl-2,3-dimethylimidazoliium, [bmimOH]: hydroxyl-functionalized butyl-3-methylimidazolium, [BF_4]: tetrafluoroborate, [PF_6]: hexafluorophosphate, [NTf_2]: trifluoromethanesulfonimide, [OTf]: triflate, [$N(CN)_2$]: dicyanamide, [NO_3]: nitrate, [HSO_4]: hydrogen sulphate, [$EtOSO_3$]: ethyl sulphate, [$BuOSO_3$]: butyl sulphate, [$HexOSO_3$]: hexyl sulphate, [$OctOSO_3$]: octyl sulphate, TOF: turn over frequency, TON: turn over number, BINAP: 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl, COD: 1,5-cyclo-octadiene, ee: enantiomeric excess, CIL: chiral ionic liquid, $scCO_2$: supercritical carbon dioxide, IPA: isopropanol, SILC: supported ionic liquid catalysts, SILP: supported ionic liquid phase, SSILP: structured supported ionic liquid-phase, SCILL: solid catalyst with ionic liquid layer, CTH: catalytic transfer hydrogenation, OSN: organic solvent nanofiltration, TSIL: task-specific ionic liquid, COE: cyclooctene, COA: cyclooctane, PVP: poly(*N*-vinyl-2-pyrrolidone), [N_{6222}]: triethylhexylammonium, [N_{22212}]: triethyldodecylammonium, [N_{22214}]: triethyltetradecylammonium, MAA: methyl acetoacetate, Ts-DPEN: *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine, [$P_{14,6,6,6}$]: trihexyltetradecylphosphonium, [$P_{4,4,4,4}$]: tetrabutylphosphonium, [P1,*i*4,*i*4,*i*4]: tri-*iso*-butylmethylphosphonium, ECOENG 500™: Peg-5 cocomonium methosulfate.

2. Kinetic and Thermodynamic properties:

A major advantage of ionic liquids as the solvent in hydrogenation reactions is the ability to fine tune the properties of the solvent by altering the structure. Hence it becomes very important for a chemist to investigate the kinetic and thermodynamic aspects of the reactions. Although only few detailed studies of the kinetics of hydrogenation reactions in ionic liquids have been reported, from available results it can be shown that the reaction kinetics, product selctivity, reaction yields, TOFs of catalysts are greatly influenced by the cations and anions of ionic liquids and their concentration in the reaction system.
It is also important to compare the trends of H_2 gas solubilities in ionic liquids and molecular solvents, while studying reaction kinetics. Table 1 summarizes the H_2 solubilities in various solvents, along with densities and viscosities. [10]

Solvent	Henry's Constant, k_H/MPa[a]	$10^3[H_2]$ (M)	Density (g/Ml)	Viscosity (cP)	Ref.
Water[b]	6.8 x 10^3	0.81	0.9982[11]	0.89[c],[12]	[13]
Methanol[b]	6.6 x 10^2	3.75	0.7914[11]	0.55[c],[12]	[14]
Ethanol[b]	5.9 x 10^2	2.98	0.7893[11]	1.06[c],[12]	[14]
Toluene[b]	2.69 x 10^2	3.50	1.4961[11]	0.45[b],[12]	[14]
Benzene[b]	4.47 x 10^2 (4.39 x 10^2)	2.54 (2.57)	0.878[11]	0.60[c],[12]	[10,13]
Cyclohexane[b]	2.57 x 10^2 (2.55 x 10^2)	3.63 (3.66)	0.777[11]	1.62[b],[12]	[10,13]
[bmim][BF_4][b]	5.8 x 10^2 (1.63 x 10^2)	0.86[d] (3.0)	1.12[15]	219[c],[15]	[10,16]
[bmim][PF_6][b,c]	6.6 x 10^2 (5.38 x 10^2)	0.73[d] (0.88)	1.363[15]	450[c],[15]	[10,16]
[bmim]Tf_2N[c]	4.5 x 10^2	0.77[d]	1.433	69[c],[15]	[10]
[bm_2im][Tf_2N][c,e]	3.8 x 10^2	0.86[d]	1.421	97.1[c],[17]	[10]
[bupy][Tf_2N][c,f]	3.9 x 10^2	0.89[d]	1.449	57[c],[18]	[10]
[bmpy][Tf_2N][c,g]	3.7 x 10^2	0.90[d]	1.387	85[c],[19]	[10]
[bmim][SbF_6][c]	4.9 x 10^2	0.93[d]	1.699	95	[10]
[bmim][CF_3CO_2][c]	4.9 x 10^2	0.98[d]	1.198	73[b],[20]	[10]
[hmim][BF_4][c,h]	5.7 x 10^2	0.79[d]	1.14[21]	314.0[b],[22]	[10]
[omim][BF_4][c]	6.4 x 10^2	0.62[d]	1.106	135.0[b],[22]	[10]
[bmim][CF_3SO_3][c]	4.6 x 10^2	0.97[d]	1.290[20]	90[b],[20]	[10]
[$P(C_6H_{13})_3(C_{14}H_{29})$] [$PF_3(C_2F_5)_3$][c]	0.7 x 10^2	1.84[d]	1.196	498[b],[21]	[10]

[a] $k_H = P_{H_2}/X_{H_2}$, where the partial pressure of hydrogen is expressed in MPa. [b] 293 K.
[c] 298 K. [d] Calculated from the solubility under 10.1 MPa, supposing that it changes linearly with the partial pressure. [e] [bm_2im]$^+$ = 1,2-Dimethyl-3-butylimidazolium.
[f] [bupy]$^+$ = *N*-Butylpyridinium. [g] [bmpy]$^+$ = *N*-Butyl-*N*-methylpyrrolidinium.
[h] [hmim]$^+$ = 1-Hexyl-3-methylimidazolium.

Table 1. Solubility of H_2 in water, organic solvents and ionic liquids, at 0.101 MPa (1 atm)

Table 1 shows that H_2 solubility in ionic liquids is typically much lower than in molecular solvents, which can lead to low reaction rates. Mass transfer effects associated with low gas solubility play a key role in hydrogenation, and may be critical when processes such as catalytic asymmetric hydrogenation are carried out in ionic liquids. Blackmond and co-workers[23] described in detail the key kinetic parameters affecting enantioselectivity in asymmetric hydrogenations, namely the concentration of molecular H_2 in the liquid phase, itself related to the pressure of the system, the rate of mass transfer and the intrinsic kinetics of competing reactions. Blackmond also determined that in cases where the enantioselectivity decreases with increasing H_2 pressure, the system can benefit from H_2-starved conditions. In other words a diffusion-limited regime could be beneficial because the rate of consumption of H_2 by the reaction would be higher than the rate of diffusion of H_2 in the liquid phase. For other reactions requiring high H_2 concentrations, low solubility problems can be solved by carrying out reactions at elevated pressures, which raises the H_2 solubility.[16] Interestingly in many cases product selectivities are achieved due to solubility differences between the intermediate and fully hydrogenated products.[24] For example, in the partial hydrogenation of 1,3-butadiene using Pd(0) nanoparticles in [bmim][BF_4], it was observed that 1,3-butadiene is at least three times as soluble in the ionic liquid as the intermediate butenes, inhibiting further hydrogenation and leading to product selectivity.[25]

The high viscosity of ionic liquids can also be a limitation for in hydrogenation reactions as diffusion of reactants through the medium is restricted. Temperature also plays an important role in hydrogenation, following the usual trend that at higher temperatures a high reaction rate is observed. However, the viscosity of the ionic liquid also decreases as temperature increases, facilitating mass transport of the reactants.

The choice of the anion is another crucial aspect of selecting an ionic liquid for hydrogenation studies. For example, in heterogeneous catalytic hydrogenations, the reaction occurs at the surface of the catalyst and the solvent cannot directly affect the energy of the activated complex. Nevertheless, solvent polarity (which varies from one anion to another) still plays an important role because polar solvents facilitate the adsorption of nonpolar substrates on the catalyst, while non-polar solvents have the opposite effect.[26] Gas solubility (*vide infra*) also varies with the anion, and it can be seen from Table 1 that ionic liquids with ditriflimide [NTf_2^-] as the counter anion have greater H_2 solubility than ILs with tetrafluoroborate [BF_4^-]. Anions can also have more specific interactions with the catalyst, which can control the conversion and enantiomeric excess of the product.[27]

Kinetic studies into the heterogeneous catalytic hydrogenation of cyclohexene in ionic liquid-alcohol mixtures have also been carried out by Khodadadi-Moghaddam *et al.*[28] with a Pt/Al_2O_3 catalyst in the IL, 2-hydroxy ammonium formate and the alcohols, methanol, ethanol or propan-2-ol at 25 °C. Mass transfer limitation effects of H_2 solubility and solvent polarity on reaction rates were studied. The rotation speed of the reaction mass was used to determine the mass transfer barriers as the hydrogen transfers from gas phase to liquid phase. It was found that there is a linear relationship between observed rate constant and rotation speed up to 700 rpm, after which the rate constant becomes independent of the rotation speed up to 1250 rpm, which suggests that the reaction is under kinetic control and takes place without external mass transfer limitations. The H_2 solubility was measured for the IL-alcohol mixtures which shows that increase in mole fraction of the IL increases the solubility and ultimately in pure IL the solubility was maximum (0.01 mL of H_2 gas in 20 g IL at 25 °C and 1 atm). A rate expression was derived considering the RDS as dissociative adsorption of hydrogen on catalyst as follows,

$$K_{obs} = K_{app} \left(\frac{H_{H_2}}{H_T} \right) C_{H_2}$$

Where k_{obs} = observed rate constant
k_{app} = apparent rate constant (incudes other concentrations and parameters)
H_{H_2} = Henry's law constant for H_2 in the solvent.
H_T = Henry's law constant for the transition state.
C_{H_2} = Concentration of H_2 in liquid phase.

Based on this equation the rate constant was found to be proportional to H_2 concentration in liquid phase and the reaction was first order with respect to H_2. (Figure 1)

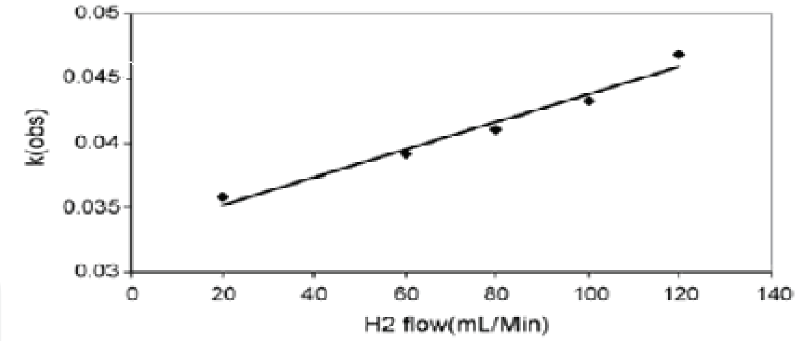


Fig. 1. Dependence of k_{obs} on hydrogen flow in ionic liquid at 25 °C (solvent 20 g, cyclohexene 0.1 g, rotation speed 1250 rpm and catalyst 0.02 g).

Furthermore the rate constants were calculated for three mixtures of IL-alcohol with increasing mole fractions of the IL (Table 2). The results indicated that with increasing mole fraction of IL, π* (dipolarity/polarizability) increases, leading to an increase in rate constant. In heterogeneous catalysis the reaction occurs on the catalyst surface, and polar solvents facilitate non-polar substrate adsorption on the catalyst.[26] Hence, Kishida linked the increase in rate constants to increased solvent polarity.

X_{IL}	IL-methanol mixture					IL-ethanol mixture					IL-propan-2-ol mixture				
	k x 10^{-2} s^{-1} g^{-1}	E^N	Π*	β	α	k x 10^{-2} s^{-1} g^{-1}	E^N	Π*	β	α	k x 10^{-2} s^{-1} g^{-1}	E^N	Π*	β	α
0.0	0.80	0.76	0.57	0.81	1.16	1.03	0.65	0.51	0.91	0.97	0.26	0.54	0.49	1.07	0.74
0.1	1.20	0.88	0.71	0.82	1.31	1.17	0.84	0.63	0.91	1.27	0.35	0.80	0.56	1.04	1.23
0.2	2.43	0.89	0.80	0.80	1.25	1.29	0.85	0.68	0.93	1.27	0.50	0.81	0.60	1.02	1.24
0.3	2.97	0.89	0.87	0.78	1.20	2.41	0.85	0.72	0.91	1.22	0.62	0.82	0.66	0.98	1.21
0.4	3.31	0.89	0.88	0.77	1.20	3.17	0.85	0.79	0.87	1.18	0.97	0.82	0.71	0.95	1.18
0.5	3.60	0.89	0.95	0.74	1.15	3.24	0.86	0.81	0.89	1.18	1.32	0.83	0.76	0.91	1.16
0.6	4.03	0.89	1.01	0.67	1.10	3.24	0.85	0.89	0.81	1.12	1.59	0.84	0.80	0.89	1.15
0.7	4.23	0.89	1.04	0.66	1.09	3.12	0.87	0.94	0.79	1.11	3.00	0.84	0.87	0.83	1.11
0.8	4.62	0.90	1.05	0.67	1.11	3.30	0.87	1.01	0.72	1.07	5.73	0.86	0.95	0.76	1.09
0.9	5.19	0.90	1.03	0.71	1.11	3.31	0.89	1.04	0.71	1.08	6.59	0.88	0.98	0.74	1.10
1.0	7.25	0.89	1.15	0.59	1.01	7.25	0.89	1.15	0.59	1.01	7.25	0.89	1.15	0.59	1.01

K = Rate constant, E^N = Normalized polarity parameter, Π* = Dipolarity/polarizability,
β = Hydrogen-bond acceptor basicity, α = Hydrogen-bond donor acidity.

Table 2. First-order rate constant of the reaction in the RTIL mixed with methanol, ethanol or propan-2-ol, together with solvatochromic parameters for the media

Similarly Fonseca *et al.*[29] carried out hydrogenation of 1-decene on Ir(0) nanoparticles in [bmim][PF_6] at 75 °C with varying pressures of H_2. They observed an increase in initial reaction rates with increase in H_2 pressures upto 4 atm, which was expected. However, above 4 atm the reaction rate is independent of the H_2 pressure, which can be ascribed to the surface saturation of the Ir(0) nanoparticles with H_2 gas. Thus at elevated pressures, (> 4 atm), a monomolecular mechanism is proposed (Figure 2) for hydrogenation occurring at the surface of catalytic nanoparticles within the IL.

$$S + C \underset{K_{a-1}}{\overset{K_{a1}}{\rightleftharpoons}} SC \xrightarrow{K_C} P$$

Fig. 2. Monomolecular mechanism

Where S = substrate, C = activated catalyst, P = final product, K_a = adsorption rate constant, K_{a-1} = desorption rate constant and K_c = catalytic rate constant.
When K_c was calculated at various pressures, it was found that for pressures ≥ 4 atm, K_c is almost identical (0.45 ± 0.06 min^{-1}) and at low pressures (2 atm) reaction rates decreased significantly, indicating that below 4 atm the hydrogenation is controlled by a mass transfer process.
In the case of fibre-supported Rh catalysts the rate of homogeneous hydrogenation was found to be dependent on the ligand to metal ratio and acid to IL ratio. Ruta *et al.*[30] when carried out gas phase hydrogenation of 1,3-butadiene using $SMF_{Inconel}$ supported $[Rh(nbd)Cl]_2$ catalyst, PPh_3 as ligand and an acid (H_3PO_4 or HBF_4) in ionic liquids ($[bmim][BF_4]$ and $[bmim][PF_6]$) , found that with $[bmim][BF_4]$:HBF_4 of 0.5 and PPh_3:Rh of 8, the reaction was fast *i.e.* 285 h^{-1}. Further investigation showed that addition of excess acid favoured the formation of a cationic dihydride species (Figure 3).

$$[Rh(H)_2L_n]^+ \rightleftharpoons RhHL_n + H^+$$

Fig. 3. Acid equilibrium for cationic dihydride species

Excellent work was carried out by Kernchen *et al.*[24] in which the hydrogenation of 1,4-cyclooctadiene was performed using a $[bmim][n\text{-}C_8H_{17}OSO_3]$ coated Ni catalyst in *n*-dodecane. This IL/ *n*-dodecane biphasic system allows effective partitioning of the intermediate (in this case cyclooctene) into the hydrocarbon layer, preventing over-reduction to cyclooctane. Table 3 depicts the values of partition coefficients of COD, COE and COA.

T in °C	K_N in (kg i/kg IL)/(kg i/kg *n*-dodecane) With i = COD, COE or COA		
	COD	COE	COA
20	0.30	0.25	0.20
50	0.37	0.31	0.25

Table 3. Nernst participation coefficients K_N for COD, COE and COA in biphasic system *n*-dodecane and ionic liquid $[bmim][n\text{-}C_8H_{17}OSO_3]$

For the hydrogenation of COD with uncoated Ni catalyst at 50 °C Kernchen obtained 40 % yield for COE (c.f. IL coated catalyst under the same conditions, 70 % yield). The K_N values from Table 3 offer a reasonable explanation for the results obtained. The low solubility of COE in the ionic liquid facilitates transfer to the n-dodecane layer and hence over-reduction is avoided. Further studies showed that the reaction follows first order kinetics with respect to COD and is zero order with respect to H_2 gas. An example of arene reductions by Rh nanoparticles supported on an ionic liquid-like co-polymer was reported by Zhao *et al*.[31] In this case most of the intermediate dienes were found to be soluble in [bmim][BF_4] which was used as a solvent, hence hydrogenation did not stop at the diene and further hydrogenated products predominate. Dyson *et al*.[32] have also performed reductions of benzene, exploiting solubility differences using K_2PtCl_4/[*N*-octyl-3-picolinium][$AlCl_4$]. The group also put forward a mechanism to account for the superior activity of K_2PtCl_4 (99 % yield of cyclohexane, at 100 °C, 50 bar H_2 in 240 mins) over other catalysts screened (Figure 4) in which a trimetal face is coordinated by the aromatic π-system of benzene.

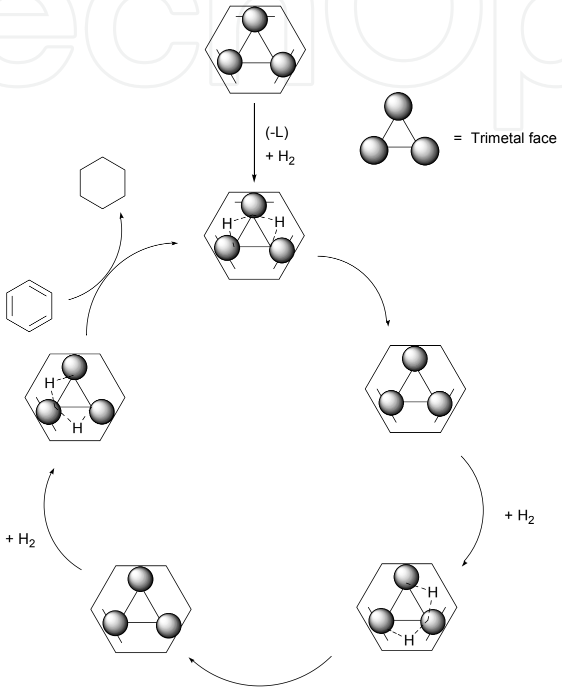


Fig. 4. The arene-exchange mechanism that could operate at a metal face

Interestingly when Silveira *et al*.[33] studied the partial hydrogenation of benzene to cyclohexene using Ru(0) nanoparticles, under solvent-free conditions and in ionic liquids ([bmim][PF_6] and [bmim][BF_4]) at 75 °C and 4 atm H_2, it was found that in the absence of a solvent, the reactions were faster (Table 4). Similar results were observed for the reduction of cyclohexanone using Ir(0) nanoparticles[34] and for other arenes using Ir(0) and Rh(0) nanoparticles.[35] The authors indicate that the reactions in ionic liquids may have been slowed by mass transfer effects. Correspondingly, when the reduction of 1,3-butadiene was attempted using Pd(0) particles at 40 °C and 4 atm H_2[25] under solvent-free conditions, 1,3-butadiene was consumed in under 2 h, compared to 6 h when [bmim][BF_4] was used as the solvent.

Mass transfer limitations have been a major challenge in many ionic liquid-based hydrogenations. For example, even in the biphasic reduction of caffeate in [bmim][PF_6] and tetradecane although the initial reaction rate was high (880 mmol kg^{-1} h^{-1}), after 1 hour this decreased to 12.4 mmol kg^{-1} h^{-1}[36]. Wolfson *et al*.[37] have overcome this problem by addition of water in their biphasic asymmetric hydrogenation reactions which were carried out with 2-acetamidoacrylate using Rh-EtDuPHOS as a catalyst in [bmim][PF_6]. When the reaction was performed with the ionic liquid in isolation, no conversion was observed. However, when water was included as a cosolvent, the product was isolated in 68 % yield with 96 % ee, with a 50 % v/v ratio of ionic liquid to water giving optimal reaction rates (TOF ≈ 1000 h^{-1} at 20 °C and 5 bar H_2).

Entry	Medium	Substrate	t [h]	Conv. [%]	TON[a]	TOF [h^{-1}][b]
1	-	1-hexene	0.7	> 99	500	714
2	[bmim][BF_4]	1-hexene	0.6	> 99	500	833
3	[bmim][PF_6]	1-hexene	0.5	> 99	500	1000
4	-	cyclohexene	0.5	> 99	500	1000
5	[bmim][BF_4]	cyclohexene	5.0	> 99	500	100
6	[bmim][PF_6]	cyclohexene	8.0	> 99	500	62
7	-	2,3-dimethyl-2-butene	1.2	76	380	316
8	-	benzene	5.5	90	450	82
9	[bmim][BF_4]	benzene	17.3	30	150	9
10	[bmim][PF_6]	benzene	18.5	73	365	20
11	[bmim][CF_3SO_3]	benzene	17.5	50	240	14
12	-	benzene[c]	2.0	> 99	250	125
13	-	toluene[c]	5.6	> 99	250	45
14	-	isopropylbenzene[c]	6.4	> 99	250	39
15	-	*tert*-butylbenzene[c]	14.1	> 99	250	18
16	-	anisole	18	< 1	-	-

[a] Turnover number TON = mol of hydrogenated product/mol of Ru.
[b] Turnover frequency TOF = TON/h. [c] Arene/Ru = 250.

Table 4. Hydrogenation of alkenes and arenes by Ru^0 nanoparticles under multiphase and solventless conditions (75 °C and 4 atm, constant pressure, substrate/Ru = 500)

While studying the asymmetric hydrogenation of acetophenone Fow *et al.*[38] investigated supported Ru and Rh-based catalysts containing either BINAP or chiraphos ligands immobilised in phosphonium ionic liquids, with the bases, K_2CO_3 and K_3PO_4 as additives. Fow proposed a kinetic model to rationalise the results of these experiments (Figure 5). For full details for catalysts structure and preparation see Fow *et al.*[38]

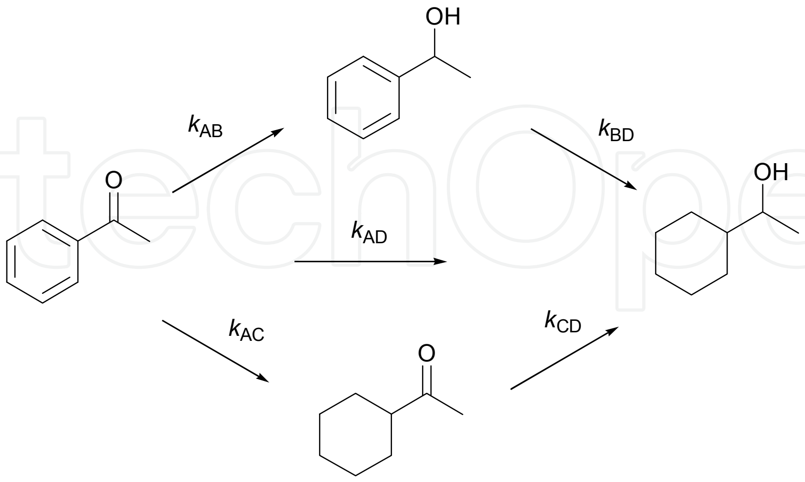


Fig. 5. Kinetic model for the reduction of acetophenone with supported catalysts.

Using a series of supported Ru and Rh catalysts immobilised in ionic liquids, reductions were carried out at between 30 and 80 °C (results Table 5) and rate constants were calculated (Table 6).

Catalyst	Temp. (°C)	Time (h)	Conv. (%)	Selectivity[a] (%)	ee[b] (%)	Configuration[b]
Ru/dec/PO_4	50	15	22	35	49	*S*
Ru/tos/CO_3	50	17	36	19	55	*S*
Rh/dec/PO_4	30	30	95	41	13	*R*
Rh/dec/PO_4	50	15	90	70	30[c]	*R*
Rh/dec/PO_4	80	4	100	45	5	*R*
Rh/dbp/PO_4	30	29	20	58	19	*R*
Rh/tos/CO_3	50	22	100	6	74	*S*
Rh(chi)/tos/CO_3	50	24	63	38	2	*S*

[a] Chemoselectivity to 1-phenylethanol, [b] Enantiomeric excess (ee) and configuration of 1-phenylethanol were determined by gas chromatography, [c] 49 % ee at 10 % conversion

Table 5. Conversion and selectivity in the hydrogenation of acetophenone

Catalyst	Temp (°C)	k_{AB} (h^{-1})	k_{AC} (h^{-1})	k_{BD} (h^{-1})	k_{CD} (h^{-1})	k_{AD} (h^{-1})	Ratio (k_{AB}/k_{AC})	Ratio (k_{AB} + k_{CD})/ (k_{AC} + k_{BD})
Rh/dec/PO_4	30	0.064	0.038	0.018	0.043	0.006	1.7	1.9
Rh/dec/PO_4	50	0.169	0.046	0.008	0.065	0.005	3.7	4.3
Rh/dec/PO_4	80	0.678	0.177	0.062	0.038	0.299	3.8	3.0
Rh/dbp/PO_4	30	0.185	0.099	0	0.391	0.036	1.9	5.8
Rh/tos/CO_3	50	0.136	0.117	0.137	0.017	0	1.2	0.6
Ru/dec/PO_4[a]	50	0.108	0.109	0.100	0.012	0.045	1.0	0.6
Ru/tos/CO_3[a]	50	0.044	0.145	0	0.356	0.036	0.3	2.8

[a] Catalyst deactivation was taken into account.

Table 6. Rate constants for the hydrogenation of acetophenone with supported catalysts

As expected the reaction rates are temperature dependent. A higher ratio for k_{AB}/k_{AC} supports the obtained selectivities of 2-phenylethanol. It was found that Rh/dec/PO_4 proved a more effective catalyst for the reduction at 50 °C in terms of reaction rate, conversion and selectivity. The activation energies calculated for reaction AB (42 $kJmol^{-1}$) were measured higher than reactions AC and BD (28 and 24 $kJmol^{-1}$ respectively) which again supports the higher selectivities at high temperatures.

When chemoselective hydrogenation of cinnamaldehyde was carried out by Kume *et al.*[39] using Pd nanoparticles at 80 °C and 5 MPa of H_2, they found that the reaction which uses Pd nanoparticles immobilized on ionic liquid modified silica gel in *m*-xylene has high reaction rates than that of reactions with $Pd(OAc)_2$ immobilized in ionic liquids in terms of TOFs (Table 7). In case of Pd/SiO_2-IL (PF_6) the reaction took only 20 minutes for completion with TOF > 47,000 h^{-1} whereas the analogous reaction in [bmim][PF_6] using $Pd(OAc)_2$ as catalyst took 6 h to complete with TOF 18 h^{-1}. The increase in reaction rates are proposed to be due to the high surface area of the silica gel which promotes adsorption of substrate and H_2 on to the Pd nanoparticles. The low yields in cases when ionic liquids were used as the solvent were ascribed to low solubility of H_2 in the medium.

Run	Catalyst	Time	Yield (%)	TOF (h^{-1})
1[b]	Pd/[bmim][Cl]	6 h	56.2	18
2[b]	Pd/[bmim][PF_6]	6 h	100	33
3[b]	Pd/[bmim][BF_4]	6 h	75.3	23
4[b]	Pd/[bmim][NO_3]	6 h	90.1	29
5[c]	Pd/SiO_2-IL[Cl]	20 min	20.7	270
6[d]	Pd/SiO_2-IL[PF_6]	20 min	100	> 47,000
7[e]	Pd/SiO_2-IL[BF_4]	20 min	70.8	24,260
8[e]	Pd/SiO_2-IL[NO_3]	20 min	100	> 33,000
9[e]	Pd/SiO_2	20 min	64.8	22,200

[a] Temperature 80 °C; H_2 5 MPa; cinnamaldehyde 2.7 mmol; *m*-xylene 2 g, [b] $Pd(OAc)_2$ 0.0134 mmol; ionic liquid 5 mmol., [c] Pd 0.108 mg, [d] Pd 0.016 mg, [e] Pd 0.022 mg.

Table 7. Hydrogenation of cinnamaldehyde catalyzed by Pd catalyst

While discussing reaction rates, one has to consider the rates of formation of metal nanoparticles as well. When Scheeren *et al.*[40] studied the hydrogenation of cyclohexene by catalyst precursor PtO_2 dispersed in [bmim][PF_6] at 75 °C, they proposed a mechanism of formation of Pt(0) nanoparticles and calculated the rate of their formation. This mechanism suggests nanoparticles are formed in four stages, nucleation, autocatalytic surface growth, agglomeration and autocatalytic agglomeration to form large agglomerates (Figure 6).

$$\text{(a)}\quad A \xrightarrow{k_1} B$$

$$\text{(b)}\quad A + B \xrightarrow{k_2} 2B$$

$$\text{(c)}\quad B + B \xrightarrow{k_3} C$$

$$\text{(d)}\quad B + C \xrightarrow{k_4} 1.5C$$

* The four equations correspond to: (a) slow nucleation of catalyst precursor A to a nanocluster B, (b) autocatalytic surface growth, (c) agglomeration step leading to the formation of bulk metal C, and (d) autocatalytic agglomeration of smaller nanoparticles with larger bulk metal particles.

Fig. 6. Four-step mechanism for transition-metal nanocluster nucleation, growth and agglomeration

Rate constants were calculated for the four step formation of nanoparticles. The kinetic data was found to be consistent with formation of large agglomerates of bulk metal catalyst (Table 8) and shows that the autocatalytic surface growth is faster than other steps.

Floris *et al.*[41] have discussed the effect of ion pairs of the catalyst and ionic liquid in the asymmetric hydrogenation of methyl acetoacetate at 60 °C and a hydrogen pressure of 50 bars. The [PF_6^-] based ionic liquids showed around 50 % lower activity in terms of TOF than [NTf_2^-] salts. (Table 9)

PtO_2/ C_6H_{12} (molar ratio)	Equations in kinetic model[a]	k_1 (h^{-1})[b]	k_2 ($M^{-1}h^{-1}$)[b]	k_3 ($M^{-1}h^{-1}$)[b]	k_4 ($M^{-1}h^{-1}$)[b]
1/4000	a, b	0.143	204.00	-	-
1/4000	a, b, c	0.184	329.88	15.96	-
1/1000	a, b	0.094	58.10	-	-
1/1000	a, b, c	0.086	78.72	7.26	-
1/1000	a, b, c, d	0.677	904.39	9.40	146.17

[a] From Figure 6. [b] Rate constants corrected for reaction stoichiometry

Table 8. Kinetic constants for hydrogenation of cyclohexene by PtO_2 in [bmim][PF_6][a]

IL	TOF_{90} (h^{-1})	ee_{90} (%)	S_{90} (%)	$ee^{re\text{-}use}$ (%)
MeOH	1100	98	79	-
[N_{6222}][NTf_2]	390	93	87	54
[bmim][NTf_2]	340	97	91	54
[N_{6222}][PF_6]	210	55	86	-
[bmim][PF_6]	160	78	88	32

Reaction conditions: 2 g MAA, 17 mL IL-MeOH 1/1 wt., S/C = 1580, 333 K, 50 bar H_2.

Table 9. The ion pair effect

There are two rate limiting factors which can be considered. First is the hydrogen gas solubility, and second is the structural modification of active catalytic centre by anion pairing. Figure 7 depicts plausible catalyst-IL interactions in the case of the [NTf_2^-] based IL.

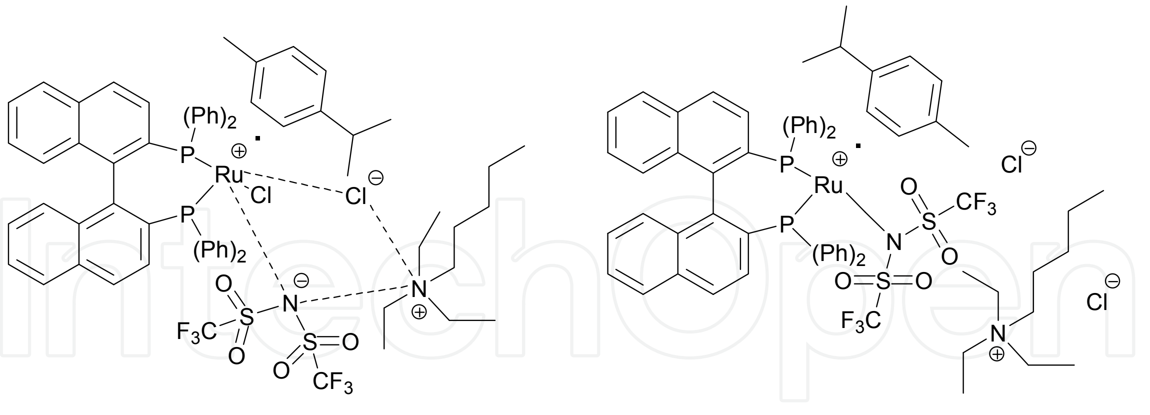


Fig. 7. Plausible catalyst-IL interactions in an [NTf_2^-] IL

3. Transition metal catalysis in ILs

Commonly used heterogeneous catalysts such as palladium or platinum on solid supports are among the catalysts employed for the hydrogenation of substrates in ILs. Although increased temperature and pressure may be a requirement when using the IL, classic palladium, platinum and ruthenium catalysts have been shown to give superior results when used in an IL compared with a common organic solvent.

Xu *et al.*[42] used a range of imidazolium ILs containing $[BF_4]$ and $[PF_6]$ anions for the catalytic heterogeneous hydrogenation of halonitrobenzenes to the corresponding haloanilines (Figure 8).

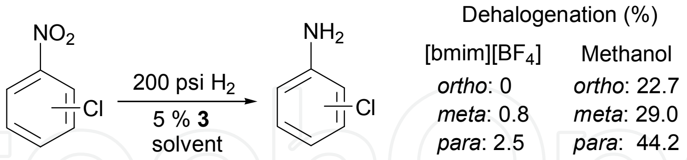
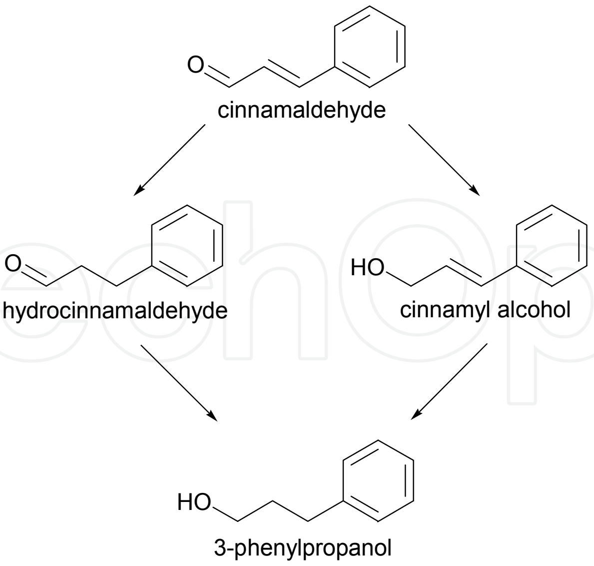


Fig. 8. Hydrogenation of halonitrobenzenes to haloanilines

Raney nickel (**1**), platinum on carbon (**2**) and palladium on carbon (**3**) were employed as metal catalysts, and methanol was used as a reference organic solvent due to its wide application in heterogeneous catalytic hydrogenations. Although increased temperatures and pressures were required for the IL systems (100 °C, 31.0 bar (**1**), 13.8 bar (**2** and **3**)) in comparison with the methanol systems, i.e. 80 °C, 13.8 bar for (**1**) and 30 °C, 2.8 bar for (**2**) and (**3**), the ILs performed better as solvents for these reactions, with the undesirable dehalogenation being greatest for all substrates tested in methanol rather than the ILs (Figure 8). Taking for example *ortho*-, *meta*- and *para*-chloronitrobenzene, and 5 % (**3**), for which the greatest differences in results between IL and organic solvent were evident, in $[bmim][BF_4]$ dehalogenation ranged from as little as 0 % with *o*-chloronitrobenzene to 0.8 % with the *meta* derivative and at most 2.5 % with the *para* substituted derivative. However, when methanol was used as the solvent, dehalogenation ranged from 22.7 % for *ortho* to 44.2 % for the *para*-chloro isomer (Figure 8). The same trend was evident using 5 % (**2**) and (**1**) as catalyst, albeit to a lesser extent. The reaction rates were found to be lower in $[bmim][BF_4]$ than in methanol, which was attributed to mass transfer processes.

Anderson *et al.*[43] selected the α,β-unsaturated aldehydes, citral and cinnamaldehyde (Figure 9 and Figure 10), to demonstrate the superior selectivity obtained using pyridinium, imidazolium and ammonium ILs over common organic solvents in hydrogenation reactions. A palladium on carbon catalyst (**3**) was used for the reactions.

In the case of cinnamaldehyde, although the temperature was increased for the reaction carried out in the IL (60 ºC), superior selectivity towards hydrocinnamaldehyde was obtained (78-100 %) compared with several conventional organic solvents (78-89 %). Worth noting for these hydrogenations is the variation of selectivities across a series of [bmim] ILs. $[Bmim][PF_6]$ showed a selectivity of 100 %, [bmim][OTf] 91 %, and [bmim][OAc] 78 % for formation of hydrocinnamaldehyde. Recycling of the $[bmim][BF_4]$ system showed catalyst activity to decrease by 50 % upon the first recycle but remained constant thereafter for five successive reactions. The selectivity however remained almost constant for all recycles carried out. The authors note that if the IL system without a substrate is treated with hydrogen gas for one hour prior to the reaction, the recycling ability of the system can be improved. In the case of citral hydrogenation, similar trends were observed. The selectivity towards citronellal obtained using ILs ($[bmim][PF_6]$, $[bmim][BF_4]$, $[C_8Py][BF_4]$, $[C_6mim][NTf_2]$, and $[emim][NTf_2]$) ranged from 81-100 %, with the organic solvents giving only 62-77 % selectivity (cyclohexane: 62 %, toluene: 77 %, and dioxane: 77 %). The authors concluded that due to the high viscosity of the ILs the rate of diffusion of aldehyde was reduced compared with conventional solvents and reactions rates were correspondingly lower. Using the dicyanamide IL $[bmim][N(CN)_2]$ Arras *et al.*[44] also achieved the selective

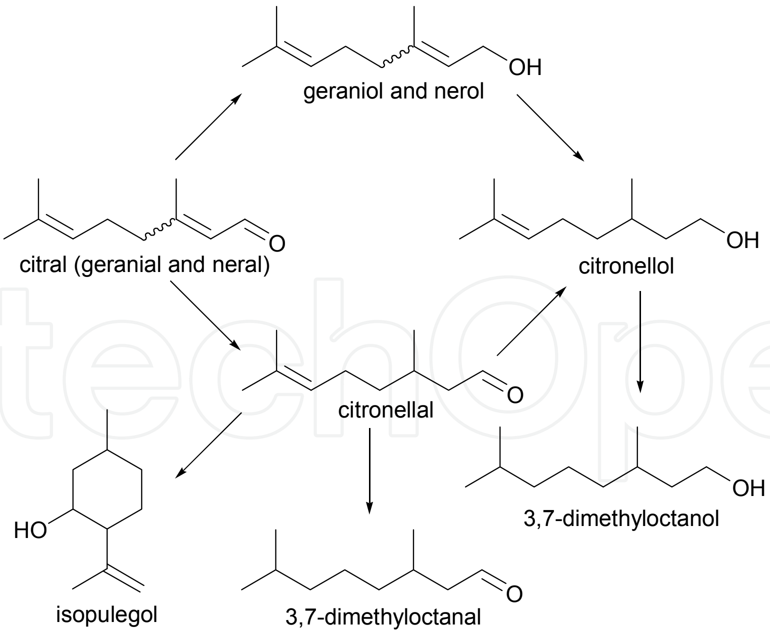


hydrocinnamaldehyde selectivity (%)

organic solvent 78-89 %

IL 78-100 %

Fig. 9. Reaction pathway of cinnamaldehyde hydrogenation



citronellal selectivity (%)

IL 81-100 %

organic solvent 62-77 %

Fig. 10. Reaction pathway of citral hydrogenation

hydrogenation of citral to citronellal using 10 % (**3**) at 50 °C and 1.0 MPa H_2. In the IL-free system 100 % conversion and 41 % selectivity towards the desired product was obtained. They found that with the IL as bulk solvent, 100 % conversion was obtained with 97 % selectivity. However, using the catalyst coated with IL the selectivity increased to > 99 % with 100 % conversion. When the IL was only present as an additive a reduction in the conversion (42 %) was observed while the selectivity remained high (> 99 %).

The same group continued this work by investigating the use of ILs as additives and coatings on palladium supported catalysts for the hydrogenation of citral.[45] They compared the results obtained by using ILs containing perfluorinated anions ([bmim][NTf_2], [bmim][PF_6] and [BMPL][NTf_2]) and the dicyanamide anion ([bmim][$N(CN)_2$], [BMPL][$N(CN)_2$] and [B3MPYR][$N(CN)_2$]). The performance of the dicyanamide ILs as either additives or coatings improved in comparison the ditriflimide or hexafluorophosphate ILs regardless of the heterocyclic cation. Using Pd/SiO_2 (**4**) as catalyst, at 50 °C and 2.0 MPa H_2, the highest conversions and selectivities towards citronellal were achieved using the dicyanamide ILs. Conversions ranging from 63 – 75 % and selectivities from 59 – 62 % were obtained using the ditriflimide or hexafluorophosphate ILs as a catalyst coating. The results for conversion obtained with [bmim][NTf_2] and [BMPL][NTf_2] were comparable with those obtained in the absence of an IL under the same reaction conditions, although the selectivity obtained was higher (79 % conversion, 45 % selectivity). Using [bmim][$N(CN)_2$], [BMPL][$N(CN)_2$] and [B3MPYR][$N(CN)_2$] conversion was > 99 % and selectivity ranged from 81 – 99 %. Almost quantitative yield of citronellal was obtained using [BMPL][$N(CN)_2$] (conversion = 100 %, selectivity = 99 %). The authors attribute the improved results of the hydrogenation using dicyanamide ILs to the sensitivity of the hydrogenation reaction to halide impurities from the fluorinated anions and also an electronic interaction between the dicyanamide anion and the palladium catalyst. Curiously the low hydrogen solubility in ILs did not affect the conversion, indicating no mass transport limitations. When the research was extended to Ru/Al_2O_3 catalyzed hydrogenation of citral in ditriflimide ILs[46], it was determined that addition of the ionic liquid reduces the initial TOF of the catalyst. For [bmim][NTf_2] the initial TOF decreased from 14.0×10^{-2} s^{-1} (initial TOF for reaction without IL) to 7.2×10^{-2} s^{-1}.

Geldbach *et al.*[32] investigated the generation of catalysts from metal chlorides in the Lewis acidic IL, [*N*-octyl-3-picolinium]$AlCl_4$ (Figure 11), by dissolving a series of metal chlorides in the IL and adding benzene as the substrate. The hydrogenation of benzene to cyclohexane is an important petrochemical process and research in this area is in continuous evolution.[47,48,49]

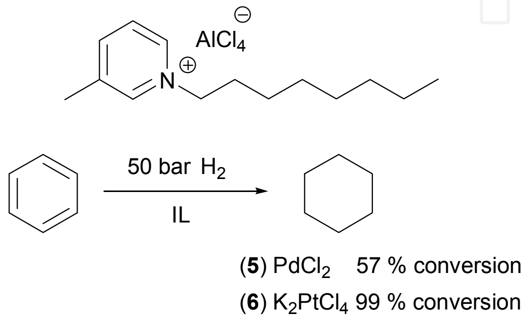


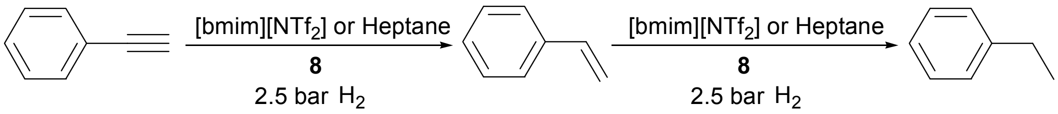
Fig. 11. [*N*-octyl-3-picolinium]$AlCl_4$ in the hydrogenation of benzene

Hydrogen was added to the biphasic mixture and the conversions to cyclohexane recorded. Of all the metal chlorides used, only the palladium catalyst, $PdCl_2$, (**5**) and platinum catalyst, K_2PtCl_4, (**6**) showed any significant activity, with 57 and 99 % conversion respectively. K_2PtCl_4 was investigated further in relation to catalyst concentration and temperature due to the impressive result. Generally, higher K_2PtCl_4 catalyst loadings gave increased conversion, and raising the temperature also led to an increase in conversion (e.g. 0.0071 mol% (**6**): 18 % conversion at 20 °C and 80 % conversion at 75 °C; and 0.14 mol% (**6**): 67 % conversion at 20 °C and > 99 % conversion at 75 °C). This groups research also extends to the examination of a ruthenium cluster catalyst in [bmim][BF_4] for the same hydrogenation reactions however no activity was observed using the IL.[23] The importance of the IL-promoted reduction can be appreciated when one considers that much higher temperatures have been recommended to achieve conversion of benzene to cyclohexane under conventional conditions. Jasik *et al.*[47] using a temperature of 175 °C to achieve complete hydrogenation and Bakar *et al.*[48] recommended 200 °C for maximum conversion.

Deshmukh *et al.*[50] also used a Lewis acidic IL ([bmim][$AlCl_4$]) for the hydrogenation of a selection of arenes, in the presence of a Pd/C catalyst. Although the hydrogenation of benzene can require harsh conditions, this group combined the concept of the activation of aromatics by Lewis acids (using the IL) and the activation of molecular hydrogen by Pd/C to achieve > 99 % conversion of benzene to cyclohexane under ambient conditions (1 bar H_2, RT). Under the same conditions they were able to achieve > 99 % conversion of biphenyl, naphthalene and napthacene and 97 % conversion of anthracene. Deshmukh[50] also tackled the problem of the hydrogenation of fullerene with their novel system. Harsh conditions are usually necessary for hydrogenation of this substrate (120 bar H_2, 400 °C),[51] however hydrogenation was achieved with only 5 bar H_2 at RT using this system.

Although ILs has many 'green' attributes, in hydrogenation reactions there are some cases, in which conventional organic solvents are preferred. Using the bimetallic catalyst system, Ag-In/SiO_2 (**7**) for the hydrogenation of citral to selectively form the acyclic/allylic terpene alcohols, geraniol and nerol, Steffan *et al.*[52] showed the non-polar solvent hexane to be superior to [bmim][NTf_2]. The chemoselective hydrogenation of citral to geraniol and nerol was lower in the IL compared to the organic solvent. Steffan explained the lower conversion of citral in ILs compared with hexane by suggesting that the lower solubility of hydrogen in the IL (0.77×10^{-3} $molL^{-1}$ at 298 K and 0.1 MPa of H_2, estimated from the H_2 solubility at 10.1 MPa assuming a linear relationship with partial pressure)[10] was the limiting factor. Information pertaining to hydrogen solubility in ILs can be found in recent sources.[53,54,55]

While investigating mass transfer effects in the hydrogenation of phenylacetylene to styrene and ethyl benzene (Figure 12) using a rotating disc reactor, Hardacre *et al.*[56] found [bmim][NTf_2] to give lower reaction rates than a non-polar hydrocarbon solvent.



Reaction rate: reduced in [bmim][NTf_2] compared to heptane

Fig. 12. Hydrogenation of phenylacetylene

Using palladium on calcium carbonate (**8**) as a catalyst, they investigated several parameters in [bmim][NTf_2] and heptane, including the effect of phenyl acetylene concentration in the solvent and the rotation speed. The rate of reaction was reduced in the IL (0.942 mmol min^{-1} at 6.0 bar) compared with the organic solvent (12.976 mmol min^{-1} at 5.5 bar), postulated to be due to the varying rate of diffusion of gaseous hydrogen through the liquid medium to the catalyst surface. The liquid to solid mass transfer coefficient ($k_{LS}a$) was calculated to vary from 0.144 to 0.150 s^{-1}, over a range of phenylacetylene concentrations and hydrogen pressures. These values indicate that the reaction is limited by liquid to solid mass transfer process, in particular the transport of dissolved hydrogen. This fact was supported by the calculated activation energies for conversion of phenylacetylene to ethyl benzene in heptane and [bmim][NTf_2] obtained between 9 and 33 kJ mol^{-1}.

Recently Khodadadi-Moghaddam *et al.*[28] investigated the kinetic parameters of the hydrogenation of cyclohexene, in mixtures of 2-hydroxyethylammonium formate and various alcohols (methanol, ethanol and IPA). Using a Pt-Al_2O_3 (**9**) catalyst, the rate constant for the reaction carried out in the IL/IPA mixture was twenty eight times higher than when IPA was used as the reaction medium. From studying solvent effects on the reaction the authors explain the discrepancy in rate to be due to the varying polarities of solvent and substrate – specifically that because of the polarity of the IL, the non-polar cyclohexene is more abundant on the catalyst surface, promoting the reaction. Furthermore, Khodadadi-Moghaddam and co-workers state that low gas solubility in many ILs is compensated by fast gas diffusion in reactions involving hydrogen gas.[57] This group extended their work to investigate this effect using acetone as the hydrogenation reaction substrate.[58] They postulate that the presence of the polar carbonyl group in acetone lowers the extent of adsorption on the catalyst surface compared with cyclohexene. The first-order rate constant of the hydrogenation reaction of cyclohexene to cyclohexane was found to be 8.7 times higher using the IL as solvent than compared to IPA. The rate constant of the hydrogenation reaction of acetone to propan-2-ol was also higher in the IL than IPA, albeit only 3.3 times.

Biphasic reaction conditions are one important method for hydrogenations using homogeneous catalysts when efficient recycling of catalyst is of importance. Hydrogenation reactions have been carried out using rhodium and ruthenium catalysts in biphasic systems using imidazolium based ILs ([bmim], [hmim] and [omim] [BF_4]). With the use of a rhodium catalyst ([Rh(η^4-C_7H_8)(PPh_3)$_2$][BF_4]) (**10**), Dyson *et al.*[59] demonstrated a biphasic hydrogenation of an alkyne using [omim][BF_4] containing the catalyst and an aqueous phase containing the substrate, 2-butyne-1,4-diol (Figure 13).

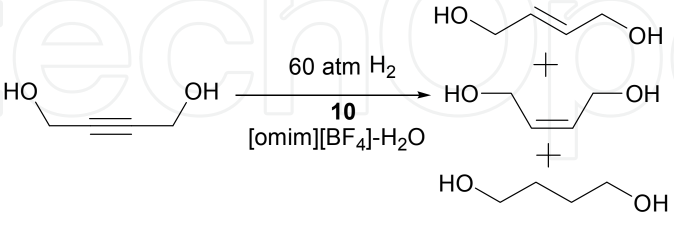


Fig. 13. Hydrogenation of butyne-1,4-diol

At room temperature, the phases were immiscible; however at the reaction temperature of 80 °C homogeneity was attained. Hydrogenation reactions were carried out under 60 atm H_2 with facile separation of the reduced products from the catalyst/IL phase being achieved simply by cooling the reaction. The products dissolved in the aqueous layer were isolated and reuse of the IL/catalyst system demonstrated. The limitations of this system were shown with maleic acid, when the reduced product, succinic acid, was found to be soluble in both the IL and aqueous phase. This type of cationic rhodium catalyst has been also used by Esteruelas *et al.*[60] employing an organic solvent to selectively hydrogenate phenylacetylene to styrene ([Rh(2,5-norbornadiene)(PPh_3)$_2$] (**11**) in DCM at 25 °C and 1 atm. H_2 pressure). At 50 °C and 39.48 atm. H_2 with $scCO_2$ as reaction solvent (157.91 atm. CO_2) Zhao *et al.*[61] selectively hydrogenated the same substrate as Dyson *et al.*,[59] 2-butyne-1,4-diol, to butane-1,4-diol (84 % at 100 % conversion) using a stainless steel reactor wall (SUS 316) to promote the reaction with no catalyst.

Wolfson *et al.*[37] used [bmim][PF_6] as reaction medium in the hydrogenation of 2-cyclohexen-1-one with $Rh(PPh_3)_3Cl$ (**12**) (Wilkinson's catalyst) (Figure 14) and methyl 2-acetamidoacrylate with Rh-EtDuPHOS (**13**).

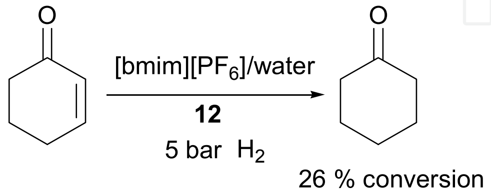


Fig. 14. Hydrogenation of 2-cyclohexen-1-one

As water was shown by this group to enhance the activity of Wilkinson's catalyst (**12**), they studied this parameter in the biphasic hydrogenation of 2-cyclohexen-1-one. Diethyl ether and hexane were screened but demonstrated low hydrogenation activity. The conversion to cyclohexanone increased from 4 % (100 % selective) in diethyl ether and 7 % (100 % selective) in hexane as co-solvent to 26 % in water (90 % selective). In the analogous homogeneous reaction with Wilkinson's catalyst (**12**) and only ethanol as solvent, 100 % conversion was achieved, albeit with low selectivity (27 %). Increased selectivity was achieved using DCM as solvent (100 %), although a compromise in conversion was observed (17 %).

Water was also used as solvent in conjunction with the [bmim][PF_6] for the biphasic hydrogenation of methyl 2-acetamidoacrylate at 5 bar H_2 and 20 °C. 68 % conversion was obtained (66 % upon re-use) with 96 % ee (97 % upon re-use). The group proposes that the use of water as the second solvent in biphasic IL reactions has a beneficial effect on activities due to the creation of a well mixed 'emulsion-like' system. Using methanol as the sole phase in a homogeneous reaction, 54 % conversion with 97 % selectivity was obtained. However, using the IL as sole reaction phase, no reaction was observed.

Scurto *et al.*[62] used biphasic hydrogenation conditions with $scCO_2$ and a rhodium catalyst (**14**) for the hydrogenation of 2-vinyl-naphthalene (Figure 15).

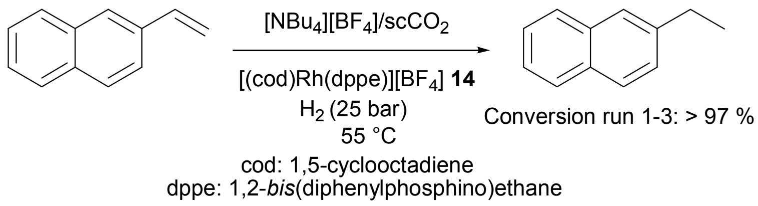


Fig. 15. Hydrogenation of 2-vinyl-naphthalene

[TBA][BF_4] was pressurised with CO_2 to give a high melting point depression of the salt for subsequent use as a reaction solvent in the liquid phase. Conversions for the first three runs using the IL were high (> 93 %). The authors explained that the drop in conversion to 62 % by the fifth run may have been due to accidental oxygen introduction or loss of catalyst during the recycling procedure.

Suarez *et al.*[63] used a ruthenium catalyst ($RuCl_2(TPPMS)_3(DMSO)$) (**15**); TPPMS: triphenylphosphine monosulfonate) immobilised in $[bmim][PF_6]$ for the biphasic hydrogenation of 1-hexene (Figure 16).

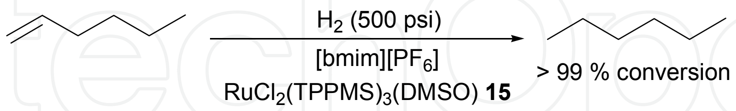


Fig. 16. Hydrogenation of 1-hexene

They investigated the effect of different parameters on the hydrogenation rate and conversion. It was observed that with increasing temperature, the viscosity of the IL decreased, therefore the conversion rate increased. However at the upper limit of temperature, 120 °C, decomposition of the catalyst was observed. Increasing the pressure also increased the conversion, until it levelled off at pressures higher than 500 psi. Overall, greater than 99 % conversion was observed for the hydrogenation of 1-hexene in the IL. However, upon recycling, the total conversion decreased (70 % after six reuses). The catalytic activity of the system using this catalyst (**15**) with the IL is, however, lower in comparison to using (**15**) in a toluene/water biphasic system.[64] Two other substrates were also investigated (cyclohexene and crotonaldehyde). 34 % conversion was achieved with cyclohexene, while only 25 % was achieved using crotonaldehyde, although good selectivity was attained with 1-butanol formed as the only product.

The tailoring of ILs to carry out a specific role together with acting as reaction medium is emerging as an efficient way to limit the number of reagents required in a chemical reaction.[9] One example is the synthesis of imidazolium IL (1-(*N,N*-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate, [mammim][OTf]) for the hydrogenation of carbon dioxide to form formic acid[65] (Figure 17). This reaction is thermodynamically unfavourable because the standard Gibbs free energy ΔG_{298}° of reaction is + 32.9 kJ mol^{-1}.

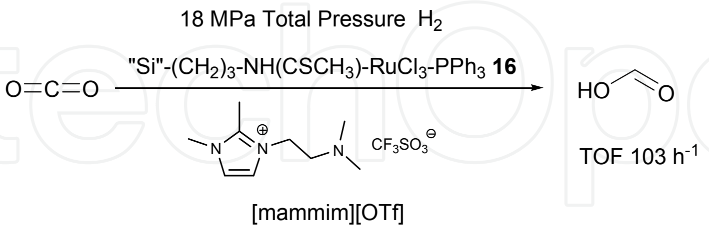


Fig. 17. Hydrogenation of carbon dioxide

The IL acts as a base for the promotion of the hydrogenation reaction which was carried out at 60 °C. A ruthenium catalyst immobilised on silica (**16**) was used as heterogeneous catalyst phase dispersed in a solution of aqueous IL. It was shown that water was necessary for the success of the reaction, the reason attributed to the lower viscosity of the IL. The basic IL [mammim][OTf] favoured the synthesis of the product, with the formation of a formate salt driving the reaction. TOFs as high as 103 h^{-1} were reached. Higher TOFs were, however, observed using other ruthenium catalysts in organic solvents (e.g. acetone, NEt_3, $[Ru_2(\mu$-

CO)(CO)$_4$(μ-dppm)$_2$], 38.11 atm. H_2 and CO_2, TOF = 130 h^{-1})[66] and $scCO_2$ ([$RuH_2(PMe_3)_4$], 80 – 85 atm H_2, TOF = 630 h^{-1})[67] for the hydrogenation of carbon dioxide to formic acid. An increase in H_2 and CO_2 pressure together with increasing the amount of IL was found to favour higher TOFs. The process was shown to be suitable for recycling procedures, with no significant reduction in TOF being observed after four recycles. Based on the assumption that the efficiency of CO_2 hydrogenation would increase if the IL contained more than one basic group, Zhang[68] synthesised a novel IL containing two tertiary amino groups, 1,3-di(*N*,*N*-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate [DAMI][OTf] (Figure 18). It was indeed shown that increasing the number of basic groups in the IL increased the formation of formic acid. A formic acid to IL ratio of 0.145:1 HCO_2H/[mammim][OTf] (wt/wt) was achieved in one reaction cycle. Using [DAMI][OTf] containing two basic groups this increased to 0.246:1.

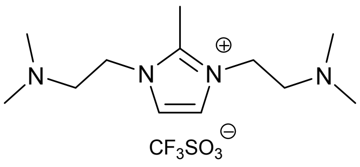


Fig. 18. [DAMI][OTf]

Obert *et al.*[69] used a ruthenium on carbon catalyst for the selective hydrogenation of propionitrile to propylamine under biphasic reaction conditions. In 1998 Dow Chemical Co. patented a process for this hydrogenation using a biphasic system of water and organic solvent where selectivities towards propylamine of > 80 % were achieved.[70] The work carried out by this group was based on two approaches encompassing the use of Brønsted-acidic ILs (dimethylcyclohexylammonium hydrogensulfate and 1-butylimidazolium hydrogensulfate) or neutral ILs ([emim][$EtOSO_3$]). The Brønsted-acidic IL was used for protonation of the primary amine in order to prevent its subsequent over-reduction to di- and tri-propylamine. The neutral IL [emim][$EtOSO_3$] was used as a medium from which the primary amine could be extracted by an organic solvent. Control experiments were carried out using one phase consisting of an organic solvent. At full conversion up to almost 50 % selectivity for propylamine was observed using a system of 1,2,4-trichlorobenzene (48.3 %), methanol (26.8 %), and cyclohexane (34.8 %). The best results were achieved using a biphasic system of 1,2,4-trichlorobenzene and the Brønsted-acidic IL, 85 % selectivity was obtained at full conversion. Using the biphasic neutral IL, the selectivity decreased to 70 %. Recycling of the neutral IL biphasic system was again demonstrated. However, the use of the Brønsted-acidic IL system required a laborious basic aqueous work-up.

Bouquillon *et al.*[71] used novel ILs, including a readily biodegradable IL for the hydrogenation of phenoxyocta-2,7-diene (Figure 19). The work for the preparation of these biodegradable solvents began with Gathergood and Scammells in 2002[72] where the same principles that are used in the synthesis of biodegradable surfactants were applied to the design of environmentally friendly ILs. Subsequent studies showed the presence of an ester linkage in the side chain of the IL cation promoted biodegradation.[73] The counterion was also a significant factor, with the octylsulfate anion present in examples which were readily biodegradable. Impressive conversions were obtained by Bouquillon *et al.*[71] for the hydrogenation of phenoxyocta-2,7-diene using a palladium catalyst (**17**). The biodegradable octylsulfate imidazolium IL displayed superior conversion (85 %) to the ditriflimide derivative (75 %). The potential for reuse of the IL/catalyst system was exemplified by the recycling of the octylsulfate system, albeit with a significant decrease in conversion to 55 % observed.

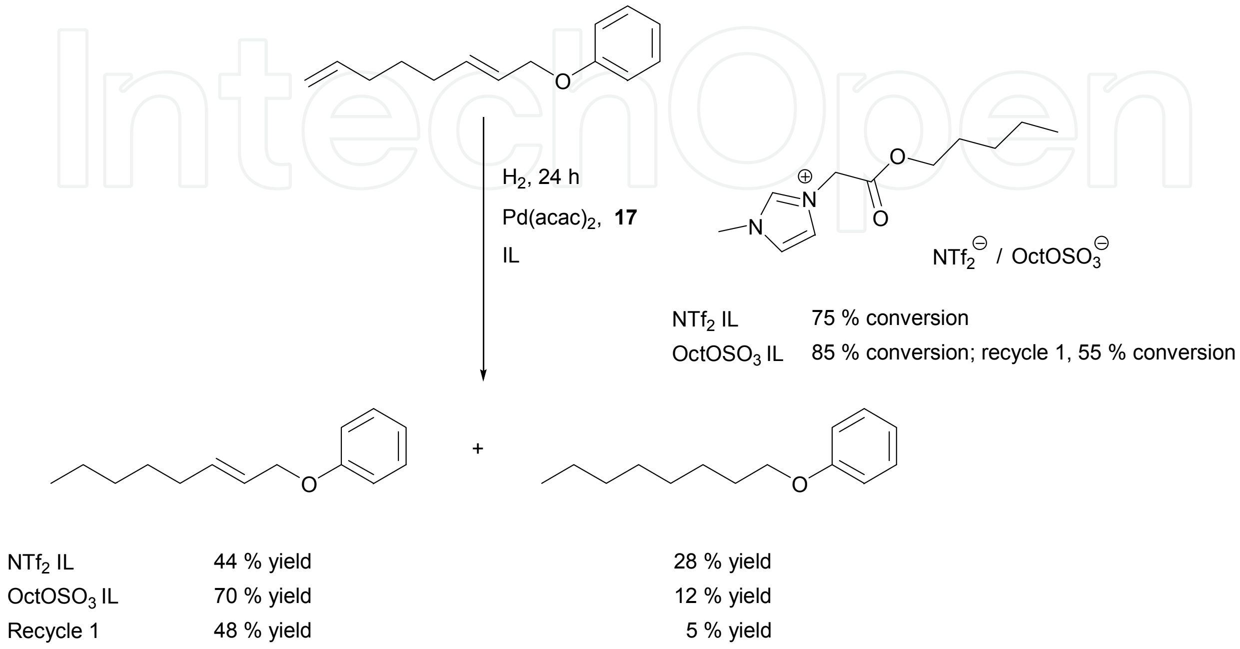
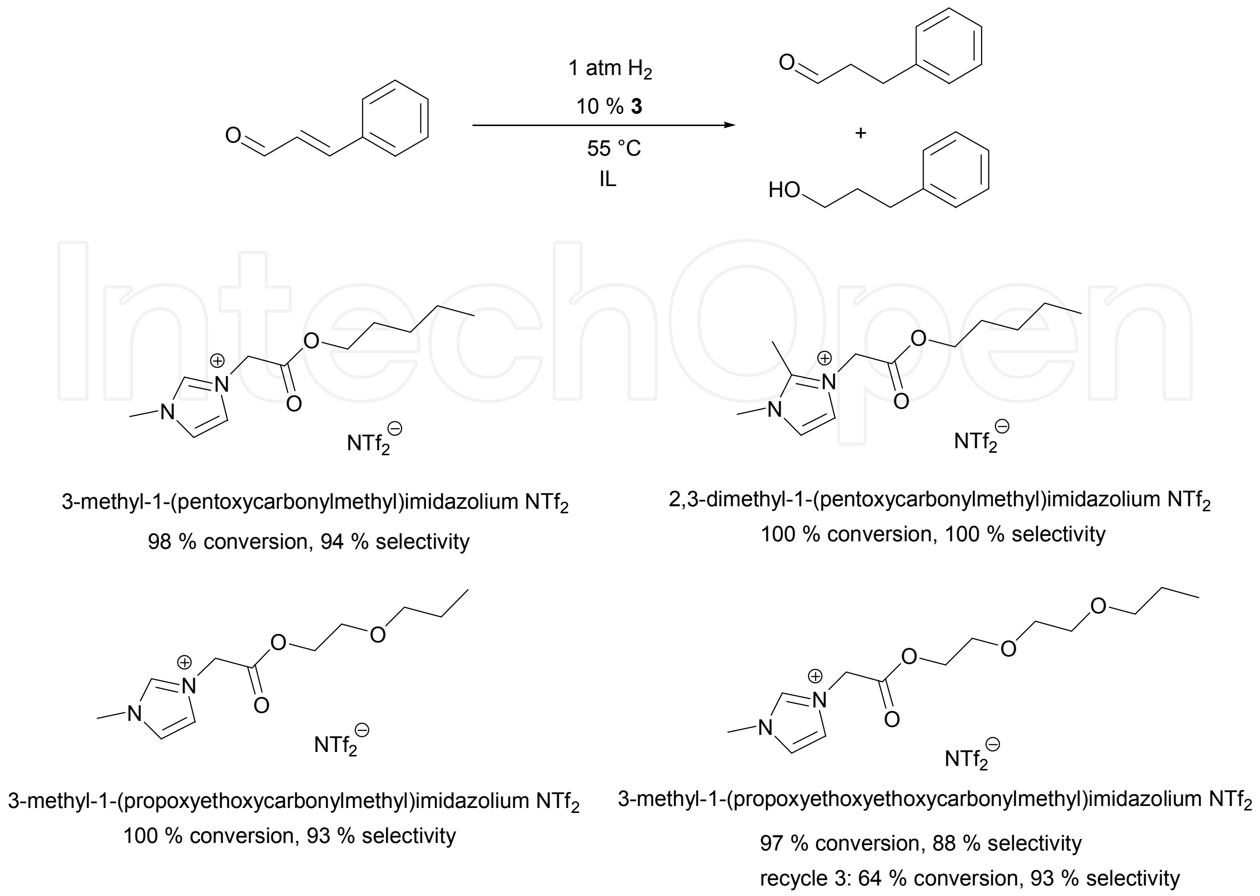


Fig. 19. Hydrogenation using ester-functionalised ILs

The potential of ILs with ester functionalities as solvents for hydrogenation reactions has been recently shown to cover a wider range of substrates. In their communication, Morrissey *et al.*[74] used the previously mentioned imidazolium ILs together with other novel ILs containing ester groups for the hydrogenation of *trans*-cinnamaldehyde, and a range of cinnamate esters. The use of these novel ILs was shown to give superior selectivity towards hydrocinnamaldehyde in the reduction of *trans*-cinnamaldehyde when compared with commercially available [bmim][NTf_2] and [bmim][$OctOSO_3$] ILs and the common organic solvent, toluene. Using a Pd/C catalyst [10 % (**3**)] at 1 atm H_2 pressure, impressive conversions (97 - 100 %) and selectivities (88 - 100 %) were obtained using the ester functionalised imidazolium ILs (Figure 20). A comprehensive review of the hydrogenation of α,β-unsaturated aldehydes comprising *trans*-cinnamaldehyde has been published by Gallezot *et al.*[75]

The hydrogenation of benzyl cinnamate was investigated by the same group, who found that selective hydrogenation of the olefin in the presence of the benzyl group was not possible using either the commercial ILs ([bmim][NTf_2] and [bmim][$OctOSO_3$]) or common organic solvents (e.g. THF, ethyl acetate, and methanol). Instead, complete hydrogenolysis of the benzyl group was observed under these conditions. However, by using the ester-functionalised ILs, 3-methyl-1-(propoxyethoxycarbonylmethyl)imidazolium [NTf_2^-] and [$OctOSO_3^-$] hydrogenation of the olefin occurred with complete selectivity, leaving the benzyl ester intact (Figure 21).



3-methyl-1-(pentoxycarbonylmethyl)imidazolium NTf_2
98 % conversion, 94 % selectivity

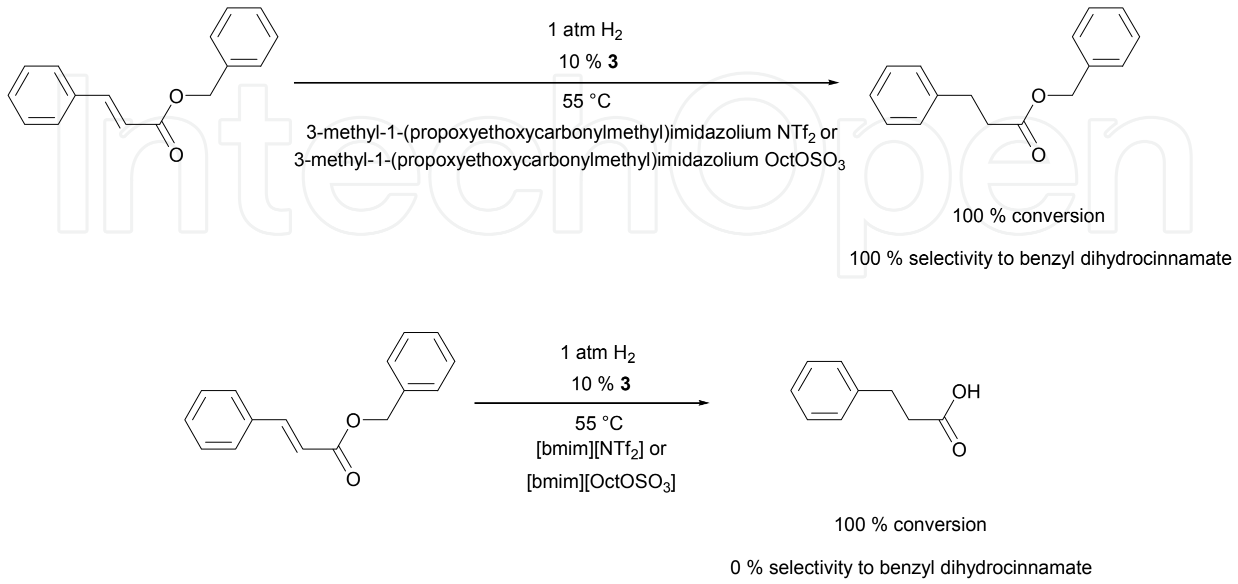
2,3-dimethyl-1-(pentoxycarbonylmethyl)imidazolium NTf_2
100 % conversion, 100 % selectivity

3-methyl-1-(propoxyethoxycarbonylmethyl)imidazolium NTf_2
100 % conversion, 93 % selectivity

3-methyl-1-(propoxyethoxyethoxycarbonylmethyl)imidazolium NTf_2
97 % conversion, 88 % selectivity
recycle 3: 64 % conversion, 93 % selectivity

[bmim][NTf_2]	100 % conversion, 87 % selectivity
[bmim][$OctOSO_3$]	100 % conversion, 69 % selectivity
Toluene	100 % conversion, 67 % selectivity

Fig. 20. Hydrogenation of *trans*-cinnamaldehyde using ester-functionalised ILs



100 % conversion
100 % selectivity to benzyl dihydrocinnamate

100 % conversion
0 % selectivity to benzyl dihydrocinnamate

Fig. 21. Hydrogenation of benzyl cinnamate using ester-functionalised ILs

4. Asymmetric Hydrogenation in ILs

Asymmetric hydrogenation is one of the most reliable methods for the synthesis of enantiomerically pure products.[76] For the greater part, the source of chiral induction originates from chiral ligands coordinated to a metal catalyst.[77,78] Extensive research into the hydrogenation of prochiral substrates in ILs has been carried out in recent years. The majority of this work has employed ruthenium or rhodium based catalysts.

4.1 Hydrogenation using rhodium catalysts

Rhodium catalysts, DiPFc-Rh (**18**), and EtDuPHOS-Rh (**13**) were compared by Boyle *et al.*[79] for the hydrogenation of α-benzamido cinnamate in [bmim][BF_4] and [emim][OTf] (Figure 22). The conversion was negligible using the IL [bmim][BF_4] (0 - < 2 %), and [emim][OTf] became the focus of the following reactions, giving a conversion of 95 % and 89 % ee using 1 mol% (**13**) as catalyst (60 psi, 50 °C). Enamide esters were hydrogenated by Burk *et al.*[80] using the same catalyst (**13**) with methanol as the reaction solvent giving ≥ 99 % ee at 100 % conversion (30 psi H_2, 20 – 25 °C, 0.1 – 0.005 mol% (**13**) catalyst). Ru-BINAP (**19**) was also included in this study and gave the highest enantioselectivity (95 %) albeit with only 16 % conversion (60 psi H_2, RT, 1 mol% catalyst). This may be compared with a conventional organic solvent based system (THF/MeOH, 1:1 mixture) with Ru-BINAP immobilised on silica, which gave 100 % conversion and 85 % ee in the hydrogenation of α-benzamido cinnamate[81] at 29 psi H_2 pressure and 35 °C.

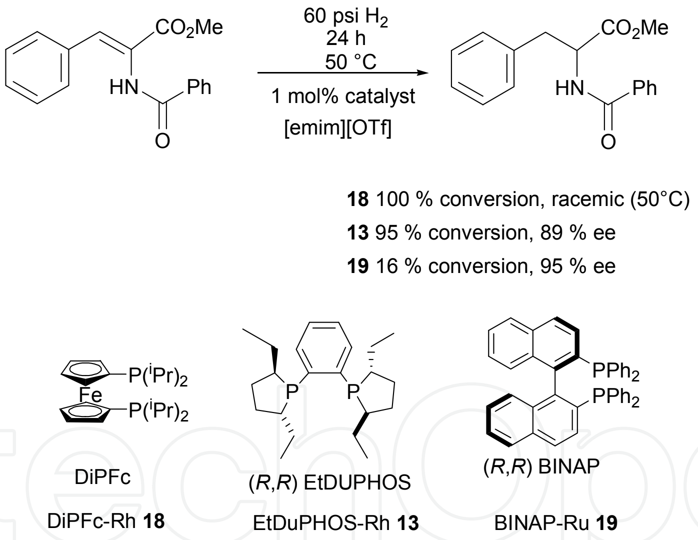


Fig. 22. Hydrogenation of α-benzamido cinnamate and Rh and Ru catalysts

Schmitkamp *et al.*[82] investigated the hydrogenation of dimethyl itaconate and methyl 2-acetamidoacrylate (Figure 23) using ditriflimide CILs derived from L-proline (*L*-prolinium methyl ester NTf_2) and L-valine (L-valinium methyl ester NTf_2) and a rhodium catalyst with tropoisomeric ligands (**20** and **21**).

They investigated the effects of using different CILs and the influence of sulfonated *tropos* ligands on the conversion and enantioselectivity of the reactions. For the hydrogenation of methyl 2-acetamidoacrylate, using (**21**), 49 (*S*) % ee was obtained using L-prolinium methyl ester [NTf_2], where a racemic mixture was obtained under the same conditions using L-valinium methyl ester [NTf_2]. This group thus used (**21**) for all subsequent hydrogenations.

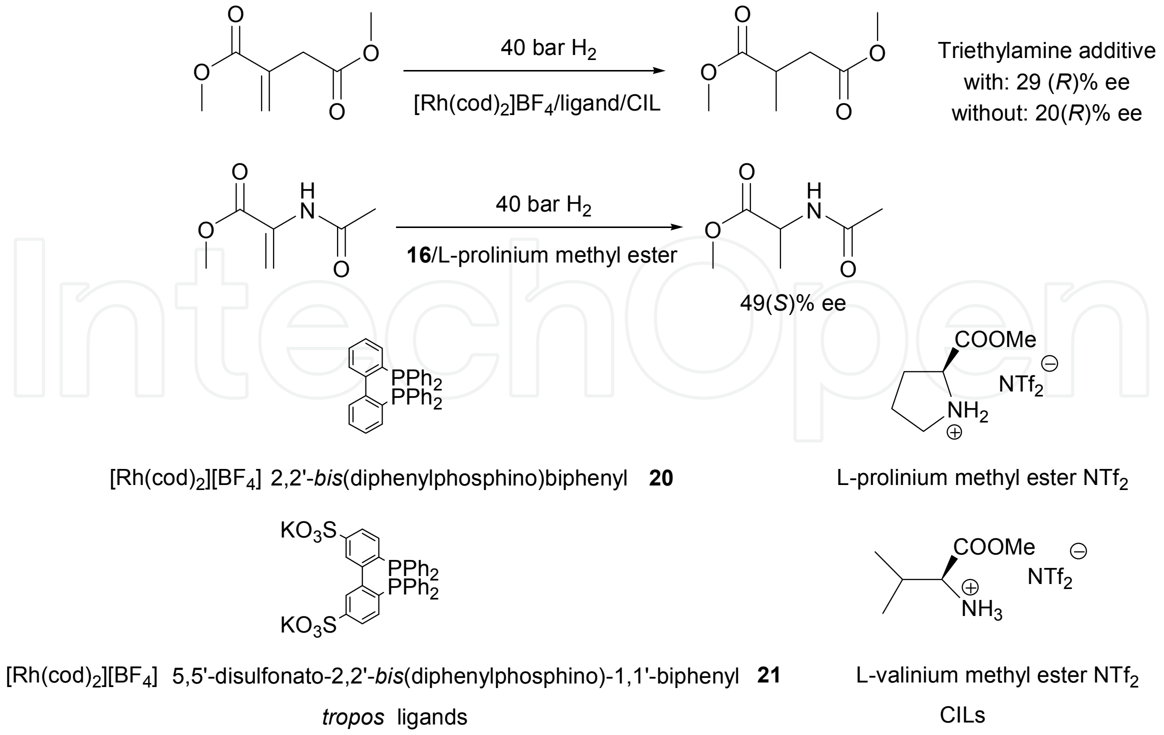
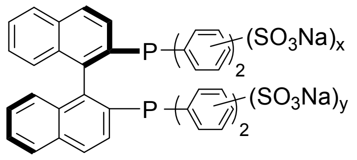


Fig. 23. Hydrogenation of prochiral substrates using CILs and a rhodium catalyst

Concerning the acrylate substrate, good enantiomeric excess (69 %) was obtained for the (*S*) enantiomer when triethylamine was used as an additive in the reaction. Using dimethyl itaconate as the substrate, the amine additive was again found to increase the enantioselectivity (from 20 (*R*) % ee without additive to 29 (*R*) % ee with additive). The sulfonate groups present in the *tropos* ligand were shown to be essential for increased enantioselectivity for both substrates. Enantioselectivity decreased dramatically when the unsulfonated 2,2′-*bis*(diphenylphosphino)biphenyl ligand (**20**) was employed. Changing from (**20**) to (**21**), a drop in enantioselectivity was observed for methyl 2-acetamidoacrylate, from 49 (*S*) to 28 (*S*) % ee, and in combination with triethylamine as an additive, from 69 (*S*) to 52 (*S*) % ee. Recycling of the system was possible by product extraction using scCO$_2$. The recycling procedure showed a reduction in conversion from > 99 % for the first run to 57 % in run three. Enantioselectivity was also moderately compromised during the recycling procedure, decreasing from 69 % to 52 % ee over three cycles.

Sulfonated ligands were also investigated by She *et al.*[83] for the hydrogenation of dimethyl itaconate. A chiral rhodium complex containing water soluble BINAPS ligand (**22**) (Figure 24) was used for the reaction in ILs [bmim][BF$_4$] and [bmim][PF$_6$].



(*R*)-BINAP-*n*SO$_3$Na, *n* = x + y = 3-4

22

Fig. 24. Water soluble BINAP ligand

An IL/IPA biphasic system was used and conversions up to 100 % were obtained, with moderate enantioselectivities (49 - 70 %). Catalytic activity began decreasing, however, after four runs of recycling the system, but the authors found that the addition of fresh ligand to the catalyst re-established its performance.

[Bmim][PF_6] was used by Wolfson *et al.*,[37] as a reaction medium in the asymmetric hydrogenation of methyl 2-acetamidoacrylate with a rhodium catalyst [Rh-EtDuPHOS, (**13**)] (Figure 25).

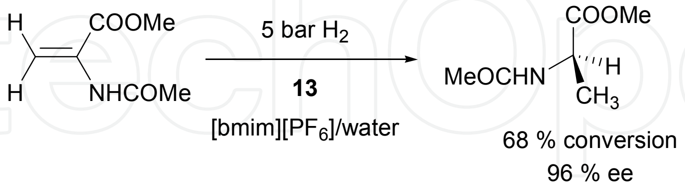


Fig. 25. Hydrogenation of methyl 2-acetamidoacrylate

The reaction did not proceed when performed in the IL alone. To enable the recycling of the catalyst immobilised in the IL, solvents immiscible in the IL were screened. Water gave the highest conversion (68 %) compared to IPA (31 %), diethyl ether (12 %) and hexane (0 %). However, the enantioselectivity remained the same (95 - 96 % ee) for the three solvents that gave conversion. The authors postulate that water is the best co-solvent due to greater mixing with the IL phase, with the water droplets dispersed more effectively than organic solvents in the IL medium.

The hydrogenation of (*Z*)-α-acetamidocinnamic acid and methyl-(*Z*)-α-acetamidocinnamate, was carried out in the ILs, [bmim][BF_4], [bmim][PF_6] and [mbpy][BF_4] using a rhodium catalyst ([Rh(COD)(DIPAMP)][BF_4]) (**23**) (Figure 26).[84]

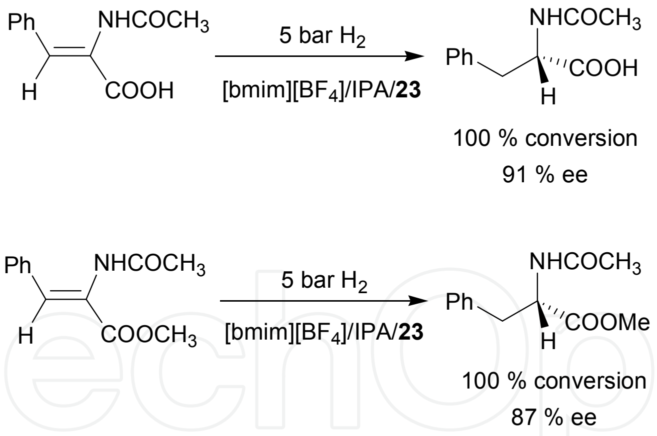


Fig. 26. Hydrogenation of (*Z*)-α-acetamidocinnamic acid and methyl-(*Z*)-α-acetamidocinnamate

In this case, IPA was used as the co-solvent in a biphasic system to facilitate recycling of the catalyst phase. A study of the effect of temperature on the enantioselectivity showed this value to peak at 55 °C. At 5 bar H_2 pressure, conversion percentage was above 97 % for the both substrates in [bmim][BF_4] and [bmim][PF_6]. Enantioselectivity was also good, with enantioselectivities between 71 - 92 %. In many asymmetric reactions the enantioselectivity decreases with increasing temperature. However, in the above case the reverse trend was observed, which led Halpern to investigate the mechanism more closely.[85] Frater *et al.*[84]

demonstrated that the catalyst system retained activity up to the fourth recycle, after which the conversion decreased slightly, with enantioselectivity remaining constant for each subsequent recycle.

Shariati *et al.*[86] used a rhodium catalyst (**24**) (Figure 27) for the asymmetric hydrogenation of methyl α-acetamido cinnamate.

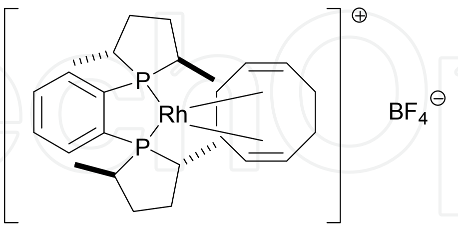


Fig. 27. Rh-MeDuPHOS (**24**)

[Bmim][BF_4] was used as the solvent and the effect of variations in the pressure of H_2 and CO_2 on the conversion and enantioselectivity of the reactions were studied. It was found that when the pressure was increased, conversion increased and selectivity decreased. Increased CO_2 pressure resulted in a decrease in conversion but an increase in selectivity. Using the IL as solvent at 20 bar H_2, 94.2 % conversion was obtained with 91.9 % ee. An increase in the pressure to 50 bar led to an increase in conversion (100 %) but a decrease in enantioselectivity (56.2 %).

4.2 Hydrogenation using ruthenium catalysts

Using methanol as co-solvent, a series of tetradecyl(trihexyl)phosphonium [P_{66614}] ILs were tested for the hydrogenation of dimethyl itaconate to dimethyl methylsuccinate (Figure 28), using the catalyst (*R*)-Ru-BINAP (**25**), at near ambient temperature (35 °C), and 20 bar H_2.[87]

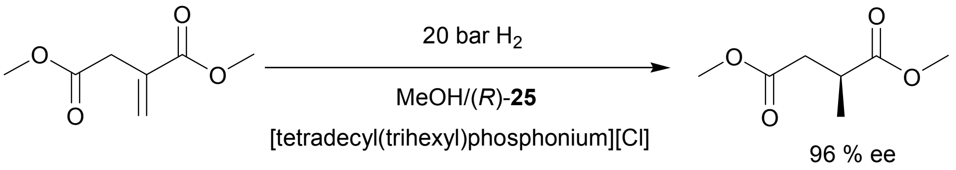


Fig. 28. Hydrogenation of dimethyl itaconate

In order to recycle the system, organic solvent nanofiltration (OSN) was used to separate the catalyst and IL from the product. Recycling of the methanol/[P_{66614}][Cl] system was achieved eight times with no loss in enantioselectivity or catalyst activity. Compared with pure methanol as solvent, the methanol/[P_{66614}][Cl] and methanol/[TBA][Cl] systems showed increased enantioselectivities, ranging from 75 % in pure methanol, to 96 % respectively in the co-solvent systems. The authors demonstrated the dependence of catalytic activity on the anion of the IL. Using [tetradecyl(trihexyl)phosphonium][Cl], good enantioselectivities and yields were obtained. However, in the case of [P_{66614}][decanoate], [P_{66614}][PF_6] and [P_{66614}][BF_4] (Figure 29), no improvement in enantioselectivity or yield was observed.

The hydrogenation of ethyl 4-chloro-3-oxobutyrate to give ethyl 4-chloro-3-hydroxy butyrate (Figure 30) was investigated by Starodubtseva *et al.*[88] using a Ru-BINAP (**25**) catalyst in various IL systems.

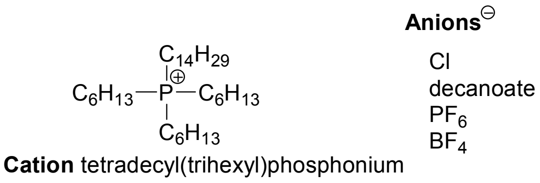


Fig. 29. Tetradecyl(trihexyl)phosphonium ILs

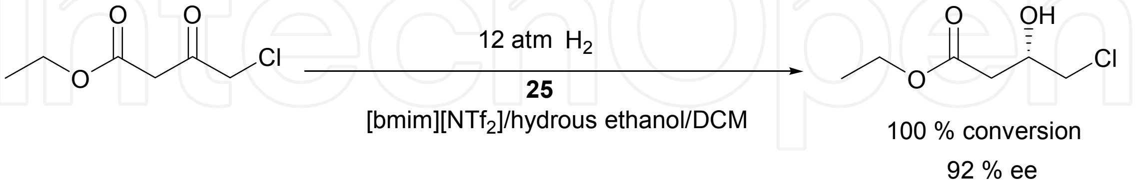


Fig. 30. Hydrogenation of ethyl 4-chloro-3-oxobutyrate

Hydrogenation results were poor using the ILs neat or in combination with an aprotic co-solvent. Starodubtseva then examined the use of [bmim][PF_6], [bmim][NTf_2] and [TEA][Br] with protic solvents, in particular ethanol. It was found that water content was also important, with superior results obtained for wet ethanol compared to anhydrous ethanol. The anhydrous ethanol formed a biphasic system with the IL and catalyst. When wet ethanol was used a homogeneous mixture with the IL/catalyst system formed. 100 % conversion, 100 % selectivity and 92 % enantioselectivity were observed in the case of the [bmim][NTf_2]/hydrous ethanol/DCM system. The conversion however decreased by more than half its original value (to 46 %) upon the third run. Selectivity remained excellent (100 %) for all three runs, and the enantioselectivity only slightly decreased to 85 % for run three. Using the [TEA][Br] IL as an example, the authors showed increasing temperature to be important for enhanced catalyst activity. By increasing the temperature from 30 °C (conversion = 42 %, selectivity = 93 %, ee = 85 %), to 70 °C (conversion = 100 %, selectivity = 100 %, ee = 96 %) improvements in catalytic performance were evident.

With their novel ruthenium catalyst [($RuCl_2$(TPPTS)$_2$)$_2$-(1*S*,2*S*)-DPENDS-KOH; TPPTS: P(*m*-$C_6H_4SO_3Na$)$_3$ and DPENDS: (1*S*,2*S*)-1,2-diphenyl-1,2-ethylene diamine sulfonate disodium) (**26**), Xiong *et al.*[27] carried out the hydrogenation of aromatic ketones (acetophenone, propiophenone, 2-fluoroacetophenone, 2-chloroacetophenone, 2-bromoacetophenone, 2-(trifluoromethyl)acetophenone, 4-(trifluoromethyl)acetophenone, 2-methoxyacetophenone, and 4-methoxyacetophenone) using a selection of ILs ([emim], [bmim], [omim] and [dodecylmim][OTs] and [bmim][BF_4] and [PF_6]) (Figure 31).

The best results were found using the tosylate ILs, with a large decrease in conversion and enantioselectivity obtained with [bmim][PF_6]. The authors attributed this to the hydrophobicity of [bmim][PF_6] hindering the activity of the hydrophilic catalyst. A decrease in enantioselectivity was observed with an increase in alkyl chain length of the cation of the IL. Various parameters were investigated as a function of catalyst activity in the IL that showed the most promising results, namely [bmim][OTs]. Increasing temperature brought about a decrease in enantioselectivity. An increase in the amount of base added (KOH) significantly increased the conversion and the enantioselectivity, as did the addition of (1*S*,2*S*)-DPENDS. The most effective catalyst precursor was shown to be [$RuCl_2$(TPPTs)$_2$]$_2$ with a conversion of 100 % and 79.2 % ee (5 MPa H_2, 50 °C). Nine aromatic ketones were tested, giving good conversions (68.0 - 100 %) and moderate enantioselectivities (40.0 – 80.6

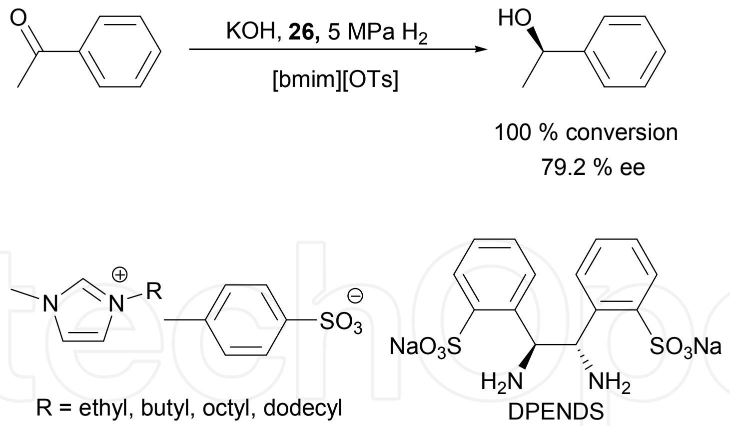


Fig. 31. Hydrogenation of acetophenone using tosylate imidazolium ILs and DPENDS

%). Recycling of the IL/catalyst system over nine runs showed conversions ranging between 100 % and 68.7 %, where even the lowest value of 68.7 % conversion was redeemed by the addition of more KOH. Wang *et al.*[89] used their novel catalyst for the hydrogenation of α,β-unsaturated ketones using ILs. Using benzalacetone as a reference substrate (Figure 32), they found that the lipophilic chains on the cations of the ILs influenced the enantioselectivity.

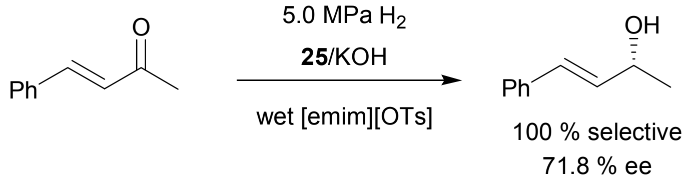
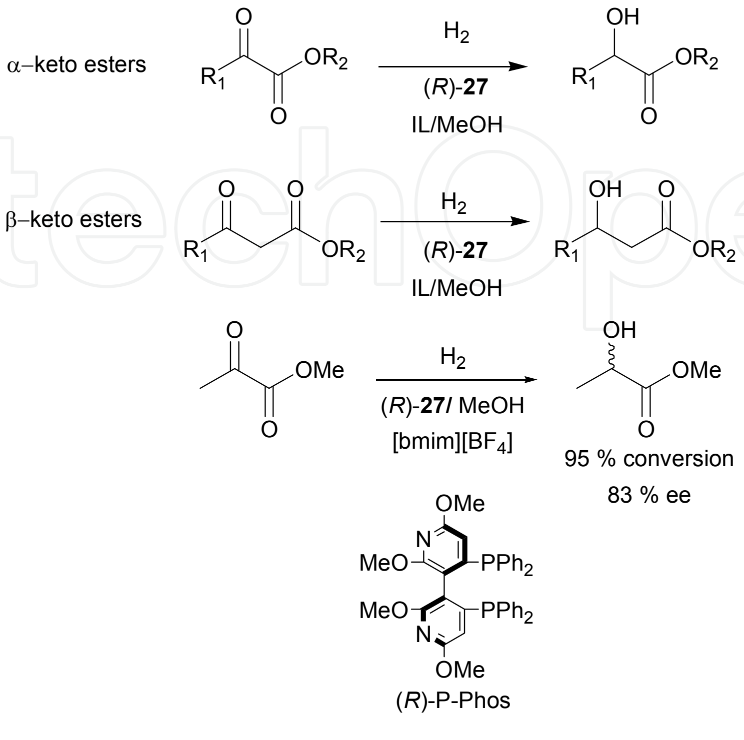


Fig. 32. Selective hydrogenation of benzalacetone

Although selectivity was high for all the unsaturated alcohols screened, enantioselectivity decreased as the ILs alkyl chain length increased (from 71.8 % ee for ethyl to 59.9 % for the dodecyl chain). This group also investigated the effect of base and water content on the reaction. 100 % conversion was reached using strong bases such as NaOH and KOH, while only 4.6 % conversion was obtained in the presence of K_2CO_3. Higher enantioselectivities (70.5 – 71.8 %) were also observed with the hydroxide bases compared to 58.7 % ee for K_2CO_3. Water was found to be a valuable co-solvent, and optimised conditions led to 100 % conversion, 100 % chemoselectivity and 75.9 % ee. Using only water as solvent 79.4 % conversion was obtained with 91.1 % selectivity towards the unsaturated alcohol and 66 % ee (5 MPa H_2, 40 °C). Consistent with Xiong *et al.*[27] favourable results were obtained using $[RuCl_2(TPPTS)_2]_2$ as precatalysts (100 % conversion, 100 % selectivity to unsaturated alcohol, 75.9 % ee in [emim][OTs]). The scope of the reaction was extended to other α,β-unsaturated ketones with good results. Hydrogenation of 2-cyclohexen-1-one gave good conversion (100 %) and chemoselectivity (94.1 % for the unsaturated alcohol), albeit with a moderate ee (48.1 %). 4-Methyl-3-penten-2-one showed good enantioselectivity (84.7 %) and chemoselectivity (84.9 %), however with only poor conversion (29.1 %). The IL/catalyst system was efficiently recycled eight times with conversion dropping from 100 % to 87.9 %. A slight decrease in the chemoselectivity (from 100 % to 99.1 %) was observed and the enantioselectivity remained almost constant for each successive recycle.

Lam *et al.*[90] used a ruthenium catalyst with a dipyridylphosphine ligand (P-Phos) (**27**) for the asymmetric hydrogenation of α- and β-keto esters (Figure 33).



Ru-(P-Phos)Cl_2 **27**

Fig. 33. Asymmetric hydrogenation of α- and β-keto esters using a Ru catalyst

Methyl pyruvate was taken as an example from the α-keto esters and the hydrogenation was carried out using Ru((*R*)-P-Phos)Cl_2 ((*R*)-**27**) and a reference ruthenium BINAP catalyst (**25**). It was found that a co-solvent was crucial for these hydrogenations, as using only the IL as solvent gave negligible conversion. Methanol was used in equal volumes as co-solvent and using (**27**), good conversions were obtained (73 and 95 % conversion for [bmim][PF_6] and [bmim][BF_4] respectively) with good enantioselectivity (86 and 83 % ee). Enantioselectivies decreased when moving to the BINAP ligand, although conversions achieved were higher. The IL used was observed to have an effect on conversion using [bmim][BF_4] and [bmim][PF_6] and methyl 2-oxo-2-phenylacetate as substrate, conversions of 18 and 65 % respectively were obtained with enantioselectivity being relatively unaffected (90 and 93 % respectively). The best conversion (65 %) and enantioselectivity (93 %) were obtained with methyl 2-oxo-2-phenylacetate in [bmim][PF_6]. Methyl acetoacetate was used as a reference substrate for the hydrogenation of β-keto esters. Conversions and enantioselectivities were greater than 98 % with either Ru((*R*)-P-Phos)Cl_2 ((*R*)-**27**) or Ru-BINAP (**25**) as the catalyst. In general, the range of β-keto esters subjected to hydrogenation using (**27**) displayed improved results, with most conversions reaching at least 70 %, and enantioselectivities exceeding 99 %. The hydrogenation of methyl acetoacetate was investigated in [bmim][PF_6] and [bmim][BF_4] for recycling ability. Both IL systems were recycled nine times with similar results although the conversion had dramatically decreased by run nine for both ILs (39 % for [bmim][BF_4] and 49 % for [bmim][PF_6]), enantioselectivities did not fall below 94 % for both ILs over the nine runs.

The hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate was investigated by Floris *et al*.[91] using a ruthenium catalyst in a mixed IL/methanol phase. Good stereoselectivity has been obtained with substrates consisting of keto groups β- or γ- to the carboxy function group using catalysts prepared from $[RuCl_2(p\text{-cymene})]_2$,[92] although the authors goal in this work was to demonstrate the effective re-use of the catalyst ((*R*)-[RuCl(BINAP)(*p*-cymene)]Cl) (**28**) immobilised in an IL. The ILs used were a series of *n*-alkyl-triethylammonium ditriflimide $[N_{222n}][NTf_2]$ ILs with varying alkyl chain lengths (n = 6,7,8,10,12, and 14), to investigate their effect on the reaction. The amount of IL required for satisfactory results to be obtained was investigated with the hexyl substituted ionic liquid $[N_{2226}][NTf_2]$. Using only methanol as the reaction solvent, 98 % ee and 79.4 % selectivity and TOF 1091 h^{-1} were obtained. When using a relatively low loading of IL (0.2 wt%) the TOF 850 h^{-1}, was slightly reduced, along with the enantioselectivity, 96.9 %. However the selectivity remained constant at 79.4 %. Increasing the amount of $[N_{2226}][NTf_2]$ added led to a reduction in TOF values and enantioselectivity, although the selectivity increased. A study into the effect of varying alkyl chain length from $[N_{2226}][NTf_2]$ to $[N_{22214}][NTf_2]$ on the reaction showed no apparent trends. A 1:1 ratio of methanol to IL was used for the reactions above. Although the best result in terms of TOF and enantioselectivity was obtained using only methanol as solvent (1091 h^{-1} TOF, 98.0 % ee at 59.85 °C and 5 MPa H_2), this system was deemed unrecyclable by the authors. The highest result for TOF and enantioselectivity for the mixed systems was obtained with the dodecyl example $[N_{22212}][NTf_2]$ (TOF = 509 h^{-1}, 97.5 % ee at 59.85 °C and 5 MPa H_2) and the lowest values with the tetradecyl $[N_{22214}][NTf_2]$ (TOF = 328 h^{-1}, 96.4 % ee at 59.85 °C and 5 MPa H_2). Using the $[N_{22212}][NTf_2]$ in combination with methanol as reaction solvent, the system was successfully recycled with only a slight drop in enantioselectivity upon the second run, from 97.5 % to 93.9 %.

Methyl acetoacetate was again used as a substrate to investigate hydrogenation using mixtures of ILs and methanol with a ruthenium catalyst (**29**).[93] The catalyst was prepared *in situ* in the presence of HBr from one equivalent of [*bis*(2-methylallyl)(1,5-cyclooctadiene) ruthenium(II)] and two equivalents of phenyl-4,5-dihydro-3H-dinaphtho[2,1-c;1'2;-e]phosphepine (phenyl-phosphepine). Various ILs based on ditriflimide (eg. $[bmim][NTf_2]$ and $[N_{1111}][NTf_2]$) were investigated because the mildly coordinating ditriflimide anion had a beneficial effect on the reaction. Although poorer results were obtained using mixed IL systems in comparison with methanol as a sole reaction solvent, the recyclability of the IL systems was demonstrated. Using methanol as solvent for the reduction of this substrate to methyl hydroxybutyrate gave 100 % yield, 100 % conversion and 92.4 % ee. These values however drastically decreased to 35.8 % yield, 85.6 % conversion and 85.3 % ee upon the first recycle of the system. Impressive results for up to 3 recycles were obtained using the IL system of [*bis*(hydroxyethyl)dimethylammonium]$[NTf_2]$. The yield decreased from 99.5 % upon the first run to 93.2 % upon run 3. The conversion decreased from 100 % to 94.2 % and the ee merely decreased from 93.0 to 91.3 % upon the third run.

Zhou *et al*.[94] demonstrated a phosphine-free catalytic system for the hydrogenation of quinolines in the IL $[bmim][PF_6]$ (Figure 34). Using 50 atm. of H_2 at 25 °C, 100 % conversion and 99 % enantioselectivity was obtained for the preparation of (*S*)-1,2,3,4-tetrahydro-2-methylquinoline. The use of the IL facilitated the recycling of the catalyst/IL system even with prolonged exposure to air. Upon recycling of the system by the 8th recycle, the conversion had decreased from 100 to 82 % with only a slight decrease in ee to 97 %. Zhou *et al.* have proposed a mechanism for this reaction. (Figure 35)

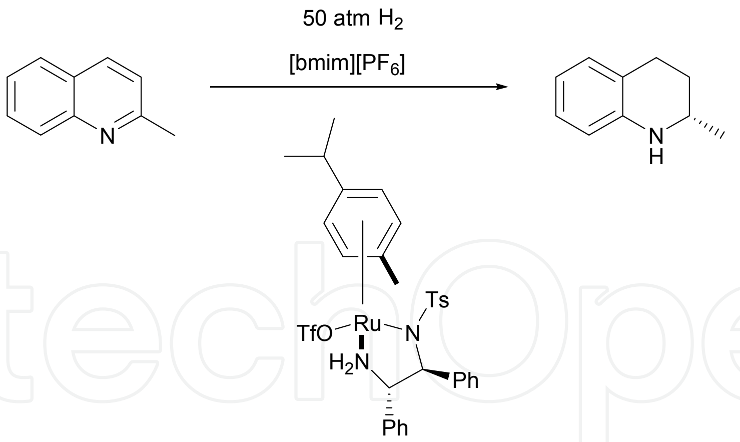


Fig. 34. Hydrogenation of 2-methylquinoline with Ru/Ts-DPEN catalysts [Ts-DPEN: *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine]

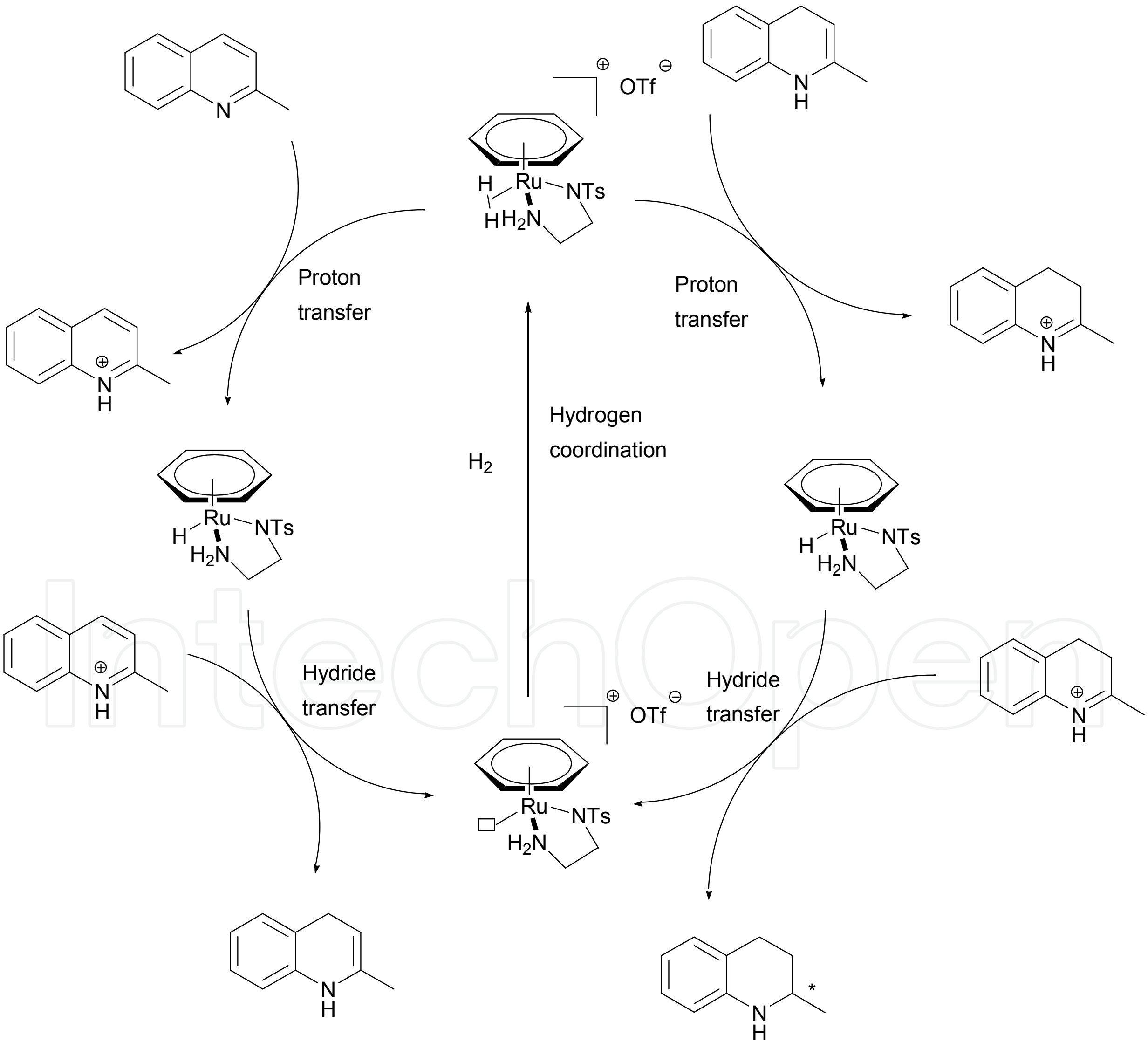


Fig. 35. Proposed mechanism for the reaction in Figure 34

When Dupont *et al.*[16] carried out asymmetric hydrogenation of (*Z*)-α-acetamido cinnamic acid using Ru-(tolyl-BINAP) in [bmim][BF_4] and IPA mixture at RT, they observed that the reduction was accompanied by kinetic resolution of the substrate

5. Metal nanoparticle catalysed hydrogenation in ILs

Nanoparticles have properties intermediate between bulk and single particles. The advantages of using nanoparticles as catalysts are that they present high catalytic activity. However, these nanoparticles need to be stabilized against aggregation into larger particles and eventually bulk aggregates, in order to retain their catalytic activity. Aggregation occurs due to their extensively large surface area and the main means of their stabilization in solution utilizes electrostatic or steric protection. Surfactants and quaternary ammonium salts have been used for stabilization of these particles, and now this field of nanoparticles used in ILs is emerging. Hydrogenation reactions using nanoparticles in ILs may lead to increased reaction times in comparison to solventless conditions or the use of common organic solvents. IL solvents can, however, have a positive effect on product selectivity and recycling of the nanoparticles can also be facilitated. The formation and stabilization of the nanoparticles used for hydrogenation reactions in ILs is only beginning to be understood,[40] despite the fact that nanoparticles based on various transition metals have now been utilised as catalytic media for hydrogenation reactions in ILs.

5.1 Palladium nanoparticles

Umpierre *et al.*[25] prepared palladium nanoparticles in [bmim][BF_4] and [bmim][[PF_6] for use in the selective hydrogenation of 1,3-butadiene to 1-butene (Figure 36). The selective hydrogenation of 1,3-butadiene is a widely used industrial process and further improvement is required to increase the selectivity towards 1-butene. Palladium on supported catalysts in conjunction with promoters or modifiers[95,96] have also been used, however the selectivity towards 1-butene is impeded by isomerisation of 1-butene and complete hydrogenation to 1-butane.

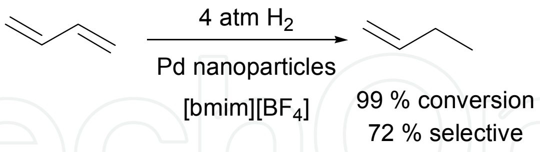


Fig. 36. Selective hydrogenation of 1,3-butadiene

The prepared nanoparticles synthesized by Umpierre *et al.*[25] could be re-dispersed in the ILs or used under solventless conditions. It was found that the reactions carried out in ILs required extended reaction times (6 h) in comparison to reactions carried out under solventless conditions (< 2h). The significant difference is the selectivity achieved in the IL case. Less than 2 % butane was obtained using the IL system, with the 1-butene product formed in high yield. However, even at low conversions and under solventless conditions, a significant amount of butane was formed. The authors suggest the higher selectivity in the IL is due to the lower solubility of butane compared to 1,3-butadiene in the IL. Butenes also did not undergo isomerisation in the ILs, whereas under solventless conditions, isomerisation to 2-butenes occurred after complete conversion of the diene substrate.

Huang *et al.*[97] used phenanthroline ligand-stabilised palladium nanoparticles for the reduction of olefins (cyclohexene, 1-hexene and 1,3-cyclohexadiene) in the IL [bmim][PF_6]. Within the temperature range 20-60 °C and a hydrogen pressure of one bar, conversions of up to 100 % were obtained. For the hydrogenation of 1,3-cyclohexadiene to cyclohexene, a selectivity of 95 % was reached. Aggregation of the palladium nanoparticles was not observed, shown by the recycling of the catalyst media nine times with no loss in catalyst activity. The effect of the ligand on the hydrogenation was investigated, including a study investigating the absence of the ligand on the recyclability of the system. Using the phenanthroline ligand, a conversion of 100 % was reached for the first cycle; the ligand-free system displayed a similar value of 95 %. However, a marked loss in activity was observed upon the first recycle using the ligand-free system (only 35 % conversion). A system without the IL was investigated, using acetic acid as reaction solvent in its place. Aggregation of the nanoparticles was observed during the course of the reaction, and a low conversion of only 5 % was reached.

Hu *et al.*[98] incorporated a bidentate nitrogen ligand into an IL, forming a novel IL capable of stabilizing Pd nanoparticles. The functionalized IL (Figure 37) stabilized nanoparticles were prepared *in situ* in [bmmim][PF_6].

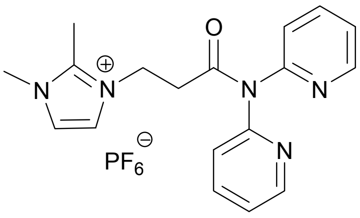


Fig. 37**.** 2,3-Dimethyl-1-[3-*N,N-bis*(2-pyridyl)-propylamido]imidazolium hexafluorophosphate

The stabilized nanoparticles were then used as catalysts for the hydrogenation of cyclohexene, styrene and ethyl acrylate. 100 % yield of reduced product was obtained for each olefin hydrogenation.

This group continued their study of this functionalised IL and investigated the recyclability of the nanocatalysts.[99] Using the IL as ligand for the palladium catalyst in neat [bmmim][PF_6] the selective hydrogenation of functionalised alkenes was investigated. Using this system, the selectivity towards reduction of the C=C bond of α,β-unsaturated aldehydes, esters and ketones was demonstrated. In the case of cinnamaldehyde hydrogenation using a Pd/C catalyst (1.5 MPa H_2 and 35 °C) 55 % conversion was obtained with 35.2 % yield of hydrocinnamaldehyde and 19.4 % yield of 3-phenylpropanol. Using palladium with the functionalised IL as ligand, 75 % conversion was obtained, with 64.5 % yield of hydrocinnamaldehyde and only 10.1 % yield of the fully reduced product, 3-phenylpropanol under the same conditions. The IL-stabilized nanocatalysts were demonstrated to be effective over 7 recycles of the hydrogenation of 2-cyclohexen-1-one. The yield of cyclohexanone remained > 95 % over the recycling procedures.

Chun *et al.*[100] formed palladium nanoparticles deposited on imidazolium-functionalised multi-walled carbon nanotubes (Figure 38) by the reduction of Na_2PdCl_4 with H_2. Direct anion exchange was possible with the bromide functionalised IL on the multi-walled carbon nanotubes, without changing size and distribution of the palladium nanoparticles, to yield hydrophobic [NTf_2^-] and [SbF_6^-] derivatives.

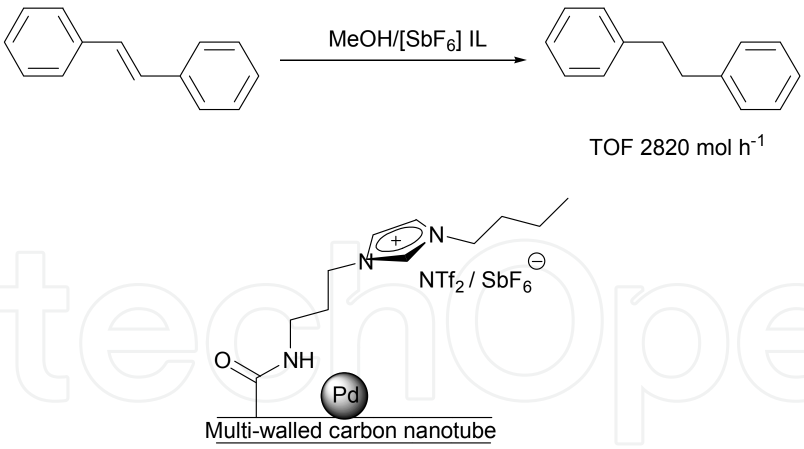


Fig. 38. Imidazolium-functionalised multi-walled carbon nanotubes in the hydrogenation of stilbene

Trans-stilbene was used as a test substrate for the use of the nanoparticles in hydrogenation reactions. Using methanol as a solvent, TOFs up to 2820 mol h^{-1} were attained using the [SbF_6^-] catalyst. When a [bmim][NTf_2]/methanol mixture was used as the solvent, conversion rose from 65 to 100 % for the [NTf_2^-] catalyst and the TOF also rose from 390 to 600 mol/h. The [SbF_6^-] IL was recycled ten times with no loss of catalytic activity. A range of substrates were hydrogenated using this recycled system with a TON of 5000 reached. IL leaching was identified as a minor problem, and additional IL was added upon each cycle of twenty runs. Aggregation of the nanoparticles was postulated to be responsible for the decreased conversion (65 %) for run 50.

Huang *et al.*[101] used palladium nanoparticles immobilized on molecular sieves by the IL, 1,1,3,3-tetramethylguanidinium lactate (Figure 39), for the hydrogenation of olefins (cyclohexene, cyclohexadiene, and 1-hexene).

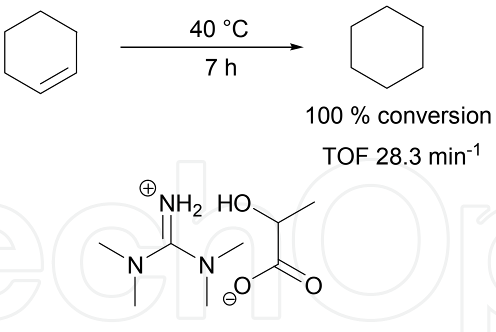


Fig. 39. 1,1,3,3-tetramethylguanidinium lactate and cyclohexene hydrogenation

The synergistic effects of the nanoparticles, molecular sieves and the IL yielded impressive results. Using cyclohexene as a substrate, the system was reused four times with no loss in activity (100 % conversion and 20.0 min^{-1} TOF maintained under a reaction temperature of 20 °C). Cyclohexadiene was selectively reduced to cyclohexene at 20 °C in 3 hours reaching 98 % conversion and 65.3 min^{-1} TOF,

Tao *et al.*[102] also used three guanidinium ILs ([1,1,3,3-tetramethylguanidine][TFA]/[lactic acid]/[acetic acid]) for the preparation of palladium on sepiolite nanoparticles and investigated their use in the hydrogenation of a range of substrates (cyclohexene, styrene, 1-hexene and 1,3-cyclohexadiene). The TFA based IL nanocatalyst was used for most of the investigative hydrogenations. 1-Hexene and styrene were both hydrogenated to hexane (> 99.0 % conversion, 10,000 h^{-1} TOF) and ethyl benzene (> 99.0 % conversion, 10,000 h^{-1} TOF) under the same conditions (2 MPa H_2, 60 °C, 0.5 h). The selectivity of the catalyst was investigated using the substrate 1,3-cyclohexadiene, where the predominant product obtained was cyclohexene at > 99 % conversion after 3.5 hours. The catalyst system was also applied to the cyclohexene to cyclohexane hydrogenation to probe recyclability. Impressive stability of the catalyst was observed when it was successfully used over five recycling experiments with no loss of catalytic activity (> 99 % conversion, 5,000 h^{-1} TOF). This group showed the superiority of their nanocatalyst system when, using the commercially available 5 % Pd/C for the hydrogenation of cyclohexene, a conversion of only 80.2 % was observed in comparison with 95.0 % conversion obtained under the same conditions using the nanocatalyst. The authors suggested that the cation of the IL was primarily responsible for the successful immobilisation of the palladium on sepiolite as results obtained using lactic and acetic acid derived ILs are almost identical to the TFA-based IL.

Palladium nanoparticles in [bmim][PF_6] were used in combination with gold nanoparticles by Dash *et al.*[103] for the hydrogenation of a range of substrates including allyl alcohol, 1,5-cyclooctadiene, *trans*-cinnamaldehyde and 3-hexyn-1-ol. Even in the presence of poly(vinylpyrrolidene), which was used as a stabilizer, the direct synthesis of the IL led to problems in terms of nanoparticle polydispersity. The preferred alternative mode of synthesis for these nanoparticles was initial preparation in methanol, then switching the solvent to an IL. Gold was found not to induce catalytic activity when used as sole metallic source. TOF results showed a high ratio of palladium to gold with 3:1 furnishing the highest TOF values for all substrates. The lowest catalytic activity was observed for *trans*-cinnamaldehyde and 3-phenylpropanal and 3-phenyl-1-propanol were formed in a 1:1 ratio. The selectivity for the alcohol increased slightly when using the bimetallic catalyst in the 1:1 ratio of Au:Pd. The hydrogenation of 3-hexyn-1-ol furnished 3-hexen-1-ol in significantly higher selectivity compared to 1-hexanol with all catalyst ratios and also using palladium as sole metallic source. Cyclooctene was formed in superior selectivity to cyclooctane for the hydrogenation reactions of 1,3-cyclooctadiene. 100 % selectivity for cycloctene was reached using the bimetallic catalyst in a ratio of 1:3 Au:Pd (Figure 40).

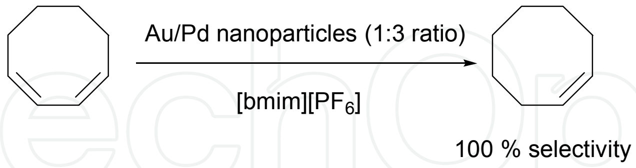


Fig. 40. Hydrogenation of 1,3-cyclooctadiene

The authors report water displays similar TOFs to [bmim][PF_6] (water TOF: 284 h^{-1}, [bmim][PF_6] TOF: 266 h^{-1}), although the IL gave superior recyclability of the system. The catalyst activity was seen to only decrease by less than 4 % for the hydrogenation of allyl alcohol for the first recycle. Several studies have shown that H_2 has low solubility in [bmim] based ILs [10,104], thus hydrogenation reactions in ILs are often mass transfer limited. Under these mass-transfer limited conditions, with respect to H_2 gas, catalyst concentrations were selected in order to optimize both catalyst stability and overall conversion of substrates.

Kume *et al.*[39] prepared palladium nanoparticles immobilized on IL modified-silica gel (Figure 41) for hydrogenation reactions at 80 °C and 5 MPa H_2.

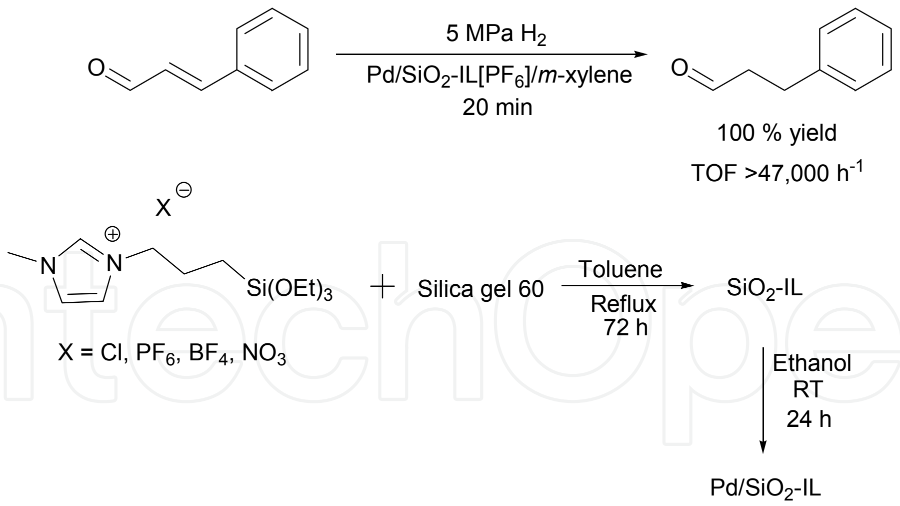


Fig. 41. Preparation of palladium nanoparticles immobilized on IL modified SiO_2 and hydrogenation of cinnamaldehyde

The prepared nanoparticles were used for the hydrogenation of cinnamaldehyde using *m*-xylene and ILs ([bmim][Cl], [bmim][NO_3], [bmim][BF_4], [bmim][PF_6]). Reactions carried out in the neat ILs gave poor catalytic activity, with TOFs of less than 33 h^{-1} after six hours, for all ILs tested. However, TOFs of 47,000 h^{-1} were achieved using the biphasic method in just 20 mins. Using xylene as the only solvent, after 20 minutes a TOF of 22,200 h^{-1} was attained. Hydrocinnamaldehyde was the only product observed for the reaction, and a correlation between the IL anion and TOF was evident. Although the TOF values obtained using neat IL were much less than those obtained using the biphasic system with the IL modified-silica gel, the same trend was evident: TOF values decreased in the order of the following anions used [Cl] < [BF_4] < [NO_3] < [PF_6]. The remarkable improvement in reaction rate when using IL modified-silica gel can be attributed to the high surface area of silica gel, which leads to enhanced contact of substrate and H_2 over the Pd nanoparticles. The silica gel system with the [bmim][PF_6] was successfully recycled nine times with 100 % yield, and a TON of nearly 500,000 achieved.

5.2 Iridium nanoparticles

Fonseca *et al.*[29] formed iridium nanoparticles in [bmim][PF_6] and investigated their application in the catalytic hydrogenation of 1-methylcyclohexene, cyclohexene, 1-decene, and 2,3-dimethyl-2-butene (Figure 42).

They found that increased steric hindrance around the double bond decreased the reaction rate, and increased pressure increased the rate of the reaction up to a certain saturation point. From their studies on the substrate/catalyst concentration ratio they concluded a limiting factor to be also the miscibility of the substrate in the IL. The same group[34] also prepared iridium nanoparticles in [bmim][PF_6] for hydrogenation of ketones. The prepared solid reduced iridium catalyst was removed from [bmim][PF_6] to be used in solventless reactions. One reaction was performed where they re-dissolved the prepared catalyst in [bmim][PF_6]. Comparing the reaction performed under solventless conditions and in [bmim][PF_6], it was seen that the reaction time increased greatly when using the IL (from as low as two hours for solventless conditions, to 17.5 hours for [bmim][PF_6]). The catalyst immobilised in [bmim][PF_6] could, however, be reused fifteen times with almost no loss in

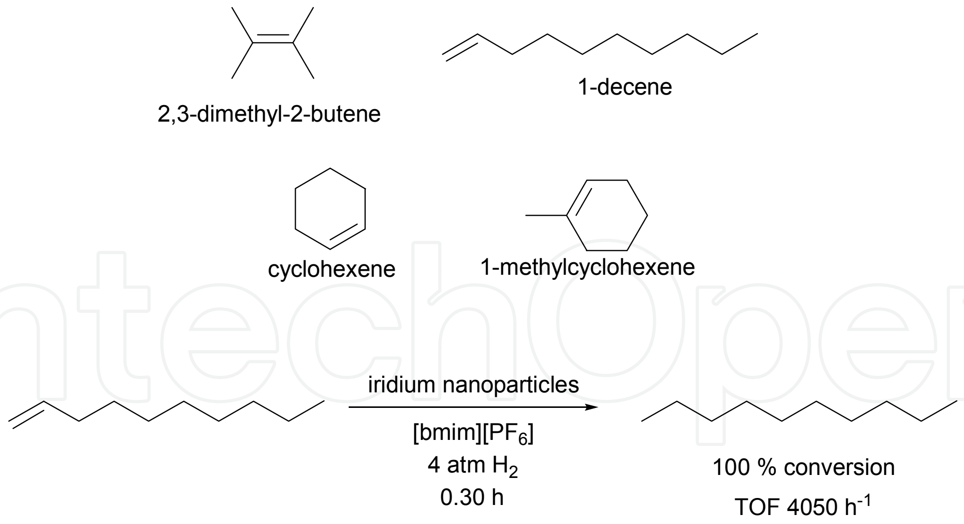


Fig. 42. Substrates used for hydrogenation by Fonseca *et al.*[29] and hydrogenation of 1-decane

activity compared to the catalyst used alone, which showed decreased activity after the third recycle. Increased reaction times were also required when the same group[35] prepared iridium nanoparticles in [bmim][PF$_6$]. The nanoparticles were subsequently used for the hydrogenation of various arenes by re-dispersion in the IL (reduction of benzene to cyclohexane at 75 °C and 4 atm H_2 after 14 hours, 85 h^{-1} TOF), in an organic solvent (after 2.5 hours in acetone, 200 h^{-1} TOF) or under solventless conditions (after 2 hours, 125 h^{-1} TOF). This was again demonstrated in [bmim][PF$_6$] hydrogenation reactions. Prolonged reaction times were required, compared with the use of an organic solvent or solvent-free conditions. Also was shown that the iridium nanoparticle catalysts could be reused after the solvent-free hydrogenation reactions (up to seven times) with little loss in catalyst activity. Iridium nanoparticles employed in the [bmim][PF$_6$] reaction showed a significant loss in activity due to the decomposition of the IL and the nanoparticles.

Dupont *et al.*[105] also prepared iridium nanoparticles in [bmim][PF$_6$]. These nanoparticles were subsequently used in the hydrogenation of olefins (1-decene, styrene, cyclohexene, methyl methacrylate, 4-vinylcyclohexene) in [bmim][PF$_6$] (Figure 43).

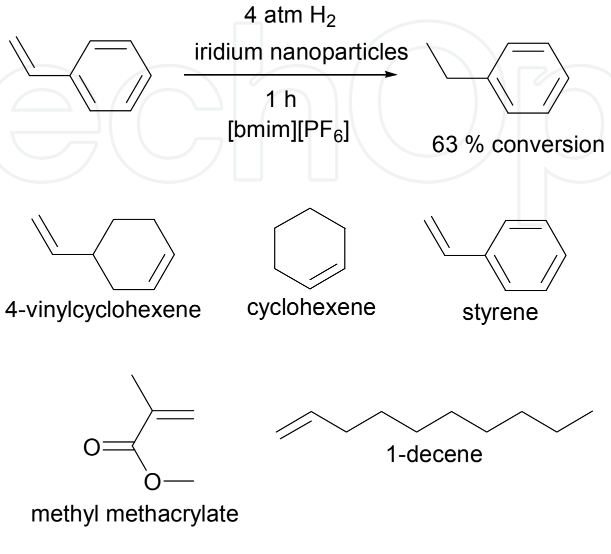


Fig. 43. Substrates used for hydrogenation by Dupont *et al.*[105] and hydrogenation of styrene

Good conversions were obtained (56 – 100 %) within 4 hours. The catalyst system was also shown to maintain efficiency over seven recycles.

5.3 Rhodium nanoparticles

Leger *et al.*[106] employed 2,2′-bipyridine ligands to stabilise zerovalent rhodium nanoparticles for the hydrogenation of aromatic compounds in ILs using biphasic conditions. They investigated the effects of varying anions and cations of the IL on catalytic activity and found the composition of the IL to have a significant influence on selectivity. Using the [bmim] cation, [BF_4] was shown to be the most effective anion favouring hydrogenation of the aromatic double bonds of styrene together with the exocyclic olefinic bond (ethylbenzene/ethylcyclohexane, 8/92 selectivity). With the dicyanamide anion, 100 % selectivity was observed for the product ethylbenzene. Concerning the cationic species of ditriflimide ILs, imidazolium and pyrrolidinium cations displayed identical results (ethylbenzene/ethylcyclohexane, 70/30 selectivity). The pyridinium cation-containing IL displayed superior catalytic activity, with ethylbenzene being formed with 85 % selectivity using [pyridinium][NTf_2]. Leger demonstrated that their catalyst system was viable for a range of aromatic compounds, and they observed that increased steric hindrance due to bulky substituents on the aromatic rings of substrates led to decreased catalytic activity. The catalytic medium was also recycled once with no decrease in catalyst activity.

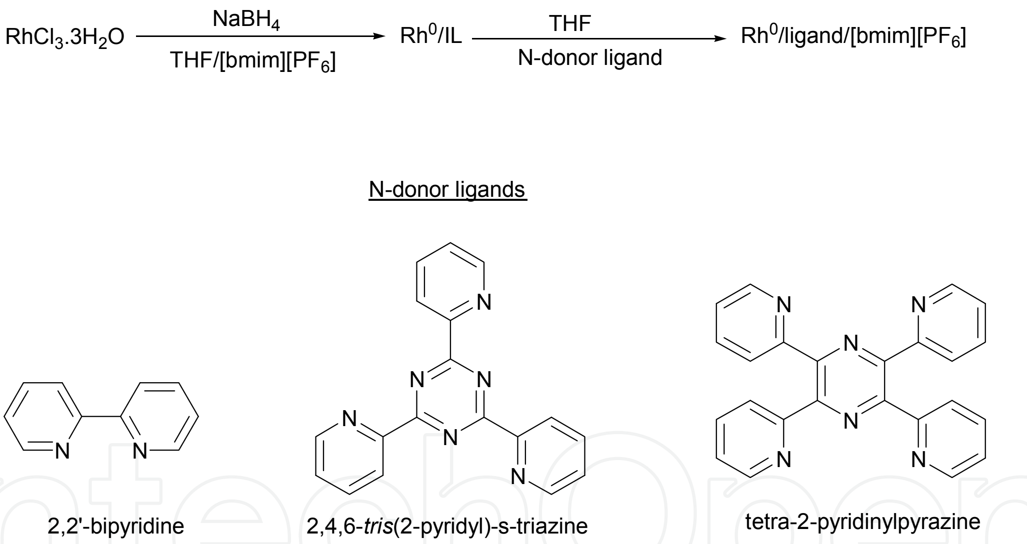


Fig. 44. Synthesis of rhodium ligand-stabilized Rh nanoparticles

Leger *et al.*[107] continued this work by using polynitrogen ligands (Figure 44) in [bmim][PF_6] for the stabilization of zero-valent Rh^0 colloids. When using the tetra-2-pyridinylpyrazine ligand, styrene was selectively hydrogenated to ethylcyclohexane (98 % yield) and ethylbenzene (2 % yield) under 40 bar H_2 at 80 °C. Benzene was reduced to cyclohexane and toluene was reduced to methylcyclohexane with 100 % conversion using either ligands, 2,2′-bipyridine or 2,4,6-*tris*(2-pyridyl)-*s*-triazine. Greater conversion was achieved using 2,4,6-*tris*(2-pyridyl)-*s*-triazine (100 %) for the reduction of ethylbenzene to ethylcyclohexane, than using 2,2′-bipyridine (60 %). Rhodium nanoparticles were stabilised by an IL-like co-polymer (Figure 45) in [bmim][BF_4] and demonstrated high activity for the hydrogenation of various arenes.[31] A record total turnover was obtained (20,000) for the hydrogenation of benzene using this system. Superior results were obtained when using the stabiliser in the IL with the nanoparticles. The solubilities of arenes in reaction media and steric, electronic properties of the substituents on aromatic ring influence the reaction rates.

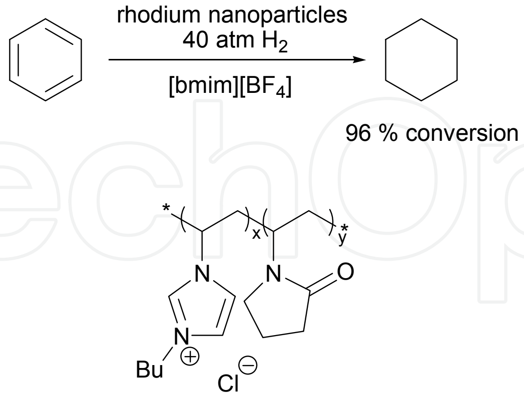


Fig. 45. Poly[(*N*-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride)] in the hydrogenation of benzene

Cimpeanu *et al.*[108] used compressed CO_2 to decrease the melting point of ammonium salts for hydrogenation reactions using a Rh nanocatalyst. [Rh(acac)(CO_2)] (**30**) was used as a catalyst precursor and various ammonium bromide salts and organic impurities were subsequently removed by extraction with supercritical CO_2. Together with the desirable decrease in melting points of the ammonium salts to facilitate the dissolution of the rhodium precursor, the supercritical CO_2 is known to enhance the hydrogen availability in the IL.[109] Using cyclohexene and benzene to test their system, results were obtained that were in line with data reported previously using Rh nanoparticles in standard ILs. Interesting selectivity was however obtained for the hydrogenation of (*E*)-2-(benzoylamino)-2-propenoic acid derivatives using the novel system in comparison to commercially available rhodium catalysts. Whereas Wilkinson's catalyst (**12**) shows poor conversion (< 5 % after 3 days) and Rh/Al_2O_3 shows no selectivity between the olefinic and aromatic double bonds, the rhodium nanoparticles stabilised by the ammonium salts demonstrated selectivity between the differing double bonds. Using the rhodium catalyst stabilised in the tetrabutylammonium bromide salt ([Bu_4N][Br]), impressive selectivity was obtained where the phenyl aromatic ring was almost exclusively hydrogenated (Figure 46).

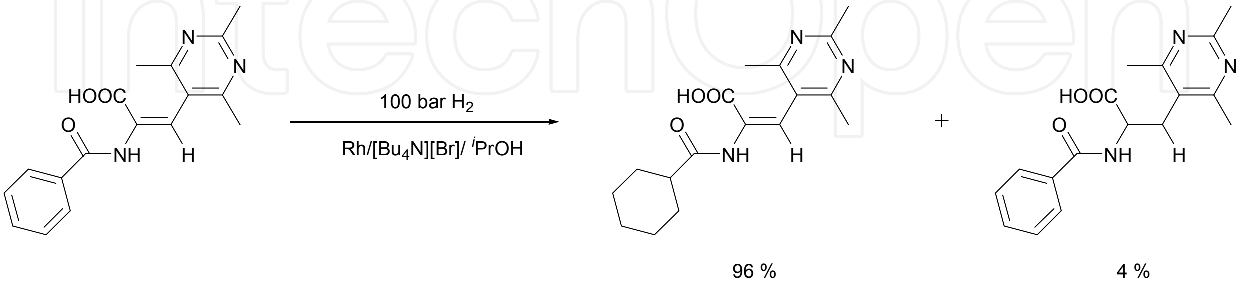


Fig. 46. Selective reduction of aromatic ring

5.4 Platinum nanoparticles

The hydrogenation of *o*-chloronitrobenzene was used to test the performance of Pt(I) and Pt(II) nanoclusters stabilised by an IL-like copolymer in [bmim][BF_4][110] (Figure 47).

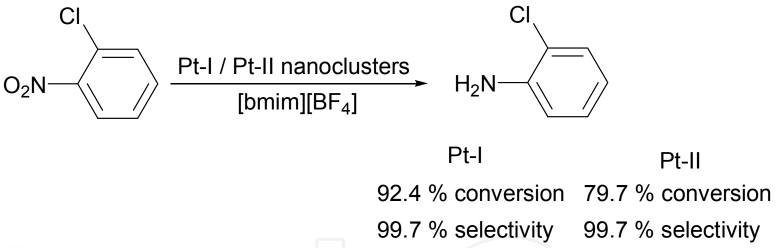


Fig. 47. Selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline

The IL-like copolymer (poly[(*N*-vinyl-2-pyrrolidone)-*co*-(1-butyl-3-vinylimidazolium chloride)]) displayed good solubility in [bmim][BF_4] and was synthesised by Kou and coworkers[110] to surmount the problem of poor solubility of PVP (poly(*N*-vinyl-2-pyrrolidone) polymer. The conversion and selectivity towards *o*-chloroaniline using these catalysts in the IL were superior to results obtained using the conventional PVP-Pt catalyst. The selectivity obtained for *o*-chloroaniline was high using both Pt(I) and Pt(II) nanoclusters (99.7 and 99.1 % respectively), although a drop in conversion was observed moving from Pt(I) (92.4 %) to Pt(II) (79.7 %). From IR studies carried out, the increased selectivity towards *o*-chloroaniline was attributed to interactions between the IL and the substrate.

Scheeren *et al.*[111] prepared platinum nanoparticles for use in the hydrogenation of alkenes and arenes in [bmim][PF_6]. Following the preparation of the nanoparticles, they were re-dispersed in either IL, acetone or used under solventless conditions for the hydrogenation reactions. The prepared nanoparticles proved to be more active than the more commonly used Adam's catalyst. From investigation of the time taken for the hydrogenation of substrates, it was found that the [bmim][PF_6] system displayed the longest reaction time in comparison to the organic solvent system, or solventless conditions. The time taken to reach 100 % conversion, for example, of 1-hexene to hexane was 0.25 hours for acetone and solventless conditions, but 0.4 hours for the IL system. A more dramatic difference in results was shown in the hydrogenation of 2,3-dimethyl-1-butene to 2,3-dimethyl-1-butane, where it took 0.6 hours to achieve 100 % conversion under solventless conditions but 3 hours to obtain only 82 % conversion using [bmim][PF_6]. Only a slight reduction in catalyst activity was noticed upon reuse from solventless conditions. The difference between reaction times was attributed to the typical biphasic conditions of the reactions performed in the ionic liquid, which can be a mass-transfer controlled process.[105]

Abu-Reziq *et al.*[112] used platinum nanoparticles supported on magnetite (Fe_3O_4) modified with functionalised ionic liquids (Figure 48). The ILs were readily synthesised by substitution reaction of the desired alkylimidazole with the alkyl chloride to furnish the alkylimidazolium chloride ILs.

The length of the alkyl chain facilitated regulation of the solubility of the resulting nanoparticles. These supported nanoparticles chemoselectively reduced alkynes to *cis*-alkenes and α,β-unsaturated aldehydes to allyl alcohols, with the added advantage of clean catalyst recovery from the reaction mixture by the application of an external magnetic field. Using their magnetite nanoparticles, impressive chemoselectivity was obtained with a range of substrates; cinnamaldehyde, for example, was selectively hydrogenated to 3-phenylprop-2-en-ol in 99 % yield and diphenylacetylene was hydrogenated to stilbene, the isomeric ratios being *cis*:*trans* 95:5. The latter system was recycled three times, the conversion decreasing a mere 3 %, from 100 % for run one, to 97 % upon the third recycle. The ratio of the *cis* and *trans* product remained almost constant upon recycling. Authors state that the magnetite nano-support can polarize the surface of the platinum nanoparticles and make them partially positive which can lead to selective adsorption and activation of the polar functional groups of the substrate.

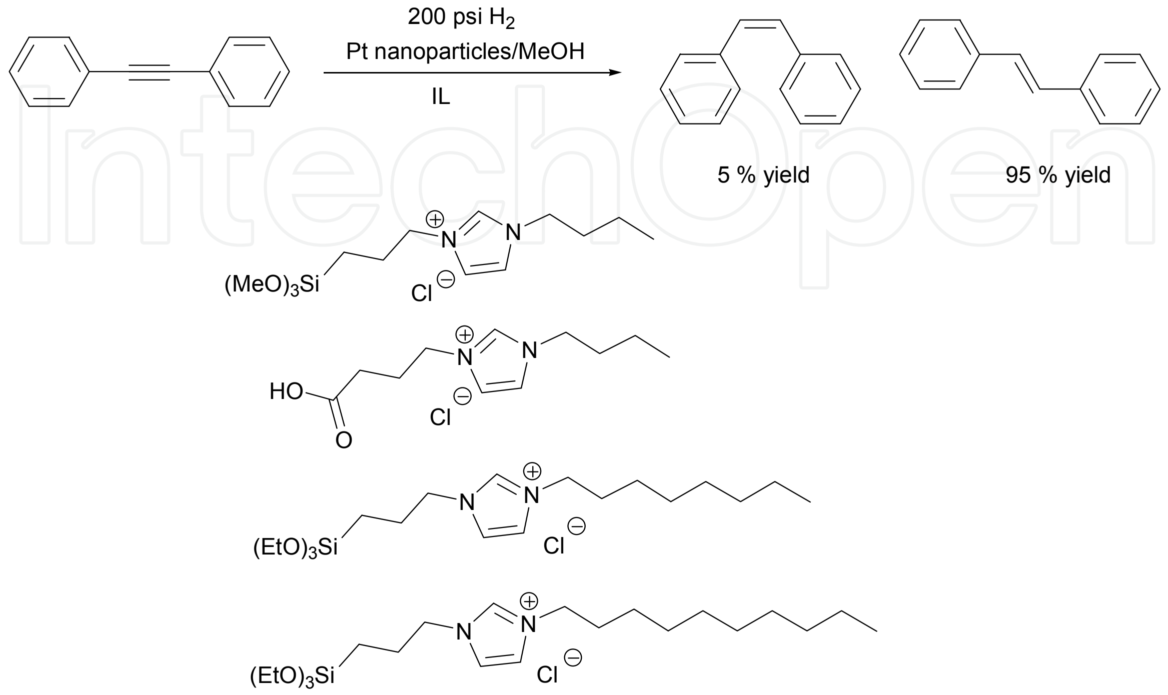


Fig. 48. Functionalised ILs and hydrogenation of diphenylacetylene

5.5 Ruthenium nanoparticles

Silveira *et al.*[33] prepared ruthenium nanoparticles in [bmim][BF_4] and [bmim][NTf_2]. They investigated the hydrogenation of benzene and olefins (1-hexene, cyclohexene, 2,3-dimethyl-2-butene, toluene, *iso*-propylbenzene, *tert*-butylbenzene, and anisole) with these nanoparticle catalysts re-dispersed in the IL and under solventless conditions. Excellent results were obtained for the conversion of hexene, cyclohexene and 2,3-dimethyl-2-butene in [bmim][PF_6] and under solventless conditions (> 99 %). Although the reactions occurred faster under solventless conditions, the catalyst could be reused up to eight times in the IL system with no significant loss in activity. Also investigated was the partial hydrogenation of benzene to cyclohexene, where the IL displayed better selectivity than solventless conditions. For example, at 75 °C and 4 atm H_2 after 2.0 hours at 10 % conversion, 15 % selectivity was obtained for the nanoparticles in the IL. However, under the same conditions after 1.0 hour and at 9 % conversion, solventless conditions furnished cyclohexene in only 4 % selectivity.

Ruthenium nanoparticles were prepared from a ruthenium dioxide precursor in imidazolium ILs.[113] The nanoparticles were subsequently prepared under solventless conditions or under IL biphasic conditions. Although harsh conditions are normally required for benzene hydrogenation, this group successfully hydrogenated benzene to cyclohexane under relatively mild conditions (75 °C, 4 atm H_2) using their ruthenium catalyst. Using [bmim][PF_6] as solvent the highest conversion and TOF (96 % and 49 h^{-1}) of benzene to cyclohexane was obtained in comparison to [bmim][BF_4] (46 % and 15 h^{-1}) or [bmim][OTf] (40 % and 22 h^{-1}). The same catalyst used under solventless conditions displayed 100 % conversion with a TOF of 953 h^{-1} after only 0.7 h. However, selectivity to cyclohexene was obtained using the IL [bmim][BF_4]. This group found that an increase in the temperature of the reaction up to a certain point had a positive effect on the selectivity of the reaction. The kinetic studies completed proved that the hydrogen mass transfer governs the overall reaction rate and product selectivity is not influenced by hydrogen pressure.

Prechtl *et al.*[114] used the ILs [bmim][NTf_2], [bmim][BF_4], [dmim][NTf_2] and [dmim][BF_4] to immobilise Ru(0) nanoparticles for hydrogenation reactions. Biphasic conditions were used for the hydrogenation of arenes at temperatures ranging from 50 – 90 °C at low hydrogen pressure (4 bar). [Bmim][BF_4] containing the nanoparticles showed the lowest conversion (40 %) after 18 hours for the hydrogenation of toluene to methylcyclohexane in comparison with the three other IL systems. Using the [bmim][NTf_2] system, after 24 hours, 50 % conversion was reached. However, the [dmim] ILs better conversion was evident after 18 hours (76 % for [BF_4^-] and 90 % for [NTf_2^-]. After several runs of the nanoparticles in the ILs the particle size and agglomeration state remained nearly unchanged. The systems were also reused successfully several times with little loss in catalytic activity.

Ruthenium nanoparticles were prepared by Prechtl *et al.*[115] by the treatment of [Ru(COD)(2-methylallyl)$_2$] (**31**) with H_2 in a nitrile functionalised IL to form Ru nanoparticles for the hydrogenation of nitrile functionalities. Using benzonitrile as a substrate this group demonstrated the preferential hydrogenation of the nitrile functionality over the aromatic group by the Ru nanoparticles in ILs (Figure 49).

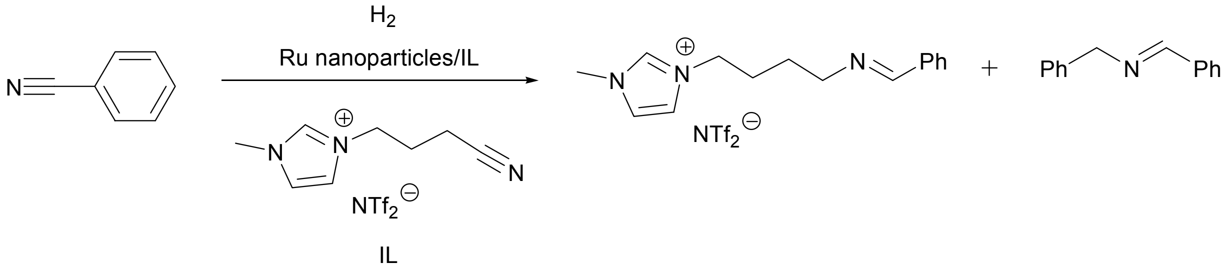


Fig. 49. Selective reduction of nitrile group. (Nucleophilic subsititution with benzyl amine, followed by evolution of ammonia was also observed)

They attribute this to the use of a nitrile functionalised IL giving rise to preferential hydrogenation of the nitrile group whereas arenes are normally hydrogenated by Ru nanoparticles in non-functionalised ILs. Additionally the activation energy for toluene hydrogenation with the ruthenium catalyst in IL is approximately 20 % lower than the activation energy for hydrogenation of nitrile groups in the ILs.[69,114] They found that the selectivity is dependent on the IL support and not on the Ru nanomaterial. For the hydrogenation of benzonitrile to (*E*)-*N*-benzylidene-1-phenylmethanamine, *via* displacement of ammonia, their hypothesis is that the strong coordination of the nitrile group to the ruthenium surface prevents displacement by the aromatic ring of benzonitrile.

5.6 Nickel nanoparticles

Migowski *et al.*[116] demonstrated that the organisation range order of an IL influences the diameter and size distribution of nickel nanoparticles prepared within. 1-Alkyl-3-methylimidazolium [NTf_2] ILs of side chain lengths varying from *n*-butyl to *n*-hexadecyl were used to test this dependency. It was found that an increase in alkyl chain length of the IL up to C_{14} led to a decrease in diameter and size distribution of the nanoparticle, although with side-chain length C_{16} the values for these parameters increased. The IL-Ni colloidal dispersion was used for the biphasic hydrogenation of cyclohexene. TOF values (91 h^{-1}) obtained for the hydrogenation of cyclohexene to cyclohexane in [bmim][NTf_2] at 100 °C and 4 bar H_2 after 14 hours were two orders of magnitude greater than those obtained using conventional nickel supported catalysts at 80 °C and 5 bar H_2.[116] Assuming that the reaction follows a classical monomolecular surface reaction mechanism[29], the catalytic activity expressed as the kinetic constant was calculated to be 9.2 X 10^{-4} s^{-1}.

5.7 Miscellaneous nanoparticles

Redel *et al.*[117] prepared metal nanoparticles (Co, Rh and Ir) in ILs by decomposition of their corresponding metal carbonyls ($Co_2(CO)_8$, $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$) and subsequently used them as catalysts for the hydrogenation of cyclohexene to cyclohexane in ILs ([N_{1114}][NTf_2], [bmim][BF_4] and [bmim][OTf). The catalyst activity observed for the nanoparticles prepared by this route was superior to that obtained by standard metal nanocatalysts in [bmim] ILs. Using [bmim][BF_4] as reaction solvent, the iridium nanoparticles demonstrated the best catalytic activity (1940 mol product (mol metal)$^{-1}$ h^{-1} after 1 hour at 97 % conversion) in comparison to the rhodium nanoparticles (380 mol product (mol metal)$^{-1}$ h^{-1} after 2.5 hours at 95 % conversion), with the cobalt nanoparticles being particularly poor (0.16 mol product (mol metal)$^{-1}$ h^{-1} after 3 hours at 0.8 % conversion). The superior activity of the iridium in comparison with rhodium was postulated to be due to the smaller particle size of the Rh nanoparticles and therefore their accompanying larger surface-to-volume ratio. Even with the reasonably mild conditions used (4 bar H_2, 75 °C) for the hydrogenation reactions, the results obtained were superior to previous work carried out using metal nanoparticles in ILs (eg. RuO_2/Ru/[bmim][PF_6]: 943 mol product (mol metal)$^{-1}$ h^{-1}). The authors suggest the preparation route of the nanoparticles to be the determining factor for the enhanced activity of their nanoparticles. Nanoparticles prepared by the route of reduction of the precatalysts can lead to impurities residing in the IL (eg HCl) which may lower the stabilization effect of the IL and in turn result in catalyst deactivation. However, preparation of the nanoparticles by the decomposition route is safer for the catalyst, because it avoids disruption of the IL phase.

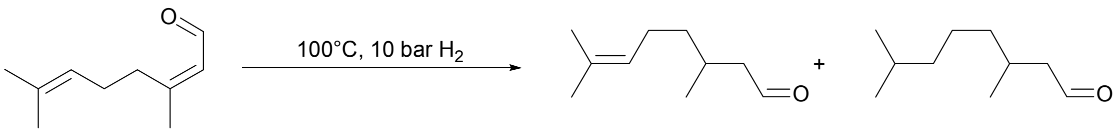
6. Hydrogenation using supported ionic liquid catalysis

An economical means of using ILs in hydrogenation catalysis has emerged. ILs containing a catalyst can be loaded onto a solid support and used for catalytic reactions, thus combining the advantages of using a solid support with the merits of using an IL media. This method of catalysis reduces the amount of IL needed in comparison with conventional IL catalytic systems.

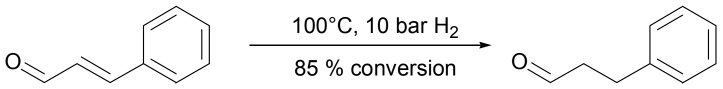
Using [tricaprylmethylammonium][PF_6], [bmim][PF_6] and [bmim][BF_4], Mikkola *et al.*[118] investigated the hydrogenation of citral using a palladium catalyst and SILC (Supported Ionic Liquid Catalysis) technology. Citronellal formation was favoured using the reaction system containing [bmim][PF_6], whereas dihydrocitronellal was favoured using [bmim][BF_4]. [Tricaprylmethylammonium][PF_6] also showed increased formation of dihydrocitronellal. The authors suggest the limiting factor to be the solubility of H_2 in the IL medium, with H_2 solubility being less in [bmim][PF_6] than [bmim][BF_4].[16,119] The cation was also shown to contribute to solubility factors as the dihydrocitronellal formation in [tricaprylmethylammonium][PF_6] was greater than in [bmim][BF_4]. When cyclohexane was used as solvent by Hao *et al.*[120] for the hydrogenation of citral using a Pd/C catalyst (5 MPa H_2, 50 °C) 60 % conversion was achieved with 78 % selectivity towards citronellal. The effect of a Lewis acid and a Brønsted acid on SILC for the one pot synthesis of menthol from citral was investigated by Virtanen *et al.*[121]. In Virtanen's system, supported Pd nanoparticles were immobilized in [*N*-butyl-4-methylpyridinium][BF_4] together with a Lewis or Brønsted acid as an ionic modifier on active carbon cloth (ACC). The initial reaction rate for the conversion of citral decreased on addition of $ZnCl_2$, and the selectivity towards dihydrocitronellal also decreased.

Virtanen *et al.*[122] used SILC technology to hydrogenate citral and cinnamaldehyde, using a palladium catalyst immobilised in [*N*-butyl-4-methylpyridinium][BF_4], [bmim][BF_4], [bmim][PF_6], [N_{1888}][PF_6] and [N_{1888}][HSO_4], tethered to an active carbon support. The stirring rate during each experiment was high (1500 rpm) so that external mass transfer limitations were eliminated. In the case of citral reduction, with all ILs tested, the percentage conversion was high with the main reduced product dihydrocitronellal observed. The notable exceptions were the [PF_6] ILs, where the principle product was citronellal and with a significant decrease in conversion (39 %). The authors contribute this compromise in performance due to lower solubility of H_2 in the [PF_6] ILs. In the case of cinnamaldehyde reduction, [*N*-butyl-4-methylpyridinium][BF_4] and [bmim][PF_6] were studied and for both ILs the main product was hydrocinnamaldehyde. Better conversion results were obtained using the [*N*-butyl-4-methylpyridinium][BF_4] (87 – 100 %) in comparison with the [bmim][PF_6] (23 – 93 %). Slightly superior selectivity towards hydrocinnamaldehyde was obtained using the [bmim][PF_6] (82 – 94 %) in comparison with the [*N*-butyl-4-methylpyridinium] [BF_4] (80 – 88 %). A clear trend of catalyst deactivation was seen from the results of different hydrogenation experiments. The low activity of the palladium catalyst with ionic liquid [bmim][PF_6] was ascribed to poor solubility of hydrogen which was also supported by kinetic studies. When the same reactions were studied to compare the intial reaction rates, it was found that for the catalyst containing ionic liquid [bmim][PF_6] has reaction order close to zero and for the ionic liquid [*N*-butyl-4-methylpyridinium][BF_4] it was 0.7 with respect to hydrogen pressure showing that hydrogen pressure does not make difference in former case.[123] Five different SILC (supported ionic liquid catalyst) compounds have also been used by Virtanen *et al.*[124] to investigate the kinetics of citral hydrogenation (Figure 50) and kinetic modelling was based on the Langmuir-Hinshelwood-Hougen-Watson concept for citral hydrogenation. Palladium nanoparticles in the IL layer were immobilised on an ACC and the results of the hydrogenation compared with conventional palladium on ACC (**32**). The bulk solvent used was *n*-hexane as no leaching of the IL was observed using this solvent, except in the case of [bmim][BF_4]. Of the imidazolium, pyridinium and ammonium ILs studied, the pyridinium [BF_4] IL-containing catalyst displayed the highest TOF observed for all ILs (> 140 mol/h). Selectivity was in most cases highest with dihydrocitronellal, for which pyridinium [BF_4] exhibited the best result (89 % selectivity). All SILCs achieved greater TOF values than the palladium on ACC (**32**) reference standard.

Lou *et al.*[125] used supported ionic liquid catalysis with a ruthenium complex ($RuCl_2(PPh_3)$(*S*,*S*-DPEN), DPEN = 1,2-diphenylethylenediamine) (**33**) for the hydrogenation of acetophenone using mesoporous materials modified with an imidazolium IL (1-methyl-3-(3-triethoxysilylpropyl)imidazolium [BF_4]) (Figure 51). The ruthenium complex immobilised in [bmim][BF_4] was confined to the surface of the mesoporous material for the hydrogenation reactions (3 MPa H_2, RT, 10 h) in IPA.



Catalyst and IL	Conv. (%)	Citronellal (%)	Dihydrocitronellal (%)
Pd(acac) in [bmim][PF_6] on ACC[118]	95 %	major product	-
Pd(acac) in [bmim][BF_4] on ACC[118]	97 %	-	major product
Pd SILCA in [bmim][PF_6][122]	95 %	major product	-
Pd SILCA in [bmim][BF_4][122]	97 %	-	major product



Pd SILCA catalyst[123]
[bmim][PF_6]
84 % yield

Fig. 50. Hydrogenation of citral and cinnamaldehyde[118,122,123]

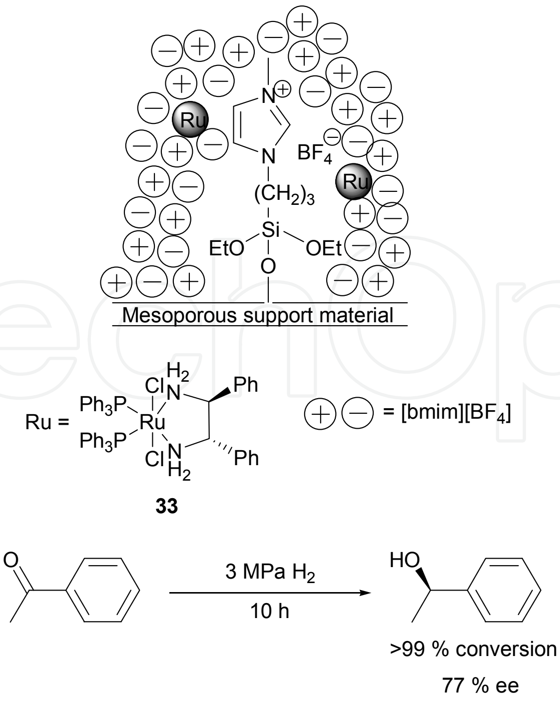


Fig. 51. Ruthenium complex used in hydrogenation of acetophenone promoted by IL-modified mesoporous materials

Lou compared the activity of their supported systems with that of the corresponding homogeneous system, with almost identical results. The homogeneous system gave a conversion of > 99 % with 78 % ee. SiO_2 showed the best activity in terms of recycling ability, compared with other mesoporous materials. The system was recycled five times with no decrease in conversion, (99 %), and little variation in enantioselectivity (79 – 75 % ee). The authors postulate that the larger pore size and complex structure of SiO_2 are the major reasons for the impressive recycling results, due to the prevention of channel blockage during recycling.

Gelesky *et al.*[126] used zerovalent rhodium nanoparticles in [bmim][BF_4] immobilized in a silica network, prepared by the acid or base catalysed sol-gel method, for the hydrogenation of alkenes (1-decene and cyclohexene). This supported ionic liquid phase (SILP) technology was compared with a commercial 5 % Rh/C catalyst and also isolated Rh(0) nanoparticles. The SILP example was found to increase catalytic activity, compared with isolated Rh(0) nanoparticles. The supported catalysts prepared by the acid catalyzed sol-gel method displayed higher IL content in the silica network, and also contained gels of larger pore diameter. Increased catalytic activity resulting from catalysts prepared *via* this route was ascribed to their relatively large pore diameter.

Fow *et al.*[38] used chiral ruthenium and rhodium catalysts immobilised in phosphonium ILs (Figure 52) supported on silica for the hydrogenation of acetophenone.

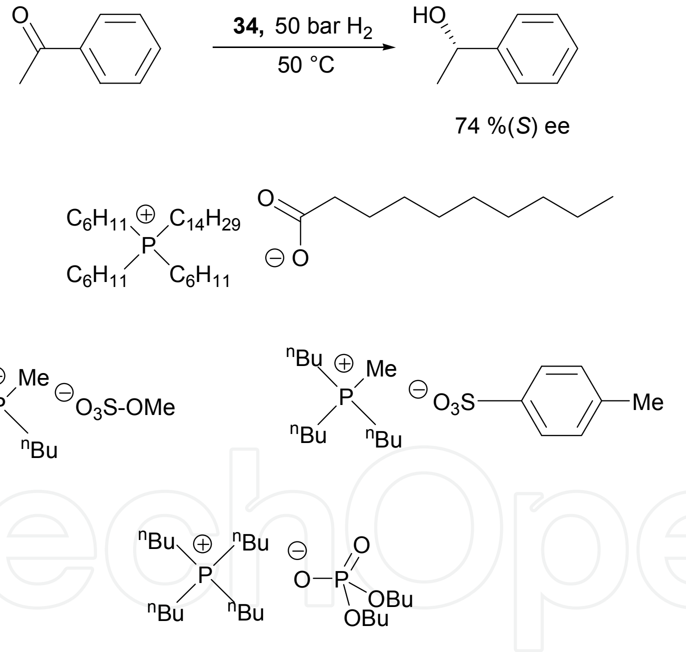


Fig. 52. Phosphonium ILs and hydrogenation of acetophenone

Basic reaction conditions were found to be essential for high conversions. Good enantioselectivity was achieved using their rhodium catalyst, [Rh((*S*)-BINAP)(COD)]$ClO_4 \cdot$ THF (**34**) (74 % ee). No enantioselectivity was observed using the corresponding homogeneous system. The authors describe formation of solvent cages in IL systems as the reason for enantioselectivity promotion with the SILCs.

Chen *et al.*[127] discovered efficient metal scavenging abilities of their task-specific ILs (TSILs) supported on a polystyrene backbone. The materials were formed by the ionic pair coupling of the imidazolium cation tethered to a polystyrene support with L-proline. The application of their novel material soaked with a palladium catalyst was used for the hydrogenation of styrene (Figure 53), where, under mild and solvent-free conditions, a good TON (5,000) and TOF (250 h^{-1}) were obtained.

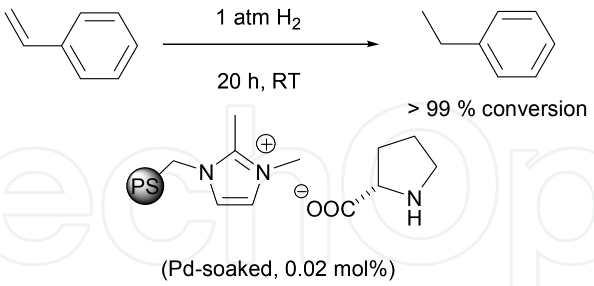


Fig. 53. Hydrogenation of styrene

Ruta *et al.*[30] demonstrated the catalytic activity of their rhodium-based structured supported ionic liquid-phase (SSILP) catalyst with the hydrogenation of 1,3-cyclohexadiene. The IL containing the metal catalyst was confined to a structured support surface consisting of sintered metal fibres. In order to obtain a homogeneous coverage of the support by the IL, these metal fibres were coated with a layer of carbon nanofibres. The hydrogenation of the selected substrate was carried out in the gas phase reaching a TOF of 150 – 250 h^{-1} and selectivity towards cyclohexene of greater than 96 %. The presence of acid and an excess of a triphenylphosphine ligand were essential for the catalytic reaction in the gas phase. Further kinetic studies showed that up to 12 % of catalyst loading the reaction is independent of gas diffusion through the IL film. Lercher *et al.*[128] reported the use of SiO_2 supported Pt nanoparticles immobilized in ionic liquid for the hydrogenation of ethylene gas. This catalyst showed similar activity to a SiO_2 supported Pt nanoparticle catalyst.

7. Transfer hydrogenation

The use of a hydrogen source other than gaseous hydrogen for hydrogen reactions in ILs has recently been explored; to the best of our knowledge, only a few publications have dealt with this subject so far.[129-134]

Catalytic transfer hydrogenations under microwave irradiation were carried out in [bmim][PF_6], using ammonium formate or triethylammonium formate as hydrogen source and 10 % palladium on carbon (**3**) as catalyst by Berthold *et al.*[129] (Figure 54) Substrates containing a wide range of functional groups were investigated, with impressive results obtained in IL systems. Hydrogenation of 4-nitrobenzoic acid methyl ester showed an increase in the yield of 4-aminobenzoic acid methyl ester from 70 % to 92 % when changing from propane-1,3-diol to [bmim][PF_6].

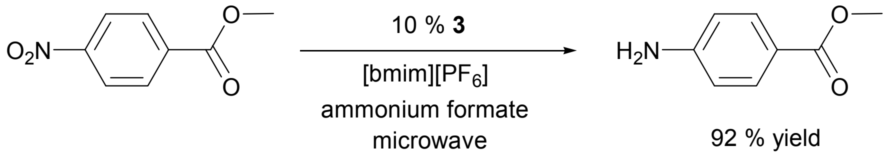


Fig. 54. Hydrogenation of 4-nitrobenzoic acid methyl ester

Baan *et al.*[130] screened six ILs ([bmim][BF_4], [bmim][PF_6], [bmim][Cl], [emim][PF_6], ECOENG™ 212, ECOENG™ 500) in the homogeneous transfer hydrogenation of cinnamic acid using a palladium catalyst (**35**) and ammonium formate as hydrogen donor. (Figure 55) Although only 2 % yield was obtained for the reduction of cinnamic acid using the [PF_6^-] ILs, > 99 % yield was obtained when [bmim][BF_4] and ECOENG™ 212 and 500 were investigated. Under similar conditions in ethanol, toluene, or chloroform negligible yields were observed. The successful reaction with the [bmim][BF_4] was then extended to other α- and aryl-substituted cinnamic acids displaying excellent results (> 99 % yield for five out of nine substrates studied).

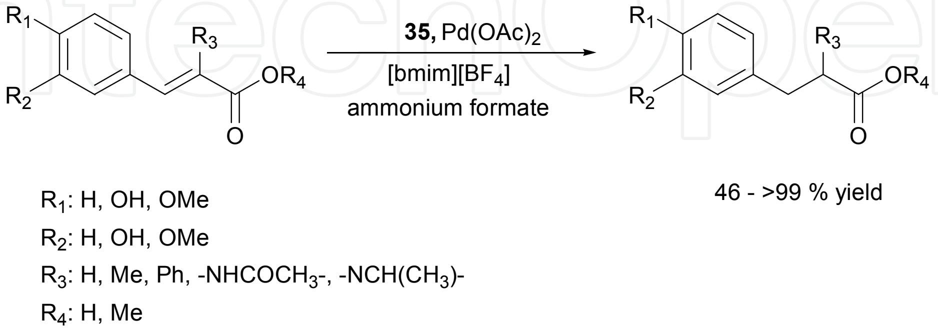


Fig. 55. Hydrogenation of substituted cinnamic acids

Cinnamic acid derivatives were hydrogenated by Baan *et al.*[131] (Figure 56) using catalytic transfer hydrogenation (CTH). Using a basic heterogeneous palladium carrier, magnesium-lanthanum mixed oxide (**36**), in [bmim][BF_4], a variety of substrates were hydrogenated in up to 99 % conversion using HCO_2NH_4. A selection of imidazolium and phosphonium ILs were investigated for the hydrogenation of cinnamic acid. Use of the imidazolium ILs led to increased activity compared with the phosphonium ILs. In [Emim][$EtOSO_3$] it was found that the source of palladium effected the reaction, with Pd^0 displaying increased conversion (85 %) in comparison with Pd^{II} (53 %). Recyclability was also shown possible by the reuse three times of the catalyst used for the hydrogenation of cinnamic acid, with no loss in activity being observed. Also in [emim][$EtOSO_3$] and an azeotropic mixture of triethylamine and formic acid and a palladium on magnesium-lanthanum hydrotalcite catalyst, the hydrogenolysis of a variety of *para*-substituted bromo and chlorobenzenes was performed. Overall, the *p*-bromobenzenes were found to be more active than their chlorinated counterparts.

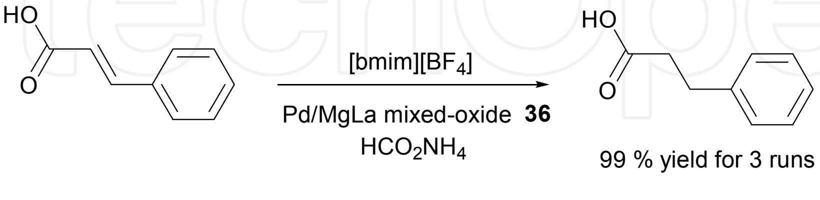


Fig. 56. Hydrogenation of cinnamic acid

Joerger *et al.*[132] used [Ru(arene)(diamine)] catalysts (**37** and **38**) for the asymmetric transfer hydrogenation of acetophenone using a range of ILs, with formic acid as the hydrogen donor. (Figure 57)

In the case of (**37**), catalyst activity was shown to be inhibited by hydrophilic ILs, for example [bmim][BF_4] (conversion < 1 %, 40 hours), [bmim][$MeSO_4$] (conversion 19 %, 48 hours) and [emim][OTf] (conversion 0 %, 24 hours). The best results using this catalyst were

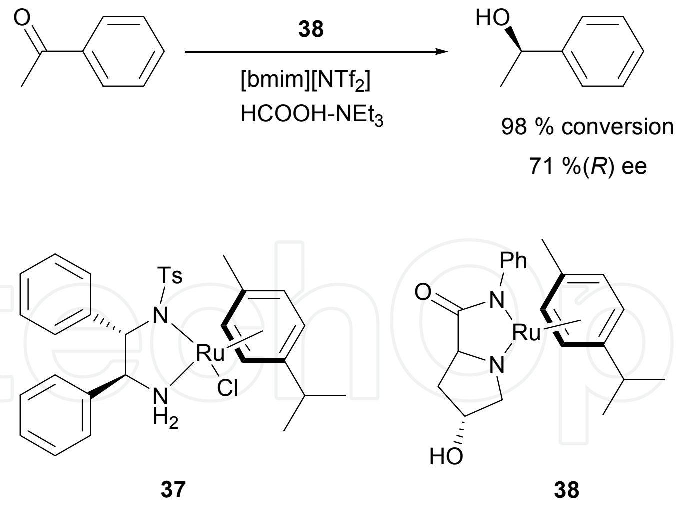


Fig. 57. [Ru(arene)(diamine)] catalysts and hydrogenation of acetophenone

thus obtained using hydrophobic ILs. Conversions of up to 99 % were reached and 97 % enantioselectivity for the hydrogenation of acetophenone to 1-phenylethanol using ILs [trimethylbutylammonium][NTf$_2$] (N_{1114}) and [methyltributylphosphonium][NTf$_2$] (P_{1444}). Without no IL 99 % conversion and 97 % ee was obtained. For the case of [N_{1114}][NTf$_2$], good recyclability was demonstrated, as long as the reaction time was increased (9 hours for run 1 to 30 hours for run 3), decreasing only from 99 % conversion in run one to 82 % conversion on the third run. A slight decrease was reported when recycling this system in terms of selectivity, from 97 % ee in run 1 to 96 % ee in run 3. Using catalyst (**38)** the highest conversion was observed using hydrophobic ILs [bmim][PF$_6$] and [bmim][NTf$_2$], with selectivity of 71 % obtained using both ILs. However, when the cation was changed from [bmim] to *N*-butylpyridinium, conversion decreased to 50 % with the lowest enantioselectivity of 65 % being observed. Upon the fifth run of [bmim][PF$_6$], the catalyst activity decreased slightly again from 72 – 68 % ee, although excellent conversion was maintained (95 %) throughout the recycling process. Using DCM as reaction solvent, 99 % conversion was achieved and 71 % ee.

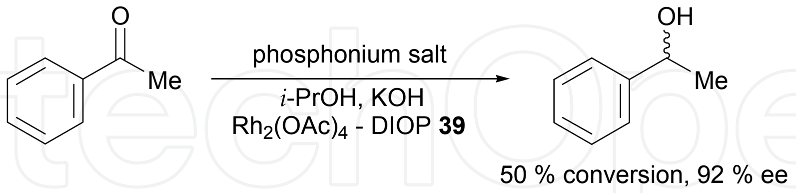


Fig. 58. Hydrogenation of acetophenone to *sec*-phenylethyl alcohol

The rhodium catalyst precursor, dirhodium tetraacetate [$Rh_2(OAc)_4$] was used by Comyns *et al.*[133] for the transfer hydrogenation of acetophenone to *sec*-phenylethyl alcohol using IPA as the hydrogen donor (Figure 58). As reaction solvents this group used a series of tetraalkyl/aryl phosphonium tosylate salts with varying melting points (Figure 59).

The authors describe the advantages of using these higher melting salts over lower melting point ionic liquids. With the ILs that were solid at room temperature, the products could be separated by simple decantation, rather than extraction during work-up. Also the inherent stability of higher melting ILs to harsher conditions provides an additional advantage.

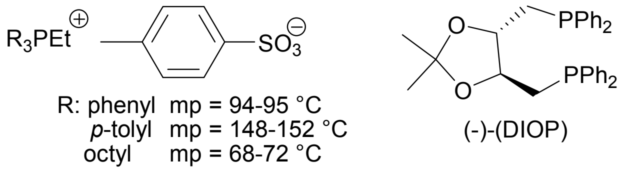


Fig. 59. Phosphonium tosylates salts and (−)-(DIOP) ligand

Reaction temperatures for the transfer hydrogenation ranged from 120-150 °C giving moderate conversions (28-50 %). Using the (−)-(DIOP) (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino)butane) (Figure 59) ligand with the ruthenium catalyst (**38**) impressive enantiomeric excesses of 92 % and 50 % conversion were obtained.

Kantam *et al.*[134] used transfer hydrogenation conditions to selectively reduce carbonyl compounds to the alcohol derivatives using Ru nanoparticles stabilized on magnesium oxide by the incorporation of a basic IL, choline hydroxide (Figure 60). Catalyst preparation involved the treatment of the magnesium oxide crystals with choline hydroxide to yield CHNAP-MgO (CH: Choline Hydroxide, NAP: nanocrystalline aerogel-prepared). CHNAP-MgO was then stirred with $RuCl_3$ solution to obtain Ru(III)-CHNAP-MgO, which in turn was reduced to yield the final catalyst, Ru(0)-CHNAP-MgO.

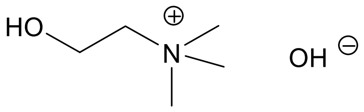
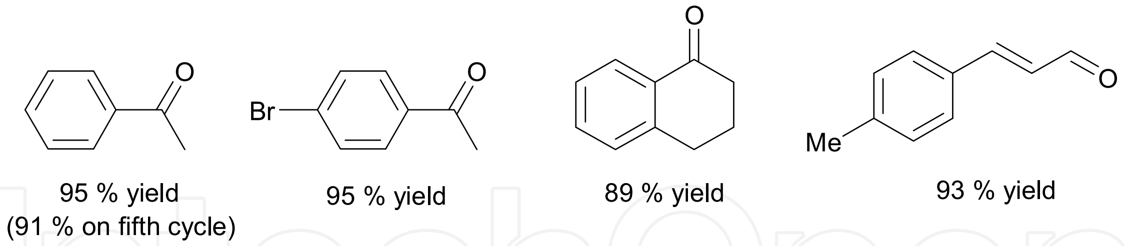


Fig. 60. Choline hydroxide

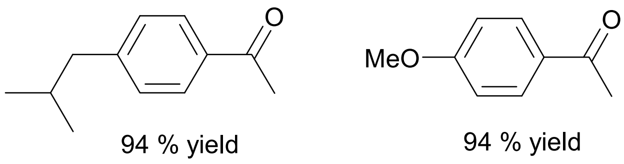
Under reflux conditions using 2-propanol and KOH in 2-propanol a number of carbonyl functionalised compounds were selectively reduced in high yields (Figure 61).



95 % yield
(91 % on fifth cycle)
95 % yield
89 % yield
93 % yield

Fig. 61. Carbonyl compounds selectively hydrogenated to alcohols

Worth noting also are the high yields that were obtained for the selective reduction of the pharmaceutically important 4-*iso*-butylacetophenone (94 %) and 6-methoxy-2-acetophenone (94 %), which are intermediate compounds in the synthesis of ibuprofen and naproxen (Figure 62).



94 % yield
94 % yield

Fig. 62. Pharmaceutically important intermediates

When Hermecz *et al.*[135] carried out hydrogenation of chalcone using Wilkinson's catalyst, they found that the reactions using only ionic liquids as solvents gave better selectivity towards 1,3-diphenylpropan-1-one than reactions performed in a mixture of molecular solvents and ionic liquids (Figure 63).

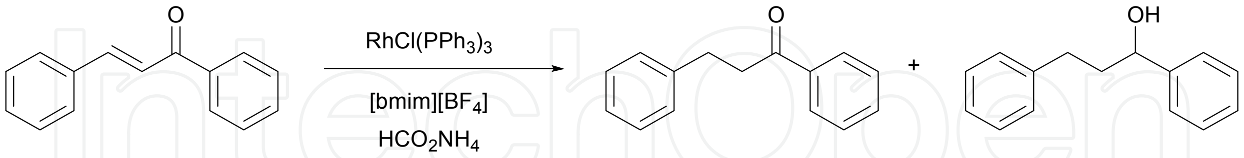


Fig. 63. Hydrogenation of chalcone using Wilkinson's catalyst

The selectivity with molecular solvents ranged from 70 % to 92 % but in ionic liquids was generally > 99 %. Furthermore, the results show that reaction rates are higher in ionic liquids, in particular, [emim][BuOSO$_3$], [emim][HexOSO$_3$] and ECOENG-500™ (Table 10).

Entry	Ionic Liquids	Reaction Time (min)^a	Conversion %	
			Ketone^b	Alcohol^c
1	[emim][EtOSO$_3$]	90	84	0
2	[emim][BuOSO$_3$]	15	> 99	0
3	[emim][HexOSO$_3$]	15	> 99	0
4	[bmim][BF$_4$]	30	> 99	0
5	[bmim]Cl	240	74	26
6	[bmim][AlCl$_4$]	240	0	0
7	[emim][PF$_6$]	240	88	3
8	[bmim][PF$_6$]	240	93	6
9	[hmim][PF$_6$]	240	60	0
10	ECOENG-500™	15	> 99	0
11	[P$_{14,6,6,6}$][Cl]	30	> 99	0
12	[P$_{14,6,6,6}$][PF$_6$]	240	55	0
13	[P$_{14,6,6,6}$][BF$_4$]	240	> 99	0
14	[P$_{4,4,4,4}$][BF$_4$]	90	> 99	0
15	[P$_{1,i4,i4,i4}$][OTs]	240	0	0

^{a} Reaction conditions: (2*E*)-1,3-diphenylprop-2-en-1-one (0.2 mmol), RhCl(PPh$_3$)$_3$ (0.02 mmol), NH$_4$CO$_2$H (0.8 mmol), ionic liquid (1 mL), 90 °C, ^{b} 1,3-diphenylpropan-1-one, ^{c} 1,3-diphenylpropan-1-ol.

Table 10. Transfer hydrogenation of chalcone in ionic liquids

The group explained the selectivity towards 1,3-diphenylpropan-1-one, by proposing a specific interaction between the ionic liquid and chalcone that prevents the reduction of carbonyl group.

8. Future prospects

This section outlines examples where ILs have been used in hydrogenations, in processes with characteristics which do not fall under the previous headings. These cases demonstrate the potential versatility of ILs and illustrate how their use can lead to innovative approaches to problems in a variety of areas.

ILs have been investigated as buffers for hydrogenation reactions in non-aqueous media.[136] Xu *et al.* demonstrated that the selectivity of the hydrogenation of *trans*-cinnamaldehyde could be modulated by using ILs with different buffering characteristics. Using the ruthenium catalyst, [RuCl$_2$(PPh$_3$)$_3$] (**40**) in DMF at 60 °C under 2 MPa H$_2$ pressure, Xu demonstrated a reversal of selectivity between the major reduction products, the unsaturated alcohol and saturated aldehyde. A range of IL buffers were synthesised by reacting basic [Rmim][OH] salts with a series of binary or polybasic acids to form IL buffers. These were then used for the hydrogenation of olefins (1-hexene, styrene and cyclohexene) to confirm the buffering ability of the IL-buffers and with *trans*-cinnamaldehyde as a substrate to investigate the dependence of selectivity on the buffer used in a non-aqueous medium. The results of the hydrogenation confirmed that the activity of the catalyst was highly buffer dependent. Notably, IL-buffers from [bmim][OH] and H$_3$PO$_4$ with log$_{10}$([base]/[acid]) of –0.073 ([bmim][H$_2$PO$_4$]) and 0.232 ([bmim]$_2$[HPO$_4$]) were found to give opposite selectivities, with [bmim][H$_2$PO$_4$] favouring reduction of the olefin over the carbonyl in the hydrogenation of *trans*-cinnamaldehyde, while [bmim]$_2$[HPO$_4$] favoured reduction of the carbonyl. When kinetic studies were carried out, the reaction rate was found to be slightly higher in the absence of the IL-buffers and notable differences in selectivity were observed between the two buffer systems. The authors proposed a catalytic mechanism to explain the reversal in selectivity using different buffering systems in non-aqueous media. (Figure 64)

It was proposed that the IL-buffer [bmim]$_2$[HPO$_4$] (log$_{10}$([Base]/[Acid]) = 0.232) is responsible for the ultimate formation of the [RuH$_4$(PPh$_3$)$_3$] which would lead to preferential reduction of the carbonyl moiety. However, the likely species formed using the IL-buffer [bmim][H$_2$PO$_4$] (log$_{10}$([Base]/[Acid]) = –0.073), [RuHCl(PPh$_3$)$_3$] promotes the reduction of the olefin. The ease of preparation of IL-buffers may well promote an increase in research in this area in order to enhance selectivity for transformations of compounds with multi-functionalised reducible groups.

The new concept of SCILL (Solid catalyst with Ionic Liquid Layer) entails the coating of an IL onto a porous solid which is also a heterogeneous catalyst and thus the drawbacks of biphasic homogeneous catalysis with IL/organic liquid systems are circumvented as the amount of ionic liquid required is reduced and mass transfer limitations are avoided due to the small IL film thickness in the pores. Kernchen *et al.*[24] used this technology for the hydrogenation of cyclooctadiene. (Figure 65)

Using a commercial nickel catalyst coated with the IL [bmim][OctOSO$_3$] they obtained poor conversion of cyclooctadiene to cyclooctane. However, no leaching of the catalyst into the organic phase occurred and the selectivity to cyclooctene increased from 40 % using the system without the IL coating to 70 % using the IL coating.

Ruta *et al.*[137] combined the catalytic activity of palladium nanoparticles with a supported IL phase, for the selective hydrogenation of acetylene to ethylene which is an exothermic reaction (ΔH_{298K} = -172 kJ/mol). Monodispersed Pd nanoparticles were obtained via reduction of Pd(acac)$_2$ dissolved in ILs ([bmim][PF$_6$] and [bmimOH][NTf$_2$]). Carbon nanofibres were used as the IL support, which were in turn anchored to sintered metal fibres. Existing problems arising from using supported palladium catalysts for this industrial hydrogenation process are the formation of active-site ensembles resulting from catalyst deactivation due to the oligomerization of ethylene.[138] High selectivity (70 – 80 %)

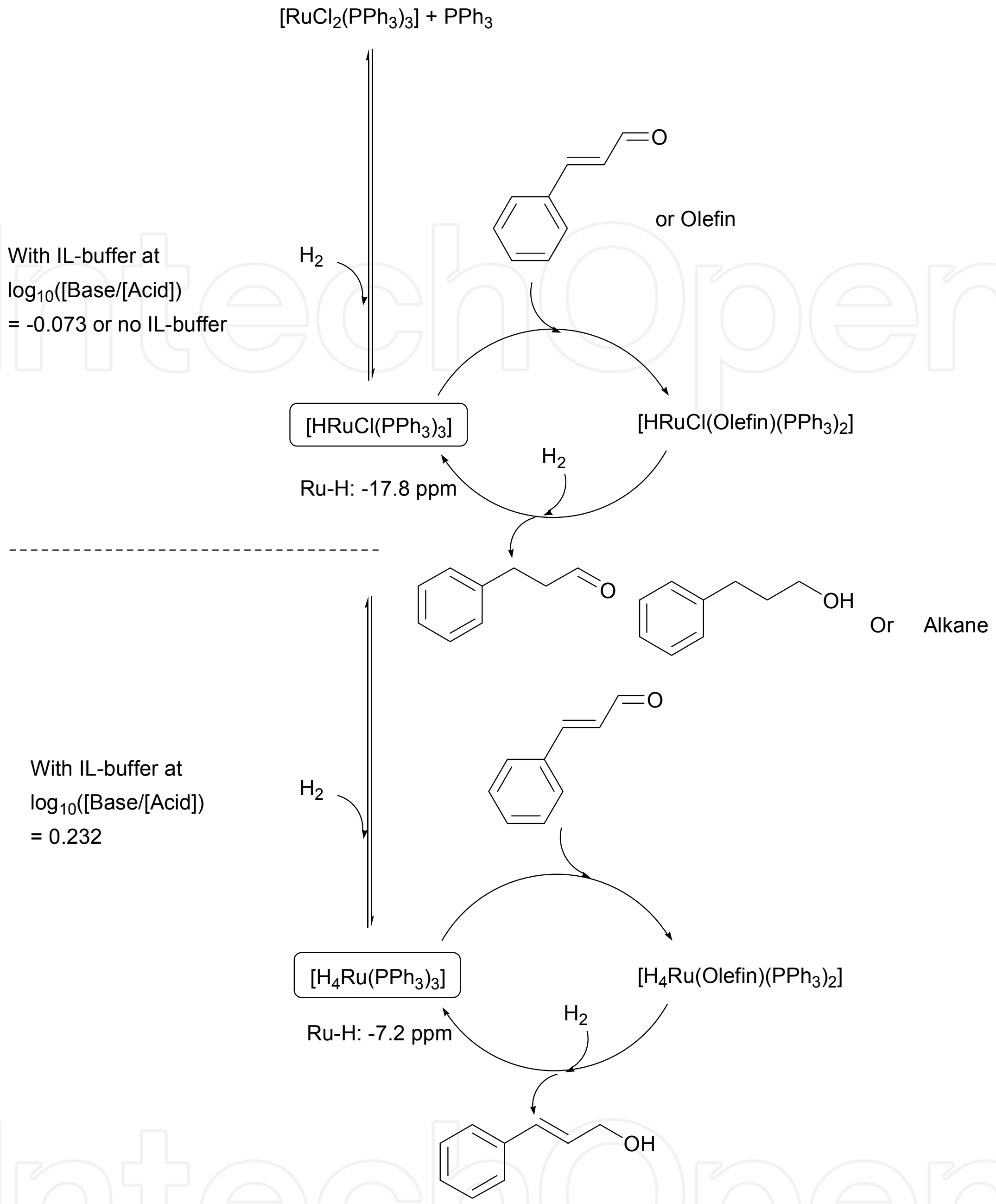


Fig. 64. Hydrogenation using IL-buffers

was obtained using their supported nanoparticle system with a maximum selectivity of 85 % (at 150 °C) being obtained using the IL [bmim][PF_6]. The impressive selectivity is due to the lower solubility of ethylene in the IL compared to acetylene which results in the lowering the subsequent hydrogenation of ethylene to ethane. The systems potential for application in industry was demonstrated by, not only its selectivity, but its long-term stability arising from the ILs preventing the formation of active-site ensembles and therefore reducing catalyst deactivation by this way.

Hamza *et al.*[139] carried out hydrogenation as part of a one-pot multistep process. The process consisted of the hydroformylation of styrene derivatives to yield branched aldehydes. The aldehydes were consequently condensed with reactive methylene compounds (malonitrile, ethyl cyanoacetate) and then hydrogenated. (Figure 66)

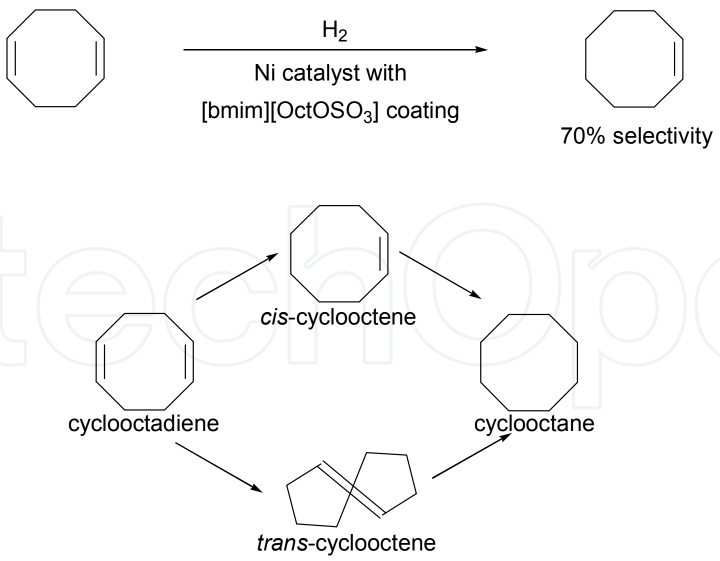


Fig. 65. Hydrogenation of cyclooctadiene

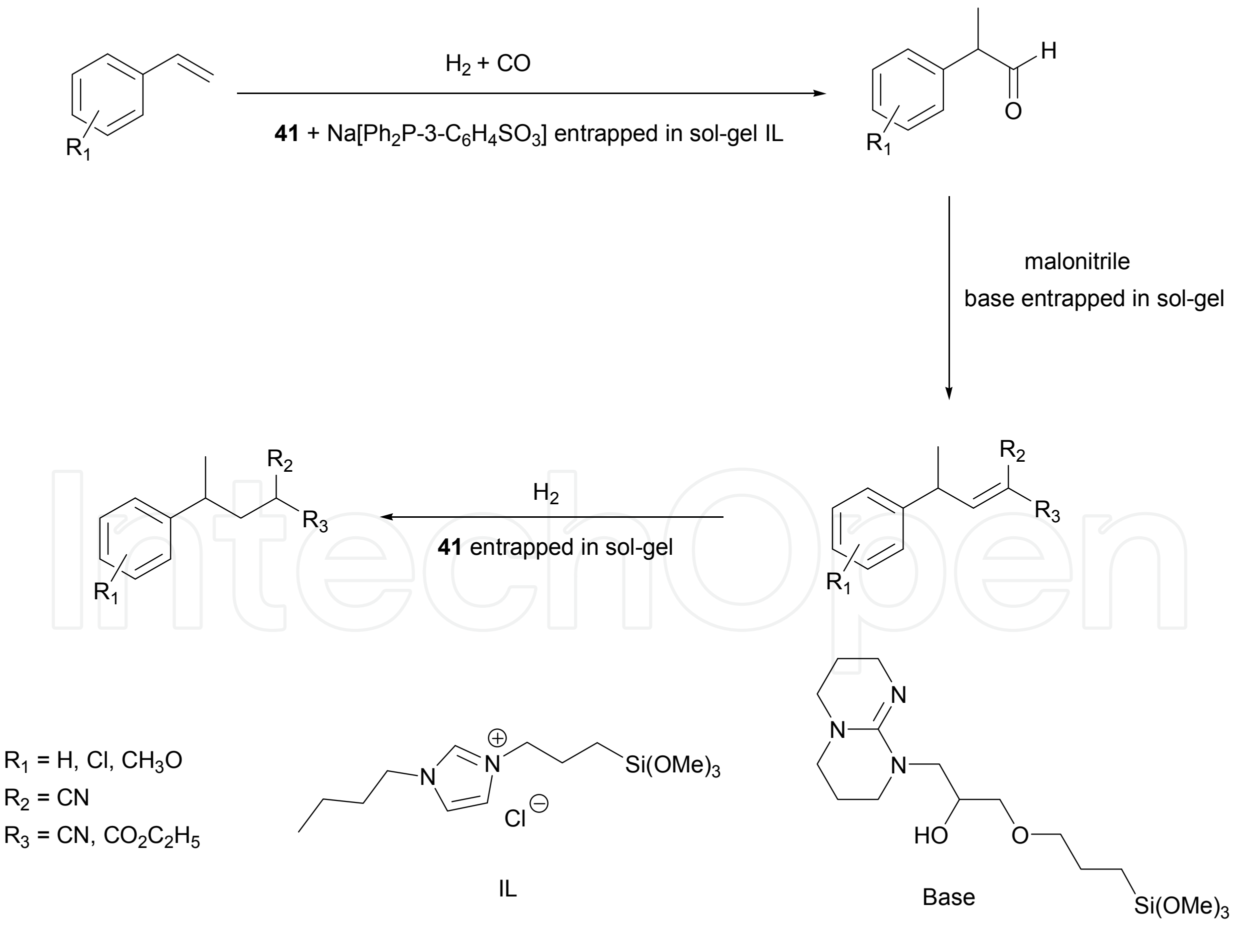


Fig. 66. One-pot multistep process

A silica sol-gel matrix containing co-entrapped $[Rh(cod)Cl]_2$ (**41**) and $Na[Ph_2P\text{-}3\text{-}(C_6H_4SO_3)]$ was confined within an IL (1-butyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride), The one-pot reaction was carried out at 80 °C with 20.7 bar H_2 and 20.7 bar CO in a mixture of 1:1 1,2-dichoroethane:THF. It was shown that the catalyst could be re-used up to four times, although renewal of the base (1,5,7-triazabicyclo[4.4.0]dec-5-ene modified with (3-glycidoxypropyl)trimethoxysilane), which was separately encaged, was required for each reaction. The authors demonstrated the success of the reaction to be dependent on the Rh catalyst being entrapped within the support and the IL being chemically bound to the sol-gel backbone. Under homogeneous conditions, where the Rh catalyst, base and IL were not entrapped in sol-gel, no reaction proceeded. The role of the IL in the reaction is proposed to be as a carbene ligand for the rhodium complex and also acting as a base that promotes the condensation of the aldehydes with malonitrile. Interesting hydrogenation selectivity was observed for this reaction. The internal double bond of the reaction intermediate was reduced, although no reduction of the external double bond of the styrene derivatives was observed.

Pt(0) and Rh(0) nanoparticles were prepared in $[bmim][BF_4]$ and redispersed in $[bmim][NTf_2]$ with cellulose acetate to create functionalised membrane films.[140] These transition metal containing films were used as catalysts for the hydrogenation of cyclohexene to cyclohexane at 75 °C and 4 atm H_2. The use of cellulose in the catalytic materials was demonstrated to be favourable to catalytic activity. Using the cellulose containing membrane with the Pt(0) nanoparticles and IL, a TOF of 7353 h^{-1} was obtained. However, using the same system without the cellulose led to a dramatic decrease in TOF to 329 h^{-1}. The recycling of their system was shown by the successful reuse of the Pt(0) based IL/cellulose membrane up to 2 times without a decrease in catalytic activity.

Craythorne *et al.*[141] co-entrapped rhodium pre-catalysts ($[RhCl(PPh_3)_3]$ (**42**) and $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**43**)) with $[bmim][NTf_2]$ by sol-gel methods and investigated their activity in the hydrogenation of styrene to ethyl benzene. The activity of the catalysts were compared to the same precatalysts prepared by doping of silica glass, the parent homogeneous catalysts, and commercially available Rh catalysts (Rh/C and Rh/alumina). Reactions were carried out using DCM as solvent at 100 °C at 27 bar H_2. In the case of the catalytic system containing the $[RhCl(PPh_3)_3]$ precatalyst, the ionogel outperformed its silica glass counterpart in terms of conversion (98 % in comparison with 75 %) and TOF (32 x 10^2 min^{-1} in comparison to 20 x 10^2 min^{-1}). Irrespective of using the silica doped system or the IL doped system, the TOF values were higher than for the parent homogeneous catalyst (5.5 x 102 min^{-1}). For the systems prepared using $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**43**) the catalyst activity for the catalyst-doped silica glasses (3.8 x 10^2 min^{-1}) and the doped ionogels (3.2 x 10^2 min^{-1}) approached that of the homogeneous catalyst (4.5 x 10^2 min^{-1}). Using heterogeneous rhodium catalysts (Rh/C and Rh/Alumina) the TOF values obtained were significantly lower in comparison to the homogeneous catalytic systems (1.2 x 10^2 min^{-1} (Rh/C) and 0.40 x 10^2 min^{-1} (Rh/Alumina)). This group investigated the capacity of their catalyst system for recycling and found no significant loss in catalytic activity, whereas the heterogeneous rhodium catalysts showed considerable loss in activity over five runs. Levoglucosenone was used to test the catalytic ionogel system using $[RhCl(PPh_3)_3]$ (**42**) in order to determine if the catalytic activity could be extended to more complex substrates. Indeed, at 110 °C and 25 bar H_2, 90 % conversion and 100 % selectivity to the olefinic bond reduced product was observed. (Figure 67)

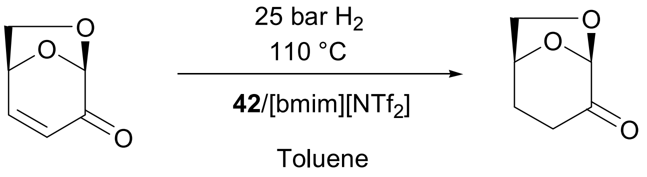


Fig. 67. Hydrogenation of levoglucosenone

Second and third generations of the catalyts were prepared by extracting the used IL with DCM and using it to prepare subsequent catalytic systems. First, second and third generations all demonstrated similar activity.

Cationic dendritic pyrphos-rhodium(norbornadiene) ([pyrphos-Rh(NBD)] (**44**)) complexes were synthesised using poly(propyleneimine) (PPI) and poly(amido amine) (PAMAM) dendrimers as supports, as catalysts for hydrogenation of (Z)-methyl α-acetamidocinnamate in methanol and a biphasic system ([bmim][BF$_4$]/IPA).[142] [Pyrphos-Rh(NBD)] complexes were also tethered to hyperbranced poly(ethylene imines) (PEI) for use as catalytic systems for the same reaction. Using methanol as reaction solvent at 25 °C and 30 bar H_2 the activity and selectivity of the PPI, PAMAM and hyperbranched PEI-bound pyrphos-Rh(NBD) complexes decreased with increasing molecular size. Studying the catalytic effects in the biphasic system, the reaction temperature was raised to 55 °C in order to facilitate a homogeneous reaction system. PPI, PAMAM and PEI-fixed systems displayed a strong negative 'dendritic effect' (Positive dendritic effect: the activity and/or selectivity of the dendritic catalyst increases in comparison to the mononuclear catalyst) with increasing molecular size in relation to catalyst activity, stereoinduction and reusability. However, the reusability of the IL/IPA biphasic system was demonstrated when the first and second generation PPI-bound pyrphos-Rh(I) complexes showed no loss of activity or selectivity after recycling twice.

Janiak *et al.*[143] reported the hydrogenation of cyclohexene by Ru and Rh nanoparticles in [bmim][BF$_4$] at 90 °C and 10 bar H_2 pressure, where the nanoparticles were decomposed using corresponding carbonyl complexes and immobilized in [bmim][BF$_4$]. The results shows that catalyst activity increases with each recycle. In case of the Ru catalysed reaction, for the first run activity was 293 [(mol of product) (mol of metal)$^{-1}$ h^{-1}] which raised to 522 [(mol of product) (mol of metal)$^{-1}$ h^{-1}] at seventh run. Authors have ascribed the raise in activity to surface restructuring of catalyst.

9. Conclusion

With increased environmental awareness throughout the chemical industry, the use of hydrogen gas for hydrogenation reactions is especially popular as it is a clean reducing agent. Coupled with the use of ILs as safer alternatives to VOCs as reaction solvents, hydrogenation reactions can be very attractive as clean, 'green' synthetic methods. It has been demonstrated that ILs can be successfully used as reaction media for a wide variety of substrates for hydrogenation reactions, including transfer hydrogenation reactions. Recyclability of the catalyst system is a major factor in the potential use of the IL. ILs provide a stabilising medium for catalysts and facilitate their immobilisation, thereby facilitating recycling procedures. IL/catalyst systems have been shown to be easily recycled in numerous cases while retaining their activity. Biphasic hydrogenations have also demonstrated recyclability, the substrates and products residing in a separate phase to the

IL and catalyst. A particularly efficient method that has been outlined is where the substrate is dissolved in the IL phase, and the reduction products form a second phase, thus facilitating clean, simple decantation of the desired product from the IL phase. However, if the products are also soluble in the IL phase and a second organic solvent is needed for extraction from the mixture, the requirement for the harmful VOC solvent detracts from the benefit of using the IL unless the recycling ability of the IL is considerable. Although ILs are duly attracting intense attention, their benefits must be balanced with their limitations, and these elements investigated if the solvents are to replace volatile organic solvents on an industrial scale. It has been depicted throughout this review that the viscosity of the ILs poses a problem in terms of increased reaction times. Although, this is an inconvenience in a research laboratory, the increase in cost associated with the heating of the solvent to decrease viscosity or the associated increased reaction times could pose a significant problem at an industrial scale.

Although the principal ILs studied for hydrogenation reactions have been the popular [bmim][BF_4] and [bmim][PF_6], novel ILs have been synthesised and studied as reaction media for these reactions. The cost of the synthesis of novel ILs should be foremost in our minds if these solvents are to be used on a large scale. A predominant factor contributing to cost reduction, and also a possible way forward, may be the use of supported systems, which require a smaller quantity of the IL.

Recycling of the IL is also important, and has significant implications for the original outlay for the material. An IL which can only maintain its required performance for 2-5 cycles has limited use. A significantly higher number of effective recycles is one of the major goals for this research area.

The ‘greenness’ of ILs has been disputed due to their possible persistence and toxicity in the environment. In our opinion, it is not only the cost and performance that should be a component in designing ILs for use in hydrogenation technologies, but toxicity, bioaccumulation and biodegradability should be given equal merit to the process selection before IL development and use in large scale chemical synthesis

The replacement of a VOC with an ionic liquid does not automatically define the synthetic method as ‘green’. Important factors include atom high economy, catalysis, selectivity, recycling, combined with low toxicity and biodegradable chemicals. Catalytic hydrogenations in ionic liquids have the potential to meet all these criteria.

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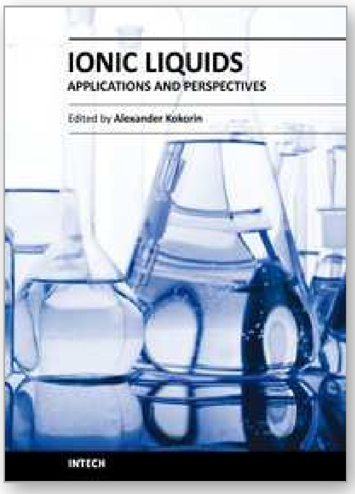

Ionic Liquids: Applications and Perspectives
Edited by Prof. Alexander Kokorin

ISBN 978-953-307-248-7
Hard cover, 674 pages
Publisher InTech

Published in print edition February, 2011

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Mukund Ghavre, Saibh Morrissey and Nicholas Gathergood (2011). Hydrogenation in Ionic Liquids, Ionic Liquids: Applications and Perspectives, Prof. Alexander Kokorin (Ed.), ISBN: 978-953-307-248-7, InTech, Available from: http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives/hydrogenation-in-ionic-liquids

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