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Catalytic Hydrogenation using Ionic Liquids as Catalyst Phase

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41.1

Introduction to Ionic Liquids

Ionic liquids are characterized by the following three definition criteria:

- they consist entirely of ions;
- they have melting points below 100 °C; and
- they exhibit no detectable vapor pressure below the temperature of their thermal decomposition.

As a consequence of these properties, most ions forming ionic liquids display low charge densities resulting in low intermolecular interaction. Some of the most common ions used to date for the formation of ionic liquids are shown in Figure 41.1.

Ionic liquids can be classified according to the different classes of cations, namely as imidazolium, pyridinium, ammonium, and phosphonium salts. These cations form low-temperature melting salts in combination with many different anions. Low-melting chloroaluminate salts can be regarded as the first ionic liquids to be studied in detail, and in the modern literature they are often referred to as “first-generation ionic liquids”. They were described as early as in 1948 by Hurley and Wier at the Rice Institute in Texas as bath solutions for the electroplating of aluminum [1, 2]. Later, during the 1970s and 1980s, these systems were intensively studied by the groups of Osteryoung [3, 4], Wilkes [5], Hussey [6–8], and Seddon [9].

In 1992, ionic liquid methodology received a substantial boost when Wilkes and Zaworotko described the synthesis of non-chloroaluminate, room-temperature liquid melts (e.g., low-melting tetrafluoroborate melts) which may be regarded as “second-generation ionic liquids” [10]. Nowadays, tetrafluoroborate and (the slightly later published [11]) hexafluorophosphate ionic liquids are still widely used in ionic liquid research. However, their use in many technical applications will be clearly limited by their slight – but clearly existing – tendency to hydrolyze. Consequently, the technical application of tetrafluoroborate and

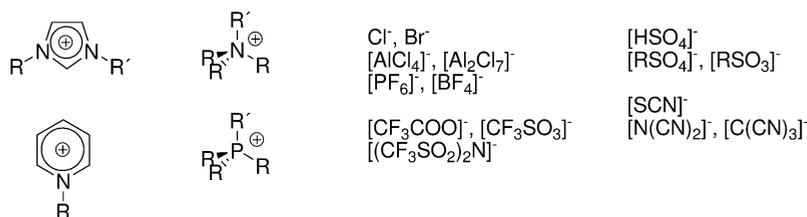


Fig. 41.1 Typical cations and anions used for the formation of ionic liquids.

hexafluorophosphate ionic liquids will be restricted to those applications where water-free conditions can be realized at acceptable costs.

In 1996, Grätzel, Bonhôte and coworkers published the synthesis and properties of ionic liquids with anions containing CF₃⁻ and other fluorinated alkyl groups [12]. These are usually highly hydrophobic melts with high stability (even under acidic conditions) against hydrolysis.

In recent times, the development of new ionic liquids has made great progress. Important developments include a range of new halogen-free ionic liquids (e.g., benzenesulfonates [13], toluenesulfonates, alkylsulfates [14], hydrogensulfate [15, 16], dicyanamides [17], thiocyanates [18], etc.), as well as functionalized (task-specific) [19–23], fluorinated [24], deuterated [25] and chiral ionic liquids [26–30].

Moreover, ionic liquids are readily commercially available today, with a number of commercial suppliers [31] offering ionic liquids, and some imidazolium-based systems being available even in ton-scale quantities. For example, Solvent Innovation offers the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate on a ton-scale; a full set of toxicological data is also available for this specific ionic liquid (for more details, see www.solvent-innovation.com). The quality of commercial ionic liquid samples has clearly improved in recent years. The fact that small amounts of impurities significantly influence the properties of the ionic liquid, and especially its usefulness for catalytic reactions [32], makes the quality of an ionic liquid an important consideration. Among the potential impurities in ionic liquids, water, halide ions and organic starting material are of great importance for transition-metal chemistry, while the color of an ionic liquid is not a critical parameter in most applications. Without any doubt, the improved commercial availability of ionic liquids is a key factor for the strongly increasing interest in this new class of liquid materials.

Due to the large number of available ionic liquids, it becomes increasingly important to understand structure–property relationships in a way that allows a specific ionic liquid to be selected or designed for a given application. In this respect, a conclusive general understanding is yet to be determined. However, during the past three years, the availability of reliable thermodynamic data has increased exponentially, providing a much better base for predictive modeling. Some key properties of well-investigated ionic liquids that may also be relevant for applications in liquid–liquid biphasic hydrogenation reactions are displayed in Table 41.1.

Table 41.1 Comparison of some properties of well-established ionic liquid systems with the 1-ethyl-3-methylimidazolium [EMIM] and 1-butyl-3-methylimidazolium [BMIM] ions.

Ionic liquid	M.p./g.p. [°C]	Viscosity [cP]	Density ^{a)} [g mL ⁻¹]	Tendency for hydrolysis ^{c)}	Reference(s)
[EMIM][AlCl ₄]	7 (mp)	18 ^{a)}	1.240	very high	5, 33
[EMIM][BF ₄]	6 (gp)	34 ^{a)}	1.240	existent	34
[EMIM][CF ₃ SO ₃]	-3 (mp)	45 ^{a)}	1.390	very low	12
[EMIM][(CF ₃ SO ₂) ₂ N]	-9 (mp)	31 ^{a)}	1.518	very low	35
[BMIM][PF ₆]	6 (mp)	207 ^{a)}	1.363	existent	36–38
[BMIM][CF ₃ SO ₃]	16 (mp)	90 ^{b)}	1.290	very low	12
[BMIM][(CF ₃ SO ₂) ₂ N]	-4 (mp)	52 ^{b)}	1.429	very low	12
[BMIM][<i>n</i> -C ₈ H ₁₇ OSO ₄]	35 (mp)	875 ^{b)}	1.060	low	14

g.p. = glass point; m.p. = melting point.

a) At 25 °C.

b) At 20 °C.

c) Very high = immediate hydrolysis, even with traces of water; existent = slow hydrolysis with water accelerated at higher temperature; low = slow hydrolysis only in acidic solutions at elevated temperature; very low = no hydrolysis even at higher temperature in acidic solutions.

n.d. = not determined.

In this chapter we will deal only with a small selection of ionic liquids, which have been successfully used in the context of hydrogenation reactions. These ion combinations, together with the abbreviations used in the following text, are displayed in Figure 41.2.

Furthermore, it is far beyond the scope of this chapter to provide any detailed insight into the materials science aspects of ionic liquids. However, it should be clearly stated that at least some understanding of the ionic liquid material is a prerequisite for its successful use as a catalyst layer in hydrogenation reactions. Therefore, the interested reader is strongly encouraged to explore the more specialized literature [39].

A significant part of the ballooning number of publications on ionic liquid chemistry (more than 1100 during 2004 according to SciFinder) deals with transition-metal catalysis in these unusual liquid materials. This intense publication activity has been documented in a number of comprehensive review articles and book chapters [39–44]. There are many good reasons for applying ionic liquids as alternative solvents in transition metal-catalyzed reactions. Besides their very low vapor pressure and their good thermal stability [45, 46], an important advantage is the possibility of tuning their solubility [47] and acidity/coordination properties [48] by varying the nature of the anions and cations systematically.

Depending on the acidity/coordination properties of the anion and on the reactivity of the cation (the possibility of carbene ligand formation from 1,3-dialkylimidazolium salts is of particular importance here [49–56]), the ionic liquid

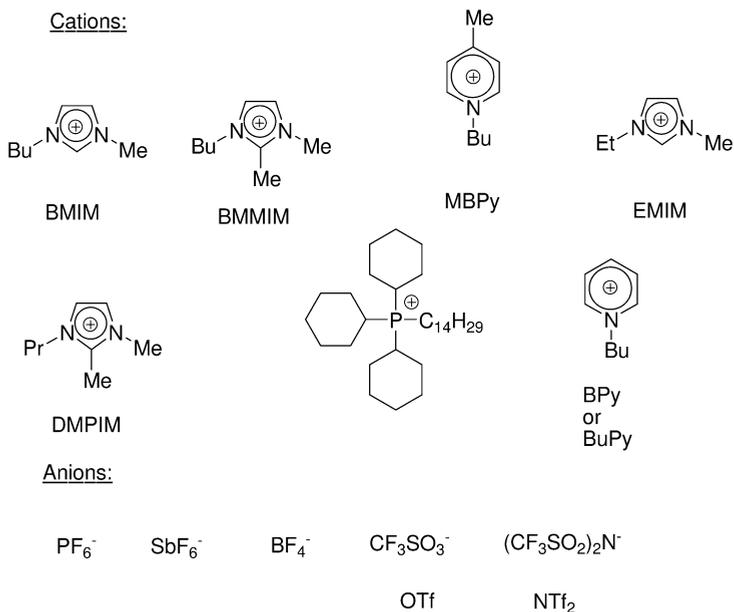


Fig. 41.2 Ionic liquids referred to in the text, and their abbreviations.

can be regarded as an “innocent” solvent, as a ligand precursor, as a co-catalyst or as the catalyst itself.

Ionic liquids with weakly coordinating, inert anions (e.g., $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ under anhydrous conditions) and inert cations (cations that do not coordinate to the catalyst themselves and that do not form species under the reaction conditions that coordinate to the catalyst) can be considered as “innocent” solvents in transition-metal catalysis. In these cases, the role of the ionic liquid is solely to provide a more or less polar, more or less weakly coordinating medium for the transition-metal catalyst that additionally offers special solubility for the feedstock and products.

However, unlike most conventional solvents, many ionic liquids combine high solvating power for polar catalyst complexes (polarity) with weak coordination (nucleophilicity) [57]. It is this combination that enables a biphasic reaction mode with these ionic liquids even for catalyst systems which are deactivated by water or polar organic solvents. Most interestingly, the biphasic reaction mode allows, in principle, the recycling of the ionic catalyst solution and thus a significant enhancement of the efficiency of the catalyst complex applied. This option is especially interesting for biphasic hydrogenation reactions, since the polarity of the reactants decreases during the reaction so that the less-polar products show lower solubility in the ionic catalyst phase than the substrate. Therefore, product isolation can be carried out by simple decantation in most cases and the catalyst containing ionic liquid can be reused immediately.

Table 41.2 Solubility of H₂ in water, organic solvents and ionic liquids, at 0.101 MPa (1 atm) [59].

Solvent	Henry's constant [k _h Mpa ⁻¹] ^{a)}	10 ³ [H ₂] [M]	Density [g mL ⁻¹]	Viscosity [cP]	Reference(s)
Benzene ^{b)}	4.47×10 ² (4.39×10 ²)	2.54 (2.57)	0.878	0.60 ^{c)}	61, 62
Cyclohexane ^{b)}	2.57×10 ² (2.55×10 ²)	3.63 (3.66)	0.777	1.62 ^{b)}	61, 62
[BMIM][BF ₄] ^{b)}	5.8×10 ² (1.63×10 ²)	0.86 ^{d)} (3.0)	1.12	219 ^{c)}	63
[BMIM][PF ₆] ^{b, c)}	6.6×10 ² (5.38×10 ²)	0.73 ^{d)} (0.88)	1.363	450 ^{c)}	63
[BMIM][Tf ₂ N] ^{c)}	4.5×10 ²	0.77 ^{d)}	1.433	69 ^{c)}	63
[BMMIM][Tf ₂ N] ^{c, e)}	3.8×10 ²	0.86 ^{d)}	1.421	97.1 ^{c)}	64
[BuPy][Tf ₂ N] ^{c, f)}	3.9×10 ²	0.89 ^{d)}	1.449	57 ^{c)}	35
[BMPy][Tf ₂ N] ^{c, g)}	3.7×10 ²	0.90 ^{d)}	1.387	85 ^{c)}	65
[BMIM][SbF ₆] ^{c)}	4.9×10 ²	0.93 ^{d)}	1.699	95	–
[BMIM][CF ₃ COO] ^{c)}	4.9×10 ²	0.98 ^{d)}	1.198	73 ^{b)}	12
[HMIM][BF ₄] ^{c, h)}	5.7×10 ²	0.79 ^{d)}	1.14	314.0 ^{b)}	31, 66
[OMIM][BF ₄] ^{c)}	6.4×10 ²	0.62 ^{d)}	1.106	135.0 ^{b)}	66
[BMIM][CF ₃ SO ₃] ^{c)}	4.6×10 ²	0.97 ^{d)}	1.290	90 ^{b)}	12
[P(C ₆ H ₁₃) ₃ (C ₁₄ H ₂₉)] [PF ₃ (C ₂ F ₅) ₃] ^{c)}	0.7×10 ²	1.84 ^{d)}	1.196	498 ^{b)}	31

a) $k_H = P_{H_2}/X_{H_2}$, 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 solubility changes linearly with the partial pressure.

e) [BMMIM]⁺ = 1,2-dimethyl-3-butylimidazolium.

f) [BuPy]⁺ = *N*-butylpyridinium.

g) [BMPy]⁺ = *N*-butyl-*N*-methylpyrrolidinium.

h) [HMIM]⁺ = 1-hexyl-3-methylimidazolium.

In this chapter we will focus uniquely on the application of ionic liquids in transition metal-catalyzed hydrogenation reactions. In this context, the hydrogen solubility in ionic liquids is an important issue. However, very few publications deal with this matter so far [58–60]. For the ionic liquid [BMIM][PF₆], the solubility of hydrogen has been found to be very low [58]. With the gravimetric microbalance method used by Brennecke et al. the solubility was even undetectable due to uncertainties in density measurement of the ionic liquid. This led, in the case of low-solubility gases, to large uncertainty (up to 75%) in determination of Henry's constant. In fact, these authors reported that the solubility of hydrogen in [BMIM][PF₆] is lower than in all conventional organic solvents.

In another publication, Dyson et al. [59] reported on hydrogen solubilities in several ionic liquids obtained by the use of ¹H-NMR technique. The results are summarized in Table 41.2.

Since the solubility of hydrogen in ionic liquids is very low, hydrogenation in ionic liquids takes place at low hydrogen concentrations. This is a disadvantage as higher pressures may be required in some cases. However, the diffusivity of hydrogen into ionic liquids can be expected to be high. According to Scovazzo and coworkers, the diffusivities of gases in ionic liquids depend strongly on the solute size as well as on the viscosity of the ionic liquid and the temperature [67]. The

high diffusivity of hydrogen results in high hydrogen transfer rates into the catalyst layer so that – during a hydrogenation reaction – the consumed hydrogen can be replenished rapidly. This fact explains the many successful hydrogenation reactions that have been reported in ionic liquids (see below), despite the low hydrogen solubility in these media. Indeed, hydrogenation reactions in ionic liquids proceed in many examples in comparable rates to those in conventional organic solvents, even though on occasion longer reaction times have been reported.

41.2

Homogeneous Catalyzed Hydrogenation in Biphasic Liquid–Liquid Systems

41.2.1

Hydrogenation of Olefins

The first investigations of biphasic hydrogenation reactions with ionic catalyst phases were reported by Chauvin et al. [68]. In general, the correct immobilization of a transition-metal catalyst in an ionic liquid requires either the use of an ionic catalyst complex or a polar or ionic modified ligand. Chauvin et al. studied the ionic Osborne complex $[\text{Rh}(\text{nbnd})(\text{PPh}_3)_2][\text{PF}_6]$ (nbnd = norbornadiene) for the hydrogenation of pent-1-ene in several ionic liquids (Table 41.3). The authors reported the hydrogenation in ionic liquid to be almost five-fold faster in $[\text{BMIM}][\text{SbF}_6]$ than the conventional homogeneous reaction in acetone. However, the reaction was found to occur much more slowly using a hexafluorophosphate ionic liquid. This effect was attributed to the better solubility of pen-

Table 41.3 Rh-catalyzed hydrogenation of pent-1-ene [68].

No.	Solvent	Conversion [%]			
		Pent-1-ene	Yield ^{a)}		TOF [min ⁻¹] ^{b)}
			Pentane	Pent-2-ene	
1 ^{c)}	Acetone	99	38	61	0.55
2	$[\text{BMIM}][\text{SbF}_6]$	96	83	13	2.54
3	$[\text{BMIM}][\text{PF}_6]$	97	56	41	1.72
4	$[\text{BMIM}][\text{BF}_4]$	10	5	5	0.15
5 ^{d)}	$[\text{BMIM}][\text{Cl}]:\text{CuCl}$	18	0	18 (98% <i>cis</i>)	0
6 ^{e)}	$[\text{BMIM}][\text{PF}_6]$	99	25	74	0.73

a) Catalyst 0.05 mmol; pent-1-ene: 8.4 mmol; solvent: 4 mL, T = 30 °C, p(H₂) = 0.1 MPa; t = 2 h.

b) TOF = mol (pentane) per mol (rhodium) and time [min].

c) 10 mL acetone, 9.2 mmol pent-1-ene.

d) The molten salt was synthesized from 1.5 equiv. CuCl and 1 equiv. $[\text{BMIM}][\text{Cl}]$.

e) In the presence of 2 mL acetone.

tene in the hexafluoroantimonate ionic liquid. The very poor yield in [BMIM][BF₄], however, was due to a high level of residual Cl⁻ ions in the used ionic liquid, leading to catalyst deactivation. At that time the preparation of this tetrafluoroborate ionic liquid in chloride-free quality was clearly a problem.

To date, several reports have been published dealing with the non-stereoselective hydrogenation of olefins in a liquid-liquid biphasic system containing ionic liquids [69–72].

The immobilization of Pd(acac)₂ as hydrogenation catalyst in the ionic liquids [BMIM][BF₄] and [BMIM][PF₆] was reported by Dupont et al. in 2000 [70]. These authors compared the biphasic hydrogenation of butadiene with the homogeneous system with all reactants being dissolved in CH₂Cl₂, with the reaction in neat butadiene and with a heterogeneous system using Pd on carbon as catalyst. The report showed that, for 1,3-butadiene hydrogenation, the selectivities achieved with Pd(acac)₂ dissolved in ionic liquids were similar to those observed under homogeneous conditions and were higher than under heterogeneous conditions (using Pd on carbon as the catalyst) or in neat 1,3-butadiene (Table 41.4).

The authors extended their investigations to a series of functionalized dienes such as sorbic acid, methyl sorbate, 1-nitro-1,3-butadiene, and cyclic dienes.

The group of Dupont also studied the catalytic activity of RuCl₂(PPh₃)₃ and K₃Co(CN)₅ in [BMIM][BF₄] for the hydrogenation of a number of unfunctionalized, unsaturated hydrocarbon compounds [69]. It was found that, in case of the ruthenium complex being the catalyst, the interaction of RuCl₂(PPh₃)₃ with the ionic liquid led to a stable, ionic purple solution, and no leaching of the Ru-complex could be detected by extraction with hydrocarbon solvents. Compared to the classical water-soluble catalysts (based on transition-metal complexes modified with water-soluble phosphane ligands [73, 74]), relatively high turnover frequencies (TOFs) of up to 537 h⁻¹ were achieved. It is also noteworthy that the hydrogenation in ionic liquid required less drastic conditions (temperature

Table 41.4 Comparison of the hydrogenation of 1,3-butadiene to butenes in different solvents [70].

Entry	Solvent	Time [h]	Conversion [%]	Selectivity [%]				TON
								
1	[BMIM][BF ₄]	12	98.2	55.5	5.1	35.2	4.2	982
2	[BMIM][PF ₆]	13	88.5	46.2	8.5	38.2	7.1	885
3	CH ₂ Cl ₂	13	93.0	44.2	6.3	47.3	2.2	930
4	a) —	13	82.4	46.8	4.7	35.4	13.1	824
5	b) —	1	61.9	24.2	7.2	30.8	37.8	619

Conditions: 50 °C, p(H₂) = 20 bar; 0.08 mmol Pd(acac)₂; diene/Pd = 1000.

TON = Turnover number = mol hydrogenated substrate per mol catalyst precursor.

a) In liquid 1,3-butadiene.

b) In liquid 1,3-butadiene using Pd/C as catalyst.

Table 41.5 Hydrogenation of several olefins with $\text{RuCl}_2(\text{PPh}_3)_3$ in $[\text{BMIM}][\text{BF}_4]$ [69].

Entry	Olefin	Conversion ^{a)} [%]	[Ru] [mmol]	Time [h]	Selectivity [%]			TOF ^{b)} [h ⁻¹]
					But-1-ene	But-2-enes	n-Butane	
1	Hex-1-ene	100	0.041	6				328
2	Hex-1-ene	84 ^{c)}	0.041	3				537
3	Cyclohexene	30	0.041	4.5				170
4	Cyclohexene	100 ^{d)}	0.065	20				73
5	Butadiene	18	0.041	1	22	33	45	543
6	Butadiene	68	0.041	4.5	29	42	29	493
7	Butadiene	100 ^{e)}	0.041	8	20	67	13	377

Conditions: T = 30 °C; p(H₂) = 25 bar.

- a) Conversion of butadiene was calculated for the hydrogenation of only one double bond.
 b) Turnover frequency = mol (product) × mol (Ru)⁻¹ h⁻¹.
 c) Only n-hexane and hex-1-ene were detected.
 d) At 60 °C.
 e) 40 atm H₂.

and hydrogen pressure) compared to the hydrogenation in the aqueous medium using the water-soluble catalyst. Selected results of the Ru-catalyzed hydrogenation in $[\text{BMIM}][\text{BF}_4]$ are shown in Table 41.5.

Hydrogenation of butadiene with $\text{K}_3\text{Co}(\text{CN})_5$, which is known to hydrogenate selectively conjugated dienes [75], was possible with 100% conversion and selectivity and a TOF up to 72 h⁻¹ in the ionic liquid $[\text{BMIM}][\text{BF}_4]$, but the catalyst was deactivated after the first run and the inactive complex $(\text{BMIM})_3\text{Co}(\text{CN})_5$ was formed [69].

Many low-oxidation state transition-metal (carbonyl) clusters are salts and can be stabilized in ionic liquids due to their ionic character. Interestingly, Dyson et al. revealed that the activity of certain clusters in the hydrogenation of alkene substrates is up to 3.6-fold faster when these clusters were immobilized in ionic liquids, compared to their activity observed in organic solvents [72]. These authors evaluated the clusters $[\text{HFe}(\text{CO})_{11}]^-$, $[\text{HWOs}_3(\text{CO})_{14}]^-$, $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ as catalysts/precatalysts in the hydrogenation of styrene to ethylbenzene in $[\text{BMIM}][\text{BF}_4]$, octane and methanol, respectively. Using $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ as catalyst precursor in $[\text{BMIM}][\text{BF}_4]$, the same research group also obtained good results for the partial reduction of cyclohexadienes to cyclohexene. However, by poisoning the catalytic phase with mercury and by means of high-pressure ¹H-NMR experiments, they showed that under the reaction conditions Ru-colloids/Ru-nanoparticles were formed and the latter acted as the catalyst in these reactions. These studies represent therefore examples of heterogeneous catalysis with nanoparticles in ionic liquids. In this context it should be mentioned that several other reports have been made about the formation, stabilization and immobilization of nanoparticles in ionic liquids. Several of these suspensions have been successfully applied in different hydrogenation reactions [40, 71, 76–85], but as these reactions are clearly

Table 41.6 Hydrogenation of styrene to ethylbenzene using $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ as a catalyst precursor in various ionic liquids [72].

Ionic liquid	TOF [mol mol ⁻¹ h ⁻¹]
[BMIM][BF ₄]	587
[BMIM][PF ₆]	522
[BMIM][(CF ₃ SO ₂) ₂ N]	587
[BMMIM][PF ₆]	392
[BMMIM][BF ₄]	413
[BMMIM][(CF ₃ SO ₂) ₂ N]	457
[OMPy][BF ₄]	718

Conditions: $p(\text{H}_2) = 50.7$ bar, 100 °C, 4 h; cluster concentration 5×10^{-4} M, ionic liquid (1 mL), styrene (1 mL), total reactor volume (30 mL).
TOF calculated as average value over 4 h.

examples of heterogeneous hydrogenation in ionic liquids they will not be discussed here in more detail. In contrast to the ruthenium-containing cluster, a homogeneous hydride complex was characterized under reaction conditions when the osmium-containing clusters were dissolved in ionic liquids. A comparison of the TOFs of the $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ -catalyzed hydrogenation of styrene to ethylbenzene in various ionic liquids is presented in Table 41.6.

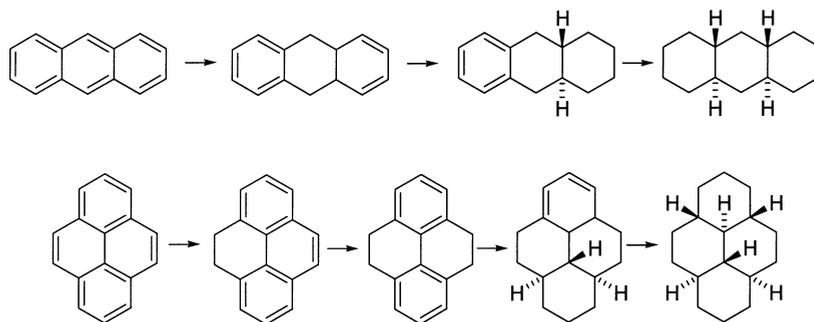
The TOFs in all ionic liquids are quite similar, although the values are somewhat lower in [BMMIM][PF₆], [BMMIM][BF₄] and [BMMIM][(CF₃SO₂)₂N] than in the [BMIM]-containing ionic liquids. The highest activity was found when [OMPy][BF₄] was used as the ionic liquid. An explanation for this could be the fact that [BMMIM]-containing ionic liquids possess the highest viscosities and therefore have the lowest mass transfer rates for hydrogen. The experiment with [OMPy][BF₄] (OMPy = 1-octyl-3-methylpyridinium cation) is special in that only for this ionic liquid can the reaction mixture form a single phase, thus preventing any liquid–liquid mass transport resistance. On the other hand, catalyst recycling by a simple decantation process is not possible in that latter case.

41.2.2

Hydrogenation of Arenes

The hydrogenation of arenes is industrially important, but so far has been dominated by the use of heterogeneous catalysts. In principle, ionic liquids offer the chance to use a liquid–liquid biphasic system where the homogeneous catalyst is immobilized and the ionic catalyst solution is reusable.

An unusual arene hydrogenation in ionic liquids was published by Seddon et al. in 1999 [86]. These authors reported a new means of hydrogenating aromatic compounds by dissolving electropositive metals in ionic liquids with HCl as the



Scheme 41.1 Reduction of anthracene and pyrene using electro-positive metals in ionic liquids with HCl as the proton source.

proton source. As the metals aluminum, zinc and lithium were used as bulk (and were converted to metal chlorides by reaction with HCl during the hydrogenation reaction), it may be a point of discussion whether the reaction can really be considered as being homogeneous. However, the authors found that the best system for hydrogenation was [EMIM][HCl₂], with additional anhydrous HCl gas as a proton source in the presence of aluminum, where the aluminum-(III)-chloride as byproduct of the reaction precipitated and the composition of the ionic liquid remained largely unaffected. In this way the complete reduction of anthracene and pyrene was carried out (Scheme 41.1).

The partial reduction of 9,10-dimethylantracene gave rise to two isomers in a 6:1 ratio. The major product was the *cis*-isomer, and the minor product the *trans*-isomer. The system is not suitable for the reduction of simple aromatics such as benzene or naphthalene. The yields there were quite low with 2% and 15%, respectively.

Dyson et al. [87, 88] applied ruthenium clusters as a catalyst for the hydrogenation of benzene, toluene, cymene, ethylbenzene, and chlorobenzene. A direct comparison of the two biphasic systems, water/organic solvent and ionic liquid/organic solvent, showed that the TOFs obtained in the ionic liquid and the aqueous media were similar [88]. The results of the hydrogenation in the two biphasic systems are listed in Table 41.7. The authors proposed that the catalytically active species was $[H_6Ru_4(\eta_6-C_6H_6)_4]^{2+}$ in the ionic liquid-containing system, as was shown for the water-containing system [89]. Again, the advantage of the ionic liquid-containing biphasic system was the easy separation of products and the possibility of reusing the catalytic active phase.

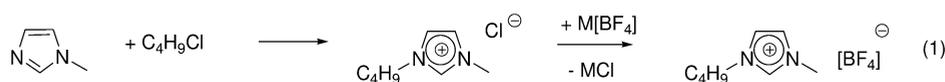
Dyson et al. also showed that it is important to account for the chloride concentration in the ionic liquid [87]. These authors proved that chloride impurities, resulting from the synthesis of the ionic liquid, have a strong influence on hydrogenation activity. This was demonstrated by a comparison of hydrogenation activity in [BMIM][BF₄] which was made via the classical ion-exchange reaction (metathesis route, Scheme 41.2 (1)), with a chloride concentration of 0.2 mol kg⁻¹, and the same ionic liquid which was made by direct conversion of

Table 41.7 Comparative studies of the biphasic hydrogenation reactions of arenes in [BMIM][BF₄] and water with [H₄Ru₄(η⁶-C₆H₆)₄][BF₄]₂ as the catalyst precursor [88].

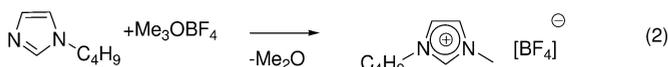
Substrate	Reaction system	Reaction conditions	Conversion [%]	Catalytic turnover ^{a)} [mol mol ⁻¹ h ⁻¹]
Benzene	Ionic liquid	60 atm H ₂ , 90 °C, 2.5 h	91	364
	Water	60 atm H ₂ , 90 °C, 2.5 h	88	352
Toluene	Ionic liquid	60 atm H ₂ , 90 °C, 3 h	72	240
	Water	60 atm H ₂ , 90 °C, 3 h	78	261
Cumene	Ionic liquid	60 atm H ₂ , 90 °C, 2.5 h	34	136
	Water	60 atm H ₂ , 90 °C, 2.5 h	31	124

- a) Catalytic turnover calculated on the assumption that the tetraruthenium catalyst does not break down into monoruthenium fragments, which is entirely consistent with the data.

Metathesis route:



Direct alkylation route:



Scheme 41.2 Metathesis route and direct alkylation route for the synthesis of [BMIM][BF₄].

butylimidazole and trimethyloxonium tetrafluoroborate (direct methylation route, Scheme 41.2 (2)), which was essentially chloride-free. The data relating to this study are presented in Table 41.8.

Based on the results of these studies it is quite evident that the reaction with ionic liquid as immobilization phase requires a chloride-free catalyst phase in order to achieve any advantage over the reaction with water as the immobilizing phase.

Very interesting results were obtained by using [Ru(η⁶-*p*-cymene)(η²-triphos)Cl][PF₆] in a biphasic system with [BMIM][BF₄] as catalyst phase [90]. The hydrogenation of benzene, toluene and ethylbenzene in this ionic liquid proved to proceed with higher yields and accordingly with higher TOFs than in the monophasic system with CH₂Cl₂ as solvent. The TOF (yield) of benzene hydrogenation was found to increase from 242 (52%) in CH₂Cl₂ to 476 mol mol⁻¹ h⁻¹ (82%) in the ionic liquid, for toluene from 74 (19%) to 205 mol mol⁻¹ h⁻¹ (42%), and for ethylbenzene from 57 (17%) to 127 mol mol⁻¹ h⁻¹ (30%), respec-

Table 41.8 The hydrogenation of various arene substrates using Ru(η^6 -C₁₀H₁₄)(pta)Cl₂ immobilized in water and in [BMIM][BF₄] of different Cl⁻ contents [87].

Substrate	Reaction conditions	TOF ^{a)} [mol mol ⁻¹ h ⁻¹]
Toluene	Water	130
Toluene	[BMIM][BF ₄] ^{b)}	54
Toluene	[BMIM][BF ₄] ^{c)}	136
Ethylbenzene	Water	122
Ethylbenzene	[BMIM][BF ₄] ^{b)}	53
Ethylbenzene	[BMIM][BF ₄] ^{c)}	145
Chlorobenzene	Water	11
Chlorobenzene	[BMIM][BF ₄] ^{b)}	6
Chlorobenzene	[BMIM][BF ₄] ^{c)}	18

Reaction conditions: catalyst (30 mg) in solvent (10 mL), substrate (1 mL), H₂ (60 atm) 90 °C, 1 h. Products formed were completely hydrogenated cyclohexane or alkane analogues of substrate.

a) Turnovers in mol substrate converted mol⁻¹ catalyst h⁻¹.

b) Made via metathesis route, [Cl]⁻ 0.2 mol kg⁻¹.

c) Made via methylation of alkylimidazole, chloride content zero.

tively. With allylbenzene as the substrate the authors observed selective hydrogenation of the benzyl group so that the unsaturated alkyl chain remained intact. The hydrogenation yielded allylcyclohexane with a quite high TOF of 329 mol mol⁻¹ h⁻¹ (84% yield), whereas the system was inactive toward arenes with *R*-alkene substituents such as styrene and 1,3-divinylbenzene.

41.2.3

Hydrogenation of Polymers

The hydrogenation in a liquid–liquid system with ionic liquids as the catalyst phase was also applied to the hydrogenation of polymers. The first studies were presented by the group of Rosso et al. [91], who investigated the rhodium-catalyzed hydrogenation of polybutadiene (PBD), nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) in a [BMIM][BF₄]/toluene and a [BMIM][BF₄]/toluene/water system. The activity of the catalyst followed the trend PBD > NBR > SBR, which is the same order as the solubility of the polymers in the ionic liquid. The values in percentage total hydrogenation after 4 h reaction time were 94% for PBD and 43% for NBR, and after a reaction time of 3 h was 19% for SBR.

For the hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block co-polymer with Ru–TPPTS complex as catalyst, Jang et al. [92] applied a polyether-modified ammonium salt ionic liquid/organic biphasic system (Fig. 41.3).

Hydrogenation conditions were optimized by addition of triphenylphosphine as promoter ligand, and the hydrogenation degree of SBS was up to 89%. Hy-

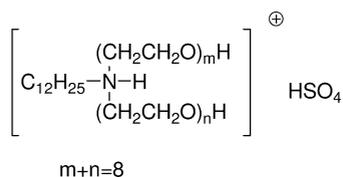


Fig. 41.3 The structure of the polyether-modified ammonium salt ionic liquid.

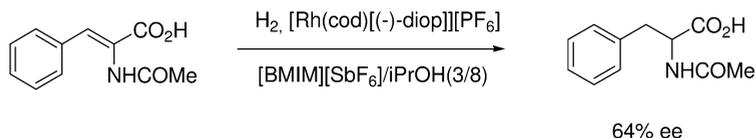


Fig. 41.4 Rhodium-catalyzed enantiomeric hydrogenation of α -acetamidocinnamic acid in the system [BMIM][SbF₆]/isopropanol system.

drogenation of the benzene ring and gel formation has not been observed. The active catalyst obviously remained in the ionic liquid and was reused three times without significant loss in catalytic activity.

41.2.4

Stereoselective Hydrogenation

Details of the first stereoselective hydrogenation in ionic liquids were published by the group of Chauvin [68], who reported the enantioselective hydrogenation of the enamide α -acetamidocinnamic acid in the biphasic system [BMIM][SbF₆]/*i*PrOH (ratio 3:8) catalyzed by [Rh(cod)]{(-)-diop}[PF₆]. The reaction afforded (*S*)-*N*-acetylphenylalanine in 64% enantiomeric excess (ee) (Fig. 41.4). The product was easily and quantitatively separated and the ionic liquid could be recovered, while the loss of rhodium was less than 0.02%.

Dupont et al. [60] studied the same reaction, but used [BMIM][PF₆] and [BMIM][BF₄] as ionic liquids. A special focus of their investigations was on the influence of H₂-pressure on conversion. The Henry coefficient solubility constant was determined by pressure drop experiment in a reactor, which is a known procedure to measure gas solubilities [93]. The values reported by these authors were $K=3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$ for [BMIM][BF₄]/H₂ and $8.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$ for [BMIM][PF₆]/H₂ at room temperature, which differ significantly from those determined by the ¹H-NMR technique (see Table 41.2) [59]. However, their values indicated that molecular hydrogen is almost four times more soluble in [BMIM][BF₄] than in [BMIM][PF₆] under the same pressure. According to the authors, this is reflected by the values of conversion (ee), which were 73% (93% ee) for [BMIM][BF₄] and 26% (81% ee) for [BMIM][PF₆] at 50 bar H₂ pressure (Table 41.9, entries 2 and 4).

The variation of hydrogen pressure in the experiments using [BMIM][PF₆] as the ionic liquid (Table 41.9, entries 1–3) also showed that conversion and enan-

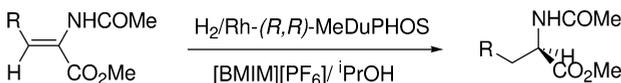
Table 41.9 The enantiomeric hydrogenation of (*Z*)- α -acetamido cinnamic acid: the effect of hydrogen concentration in the liquid phase on the conversion and the enantioselectivity.

Entry	Catalyst phase	$p(\text{H}_2)$ [atm]	Solubility H_2 [mol L ⁻¹]	Conversion [%]	ee ^{b)} [%]
1	[BMIM][PF ₆]	5	4.4×10^{-3}	7	66
2	[BMIM][PF ₆]	50	4.4×10^{-2}	26	81
3	[BMIM][PF ₆]	100	8.9×10^{-1}	41	90
4	[BMIM][BF ₄]	50	1.5×10^{-1}	73	93
5	ⁱ PrOH	50	129.3 ^{c)}	99	94

Reaction conditions: room temperature, 24 h, 950 rpm,
3 mL ionic liquid and 9 mL isopropanol, substrate/[Rh]=100.

b) Determined by chiral GC.

c) Calculated from data reported by Frölich [94].



1a. R = H

1b. R = Phenyl

Fig. 41.5 Enantiomeric hydrogenation of enamides catalyzed by Rh–MeDuPHOS complex heterogenized in [BMIM][PF₆].

tiostereoselectivity increased with the higher hydrogen availability (higher pressure, higher solubility) within the ionic liquid.

Another type of chiral rhodium complex [Rh–MeDuPHOS] was also immobilized in [BMIM][PF₆] and used in the enantiomeric hydrogenation of related enamides [95] (Fig. 41.5). Geresh et al. focused their research on the stabilization of the air-sensitive catalyst in the air-stable ionic liquid, so that the complex was protected from attack by atmospheric oxygen and recycling was possible.

The results are comparable to those of homogeneous reaction conditions (Table 41.10), and recycling of the catalyst was successful with constant ee-values over five cycles, even though conversion decreased. Amazingly, the catalyst was still active, despite being stored under atmospheric conditions for 24 h (Table 41.10, entry 7).

A special example for a regioselective hydrogenation in ionic liquids was reported by our group and by Drießen-Hölscher [96, 97]. Based on investigations in the biphasic system water/*n*-heptane, the ruthenium-catalyzed hydrogenation of sorbic acid to *cis*-3-hexenoic acid according to Scheme 41.3 in the system [BMIM][PF₆]/MTBE was studied [98].

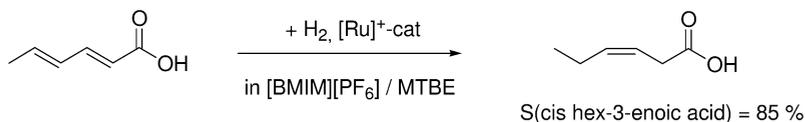
In comparison to polar organic solvents (e.g., glycol), a more than threefold increase in activity with comparable selectivity to *cis*-3-hexenoic acid was ob-

Table 41.10 Enantiomeric hydrogenation of enamides with Rh-MeDuPHOS in [BMIM][PF₆]-iPrOH [95].

Entry		1a Conversion		1b Conversion	
		[%]	ee [%]	[%]	ee [%]
1	Homogeneous ^{a)}	100	97 (<i>R</i>)	100	99 (<i>R</i>)
2	Homogeneous ^{b)}	5	57 (<i>R</i>)	–	–
3	Heterogeneous; first cycle	100	93 (<i>R</i>)	83	96 (<i>R</i>)
4	Heterogeneous; second cycle	100	80 (<i>R</i>)	64	96 (<i>R</i>)
5	Heterogeneous; third cycle			62	95 (<i>R</i>)
6	Heterogeneous; fourth cycle			60	94 (<i>R</i>)
7	Heterogeneous; fifth cycle ^{c)}			58	94 (<i>R</i>)

Reaction conditions for homogeneous catalyst: 25 °C, 2 atm H₂, 7 g iPrOH; reaction time=5 min. In the heterogeneous system, 5 g ionic liquid was added; reaction time=20 min.

- a) Preparation of the catalyst and of feeding into the reactor were performed under nitrogen.
 b) Catalyst prepared in an inert atmosphere and exposed to air for a few minutes during feeding into the reactor. For cycles 3 to 7, all manipulations were performed in air.
 c) Left to stand in air for 24 h.

**Scheme 41.3** Regioselective hydrogenation of sorbic acid in the biphasic system [BMIM][PF₆]/MTBE.

served in the ionic liquid. This is explained by a part deactivation (through complexation) of the catalytic active center in those polar organic solvents that are able to dissolve the cationic Ru-catalyst. In contrast, the ionic liquid [BMIM][PF₆] is known to combine high solvation power for ionic metal complexes with relatively weak coordination strength. In this way, the catalyst can be dissolved in a “more innocent” environment than is the case if polar organic solvents are used. After the biphasic hydrogenation of sorbic acid, the ionic catalyst solution could be recovered by phase separation and reused four times with no significant loss of selectivity, but with a decreasing conversion from 74.0 and 77.4%, to 59.6 and 35.8% in the third and fourth runs, where the autoclave containing the catalyst phase was left to stand overnight between the second and the third runs.

A comparison of hydrogenation activity in a biphasic ionic liquid-containing system and a homogeneous media was carried out by Dupont et al. [99]. These authors used a [RuCl₂-(*S*)-BINAP]₂ NEt₃ catalyst precursor dissolved in [BMIM][BF₄]. This

system hydrogenates 2-arylacrylic acids (Fig. 41.6) (aryl=Ph or 6-MeO-naphthyl) with enantioselectivities similar to or higher than those obtained in homogeneous media. After reaction, the product was completely dissolved in the isopropanol-containing phase and separated by simple decantation. The ionic catalyst solution was recycled three times, without significant changes in activity and selectivity (Table 41.11).

In enantioselective hydrogenation the substrates can be divided in two classes (Fig. 41.7):

- Class I are components which require low H₂-pressure to obtain good enantioselectivities (e.g., tiglic acid).
- Class II components require high H₂-pressure (e.g., atropic acid) [100, 101].

Under this aspect, the group of Jessop [102] investigated the influence of the ionic liquid used on enantioselectivity in the hydrogenation of atropic acid as an example

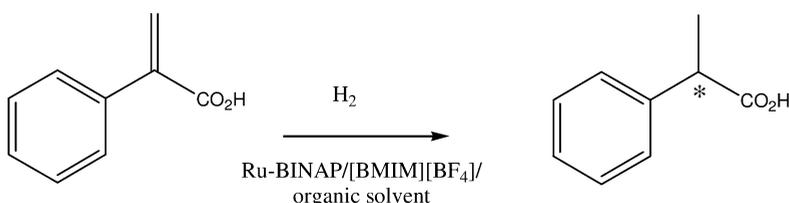


Fig. 41.6 Hydrogenation of 2-phenylacrylic acid in the system [BMIM][BF₄]/organic.

Table 41.11 Enantiomeric hydrogenation of 2-phenylacrylic acid giving 2-phenylpropionic acid. Reaction conditions: [Ru]=0.034 mmol; ROH=30 mL; [BMIM][BF₄]=3 mL; time=20 h [99].

Entry	Catalyst	Co-solvents	SCR	P [atm]	Conversion [%]	ee [%] (conf.)
1	<i>in situ</i> Ru-(S)-BINAP	MeOH	40	35	100	62 (S)
2	[Ru-Cl ₂ -(S)-BINAP] ₂ ·NEt ₃	MeOH	80	25	100	83 (S)
3	[Ru-Cl ₂ -(S)-BINAP] ₂ ·NEt ₄	<i>i</i> -PrOH	80	25	100	64 (S)
4	<i>in situ</i> Ru-(R)-BINAP	MeOH/[BMIM][BF ₄]	40	25	100	86 (R)
5	<i>in situ</i> Ru-(R)-BINAP	<i>i</i> -PrOH/[BMIM][BF ₄]	80	35	99	69 (R)
6	Recycle of entry 5	<i>i</i> -PrOH/[BMIM][BF ₄]	80	22	99	72 (R)
7	Recycle of entry 6	<i>i</i> -PrOH/[BMIM][BF ₄]	80	25	99	77 (R)
8	Recycle of entry 7	<i>i</i> -PrOH/[BMIM][BF ₄]	80	25	99	70 (R)
9	[Ru-Cl ₂ -(S)-BINAP] ₂ ·NEt ₃	<i>i</i> -PrOH/[BMIM][BF ₄]	20	50	100	78 (S)
10	Recycle of entry 8	<i>i</i> -PrOH/[BMIM][BF ₄]	20	75	100	84 (S)
11	Recycle of entry 9	<i>i</i> -PrOH/[BMIM][BF ₄]	20	25	90	79 (S)
12	Recycle of entry 10	<i>i</i> -PrOH/[BMIM][BF ₄]	20	100	95	67 (S)
13	[Ru-Cl ₂ -(S)-BINAP] ₂ ·NEt ₃	<i>i</i> -PrOH/[BMIM][BF ₄]	400	25	100	72 (S)

SCR=substrate:catalyst ratio.

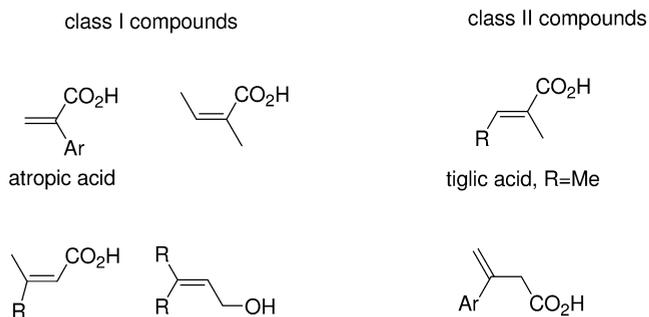


Fig. 41.7 Classification of substrates for enantioselective hydrogenation.

for Class I compounds, and of tiglic acid as an example for Class II compounds. These authors found a strong dependency of ee on the used solvent for the hydrogenation of atropic acid. The ee-values varied in the range of 72 to 95%, and increased in the following order: MeOH < [EMIM][CF₃SO₃] < [BMIM][BF₄] = [MBPy][BF₄] < [BMIM][PF₆] = [DMPIM] [(CF₃SO₂)₂N] < [EMIM][(CF₃SO₂)₂N].

For Class II components, the enantioselectivity for asymmetric hydrogenation in ionic liquids (without co-solvent) was low. The best enantioselectivities were obtained with methanol as co-solvent as the viscosity was much lower (i.e., the mass transfer was higher), and hydrogen solubility was presumably higher compared to the pure ionic liquids. For the reactions in neat ionic liquids, the selectivity was again dependent upon the choice of ionic liquid, increasing in the order: [BMIM][BF₄] < [EMIM][O₃SCF₃] < [BMIM][PF₆] = [EMIM][N(OTf)₂] < [DMPIM][N(OTf)₂].

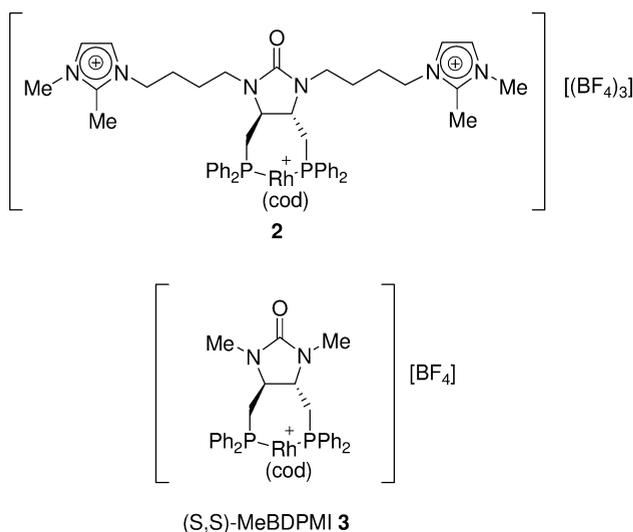


Fig. 41.8 Rh-complex with a bisphosphine-containing cation as ligand.

Table 41.12 Rh-catalyzed enantiomeric hydrogenation of *N*-acetylphenylethenamine using Rh-complex **2** and Me-BDPMI **3** in a [BMIM][SbF₆]/*i*PrOH two-phase solvent systems [103].^{a)}



Entry	Catalyst	Run	Time [h]	Conversion [%] ^{b)}	ee [%] ^{c)}
1	2	1	1	100	97.0
2		2	1	100	96.6
3		3	1	100	96.2
4		4	1	82	95.4
5		4	8	100	95.4
6	3	1	1	100	95.8
7		2	1	100	95.1
8		3	1	78	94.2
9		4	1	51	91.4
10		4	12	85	88.0
11 ^{d)}	3	1	1	100	95.6

- a) Reaction conditions: Catalyst:substrate ratio=0.01:1; [BMIM][SbF₆]/*i*PrOH=1/2 (v/v); reaction temperature: 20 °C; p(H₂)=1 atm.
 b) Determined by NMR and GC.
 c) Determined by chiral GC using CP-Chirasil Dex CB column.
 d) Reaction carried out in the presence of 0.5 mol% **3**.

These results demonstrate that the effectiveness of hydrogenation in ionic liquids is not only a parameter of H₂ availability. Indeed, many solvent parameters – including polarity, coordinating ability and hydrophobicity – should be taken into account, though these have not yet been studied.

Lee et al. [103] synthesized a chiral Rh-complex with a bisphosphine-containing cation as ligand (Fig. 41.8, **2**) to improve the immobilization of the transition-metal complex within the ionic liquid.

Immobilization of this complex in the biphasic system [BMIM][SbF₆]/*i*PrOH showed better results compared to the non-modified complex Me-BDPMI (Fig. 41.8, **3**). The ionic catalyst solution was reused three times without loss of activity (Table 41.12). At the fourth run the conversion decreased, though high conversions could be still realized by increasing the reaction time.

A broad screening of ligands and ionic liquids was carried out by Feng et al. [104]. For rhodium-catalyzed hydrogenation of enamides the best catalysts were found to be the rhodium–ferrocenyl–diphosphine complexes with taniaphos, josiphos, walphos and mandyphos as ligands (Fig. 41.9).

Screening of the reaction media showed that, with the use of an ionic liquid/water mixture (a so-called “wet ionic liquid”), recycling of the catalyst could be improved compared to the reaction in ionic liquid without co-solvent. The com-

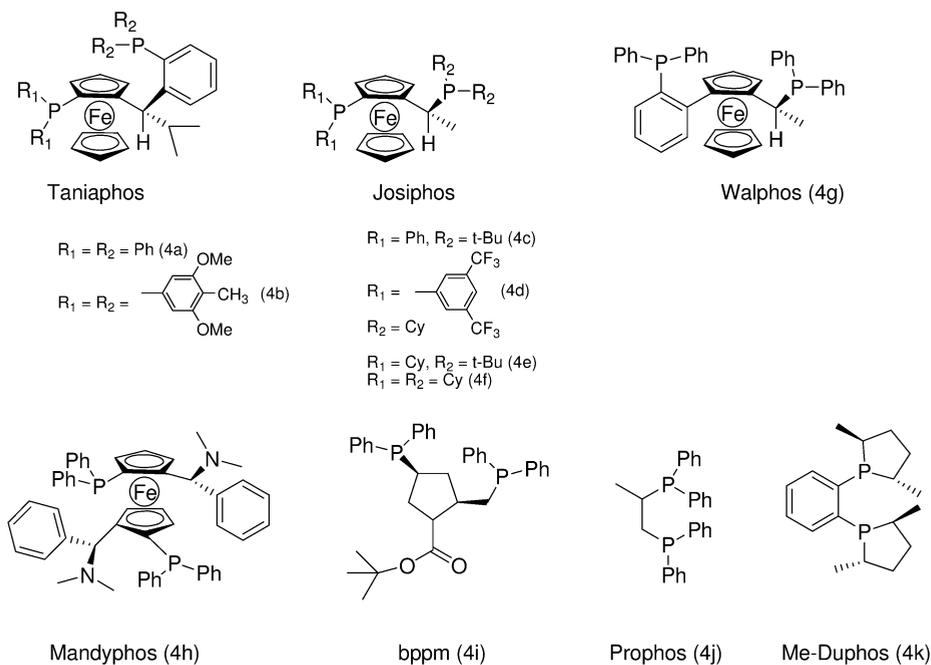


Fig. 41.9 Structures of the ligands used for enantioselective hydrogenation in the study of Feng et al. [104].

parative study with methyl- α -acetamidoacrylate hydrogenation showed that the ionic liquid/water media gave good results with regard to conversion, enantioselectivity, and catalyst separation (Table 41.13).

41.2.5

Ketone and Imine Hydrogenation in Ionic Liquids

Only one report exists on ketone hydrogenation in ionic liquids which applies Rh-complexes as catalysts [105]. The groups of Yinghuai, Ke and Hawthorne synthesized a new carborane-based room-temperature ionic liquid consisting of an *N*-*n*-butylpyridinium cation and a $[\text{CB}_{11}\text{H}_{12}]^-$ anion, and used this ionic liquid as reaction medium in the asymmetric hydrogenation of unsymmetrical aryl ketones in the presence of the chelating ligand (*R*)-BINAP and a rhodacarborane catalyst (Table 41.14). Compared to hydrogenation in tetrahydrofuran and in “classical” ionic liquids, the best results were achieved with the carborane-based ionic liquid.

Lin et al. [106] studied the hydrogenation of β -aryl ketoester using a ruthenium BINAP system with different substituents at the 4,4'-position of the BINAP ligand. The best enantioselectivities were achieved with steric demanding and electron-donating 4,4'-substituents. For example, ee-values of 97.2% and 99.5% were obtained for the hydrogenation of ethyl benzoylacetate with R =trimethylsilane (5,

Table 41.13 Enantioselective hydrogenation of enamides catalyzed by Rh-Taniaphos in various ionic liquids/water combinations and in conventional solvents [104].

Entry	Reaction medium	Conversion [%]	ee [%]	Catalyst separation	No. of phases
1	MeOH-H ₂ O ^{a)}	100	98	–	1
2	MeOH	100	97	–	1
3	<i>i</i> -PrOH	92	95	–	1
4	Toluene	47	28	–	1
5	[BMIM]BF ₄	32	>99	–	1
6	[BMIM]PF ₆	6	91	–	1
7	[BMIM]BF ₄ / <i>i</i> -PrOH	64	96	+	2
8	[BMIM]PF ₆ / <i>i</i> -PrOH	12	93	+	2
9	[OMIM]BF ₄ /H ₂ O	100	>99	++	2
10	[BMIM]Tf ₂ N/H ₂ O	97	>99	++	2
11	[BMIM]BF ₄ -H ₂ O ^{b)} /Toluene	100	>99	++	2
Reaction using ligand 4b , substrate: methyl- <i>a</i> -acetamidoacrylate					
12	MeOH	53	97	–	1
13	<i>i</i> -PrOH	84	95	–	1
14	[BMIM]BF ₄	17	98	–	1
15	[BMIM]BF ₄ / <i>i</i> -PrOH	43	99	++	2
16	[OMIM]PF ₆ / <i>i</i> -PrOH	47	98	++	2
17	[OMIM]BF ₄ /H ₂ O	70	>99	++ ^{*)}	2
18	[BMIM]Tf ₂ N/H ₂ O	90	>99	++	2
19	[BMIM]BF ₄ -H ₂ O ^{b)} /Toluene	100	>99	++	2
Reaction using ligand 4a , substrate: methyl- <i>a</i> -acetamidocinnamate					
20	<i>i</i> -PrOH	100	94	–	1
21	[BMIM]BF ₄	52	93	–	1
22	[BMIM]BF ₄ / <i>i</i> -PrOH	100	93	+	2
23	[OMIM]BF ₄ /H ₂ O	100	95	++	2
24	[BMIM]BF ₄ -H ₂ O ^{b)} /Toluene	100	94	++	2
25	[OMIM]BF ₄ /H ₂ O ^{c)} /Toluene	100	95	++	3
Reaction using ligand 4b , substrate: methyl- <i>a</i> -acetamidocinnamate					
26	<i>i</i> -PrOH	100	99	–	2
27	[OMIM]BF ₄ /H ₂ O	100	>99	++	2

ILs: ca. 2 mL, co-solvents: ca. 2–3 mL, SCR=200, [S]=0.25 M in co-solvent, room temperature, P(H₂)=1 bar, t=20 min.

“–” no, “+” good (some leaching), “++” excellent (no leaching).

a) v:v=4:1.

b) v:v=6:1.

c) v:v=3:1.

*) ICP-MS: 0.9 ppm Rh content in co-solvent.

Table 41.14 Rhodium-catalyzed hydrogenation of acetophenone (A) and ethyl benzoylformate (B) [105].

Solvent	Conversion [%] ^{b)}	ee [%] ^{c)}	TOF [h ⁻¹] ^{d)}
[OMIM][BF ₄]	100 (A, B)	97.3 (A), 99.3 (B)	194 (A), 201 (B)
[BMIM][BF ₆]	100 (A, B)	97.8 (A), 98.2 (B)	207 (A), 213 (B)
[BPy][CB ₁₀ H ₁₂]	100 (A, B)	99.1 (A), 99.5 (B)	239 (A), 306 (B)
Tetrahydrofuran	82 (A), 87 (B)	91.3 (A), 85.7 (B)	96 (A), 107 (B)

Molar ratio of catalyst/(*R*)-BINAP/acetophenone = 1 : 1.5 : 1000;
 reaction conditions: H₂ (12 atm), 50 °C, 12 h; [cat.] = 8.1 × 10⁻⁴ M.

b) Determined by GC.

c) Determined by GC on a Chirasil DEX CB column.

d) TOF = (mol hydrogenation product mol Rh h⁻¹),
 determined after 3 h.

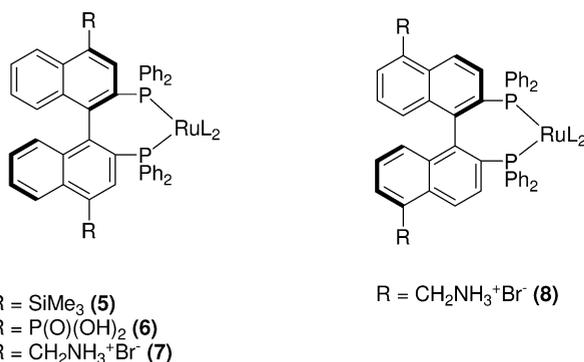
**Fig. 41.10** Ru-complexes as used by Lin et al. in the hydrogenation of β -aryl ketoester in several ionic liquids.

Fig. 41.10), and R = bisphosphonic acid (**6**, Fig. 41.10), respectively, as substituents. By immobilization of these catalysts in [BMIM][BF₄], a slight deterioration in ee-values (reduction by 1%) was observed for the trimethylsilane-substituted catalyst, while an increase (by up to 2.6%) was observed for the bisphosphonic acid-substituted catalyst. Both catalysts were recycled and reused four times and the ee (conversion) decreased from 97.3% (>98) to 95.1% (62%) in the case of trimethylsilane as substituent, and from 97.5% (98) to 74.7% (44%) for the bisphosphonic acid-substituted catalyst. In both cases no significant leaching was detected. Higher conversion rates with comparable ee-values were achieved by using [MMPIM][CF₃SO₂]₂N as ionic liquid [107]. These findings can be explained by an absence of the anions [BF₄]⁻ and [PF₆]⁻ (with their potential to liberate the catalyst poison F⁻ in a hydrolysis reaction) and substitution of the acidic proton at the 2-position of the imidazolium cation by a methyl group, which safely prevents carbene formation with the transition metal.

The same catalyst was used in the asymmetric hydrogenation of β -keto esters in [BMIM][PF₆], [BMIM][BF₄] and [MMPIM][(CF₃SO₂)₂N] with complete conversions and ee-values of up to 99.3% [108].

Another substituted derivative of BINAP was used by Lemaire et al. [109]. The ammonium salt catalysts (**7** and **8**, Fig. 41.10) were prepared *in situ* from the bromohydrates and [Ru(η^3 -2-methylallyl)₂(η^2 -COD)], and immobilized in several ionic liquids. By comparative studies of the hydrogenation of ethyl acetoacetate, the best results were obtained with imidazolium- and pyridinium-containing ionic liquids. No significant ee was observed with the phosphonium salt. This observation was attributed to problems of solubility and to the ability of complexation for the phosphonium ion. From the anionic side, use of the [BF₄]⁻ anion appeared superior compared to [PF₆]⁻ and [(CF₃SO₂)₂N]⁻.

Due to chloride impurities of the ionic liquids in use, all selectivities were lower than the selectivities in pure water. Surprisingly, the selectivity increased from 76 to 90% and from 85 to 90% with reuse of the ionic catalyst solution based on [BMIM][BF₄] and [BPy][NTf₂], respectively.

Ionic liquids have also been applied in transfer hydrogenation. Ohta et al. [110] examined the transfer hydrogenation of acetophenone derivatives with a formic acid–triethylamine azeotropic mixture in the ionic liquids [BMIM][PF₆] and [BMIM][BF₄]. These authors compared the TsDPEN-coordinated Ru(II) complexes (**9**, Fig. 41.11) with the ionic catalyst synthesized with the task-specific ionic liquid (**10**, Fig. 41.11) as ligand in the presence of [RuCl₂(benzene)]₂. The enantioselectivities of the catalyst immobilized by the task-specific ionic liquid **10** in [BMIM][PF₆] were comparable with those of the TsDPEN-coordinated Ru(II) catalyst **9**, and the loss of activities occurred one cycle later than with catalyst **9**.

Table 41.15 Recycling of **9**- and **10**-Ru in the asymmetric transfer hydrogenation of acetophenone with the azeotrope in [BMIM][PF₆] [110].

Cycle	Catalyst 9 -Ru Conversion		Catalyst 10 -Ru ^{a)} Conversion	
	[%] ^{b)}	ee [%] ^{b)}	[%] ^{b)}	ee [%] ^{b)}
1	96	93	98	92
2	99	92	>99	93
3	95	92	99	93
4	88	92	92	93
5	63	93	75	90

Reaction conditions: room temperature, 24 h, SCR=100.

a) A mixture of **10** and [RuCl₂(benzene)]₂ was used.

b) Determined by capillary GLC analysis using a chiral Cyclodex-B column.

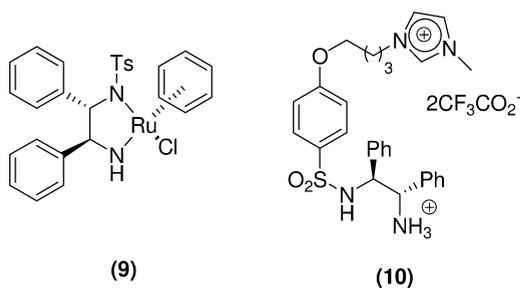


Fig. 41.11 Ru-complex and task-specific ionic liquid for the hydrogenation of acetophenone derivatives.

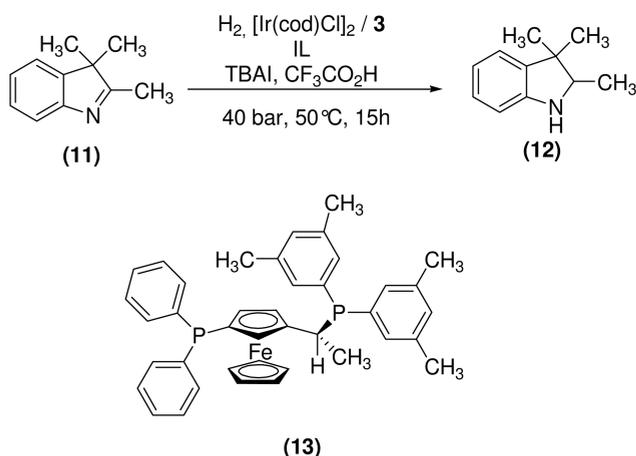


Fig. 41.12 Enantioselective hydrogenation of trimethylindolenine.

41.2.6

Imine Hydrogenation

Very few examples describe the hydrogenation of imines in ionic liquids. Giernoth et al. [111] performed a screening of eight different ionic liquids (the cations were [BMIM]⁺, [C₁₀MIM]⁺, [BMPy]⁺ and [C₁₀MPy]⁺ combined with the anions [BF₄]⁻ and [(CF₃SO₂)₂N]⁻), and compared them with toluene as solvent in the hydrogenation of trimethylindolenine (11, Fig. 41.12) with Ir-xylyphos as catalyst (13, Fig. 41.12).

Besides immobilization of the catalyst, the benefit of the ionic liquids is in this case a reduction of the reaction time from 23 h in toluene to less than 15 h in [C₁₀MIM][BF₄] with no loss of selectivity, although the ionic media require slightly higher reaction temperatures (Table 41.16). Furthermore, a stabilization of the ionic catalyst solution against atmospheric oxygen is observed. This stabilization ef-

Table 41.16 Enantioselective hydrogenation of **11** [111].

Entry	Solvent	Conversion [%]	ee [%] ^{a)}
1 ^{d)}	Toluene ^{b)}	100	90
2 ^{d)}	Toluene ^{c)}	98	86
3 ^{d)}	[BMIM][BF ₄]	100	56
4 ^{d)}	[BMIM][BF ₄]	45	56
5 ^{d)}	[BMIM][NTf ₂]	100	70
6 ^{d)}	[BMIM][NTf ₂]	91	68
7 ^{d)}	[C ₁₀ MIM][NTf ₂]	100	76
8 ^{d)}	[C ₁₀ MIM][NTf ₂]	100	72
9 ^{e)}	[C ₁₀ MIM][BF ₄]	98	84
10 ^{e)}	[C ₁₀ MIM][NTf ₂]	92	76

Reaction conditions: 0.4% catalyst loading, $p(\text{H}_2) = 40$ bar, 50 °C, 15 h.

- a) (S)-enantiomer.
 b) 23-h reaction time, 30 °C.
 c) 15-h reaction time, 50 °C.
 d) Under strictly anaerobic conditions.
 e) After 8-h reaction time and transfer through air.

fect facilitates the transfer of freshly prepared catalyst to the autoclave through air making the handling of the ionic liquid/catalyst-system much easier.

41.3

Homogeneous Catalyzed Hydrogenation in Biphasic Ionic Liquid/Supercritical (sc)CO₂ System

A very interesting way of performing homogeneous hydrogenation reactions in an ionic catalyst phase is to combine them with a compressed CO₂ extraction phase. The significant solubility of CO₂ in the ionic liquid enhances the availability of hydrogen in the ionic liquid in two ways. First, hydrogen solubility in the ionic liquid phase is greatly increased by the “co-solvent” CO₂. Second, the viscosity of the ionic liquid is drastically reduced by the presence of CO₂, thus enhancing the mass transport of hydrogen into the ionic liquid phase.

The fact that no ionic liquid is soluble in a pure compressed CO₂ phase makes the combination of both solvent systems – which are at the extreme ends of the polarity and volatility scales – especially attractive for continuous processes [102, 112–114].

41.4 Supported Ionic Liquid Phase Catalysis

A rather new concept for biphasic reactions with ionic liquids is the supported ionic liquid phase (SILP) concept [115]. The SILP catalyst consists of a dissolved homogeneous catalyst in ionic liquid, which covers a highly porous support material (Fig. 41.13). Based on the surface area of the solid support and the amount of the ionic liquid medium, an average ionic liquid layer thickness of between 2 and 10 Å can be estimated. This means that the mass transfer limitations in the fluid/ionic liquid system are greatly reduced. Furthermore, the amount of ionic liquid required in these systems is very small, and the reaction can be carried in classical fixed-bed reactors.

The SILP concept has been successfully applied to homogeneous hydrogenation by Mehnert et al. [116]. In these investigations, the hydrogenation of 1-hexene, cyclohexene and 2,3-dimethylbutene was carried out with the complex $[\text{Rh}(\text{nbd})(\text{PPh}_3)_2][\text{PF}_6]$ (nbd=norbornadiene, PPh_3 =triphenylphosphine). In comparison to the classical homogeneous and to the biphasic reaction systems, the catalyst showed enhanced activity by using the SILP concept (see Table 41.7). For example, the reaction rate for the hydrogenation of 1-hexene increased from $k_0=0.4 \text{ min}^{-1}$ at 50°C for the homogeneous phase to $k_0=11.2 \text{ min}^{-1}$ at 30°C for the SILP catalyst. This corresponded to an increase in TOF from $46 \text{ mol mol}^{-1} \text{ min}^{-1}$ for the biphasic hydrogenation of 1-hexene to $447 \text{ mol mol}^{-1} \text{ min}^{-1}$ (Table 41.17, entries 5 and 10).

The same catalyst was reused for 18 batch runs, without any significant loss of activity. The level of rhodium leaching remained below the detection limit, and the isolated organic phases did not exhibit any further reactivity, which additionally verified full retention of the active species.

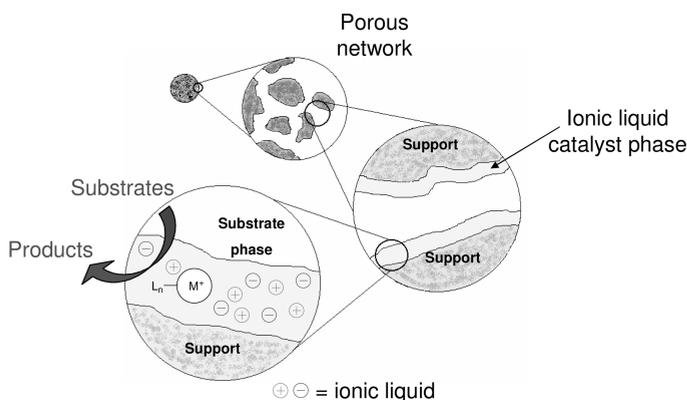


Fig. 41.13 Supported ionic liquid phase (SILP) catalyst. The ionic liquid phase containing a rhodium complex is immobilized on the surface of a silica gel support material.

Table 41.17 Comparative hydrogenation studies using supported ionic liquid catalysts, biphasic catalyst systems and the classical homogeneous catalyst systems [116].^{a)}

Entry	Substrate	Substrate [mol]	Solvent ^{b)} [mol]	Pressure [psig]	Temperature ^{c)} [°C]	Time [min]	Conversion [%]	Yield ^{d)} [%]	TOF _{ave} ^{e)} [min ⁻¹]	k _p ^{f)} [min ⁻¹]	Comments
1	1-C ₆ =	0.12	0.94	15	23 (25)	120	100	68	28	0.4	
2	1-C ₆ =	0.12	0.96	72	22 (28)	45	100	91	135	2.1	
3	1-C ₆ =	0.14	0.95	150	23 (29)	23	98	86	291	3.6	
4	1-C ₆ =	0.13	0.97	300	23 (30)	20	99	91	329	6.5	
5 ^{g)}	1-C ₆ =	0.13	0.96	600	25 (34)	16	100	99	447	11.2	
6	1-C ₆ =	0.11	0.83	900	23 (33)	7	97	94	821	21.7	
7 ^{h)}	c-C ₆ =	0.13	0.99	600	24 (31)	20	95	91	329	9	
8 ⁱ⁾	DMB	0.13	0.96	600	22 (23)	120	34	29	17	0.6	
9 ^{j)}	1-C ₆ =	0.04	0.2	600	30 (30)	120	44	20	4	–	Biphasic
10 ^{k)}	1-C ₆ =	1.2	1.5	600	50 (50)	120	96	29	46	0.4	Acetone

a) All runs conducted at stirring speed of 2200 rpm in a 300-mL autoclave equipped with a basket insert (Robinson-Mahoney reactor) and a catalyst charge of $c(\text{Rh})=0.018 \times 10^{-3}$ mol.

b) Heptane used as solvent.

c) Values in parentheses give maximum reaction temperature due to exotherm (small impact on k_p for entries 1–8; comparison with entry 10 will not be influenced).

d) Yield of hydrogenated product 2 reaction byproducts consisted of isomerized olefins (for hexene-1: *c,i*-hexene-2 and *c,i*-hexene-3).

e) TOF_{ave} defined as mol (hydrogenated product) per mol (rhodium) per min (full reaction time); reactions were stopped after 120 min or > 95% conversion.

f) k_p is initial rate constant for the appearance of hydrogenated product.

g) No transport limitation was apparent under the applied reaction conditions; the reaction was also investigated at 1800 rpm with no change of k_p .

h) Substrate: *c*-C₆=cyclohexene.

i) Substrate: DMB = 2,3-dimethyl-2-butene.

j) Liquid-liquid biphasic reaction was carried out in a 70-mL autoclave at a stirring speed of 1600 rpm with a catalyst charge of $c(\text{Rh})=0.018 \times 10^{-3}$ mol in 4 mL ionic liquid.

k) Homogeneous catalysis carried out in 300-mL autoclave at stirring speed of 2200 rpm in acetone solution with a catalyst concentration $c(\text{Rh})=0.06 \times 10^{-3}$ mol.

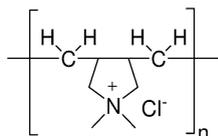


Fig. 41.14 Poly(diallyl-dimethylammoniumchloride).

Table 41.18 Homogeneous, biphasic and heterogeneous enantioselective hydrogenations of methyl acetoacetate with Ru-BINAP [117].

Entry	Reaction	Solvent	TOF [h^{-1}] (re-use)	ee [%]	Selectivity ^{a)}
1	Homogeneous	Methanol	103	99	85
2		Isopropanol	74	99	93
3		Methanol ^{b)}	88	99	91
4	Biphasic	Isopropanol	16 (15)	97	83
5	SILP	Isopropanol	29 (29)	97	87

Reaction conditions: 2 μmol complex, SCR=140, 40 bar H_2 , 60°C, 1 h. Homogeneous: 4 mL solvent. Biphasic: 1 g [BMIM][PF₆], 4 mL solvent. Heterogeneous: 0.2 g polymer, 1 g [BMIM][PF₆], 4 mL solvent.

- a) Selectivity to methyl hydroxybutyrate due to the formation of the corresponding acetal.
 b) Addition of 0.2 g polymer.

To our knowledge, there is to date only one report concerning asymmetric hydrogenation using a SILP catalyst [117]. Methyl acetoacetate was hydrogenated using Ru-BINAP dissolved in [BMIM][PF₆] and immobilized on the poly(diallyl-dimethylammonium chloride) support (Fig. 41.14).

This polymeric phase simultaneously heterogenizes the transition-metal complex and the ionic liquid, so that the catalyst is fully recyclable. The SILP-catalyst was less active than the homogeneous reference system, but clearly more active than the biphasic system (Table 41.18).

Beside SILP experiments with silica as support material, reports have also been made on the use of membranes coated with ionic liquid catalyst solution for the hydrogenation reaction of propene and ethene. The membranes were obtained by supporting various ionic liquids, each containing 16 to 23 mmol Rh(I) complex $\text{Rh}(\text{nbd})(\text{PPh}_3)_2^+$ (nbd=norbornadiene), in the pores of poly(vinylidene fluoride) filter membranes [118].

41.5

Conclusion

The use of ionic liquids has been successfully studied in many transition metal-catalyzed hydrogenation reactions, ranging from simple alkene hydrogenation to asymmetric examples. To date, almost all applications have included procedures of multiphase catalysis with the transition-metal complex being immobilized in the ionic liquid by its ionic nature or by means of an ionic (or highly polar) ligand.

A large part of the research has been dedicated to liquid–liquid-biphasic hydrogenation reactions. Hydrogenation, in principle, is very well suited for a biphasic reaction mode using ionic liquids. Many hydrogenation catalysts are ionic or polar and – most importantly – the polarity of the product is lower than the polarity of the substrate. This allows easy product separation after the reaction with low product solubility in the catalyst phase. Moreover, the formation of heavy, polar side products that would accumulate in the catalyst phase during recycling is not very likely in hydrogenation chemistry. Consequently, many of the research projects published to date have focused on aspects of recycling. Regarding the fact that not only the metal complex but also the ionic liquid itself is a valuable part of the reaction mixture, the concept aims for full and intact recovery of the ionic catalyst solution and its reuse.

Many of the examples presented in this chapter have shown much promise in this respect. It was seen that in many cases the activity and selectivity of known transition-metal complexes does not change too much in the ionic environment, indicating weak interaction of the ionic liquid ions and the complex in most cases. Selectivity optimization based on ligand design – which is especially important in asymmetric catalysis – is also possible in an ionic liquid environment. However, some important differences to the homogeneous reactions in organic solvents must be taken into account. Hydrogen solubility in ionic liquids is low compared to that in traditional solvents, and consequently the hydrogen concentration is low at the catalytic center. The mass transfer of hydrogen into the catalyst layer is affected by the viscosity of the ionic liquid (with low viscosities enhancing mass transfer), but has been found to be sufficiently rapid in most cases to reach acceptable reaction rates comparable to those obtained in organic media.

Specifically interesting variations of the hydrogenation using ionic liquids are the transition metal-catalyzed hydrogenations in the system ionic liquid/compressed CO₂ and the SILP concept. In both cases the advantages of a molecular defined, homogeneous, selective and recyclable hydrogenation catalyst are combined with very efficient, continuous catalyst recovery and recycling. Both concepts offer new approaches for process intensification in homogeneous hydrogenation catalysis.

Abbreviations

BMIM	1-butyl-3-methylimidazolium
EMIM	1-ethyl-3-methylimidazolium
NBR	nitrile-butadiene rubber
PBD	polybutadiene
SBR	styrene-butadiene rubber
scCO ₂	supercritical CO ₂
SCR	substrate: catalyst ratio
SILP	supported ionic liquid phase
TOF	turnover frequency
TON	turnover number

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