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Switching the Mechanism of Catalyst Activation by Ionic Liquids

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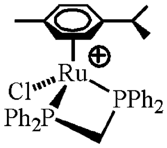
In ionic liquids (ILs), the activation of a ruthenium(II) catalyst precursor occurs via an unexpected mechanism, which is different from the activation mechanism that takes place in water. The effectiveness of a biphasic catalytic hydrogenation reaction using the ruthenium(II) precatalyst is shown to be highly dependent on the nature of both anion and cation of the IL. Evidence is provided that chloride ions are required to generate the active catalyst. Moreover, the influence of the IL cation on the rate of hydrogenation is correlated with the differences in capability of the IL to solvate chloride. A kinetic study provides insights into the mechanism of the formation of the active catalytic species.

Introduction

Solvent effects on chemical reactions have been observed since the second part of the 19th century and have frequently been reported and analyzed in terms of solvent parameters, which should be able to fully describe and predict the outcome of a reaction carried out in a particular solvent.[1] Thus, solvents have been classified according to their polarity, which is estimated using various approaches including studying the bulk properties of solvents, or according to the reactivity or spectroscopic properties of solutes.[1b,2] A change of solvent can have a drastic impact on the kinetics or thermodynamics of a chemical reaction due to different stabilization of reagents, transition states, or products by the solvent molecules.[3] Solvent effects on transition metal-catalyzed reactions may have major consequences on the activity and/or selectivity of a catalyst,[4] and the use of a particular solvent can even induce modifications in a catalytic cycle or even suppress catalytic activity altogether.

In order to combine the efficiency of homogeneous catalytic processes with the advantages of heterogeneous catalysis, the concept of biphasic catalysis has been developed.[5] This approach consists of using alternative solvents that are not miscible with the product(s) of a reaction (and often the substrates) and that provide a separate phase in which the catalyst is immobilized and is easily recycled. For example, the Ruhrchemie/Rhône-Poulenc oxo process, designed for the production of *n*-butyraldehyde from syngas and propylene, is one of the most important industrial applications of biphasic catalysis in which the rhodium catalyst is immobilized in water.[6] Ionic liquids (ILs) have demonstrated their potential utility in the field of biphasic catalysis.[7] By virtue of the ionic nature of these solvents, a large number of anion−cation combinations can be envisaged, which can yield a vast library of potential ILs. By analogy with classical solvents, the replacement of a molecular solvent by an IL can modify the reactivity of a catalyst precursor, as has been described for a ruthenium(II)-catalyzed hydrogenation.[8] This catalytic reaction, which operates in water, was shown to be inhibited in [bmim][BF_4] and [bmim][TfO] (bmim = the 1-butyl-3-methylimidazolium cation), due to the different solvation of a particular species involved in the mechanism of formation of the catalyst.[8]

Chart 1



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In this study, the effect of the IL anion and cation combination on a ruthenium(II)-catalyzed hydrogenation reaction was investigated and related to variations in the solvation of key solutes, since the replacement of one IL by another can greatly affect the properties of solutes and, therefore, the kinetics and reaction pathways that might occur.[9] Additionally, this work represents, together with a few other reports,[10] a rare example of a mechanistic study of a catalyzed reaction performed in ILs and to the best of our knowledge the first showing that a different mechanism takes place in ILs compared to other solvents.

Results and Discussion

Effect of the Anion. The arene−ruthenium(II) complex, **1** (Chart 1), which is an effective precatalyst in water, has been shown to be active in some ILs under conditions that provide a higher solvation of the dissociated chloride (i.e., by addition

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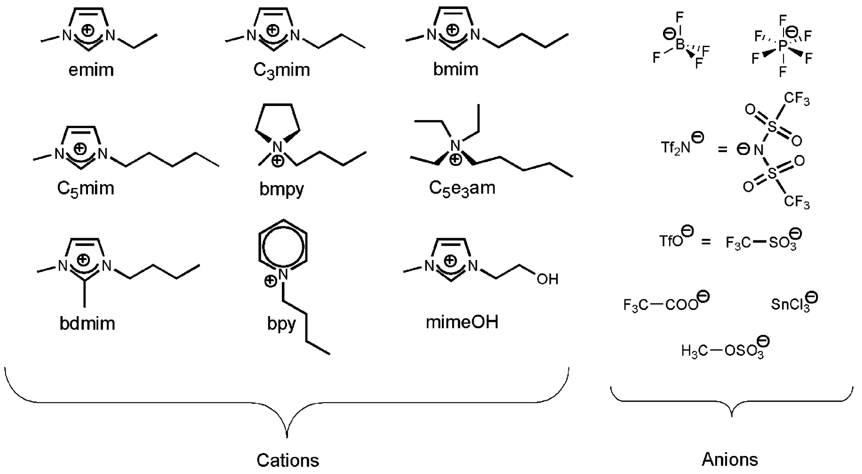
Chart 2



of water to the IL).[8] The use of ILs containing Lewis acidic anions with different properties was envisaged as an alternative method to favor the dissociation of chloride from the ruthenium precatalyst, as has been highlighted in recent studies by van Eldik on chloride substitution on platinum(II) complexes performed in chlorostannate melts and [bmim][Tf_2N].[10c,11] In this respect, hydrogenation of styrene was carried out in a series of [bmim][Anion] ILs, where Anion = PF_6, $SnCl_3$, BF_4, Tf_2N, CF_3COO, CH_3OSO_3, and TfO (**1**·Cl and **1**·BF_4 were employed as the catalyst precursors; see Charts 1 and 2 for the structures of the Ru(II) complex, **1**, and the ILs, respectively).

Table 1. Selected Solvent Properties for [bmim][Anion]

anion	π^{*a}	α^a	β^a	η/cP	$\Lambda/10^2$ S·cm^2·mol$^{-1\,c}$
BF_4	1.047	0.627	0.376	113	3.2
PF_6	1.032	0.634	0.207	225	3.8
$MeSO_4$				214[b]	
Tf_2N	0.984	0.617	0.243	54	1.5
CF_3COO					2.3
CF_3SO_3	1.006	0.625	0.464	107	2.7

[a] Ref 15. [b] From the supplier. [c] Ref 16.

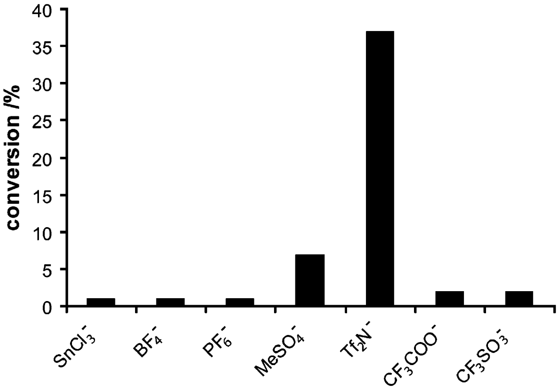


Figure 1. Influence of the IL anion on the catalytic hydrogenation of styrene to ethylbenzene using **1**·Cl in [bmim][Anion] type ILs. Conditions: 80 °C, H_2 (50 bar), [substrate]/[Ru] = 1160, 4 h. Note: under the same conditions **1**·Cl in water results in essentially quantitative conversion.

When **1**·BF_4 was used in the various ILs, no activity was observed, and changing the IL anion does not improve the dissociation of chloride from this complex. Moreover, the hydrogenation reaction was attempted in [mimeOH][Tf_2N], which displays a higher ability to solvate chloride,[12] but the catalyst precursor remained inactive. So far, addition of water seems to be the only effective method that modifies the solvent properties in order to enable the catalytic hydrogenation in ILs through the mechanistic pathway involving loss of the coordinated chloride.[8,13] However, using **1**·Cl as a precatalyst in the series of [bmim][Anion] ILs provides unexpected results, which are summarized in Figure 1. In contrast to **1**·BF_4, complex **1**, with chloride as the counteranion, displays some activity for styrene hydrogenation, notably in [bmim][Tf_2N] and other [Tf_2N]-based ILs (see below). The presence of the chloride ion appears to be necessary to provide the active catalytic species. Indeed, a catalytic experiment was performed with **1**·BF_4 in [bmpy][Tf_2N] in the presence of ca. 2.5 equiv of [bmpy][Cl], and 97% conversion was measured after 4 h reaction. These observations rule out the mechanism that requires the dissociation of chloride (i.e., the established mechanism in water). On the contrary, here chloride ions act as a cocatalyst and promote the hydrogenation of styrene. Previous NMR spectroscopic studies using **1**·Cl and the corresponding diphenylphosphinoethane (dppe) and diphenylphosphinopropane (dppp) complexes under similar conditions, for styrene hydrogenation in toluene, provided evidence for a dissociative process as the rate-limiting step.[13] This step was believed to be the dissociation of chloride, as it was observed that the chloride ligand was replaced by a hydride ligand after catalysis performed in water.[13] However, in view of these new results, it is more likely that another mechanism, activated by chloride ions, is taking place in [Tf_2N] ILs. The observed dissociative step can then be attributed to the loss of the *p*-cymene ligand rather than dissociation of chloride as established in water.

According to the results illustrated in Figure 1, there is a strong influence of the IL anion on the formation of catalytically active species. Several microscopic and macroscopic solvent properties that could help rationalize this anion effect are collected in Table 1. Viscosities are unlikely to be the main cause of the disparities in the catalytic activities (see Table 1). Although [bmim][Tf_2N] has the lowest viscosity, [bmim][$MeSO_4$] is more viscous than [bmim][BF_4] and [bmim][TfO]; however, the hydrogenation reaction performed in this IL results

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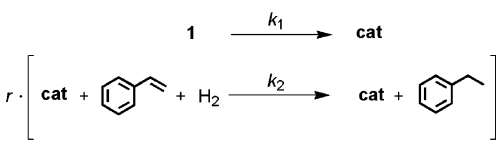
Scheme 1[a]



[a] r is the [substrate]/[catalyst] ratio.

in a higher activity than in the [bmim][BF_4] or [bmim][TfO] ILs. As chloride ions are a prerequisite to obtain catalytic activity, their solvation, which is related to their availability to react in solution, should also affect the formation of active species. The empirical solvent polarity scale, first developed by Kamlet, Abboud, and Taft (KAT),[14] has been extended to ILs by Welton and co-workers.[15] The scale consists of three parameters, π^*, α, and β, which describe the dipolarity/polarizability and hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of the solvent, respectively. The consequences of π^* and α on chloride solvation has been previously discussed.[12] The [bmim][Tf_2N] IL displays the lowest π^* and α values in the [bmim][Anion] series, which is consistent with a lower chloride solvation (higher activity). Moreover, the molar conductivity is the lowest for [bmim][Tf_2N].[16] Poor diffusion of the [bmim] cations would reduce the ability to solvate chloride ions in the IL; however, the small variations of the KAT parameters should not provide a large difference in chloride solvation. Apart from the influence on the solvation of chloride, the IL anion may have an effect on the solvation of the cationic Ru(II) precursor. The formation of a stronger ion pair (or aggregate) that might occur in the presence of spherical anions could prevent nucleophilic attack of the chloride ion at the metal center and preclude the formation of the actual catalyst. Moreover, the addition of an excess of [bmim][Cl] (15 equiv) did not improve the catalytic performances of **1**·Cl in [bmim][BF_4]. This suggests that the nature of the IL anion has a greater influence on the solvation of **1** rather than on the solvation of the chloride ions, which should not be significantly higher than in [bmim][Tf_2N].

Effect of Chloride Ions. The effect of chloride on the catalytic hydrogenation of styrene was further investigated in [bmim][Tf_2N]. Hydrogen uptake was monitored as a function of time and converted into the number of moles of styrene. The data were treated using the *pseudoelementary kinetic model* that has been previously applied by Finke to study the formation of catalytic nanoclusters.[17] This concept requires that the hydrogenation of the substrate performed in the presence of the catalyst (k_2) is fast compared to the formation of the catalyst from the precursor (k_1) (Scheme 1, where r is the [substrate]/[catalyst] ratio). In such a case, the kinetics of the overall reaction (k_{obs}) can be described by the kinetics of the first step. Considering the high [substrate]/[catalyst] ratio, the consumption of H_2 in the first step is negligible; therefore, the overall H_2 consumption corresponds to that occurring during the second step. In order to maintain a higher rate for the second step, only data prior to 50% conversion were analyzed.[17a]

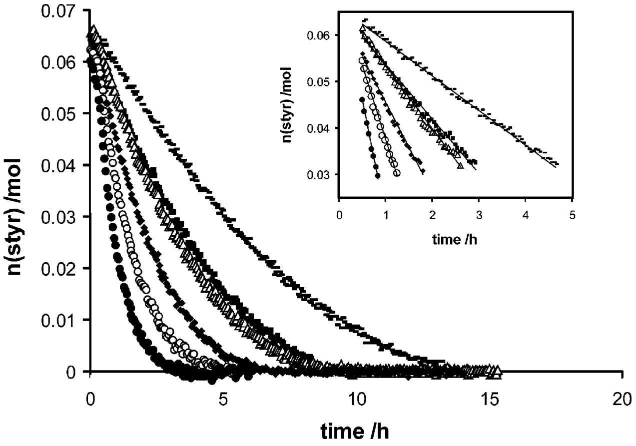


Figure 2. Effect of chloride concentration on the kinetics of styrene hydrogenation using **1**·Cl as precatalyst in [bmim][Tf_2N]. [Cl^-] = 9.8 × 10^{-6} (− dashes), 1.2 × 10^{-5} (■ filled squares), 1.5 × 10^{-5} (△ empty triangles), 2.1 × 10^{-5} (◆ filled diamonds), 3.3 × 10^{-5} (○ empty circles), 5.5 × 10^{-5} (● filled circles) mol·g^{-1}. Straight lines represent calculated moles of styrene using a linear least-squares fitting procedure (all $R^2 > 0.99$). Conditions: 80 °C, initial H_2 pressure = 50 bar, [substrate]/[Ru] = 1400.

On the basis of this model, the observed rate of reaction relates the rate of formation of the catalytically active species as expressed in eq 1, where r is the [substrate]/[cat] ratio.

$$\frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{1}{r}\,\frac{-\mathrm{d}[\mathrm{Substrate}]}{\mathrm{d}t} \tag{1}$$

The effect of IL or additives on the overall rate of reaction can then be directly ascribed to their influence on the formation of the actual catalytic species. Figure 2 shows the consumption of styrene using **1**·Cl as a precatalyst in [bmim][Tf_2N] with addition of known amounts of [bmim][Cl]. After stabilization of the temperature, the moles of styrene decrease linearly with time, which corresponds to a linear decrease of the moles of **1**·Cl with time, according to the kinetic model used. Therefore, the formation of the catalyst follows apparent zero-order kinetics (eq 2).

$$v = \frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k_{\mathrm{obs}} \tag{2}$$

The ^{31}P NMR spectra of the IL phase recorded after 2 h of catalysis in [bmpy][Tf_2N] (which provides a more active medium, as will be discussed later) with various amount of added [bmpy][Cl] show that the proportion of **1**·Cl relative to the other potential ruthenium−diphosphine species does not vary significantly (see Supporting Information). Providing that only a minor proportion of the catalyst is formed at the beginning of the reaction, it can be assumed that chloride ions, which are likely to participate in the formation of the catalyst, display a constant concentration ($\geq[\mathbf{1}]$).

Equation 3 expresses the rate law involving the concentration of chloride for the formation of the catalyst. By plotting ln v as a function of ln[Cl^-] (eq 4), the partial order of the reaction, n, can be ascertained. As presented in Figure 3, a first-order kinetics in chloride concentration is observed.

$$v = k[\mathrm{Cl}^-]^n \tag{3}$$

$$\ln v = \ln k + n \ln[\mathrm{Cl}^-] \tag{4}$$

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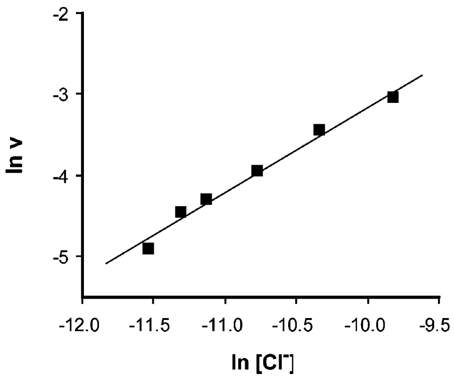


Figure 3. Dependence of the chloride concentration on the rate of formation of the catalyst. Linear least-squares fit, slope = 1.05 ± 0.07, intercept = 7.3 ± 0.7, $R^2 = 0.98$.

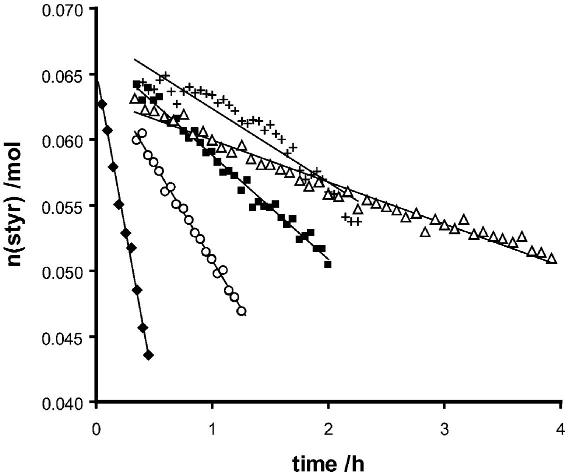


Figure 4. Influence of the IL cation on the kinetics of styrene hydrogenation using **1**·Cl as precatalyst in [Cation][Tf_2N]. Cation = bpy (△ empty triangles), bdmim (+ crosses), bmim (■ filled squares), bmpy (○ empty circles), and C_5e_3am (◆ filled diamonds). Straight lines represent calculated moles of styrene using a linear least-squares fitting procedure (all $R^2 > 0.9$). Conditions: 80 °C, initial H_2 pressure = 50 bar, [substrate]/[Ru] = 1400.

Effect of the Cation. The effect of the IL cation on the kinetics of formation of the active catalyst species was investigated, and the results from these experiments are summarized in Figure 4. The rate of reaction in various [Cation][Tf_2N] ILs, where Cation = bpy, bdmim, bmim, bmpy, and C_5e_3am, was determined by a linear least-squares fit at the beginning of the catalytic reaction according to the *pseudoelementary kinetic model*. A relatively large influence of the IL cation is observed on the reaction rate; in [C_5e_3am][Tf_2N] the rate is 15 times higher than in [bpy][Tf_2N] (see Table 2). An effect due to differences in viscosities can be ruled out in view of the values measured for [C_5e_3am][Tf_2N] and [bpy][Tf_2N] (see Table 2). A solvation scale for chloride has been previously established in the same series of [Tf_2N]-based ILs by the determination of the reaction enthalpy for the dissociation of a chloride-templated assembly.[12] The reaction enthalpy, ΔH, obtained in this study is related to the solvation enthalpy of chloride in the given IL, ΔH_{solv}, and the intrinsic reaction enthalpy corresponding to the equilibrium under investigation, ΔH_{eq}, as expressed in eq 5.

$$\Delta H = \Delta H_{equ} + \Delta H_{solv} \qquad (5)$$

The IL cation effect and the influence of chloride on the catalytic hydrogenation suggest that there is a relationship between the solvation of chloride and the rate of reaction. In fact, ln v versus ΔH displays a linear behavior, as expressed in eq 6 and illustrated in Figure 5.

Table 2. Styrene Hydrogenation Rates Using 1·Cl in [Cation][Tf_2N] ILs, Reaction Enthalpies Related to Chloride Solvation, and Viscosities of Each IL

cation	v/mol·h^{-1} ^{a}	ln v	ΔH/kJ·mol^{-1} **1**	η/cP^d
emim	4.06×10^{-3}	−5.51	5.9 ± 0.7^b	37
C_3mim	5.31×10^{-3}	−5.24	7.1 ± 0.9^b	53
bmim	7.97×10^{-3}	−4.83	8.6 ± 0.2^c	54
C_5mim	9.63×10^{-3}	−4.64	9.8 ± 1.2^b	70
C_5e_3am	4.79×10^{-2}	−3.04	16.8 ± 0.1^c	211
bmpy	1.48×10^{-2}	−4.21	12.3 ± 0.3^c	87
bpy	3.19×10^{-3}	−5.75	4.3 ± 0.2^c	59
bdmim	5.64×10^{-3}	−5.18	8.2 ± 0.08^c	118

[a] Conditions: 80 °C, initial H_2 pressure = 50 bar, [substrate]/[Ru] = 1400. [b] Calculated with the correlation shown in Figure 5. [c] From ref 12. [d] At 22 °C.

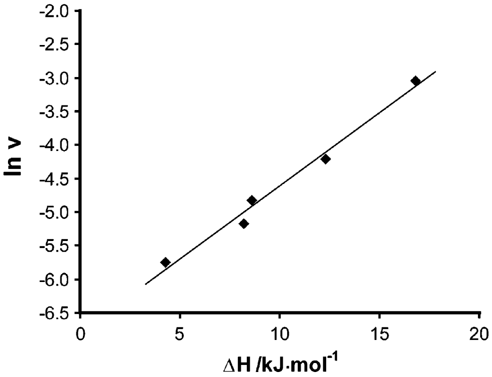
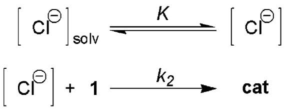


Figure 5. Correlation between the rate of styrene hydrogenation in [Cation][Tf_2N] using **1**·Cl as precatalyst and the chloride solvation enthalpy in each IL, [Cation][Tf_2N]. Linear least-squares fit, slope = 0.22 ± 0.02, intercept = −(6.8 ± 0.2), $R^2 = 0.98$.

Scheme 2



$$\ln v = \ln m + n\Delta H \qquad (6)$$

$$E_a = B(-\Delta H_{solv}) \qquad (7)$$

In agreement with Arrhenius's law, eq 6 demonstrates a proportional relationship between the activation energy of the rate-limiting step and ΔH_{solv}, as expressed in eq 7 (see Supporting Information for the details). This implies that the rate-limiting step in the formation of the catalyst is related to the (partial) desolvation of chloride, which provides species that can react with **1** in a subsequent step, as depicted in Scheme 2. This mechanism is in agreement with a previous report on nucleophilic substitution in ILs.[18]

The cation effect was further studied in a series of 1-alkyl-3-methylimidazolium, [Rmim][Tf_2N], ILs. As shown Figure 6, the reaction rate increases with the length of the alkyl side-chain. This feature is likely to be associated with a change in the chloride solvation enthalpy. Using the linear relation obtained above (eq 6, Figure 5), the enthalpy, ΔH, was estimated for each [Rmim][Tf_2N] IL, and their values are collected in Table 2. Although the ΔH values calculated with eq 6 are less

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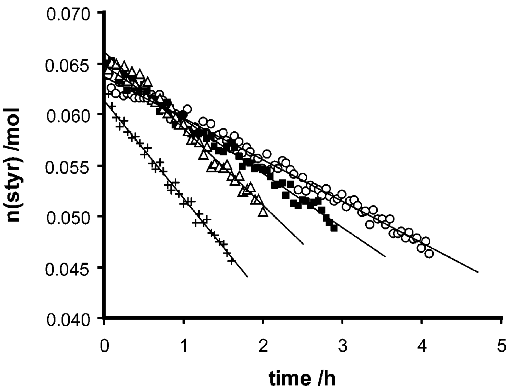


Figure 6. Influence of the alkyl chain length on the kinetics of styrene hydrogenation using **1**·Cl as precatalyst in [Rmim][Tf_2N]. R = ethyl (○ empty circles), propyl (■ filled squares), butyl (△ empty triangles), and pentyl (+ crosses). Conditions: 80 °C, initial H_2 pressure = 50 bar, [substrate]/[Ru] = 1400.

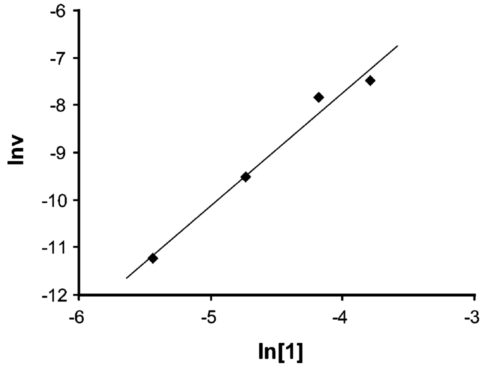
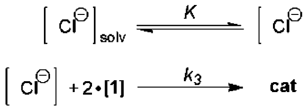


Figure 7. Dependence of ruthenium concentration on the rate of formation of the catalyst. Linear least-squares fit, slope = 2.4 ± 0.2, intercept = 1.8 ± 1.1, R^2 = 0.98.

Scheme 3



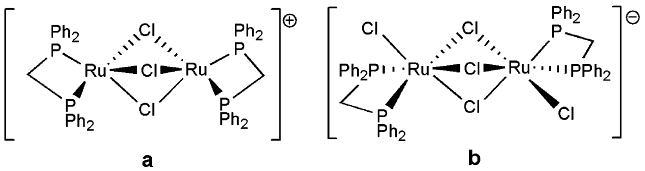
precise than the ones previously reported, this new data extend the chloride solvation scale already available.[12] The effect of the alkyl chain length on chloride solvation is, however, less significant than the nature of the cation.

The Mechanism of Catalyst Formation. The influence of the initial concentration of the ruthenium(II) complex was studied in a 0.1 M solution of [bmpy][Cl] in [bmpy][Tf_2N] in which the concentration of precursor **1**·BF_4 varied between 4.4 and 22.7 mM. The rate of formation of the catalyst was obtained by a linear least-squares fit (see Supporting Information) and was normalized by *r*, the [substrate]/[catalyst] ratio, as expressed in eq 1.

By analogy with eq 4, a linear correlation is observed when ln v is plotted as a function of ln[**1**] with a value for the slope close to 2, as shown in Figure 7. This implies a second-order kinetics in ruthenium(II), which provides, according to the results discussed above, the mechanism shown in Scheme 3 and the rate law expressed in eq 8 for the formation of the catalyst.

$$v = k_3[\mathrm{Cl}^-][\mathbf{1}]^2 = Kk_3[\mathrm{Cl}^-]_{\mathrm{solv}}[\mathbf{1}]^2 \tag{8}$$

Chart 3



The fact that catalyst formation is second-order in ruthenium(II) strongly suggests the formation of a dimeric species. Therefore, on the basis of this rate law, the formation of the cationic, electronically unsaturated species (dimer **a** depicted in Chart 3) can be postulated as a rate-limiting process in the formation of the active catalyst. Such a step is consistent with the first-order kinetics observed in chloride and the loss of *p*-cymene as mentioned above. The proposed species could further react with the chloride ions present in the reaction medium to yield the anionic dimer (**b** in Chart 3). Similar anionic species have been previously identified in ruthenium-catalyzed hydrogenation reactions[19] and have also been synthesized from the corresponding cationic arene−ruthenium diphosphine complex in the presence of chloride.[20] Subsequent steps in the catalyst formation that could lead to trimers or ruthenium nanoclusters cannot be excluded. The IL solution changes from orange before the hydrogenation reaction to dark red after the catalytic experiment is performed in the presence of an excess of chloride, and the ^{31}P NMR spectrum indicates the presence of several unidentified phosphorus species (see Supporting Information). Electrospray ionization mass spectrometry has previously been shown to detect catalysts present in ionic liquids at low concentrations,[21] and analyses of the ionic liquid phase from these experiments were performed in order to ascertain the molecular weight of these dimers, or potentially other ruthenium-containing compounds, but no ruthenium species could be observed.

Mercury poisoning experiments were performed in catalytic runs that use **1**·Cl in pure [bmpy][Tf_2N] as well as in [bmpy]-[Tf_2N] containing 2 equiv of [bmpy][Cl], and it was observed that a large excess of mercury (ca. 160 equiv) did not affect the activity of the catalyst, which discards the role of Ru(0) nanoparticles in the catalytic activity.[22] Moreover, attempts to establish the presence of ruthenium nanoparticles using transmission electron microscopy (TEM) after a catalytic experiment carried out with **1**·BF_4 in [bmpy][Tf_2N] containing an excess of chloride were unsuccessful. Combined, the nature of the catalyst is more likely to be molecular rather than involving nanoparticles, presumably a species resulting from the reaction of a dimer (Chart 3, **a** or **b**) with dihydrogen. It was observed that the addition of base also has consequences on the hydrogenation of styrene using **1**·Cl as a precatalyst. As illustrated in the Supporting Information, the presence of triethylamine enhances the catalytic activity. Bases are known to increase the activity of homogeneous hydrogenation catalysts, which require heterolytic cleavage of dihydrogen to provide active hydride species. Hence, such a step should be involved

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in the formation of the catalyst and should occur at a rate comparable to the formation of dimer **a**. A 0.1 M solution of [bmpy][Cl] in [bmpy][Tf_2N] containing the precatalyst **1**·BF_4 (7×10^{-3} mmol) was used for a catalytic experiment and recycled for further runs as shown in the Supporting Information. As a decrease in catalytic activity was observed, the color of the IL phase varied from dark red (first run) to yellow (last run) and the ^{31}P NMR spectrum of the IL phase after the forth run displayed only one singlet at 24.3 ppm (see Supporting Information).

Conclusions

This study has emphasized the crucial role that ILs can play in transition metal-catalyzed reactions. Very recently it has been shown that ILs can dramatically influence the outcome of a reaction,[23] and similarly in this study we have shown that the generation of an active catalyst is highly dependent on the nature of the IL and additionally that the active catalyst is different from the one generated in water, although the catalyst function, i.e., the hydrogenation of unsatuared organic bonds, remains the same. We have shown that the activation mechanism of a catalyst precursor that is known to operate in water or IL–water mixtures via a mechanism involving chloride dissociation is modified by the use of dry ILs. Both the cation and the anion of the IL can inhibit or promote the formation of the active catalyst; the main reason arises from the differences in solvent–solute interactions that take place in each IL. The role of chloride in the formation of the catalytically active ruthenium species was evidenced by kinetic studies, and the influence of the IL on the rate of hydrogenation was related to the different solvation capability of each IL toward chloride ions. Accordingly, higher catalytic activities were measured in ILs that provide lower chloride solvation. Although the nature of the true catalyst remains unclear, we were able to postulate a mechanism for the rate-determining step occurring in the formation of the catalyst. The kinetics are consistent with a reaction involving two cationic ruthenium(II) complexes, **1**, and a chloride ion. Moreover, the reactivity of these species was shown to be strongly dependent on the IL.

Experimental Section

All ILs were synthesized via the halide salt apart from [bmim]-[TfO],[24] which was prepared via direct alkylation from butylimidazole using methyltriflate. The halide salts of imidazolium, pyrrolidinium, pyridinium, and ammonium were prepared from the halogenoalkane in refluxing toluene following previous procedures.[25] The hydrophobic [Tf_2N]- and [PF_6]-based ILs were synthesized by metathesis in water at room temperature, according to published methods.[26] The hydrophilic [BF_4]- and [CF_3COO]-based ILs were prepared by metathesis at room temperature in dichloromethane as previously described,[25a] and [bmim][$SnCl_3$] was made from the chloride salt and $SnCl_2$ at room temperature in dichloromethane as reported elsewhere.[27] The ILs prepared by metathesis were washed with water to minimize the presence of halide impurities. All the ILs were dried under vacuum at 70 °C for several hours and characterized by ^1H NMR spectroscopy. [bmim][$MeSO_4$] was purchased from Fluka and used as received. The ruthenium(II) complexes [Ru(dppm)(*p*-cymene)Cl]Cl (**1**) and [Ru(dppm)(*p*-cymene)Cl]BF_4 (**2**) were synthesized as previously reported.[13]

NMR spectra were recorded on a Bruker Avance 400 spectrometer; ^1H chemical shifts were referenced to residual solvent peak, and ^{31}P chemical shifts were referenced to H_3PO_4 85%. Gas chromatography (GC) measurements were performed on a Varian Chrompack CP-3380 gas chromatograph equipped with a CP-sil 5CB column. Viscosity measurements were carried out at room temperature with a DV-II+ Brookfield viscometer.

Catalytic Experiments. In a home-built multicell autoclave equipped with magnetic stirrers, a solution of **1** or **2** (15×10^{-3} mmol) was dissolved in IL (1 mL) and styrene (2 mL), flushed three times with H_2, pressurized with 50 bar of H_2, and then heated to 80 °C. After 4 h at 80 °C, the hydrogenation reaction was stopped and the conversion was determined by GC analysis of the organic phase.

In a typical kinetic experiment, solutions of **1** (44×10^{-3} mmol) in IL (3 mL) with different amounts of chloride salt together with styrene (7 mL) were introduced in a single autoclave equipped with a magnetic stirrer and a pressure transducer connected to a digital data recorder. The reactor was flushed three times with H_2, heated to 80 °C. and pressurized with 50 bar of H_2 just before the monitoring of H_2 uptake was started. After the first run, the organic phase was decanted and the IL layer was reused for subsequent runs with a fresh solution of substrate. Conversion (conv) was determined by GC analysis of the organic phase. The number of moles of styrene at a given reaction time was calculated using the following equation:

$$n_{\mathrm{styr}}(t) = n_{\mathrm{styr}}(t_0)\left(1 - \frac{\mathrm{conv}}{\Delta p}(p(t_0) - p(t))\right) \tag{9}$$

where $\Delta p = p(t_0) - p_{\mathrm{final}}$.

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Supporting Information Available: ^{31}P NMR spectra of reaction mixture, derivation of eq 7, influence of ruthenium concentration on the rate of styrene hydrogenation, effect of base on the conversion, scheme of catalyst formation, as well as recycling experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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