

Fast Substitution Reactions of Pt(II) in Different Ionic Liquids. Reactivity Control by Anionic Components[†]Peter Illner,[‡] Svetlana Begel,[‡] Simon Kern,[‡] Ralph Puchta,^{‡§} and Rudi van Eldik^{‡*}

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The effect of several imidazolium-based ionic liquids on the rate and mechanism of the substitution reaction of [Pt(terpyridine)Cl]⁺ with thiocyanate was investigated as a function of thiocyanate concentration and temperature under pseudo-first-order conditions using stopped-flow and other kinetic techniques. The obtained rate constants and activation parameters showed good agreement with the ion-pair stabilization energies between the anions of the ionic liquids and the cationic Pt(II) complex derived from density-functional theory calculations (RB3LYP/LANL2DZp) and with parameters derived from the linear solvation energy relationship set by the Kamlet-Taft β parameter, which is a measure of a solvent's hydrogen bonding acceptor ability. In general, the substitution reactions followed an associative mechanism as found for conventional solvents, but the observed rate constants showed a significant dependence on the nature of the anionic component of the ionic liquid used as solvent. The second order rate constant measured in [emim][NTf₂] is 2000 times higher than the one measured in [emim][EtOSO₃]. This difference is much larger than observed for a neutral entering nucleophile studied before.

Introduction

The properties of ionic liquids (ILs) and their advantages and disadvantages are presently discussed extensively in terms of different kinds of possible applications.^{1–3} Their applicability in new technologies is being investigated, and some applications are already realized,^{4–6} whereas others may most probably never reach an implementation.⁷ They

are already used in homogeneous catalysis, as medium or as co-reactant, increasing the turnover or selectivity of such reactions. This gives rise to the question whether ILs do more than just serve as another solvent. Can they influence chemical reactions, and if so how, since some groups have reported an increase in reactivity, a changeover in mechanism, or a complete inhibition of the reaction.⁸ A further interesting aspect is the development of chiral ILs that can possibly facilitate the control of product chirality just by use of the right IL.⁹ Our goal is to quantify possible mechanistic changes and the origin of these changes when a typical reaction of a metal complex, extensively studied in conventional solvents before, is transferred into an IL. Since ILs differ significantly in their properties (viz. viscosity, melting point, coordinative properties, etc.), we selected four ILs with different solvent properties as summarized in Table 1. In

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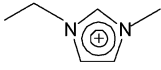
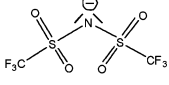
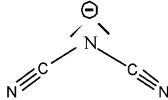
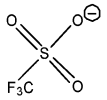
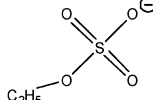
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Table 1. ILs Used in This Study and Some of Their Physical Properties¹⁰

	[emim][NTf ₂]	[emim][dca]	[emim][OTf]	[emim][EtOSO ₃]
Cation	Anion			
				
Color of IL	colorless	slightly yellow	slightly yellow	colorless
Miscibility with water	1.8 Mass. %	yes	yes	yes
Melting point [°C]	-17	-21	-12	-65
Viscosity [cP] (at 20 °C)	34	21 (at 25 °C)	45	120
Density [g/cm ³] (at 20 °C)	1.52	1.11	1.39	1.24

this way we should be able to detect essential differences between conventional solvents and ILs, and between different ILs in which only their anionic component is varied. The selected ILs are among the best studied to date and readily available. The purity of the ILs used was considered to be very important, since we found the solubility of reactants and their reaction rate to be very sensitive to even small quantities of impurities. For a test reaction to study the influence of ILs on typical substitution reactions of metal complexes in solution, it was desirable to select a simple, single step reaction for which no reverse, subsequent, or parallel reactions occur, to simplify the study and the interpretation of the data. In this way possible deviations from the expected substitution behavior of square planar complexes should be immediately noticeable. We selected a Pt(II) complex (see Figure 1) that was, along with some derivatives, studied in our group before in many different solvents and for various entering nucleophiles.^{11,12}

The complex has a labile Pt(II) center because of the influence of the π -acceptor properties of the terpyridine chelate by which electron density is drawn away from the metal center to make it more electrophilic and to enhance a nucleophilic attack by the entering ligand. On the basis of our earlier results, we expect a rapid displacement of chloride by a strong nucleophile such as thiocyanate that should proceed via an associative mechanism as it was found for

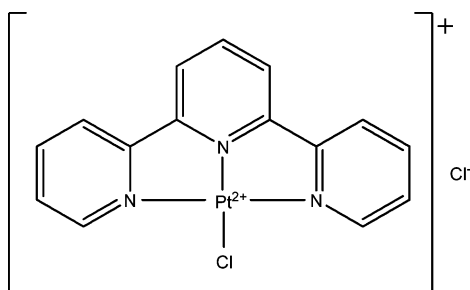


Figure 1. Schematic structure of chloro(2,2':6',2''-terpyridine)platinum(II) chloride, [Pt(ppp)Cl]Cl.

the systems studied so far.¹¹ The selected complex can therefore serve as a benchmark for other solvent systems that have not been studied before.

In a first study¹² we investigated the substitution reaction for a neutral entering ligand thiourea, observed a correlation between the stabilization of the cationic metal complex and the observed reaction rate, and observed a correlation with the β parameter derived from the linear solvation energy (LSE) relationship set by Kamlet–Taft.¹³ Thus, the attack by the uncharged nucleophile was affected by the properties of the ILs. We have now extended this work to the anionic nucleophile thiocyanate. The influence of ILs on a negatively charged nucleophile is expected to be even larger because the transition state of the substitution reaction involves charge neutralization which should be less favored in a solvent consisting of charged ions and could lead to a decrease in the reaction rate. Furthermore, a solvation shell consisting of negatively charged ions could form around the electrophilic complex and lead to repulsion of the entering charged nucleophile. And finally, the entering nucleophile could be

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highly solvated by the solvent molecules, since they are also charged ions, thus decreasing the nucleophilicity of the nucleophile and as a result, the reaction rate.

If one or more of these effects show up, we should be able to observe even larger differences than in the case of thiourea when compared to the behavior in aqueous medium.¹¹ Differences between the different ILs employed should also show up and enable us to estimate from which specific parameters or properties these differences originate.

Materials and Methods

Materials. All chemicals used were of analytical reagent grade and of the highest purity commercially available. NaSCN was used as a source for thiocyanate. The methanol used for kinetic investigations was purchased from Merck KGaA (Uvasol) with a water content of <200 ppm. The [Pt(ppp)Cl]Cl complex was synthesized and characterized as described in the literature.¹⁴ The organic solvents used for the preparation of the ILs were dried as described in the literature.¹⁵

Synthesis of the ILs. All operations were performed under nitrogen atmosphere. [emim][NTf₂] was synthesized according to an anion metathesis procedure described in the literature.¹⁶ [emim]Br and Li[bta] were obtained from Solvent Innovation, and [emim]Br was purified twice by recrystallization (before the metathesis reaction) and was obtained as white solid. The synthesized [emim][NTf₂] was treated with activated charcoal and dried under vacuum. [emim][OTf] and [emim][dca] were obtained from Solvent Innovation and purified before use by treating them with activated charcoal, drying under vacuum for 3–4 days, and finally storing them over a molecular sieve. [emim][dca] had to be cleaned of Na[dca] leftovers from the synthesis. This was achieved by addition of a 3-fold excess of dry dichloromethane to the liquid to precipitate Na[dca] and subsequent filtering. [emim][EtOSO₃] was also obtained from Solvent Innovation and dried under vacuum for 10 days before use. The water content determined by Karl Fischer titration was found to be 50–70 ppm in the case of [emim][NTf₂], 50 ppm for [emim][OTf], and 70 ppm for [emim][dca]. The water content of [emim][EtOSO₃] was adjusted to 1500 ppm to reduce the viscosity of the highly viscous IL.

Recently, a question was raised regarding the spontaneous decomposition of the [EtOSO₃][−] anion in [emim][EtOSO₃] that leads to ethanol and hydrogensulfate.¹⁷ It was reported that during long-term storage this saponification reaction can lead to a hydrogensulfate content of up to 26%. As the presence of hydrogensulfate anions could significantly affect the properties of the IL (such as viscosity or solubility of substrate), the hydrogensulfate concentration in the IL used throughout this study was determined using ion chromatography and NMR methods (see Supporting Information, Figure S1 and S2). The NMR spectra showed no decomposition of the ethylsulfate anion and no formation of ethanol. The ion chromatogram¹⁸ showed a sulfate concentration

of only 2 ppm, which is negligible and argues against decomposition of the ethylsulfate anion under our reaction conditions. This may be related to our storage conditions that excluded humidity under a permanent atmosphere of dry nitrogen.

Density-Functional Theory (DFT) Calculations. All structures were fully optimized using the B3LYP hybrid density functional^{19–21} and the LANL2DZ basis set augmented with polarization functions further denoted as LANL2DZp,^{22–27} and characterized as minima or transition state structures by computation of vibrational frequencies (for minima, all frequencies are positive, NImag = 0). The influence of bulk solvent was probed by single point calculations using the CPCM formalism²⁸ with water as solvent, that is, B3LYP(CPCM)/LANL2DZp//B3LYP/LANL2DZp. All energies were corrected for zero point energies. The Gaussian 03 suite of programs was used throughout.²⁹

Instrumentation and Measurements. Karl Fischer titrations were done on a 756 KF Coulometer. Elemental analyses (Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba)), and NMR spectroscopy (Bruker Avance DRX 400WB FT-spectrometer) were used for chemical analysis and compound characterization, respectively. The UV–vis spectra of the studied ILs were recorded on a Varian Cary 1G spectrophotometer equipped with a thermostatted cell holder. For kinetic measurements on fast reactions, a Durrum D110 (Dionex) stopped-flow instrument was used. The temperature

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of the instruments was controlled within an accuracy of ± 0.1 K. For kinetic measurements on slow reactions in the case of [emim][EtOSO₃], a Varian Cary 1G spectrophotometer equipped with a thermostatted cell holder was used. Thiocyanate was selected as an entering nucleophile since its high nucleophilicity should prevent a possible back reaction as in the case of thiourea.³⁰ The ligand substitution reactions were studied under pseudo-first-order conditions by using at least a 10-fold excess of SCN⁻. All listed rate constants represent the average value of at least six kinetic runs in the case of the stopped-flow experiments and four kinetic runs in the case of the slow reactions measured in tandem cuvettes on the UV-vis spectrophotometer.

Preparation and Analysis of the Measurements. All test solutions of ILs were degassed prior to the measurements to prevent formation of gas bubbles. The Pt(II) complex was added to the ILs and stirred overnight for all the ILs. The complex concentration was throughout around 0.3 mM in all ILs. NaSCN dissolved readily in the ILs used. Since the ILs consist entirely of cations and anions, no ionic strength adjustment was made.

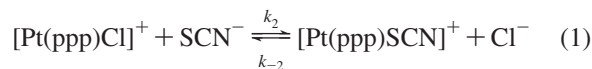
In the methanolic solutions the ionic strength was adjusted to 100 mM by addition of LiCF₃SO₃. A pH value of 2 was obtained by addition of CF₃SO₃H to prevent formation of the alcoholate complex. The Pt(II) complex had a concentration of 0.05 mM in the methanolic solution, and a 10-fold excess of LiCl (0.5 mM) was added to prevent spontaneous hydrolysis of the complex. The kinetic traces obtained were fitted with Origin 7. The kinetic traces recorded in the ILs with [dca]⁻, [TfO]⁻ and [EtOSO₃]⁻ anions fitted very well to a single-exponential function, in line with the predicted pseudo-first-order behavior of reaction 1. The kinetic traces recorded in [emim][NTf₂] and methanol showed a subsequent slow reaction and had to be fitted with two exponential functions to correct for this.

Results and Discussion

Since polarity plays an important role in all substitution reactions involving metal complexes,³¹ we correlated our data with polarity parameters obtained from a recent study by Spange et al.³² They used the polarity parameter β , derived from the linear solvation energy (LSE) relationship set by Kamlet-Taft, as a measure for hydrogen bond acceptor basicity, for a series of different imidazolium-based ILs, including the four ILs used in this study. Although this parameter was measured for ILs with [bmim]⁺ cations, the difference with our systems including the [emim]⁺ cation should only be marginal as the alkyl side-chain should not interfere with the hydrogen bond acceptor ability. To compare the measurements done in ILs with measurements in conventional solvents, the measurements were also performed in methanol, as a representative example for a molecular, protic solvent. The literature value for the β parameter of methanol is 0.66, but since a different set than the commonly used set of solvatochromic dyes was used to determine this value for the ILs, we calculated the β parameter for methanol according to the reported equation,³² using literature data for the absorption of the used dye in

methanol measured elsewhere,³³ and found a value of 0.50 for the β parameter of methanol. This parameter was used throughout for a better comparison with the values determined for the ILs, since there are large differences in these empirical values depending on the set of dyes used.^{32,34,35}

A detailed kinetic study of the substitution reaction of the [Pt(ppp)Cl]Cl complex (Figure 1) with SCN⁻ as entering nucleophile was performed in the ILs [emim][NTf₂], [emim][dca], [emim][OTf], [emim][EtOSO₃], and in methanol. The overall reaction is given in eq 1.



During the substitution process a neutral transition-state is formed. As ILs are highly charged solvents, a direct influence on the rate and activation parameters should be observed. The reaction was studied as a function of the nucleophile (SCN⁻) concentration and temperature to determine the rate constants (k_2 and k_{-2}) and the activation parameters (ΔH^\ddagger and ΔS^\ddagger). The solvent dependence of reaction 1 was studied by dissolving the isolated complex in the selected solvents and determining the rate constants and activation parameters for the reaction with thiocyanate in each solvent. Typical examples of the observed spectral changes and kinetic traces are shown in Figures 2 and 3, respectively. The spectral changes, examples for kinetic traces, and concentration and temperature dependences for the other ILs are reported in Supporting Information, Figures S3 to S11. The overall spectral changes were found to depend on the IL used. The wavelengths used for kinetic measurements are listed in Table 2.

The kinetic traces recorded in the ILs with [dca]⁻, [TfO]⁻, and [EtOSO₃]⁻ anions fitted very well to a single-exponential function, in line with a pseudo-first-order behavior of reaction 1 (see Figure 3). The kinetic traces recorded in [emim][NTf₂] and methanol showed a subsequent reaction and had to be fitted with a two-exponential function to correct for this (see Supporting Information, Figures S6 and S7). The subsequent reaction is considerably slower than the first substitution process and does not interfere with the first reaction. As the second reaction also showed a dependence on the SCN⁻ concentration (see Supporting Information, Figures S12 and S13), it could involve a second substitution step similar to reactions of different Pt(II) complexes with N-donor chelate ligands, where strong sulfur containing nucleophiles like thiourea or L-methionine are able to substitute the chelate partially or completely.³⁶ The calculated structure of a doubly substituted complex where one of the pyridine rings of the chelate is bent away from the plane, is given in Figure 4.

The square-planar geometry of the [Pt(ppp')(SCN)₂] complex is slightly distorted. The calculations predicted the conformation with a ring-opened terpyridine chelate to be about 25 kJ/mol more stable than the 5-fold coordinated

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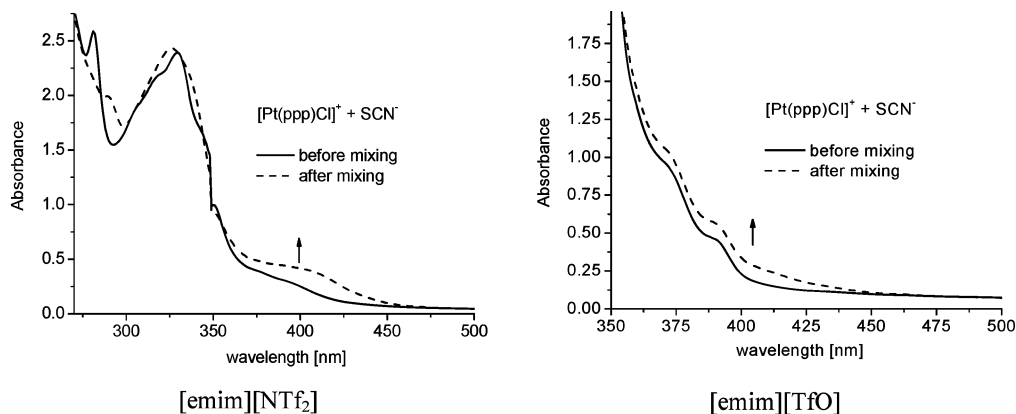


Figure 2. Spectral changes observed for the reaction of [Pt(ppp)Cl]⁺ with thiocyanate in [emim][NTf₂] and [emim][TfO].

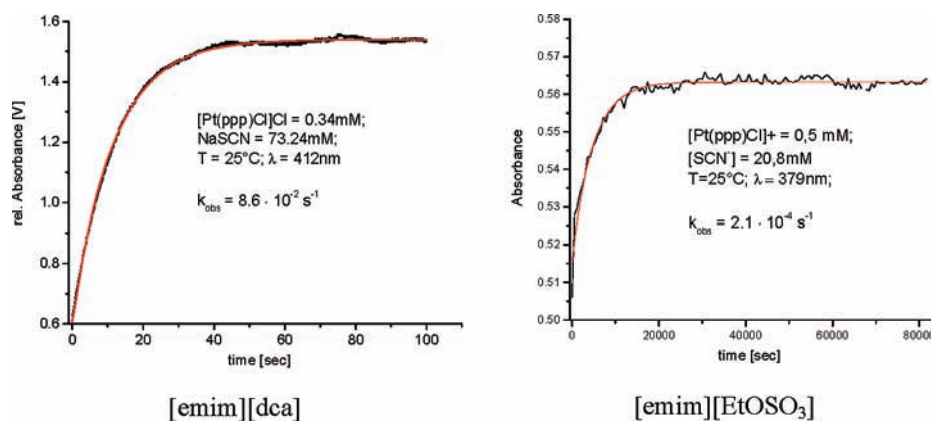


Figure 3. Typical kinetic traces recorded for reaction 1 in [emim][dca] and [emim][EtOSO₃].

Table 2. Wavelengths Selected for the Kinetic Measurements in the Different Solvents

solvent	methanol	[emim][NTf ₂]	[emim][dca]	[emim][TfO]	[emim][EtOSO ₃]
selected wavelength	343 nm 360 nm	410 nm	412 nm	394 nm	362 nm 379 nm

transition state. The theoretically possible dechelation at the inner pyridine position leading to [Pt(pp'p)(SCN)₂] was not observed during the calculations. This is in accordance with the expectation that dechelation will occur at one of the end pyridine groups because of the stability of the partially chelated ligand.

The calculated pseudo-first-order rate constants for reaction 1 were plotted against the thiocyanate concentration and showed a linear dependence with a negligible intercept for all solvents studied. Typical plots are presented in Figure 5, from which it can be concluded that $k_{-2} \approx 0$, which means that no meaningful back reaction occurs.

The observed rate constant can be expressed as a function of the concentration of the entering ligand, namely, $k_{\text{obs}} = k_2[\text{SCN}^-]$, where k_2 is the second-order rate constant for the forward reaction in equation 1. The values of k_2 for the substitution of chloride by thiocyanate in [Pt(ppp)Cl]⁺ in different ILs are summarized in Table 3. For comparison, this table also contains kinetic data for the investigated reaction in methanol. Measurements in water were not possible because the complex is not soluble in an aqueous medium containing other salts to adjust the ionic strength. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) for k_2 , determined

from the temperature dependence studies (see typical examples shown in Figure 6), are also included in Table 3.

The k_2 values for reaction 1 determined in the ILs differ by 3 orders of magnitude and are at least ten times smaller than in methanol. In general the decrease in k_2 is accompanied by an increase in both ΔH^\ddagger and ΔS^\ddagger . They are also at least five times smaller than the k_2 values reported for the reaction with thiourea in the same solvents.¹² The largest difference is found for [emim][EtOSO₃], where the reaction with thiourea is 1300 times faster than the reaction with thiocyanate.

A certain deceleration of the reaction rate on changing from a neutral to a negatively charged nucleophile was expected on the basis of the Hughes–Ingold rules.^{37,38} If the metal complex and the nucleophile are of opposite charge, the transition state for an associative mechanism is neutral and thus less favored in a solvent that has a high ionic strength. A destabilizing effect arises from the partial or complete desolvation during the formation of the transition state from the charged nucleophile and complex, which are normally well solvated in solutions of high ionic strength

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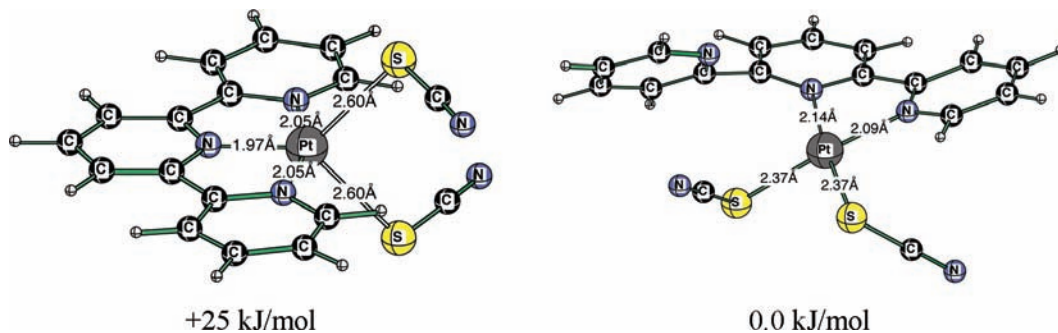


Figure 4. Schematic presentation of $[\text{Pt}(\text{ppp}')(\text{SCN})_2]$.

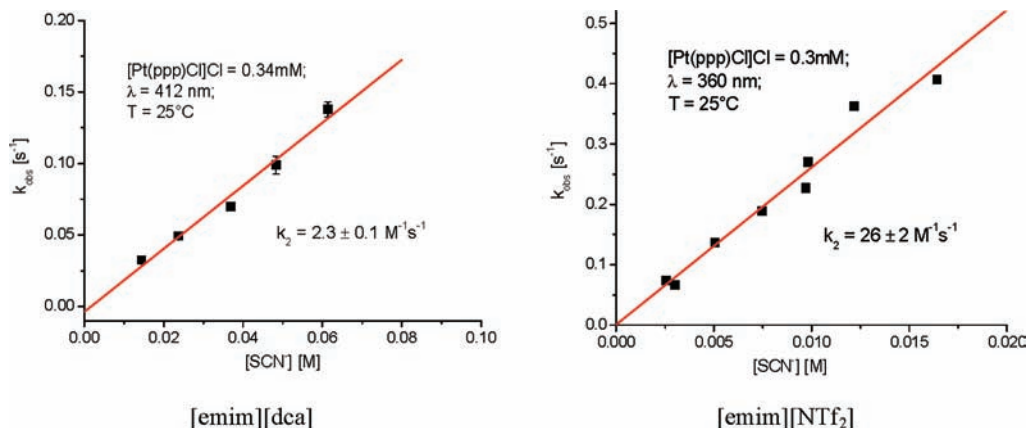


Figure 5. Typical concentration dependences for reaction 1 in $[\text{emim}][\text{dca}]$ and $[\text{emim}][\text{NTf}_2]$.

Table 3. Summary of Rate and Activation Parameters for the Reaction between $[\text{Pt}(\text{ppp})\text{Cl}]^+$ and Thiocyanate in Different ILs and Methanol As Solvent

solvent	k_2 at 25 °C $[\text{M}^{-1} \text{s}^{-1}]$	ΔH^\ddagger $[\text{kJ mol}^{-1}]$	ΔS^\ddagger $[\text{J K}^{-1} \text{mol}^{-1}]$
methanol	299 ± 7	39 ± 1	-72 ± 3
$[\text{emim}][\text{NTf}_2]$	26 ± 2	44 ± 2	-69 ± 5
$[\text{emim}][\text{dca}]$	2.3 ± 0.1	51 ± 1	-74 ± 3
$[\text{emim}][\text{OTf}]$	2.7 ± 0.2	62 ± 1	-34 ± 5
$[\text{emim}][\text{EtOSO}_3]$	$(1.32 \pm 0.08) \times 10^{-2}$	78 ± 2	-15 ± 7

and thus stabilized. Thus the ground state of the reactants (and eventually the products) is stabilized, whereas the transition state is destabilized, which increases the activation barrier and decelerates the reaction. This accounts for the observed deceleration of the reaction with thiocyanate as compared to thiourea and also for the difference between methanol and the ILs. However, why is there such a large difference between the reaction rate for the “fastest” IL $[\text{emim}][\text{NTf}_2]$ and the “slowest” IL $[\text{emim}][\text{EtOSO}_3]$?

In the case of thiourea as nucleophile, we correlated our data with one of the parameters introduced by Kamlet and Taft as a measure for a liquid’s hydrogen bond acceptor ability, namely, the β -value (see Table 4). This parameter was determined in the original study³² for a different dye that allowed to investigate highly colored ILs more easily.

A correlation between $\ln(k_2)$ for reaction 1 and the β value of the solvent is shown in Figure 7. The general trend observed from this figure is the reduction of the reaction rate with increasing β value. The observed reaction rate seems to be linked to the hydrogen bond acceptor ability of the IL or, more general, of the solvent used. A higher hydrogen bond acceptor ability results in a stronger interac-

tion with the positively charged Pt(II) complex by which it is stabilized. This means that a higher β value correlates with a stabilization of the reactants and products and a destabilization of the transition state.

For a series of ILs with the same cation, the increase in the β value is directly linked to a decrease in the α value (see Figure 8), the hydrogen bond donor ability of a solvent.^{35,39} An increase in the β value means a decrease in the α value and thus a lower hydrogen bond donor ability of the solvent.³⁵ In contrast to small anions with a high charge density, large anions which have a dispersed charge like thiocyanate, iodide, or picrate are better solvated by dipolar non-hydrogen bond donor solvents with a low α value.³⁹ This means in our case that a solvent with a lower α value and thus a higher β value should establish stronger interactions with the anionic nucleophile thiocyanate and thus hinder nucleophilic attack.⁴⁰ A strongly solvated nucleophile is restricted in its mobility and less nucleophilic. This is in agreement with the decrease in reaction rate on changing to a solvent with a higher β value, for example, $[\text{emim}][\text{EtOSO}_3]$.

A correlation of the enthalpy of activation versus the β value (Figure 9) confirms the influence on the activation barrier of the reaction. The higher the β value, the higher the activation enthalpy, thus decreasing the rate of the reaction. This is in agreement with the decrease in reaction rate with increasing β value. The reactants and products are

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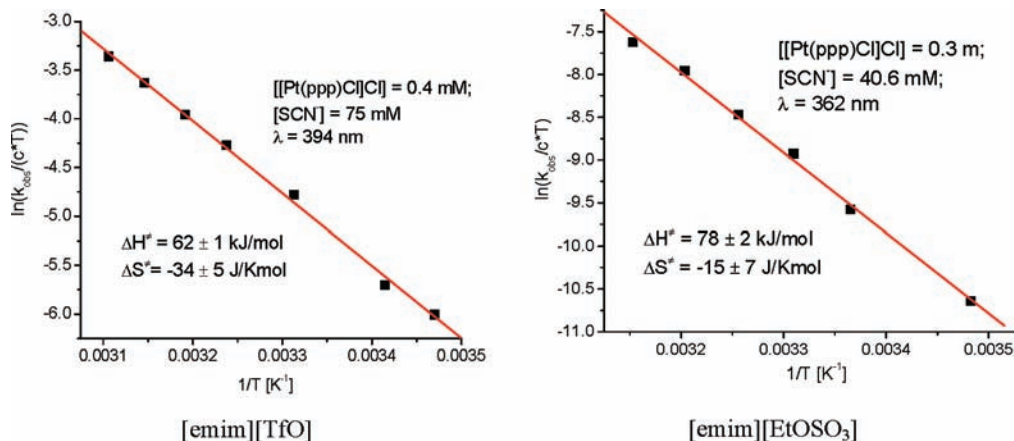


Figure 6. Typical Eyring plots for reaction 1 in [emim][TfO] and [emim][EtOSO₃].

Table 4. β Values for the Selected ILs and Methanol

solvent	methanol	[emim] [NTf ₂]	[emim] [dca]	[emim] [OTf]	[emim] [EtOSO ₃]
β -value ³²	0.50 ^a	0.42	0.64	0.57	0.71

^aThe value for methanol was calculated according to spectra and equations reported in the literature.^{13,32,33}

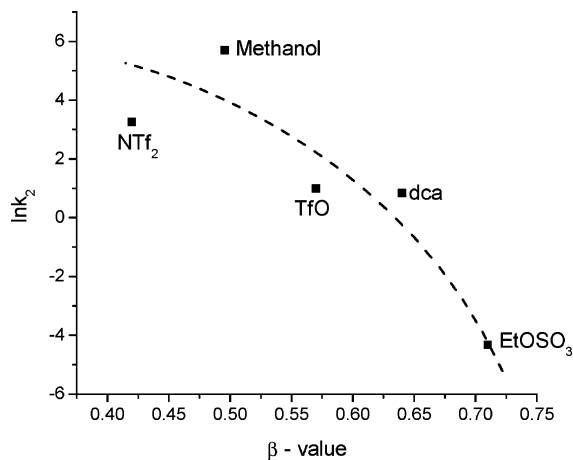


Figure 7. Correlation of $\ln(k_2)$ for reaction 1 with the β value.

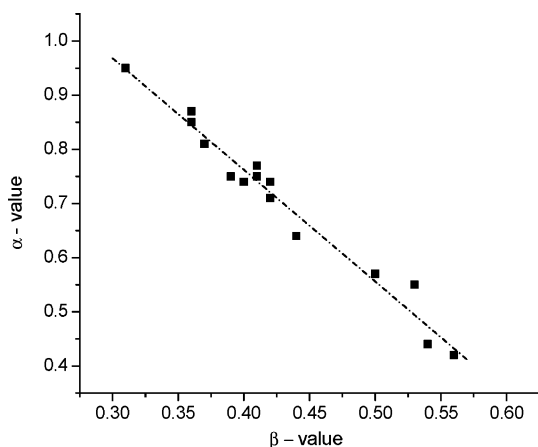


Figure 8. Linear correlation between the α and β values of the investigated [bmim]⁺ ILs.⁴⁵

better stabilized than the transition state, and as the energy of the reactant is reduced, the activation barrier is increased. Thus, the activation enthalpy can be readily correlated with the β value, whereas a rather different dependence is

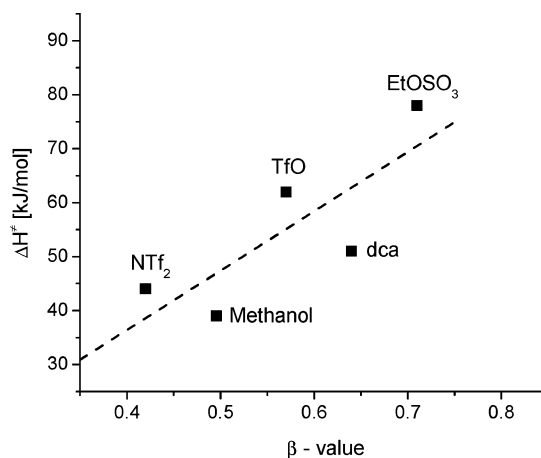


Figure 9. Correlation of the enthalpy of activation versus the β value.

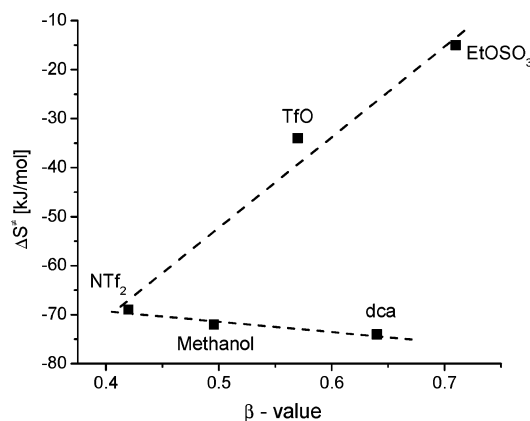


Figure 10. Correlation of the activation entropy versus the β value.

observed when the activation entropy is plotted against this polarity parameter (Figure 10).

Two different trends are observed in Figure 10. The triad consisting of [emim][NTf₂], [emim][TfO], and [emim]-[EtOSO₃] shows an increase in activation entropy with increasing β value. The triad consisting of [emim][NTf₂], methanol, and [emim][dca] shows nearly no change in activation entropy. The activation entropy consists of an intrinsic and a solvational term as summarized in eq 2. The intrinsic term is the sum of all entropy changes caused by changes in bond lengths and bond angles on formation of the activated complex. This should be almost the same for

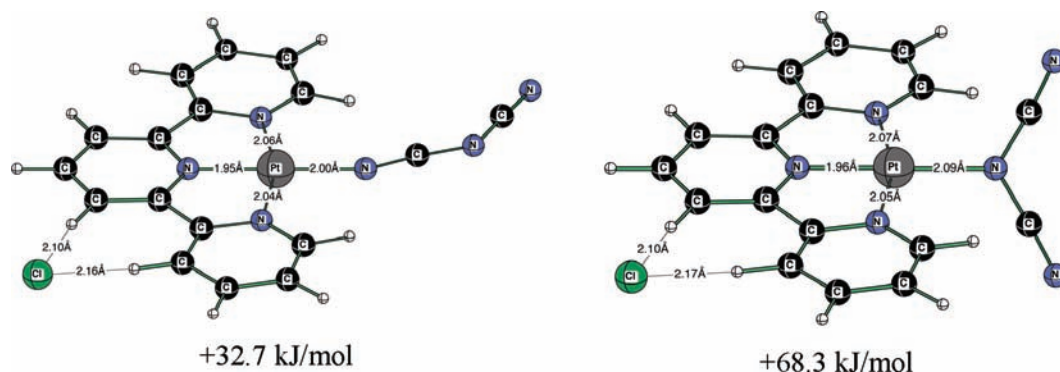


Figure 11. Calculated terminal (left) and central (right) coordination modes of [Pt(ppp)dca]Cl; energy values compared to [Pt(ppp)Cl]dca.

Table 5. Comparison of the Relative Stability for the [dca]⁻ and [NTf₂]⁻ Complexes (in kJ/mol)

	B3LYP/LANL2DZp // B3LYP/LANL2DZp + ZPE(B3LYP/LANL2DZp)				
[Pt(ppp)Cl]dca	0.0	[Pt(ppp)dca _{cent}]Cl	+ 68.3	[Pt(ppp)dca _{term}]Cl	+ 32.7
[Pt(ppp)Cl]NTf ₂	0.0	[Pt(ppp)NTf _{2-N}]Cl	+ 106.9	[Pt(ppp)NTf _{2-OO'}]Cl	+ 139.3
	B3LYP(CPCM)/LANL2DZp // B3LYP/LANL2DZp + ZPE(B3LYP/LANL2DZp)				
[Pt(ppp)Cl]dca	0.0	[Pt(ppp)dca _{cent}]Cl	+ 41.7	[Pt(ppp)dca _{term}]Cl	+ 3.7
[Pt(ppp)Cl]NTf ₂	0.0	[Pt(ppp)NTf _{2-N}]Cl	+ 75.6	[Pt(ppp)NTf _{2-OO'}]Cl	+ 101.4

all studied solvents, as the complex and the entering nucleophile remain the same. The solvational term is related to changes in electrostriction on going from the reactant to the transition state. Changes due to charge formation or charge neutralization, and also dipole formation or an increase in polarizability, can cause changes in the solvation shell and thus the activation entropy (and activation volume).

$$\Delta S^\ddagger = \Delta S_{\text{intr}}^\ddagger + \Delta S_{\text{solv}}^\ddagger \quad (2)$$

If, as in our case, two charged molecules form a neutral transition state, the solvating molecules will be released on going to the transition state. A larger number of solvent molecules bound to the reactant molecules before formation of the transition state should result in a larger increase in entropy (and volume) during the activation process. Furthermore, in ILs where all the solvent molecules are charged, the effect should be even larger since during formation of the transition state the strong interaction of oppositely charged reactant species with the solvent completely vanishes.

From Figure 10 we can conclude that the ethylsulfate or triflate containing ILs are bound stronger to the solutes than the ILs containing [dca]⁻ and [NTf₂]⁻, as a much larger increase in entropy is observed in this case. The interaction of [dca]⁻ and [NTf₂]⁻ with the metal complex could be less favored because of the structure of these anions. Dicyanamide has a repulsive π -system and a negative charge located on one nitrogen atom, whereas [NTf₂]⁻ has a sterically shielded negative charge also located on a single nitrogen atom. Thus both anions could be less favored for interaction with the Pt(II) center in contrast to the sulfate derivatives.

The abnormality of the activation entropy value found for [emim][dca] could also originate from the relatively high nucleophilicity of [dca]⁻ compared to that of the other IL anions. As reported in our earlier study,¹² we have direct spectroscopic evidence for the displacement of the chloride ligand in [Pt(ppp)Cl]⁺ by [dca]⁻ on addition of Na[dca] to an aqueous solution of this complex. We also considered the nucleophilicity of the anions of the other ILs and the

possibility of their coordination to the Pt(II) center replacing the chloride ligand. The [NTf₂]⁻ anion has several possible coordination options⁴¹ due to the negatively charged nitrogen atom and the electron pairs on the oxygen atoms. Therefore, the possible coordination of this potential ligand had to be checked as well, although no spectroscopic evidence for its coordination is available. The two anions of the other ILs, namely, [TfO]⁻ and [EtOSO₃]⁻, are expected to be very weak nucleophiles and were not investigated further. To check the plausibility of ligand displacement in [emim][dca] and [emim][[NTf₂]⁻], DFT calculations of the complex with coordinated chloride and thiocyanate, and of the complexes where the anions of the ILs are coordinated, were compared.

In the case of [dca]⁻ two coordination modes are possible, namely, one via the negatively charged central nitrogen atom and one via the terminal nitrile groups (see Figure 11). The terminal coordination mode turned out to be 35.7 kJ/mol more stable than the other one, but overall the coordination seems not to be favored since the chloride containing complex is 32.7 kJ/mol more stable than the terminal mode (see Table 5) and 68 kJ/mol more stable than the central coordination mode. However, if in the comparison between the chloride and the terminal dca complex the CPCM solvent simulation is included, the chloride complex is only 3.7 kJ/mol more stable. This difference is only marginal such that when the complex is dissolved in [emim][dca], the IL anion is present in such a large excess that a displacement of chloride could be favored. However, if the chloride anion is displaced by the [dca]⁻ anion in the first place, the substitution reaction with thiocyanate nevertheless proceeds as observed experimentally. By calculating the energy differences, we found the [Pt(ppp)dca]SCN complex to be 12.2 kJ/mol less stable than the [Pt(ppp)SCN]dca complex.

In the case of [NTf₂]⁻ coordination via the negative charged nitrogen atom ($\eta^1\text{-N}$), coordination via one oxygen atom ($\eta^1\text{-O}$), coordination via two oxygen atoms ($\eta^2\text{-O,O'}$), or even via oxygen and nitrogen ($\eta^2\text{-O,N}$) are theoretically possible (see Figure 12).⁴¹ The results show that all these

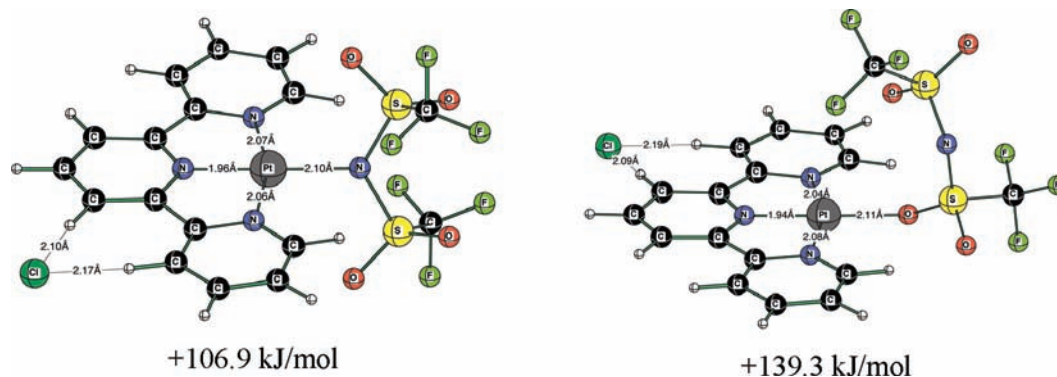


Figure 12. Calculated η^1 -N (left) and η^2 -O,O' (right) coordination modes of [Pt(ppp)NTf₂]Cl; energy values compared to [Pt(ppp)Cl]NTf₂

Table 6. Stabilization Energies of the Complex-Anion Interaction for the Different ILs¹²

IL anion	[NTf ₂] ⁻	[dca] ⁻	[TfO] ⁻	[EtOSO ₃] ⁻
ΔE [kJ/mol]	-287.0	-293.3	-300.0	-315.5

structures are clearly energetically unfavored compared to the chloride containing complex. The (η^1 -N)-mode is 106.9 kJ/mol and the (η^2 -O,O')-mode is 139.3 kJ/mol less stable than the chloride complex. When the CPCM solvent simulation is incorporated, the differences decrease to 75.6 kJ/mol for the (η^1 -N)-mode and 101.4 kJ/mol for the (η^2 -O,O')-mode, but still the chloride complex is greatly favored, so that even under a large excess of [NTf₂]⁻ no chloride displacement is likely to occur.

On the basis of these calculations, it follows that a severe influence on the mechanism can occur in [emim][dca]. However, as we found from the correlations with the β parameter, not only a substitution process but also interactions of ion pairs can result in profound changes in reaction rates. We, therefore, also calculated the ion pair stabilization energy between the IL anions and the Pt(II) complex to gain further insight on solute–solvent interactions as introduced in a previous paper.¹² Our computations indicated a strong influence of the anion on the anion–cation stabilization energy. We calculated the energies (in the gas phase) of the separated ions of the ILs and compared these with the energies of the ion pairs. We found large differences depending on the nature of the anion. If the cation–anion interaction of the IL is influenced or even controlled by the anion, the stabilization of dissolved cations such as the Pt(II) complex should also be influenced. We calculated the energies of complex-anion ion pairs, compared these values with the separated ions, and calculated the difference (Table 6) for the ion pair stabilization energy.¹²

Although the energies are surely exaggerated because of Coulomb attraction and because the values do not include dispersion, we do find good correlations with experimental properties. The ion pair stabilization energy significantly differs over a range of about 30 kJ/mol changing from [NTf₂]⁻ to [EtOSO₃]⁻. The numbers also show that [NTf₂]⁻ and [dca]⁻ are only slightly coordinative. The calculations account for the [NTf₂]⁻ and [dca]⁻ anion to interact more with the terpyridine ligand than with the Pt(II) center, reflected in a position occupied by the anion not perpendicular above the metal center but shifted more to a position

above the central pyridine unit. In contrast to this, the [TfO]⁻ and [EtOSO₃]⁻ anions show a preferred interaction with the Pt(II) center reflected in an higher interaction energy and a position perpendicular above the metal center at a rather short distance (2.9 Å to 3.0 Å). If the position of the anions in solution is similar to the calculated gas phase structure, nucleophilic attack by an entering ligand could be blocked to some extent since the [TfO]⁻ and [EtOSO₃]⁻ anions sterically protect the reactive center. Thus, the interacting IL anion first has to be removed from its blocking position for nucleophilic attack to occur. The higher the interaction energy of the anion, the slower the associative ligand substitution reaction and the higher its activation barrier (consisting of ΔH^\ddagger and ΔS^\ddagger), as shown in Figure 13.

In summary, both the interaction energy and the influence of the hydrogen bond acceptor ability influence the reaction. A stronger interaction of the solvent molecules with the dissolved species results in a decrease in the reaction rate, thus confirming the findings of the study with the uncharged nucleophile thiourea.¹² The anions of the ILs seem to play a crucial role in this context, as they seem to differ in their ability to interact with the Pt(II) complex. The largest difference exists between the [NTf₂]⁻ and [EtOSO₃]⁻ anions, which differ in their hydrogen bond donor ability and their stabilization ability, which leads to the difference in the reaction rate measured in these solvents. Overall, the reaction is slower in the ILs with oxosulfur derivatives ([emim]-[EtOSO₃] and [emim][TfO]) that possess an oxygen donor atom for interaction with the metal complex, in contrast to the two other ILs ([emim][NTf₂] and [emim][dca]) that possess a nitrogen donor atom. This suggests that the nature of the donor atom of the anionic component of the ILs is a crucial factor for the interaction with the electrophilic metal complex and thus for the overall reaction velocity. Further

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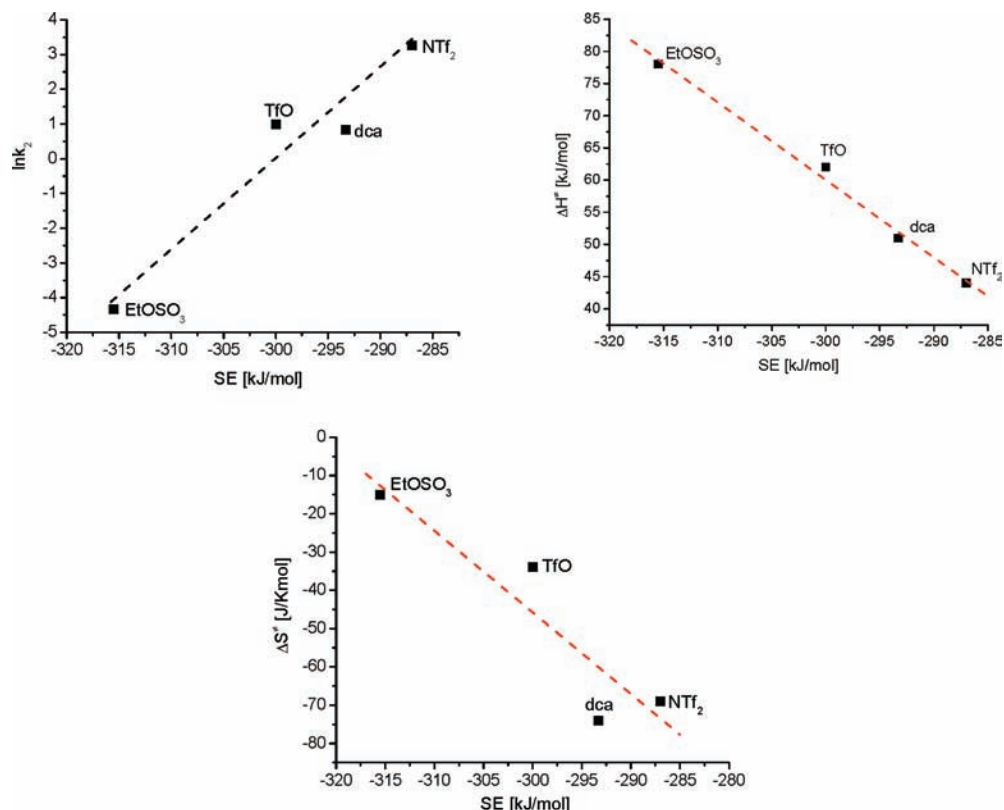


Figure 13. Plots of $\ln k_2$, ΔH^\ddagger , and ΔS^\ddagger versus the calculated ion pair stabilization energy (SE).

investigations with different ILs that contain completely different anions such as $[\text{CF}_3\text{BF}_3]^-$,⁴² $[\text{AlCl}_4]^-$,⁴³ $[\text{FAP}]^-$ (tris(perfluoroethyl)trifluorophosphate anion),⁴⁴ or with sulfur donors⁴⁵ could reveal more insight on this.

Conclusions

The results obtained demonstrate clearly that conventional research methods can be applied in the study of ILs as done for conventional molecular solvents. In the present case the numerical values indicate that there is no back reaction ($k_{-2} \approx 0$), and the forward reaction has an associative character ($\Delta S^\ddagger \ll 0$). We found evidence that the reaction rates in different ILs differ considerably from those in conventional molecular solvents. A likely reason is the influence of the anionic component of the IL that interacts with the positively charged metal complex and solvation effects in the IL that affect the nucleophilicity of the nucleophile. Furthermore, the nature of the anion of the IL seems to play a crucial role, as some anions, particularly those with oxygen donor atoms, decelerate reactions with uncharged nucleophiles, as well as reactions with charged ones, much more than other anions.

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Supporting Information Available: The ion chromatogram and NMR spectrum of $[\text{emim}][\text{EtOSO}_3]$ are given in Figures S1 and S2. Spectral changes, examples for kinetic traces, concentration and temperature dependences for the ILs not shown in the text are given in Figures S3 to S11. The concentration dependence of the subsequent reaction only observed in methanol and $[\text{emim}][\text{NTf}_2]$, is reported in Figures S12 and S13 (five pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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