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Mechanistic Studies on Fast Ligand Substitution Reactions of Pt(II) in Different Ionic Liquids: Role of Solvent Polarity and Ion-Pair Formation

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The effect of several imidazolium-based ionic liquids on the mechanism of a classical ligand substitution reaction of $[Pt(terpyridine)Cl]^+$ with thiourea was investigated. A detailed kinetic study as a function of the nucleophile concentration and temperature was undertaken under pseudo-first-order conditions using stopped-flow techniques. Polarity measurements were performed for the employed ionic liquids on the basis of solvatochromic effects, and they show similarities with conventional polar solvents. Density-functional theory calculations (RB3LYP/LANL2DZp) were employed to predict the ion-pair stabilization energy between the ionic components of the ionic liquids and/or between the anions of the ionic liquids and the cationic Pt^{II} complex. These data illustrate how the anions of the ionic liquids can affect the investigated substitution reaction. In general, the substitution mechanism in ionic liquids was found to have an associative character similar to that in conventional solvents. The observed deviations reflect the influence of the ionic liquid on the interaction between the anionic component of the liquid and the positively charged complex.

Introduction

We have developed an interest in the effect of ionic liquids (ILs) as a reaction medium on ligand substitution reactions of transition metal complexes because of their potential role in tuning the catalytic activity of metal complexes in processes involving ligand substitution reactions.[1,2] ILs are low-temperature (<100 °C), molten organic salts that represent a novel category of solvents with nonmolecular ionic properties. Over the last two decades ILs have been investigated extensively as solvents for transition metal catalyzed reactions. It was shown that the replacement of conventional organic solvents by ILs can result in a noteworthy improvement of existing procedures and can lead to a novel and unusual chemical reactivity.[2–5] Moreover, these solvents exhibit interesting physical properties, and the lack of appreciable vapor pressure illustrates their environmental-friendliness.[6–8]

Although ILs present a continuously growing area of research, the exact nature of the processes that occur within these liquids is presently not completely understood. An important question is whether the changeover from a conventional solvent to an IL can lead to a significant influence on, or even a modification of, the underlying reaction mechanism. ILs differ significantly in physical properties from classical solvents, on which basis one would expect such modifications, which can only be excluded following accurate and detailed investigations. Mechanistic studies on inorganic/bioinorganic reactions in ILs as solvents

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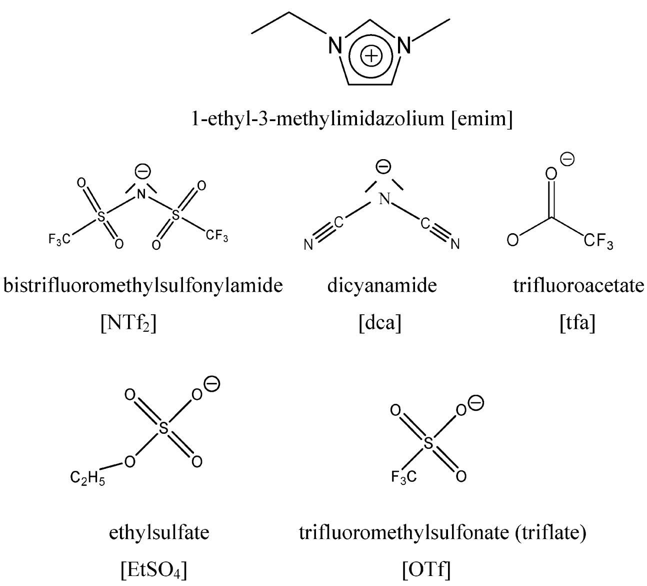
stand at the center of our present interest. The time has come where ILs should not be employed on a trial and error basis, but rather on the basis of a well-founded mechanistic understanding.

In addition, many ILs have not been sufficiently explored in a systematic manner, with the result that important data, essential to complete the characterization of the properties of the medium, are still missing. Because such characterizations are required for mechanistic investigations, the study of solvent polarity of the employed ILs as a function of temperature and pressure forms an important part of the present work. Furthermore, we report the calculated ion-pair stabilization energies of the ion-pairs in the ILs and their correlation with experimentally measured NMR data. We also report computed energies for the possible interactions between the anions of the investigated ILs and the positively charged metal complex.

The best way to investigate the potential influence of an IL as solvent on the mechanism of a reaction is to use well-studied reactions as test systems to ensure that the observed deviations and/or changes in the chemical system are caused by the applied IL. We report here detailed studies on the substitution reaction of a very labile Pt^{II} complex. Ligand substitution reactions of square-planar complexes of d^8 metal ions such as Pt^{II} and Pd^{II} play a fundamental role in many chemical processes, for instance in the treatment of tumors and in homogeneous catalysis.[9,10] For this reason they are among the best investigated dynamic processes.[11] Up to now the kinetic and thermodynamic data show that in nearly all cases the substitution mechanism has an associative character, according to which the entering nucleophile forms a bond with the metal center prior to bond cleavage with the leaving group, and therefore involves an increase in the coordination number of the Pt center from four to five in the transition state.[11,12]

Mechanistic studies on the behavior of Pt^{II} complexes have a long tradition in our group.[13] For example, we recently studied the influence of different solvents on ligand substitution reactions of Pt^{II} complexes as a function of the π-acceptor properties of the spectator chelate.[14] Moreover, we examined the influence of an ionic liquid ([bmim][NTf_2]) on substitution reactions of [Pt(apa)Cl]Cl complexes.[15] The presented work will complete and extend these studies with ligand substitution on another, much more labile Pt^{II} complex, namely, [Pt(ppp)Cl]Cl where ppp = $2.2':6',2''$-terpyridine, used as a test system. The high lability of this complex results from the strong π-back bonding by the three in-plane pyridine rings that causes a strong increase in the electrophilicity of the metal center.[13e] This was done in different ILs consisting of the $[emim]^+$ cation and a series of anions, namely, $[NTf_2]^-$, $[dca]^-$, $[OTf]^-$, and $[EtSO_4]^-$. The structure and physical properties of the ILs under investigation are presented in Scheme 1 and Table 1, respectively.

Scheme 1. Schematic Structure of the ILs under Study



Materials and Methods

Materials. All chemicals used were of analytical reagent grade and of the highest purity commercially available. The solvatochromic Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate hydrate, was obtained from Aldrich and phenol blue (N,N-dimethylindoaniline) from Acros Organics. The [Pt(ppp)Cl]Cl complex was synthesized as described in the literature.[17] The organic solvents used were of analytical reagent grade. Those used for the preparation of the ILs were dried as described in the literature.[18]

Synthesis of the ILs. All operations were performed under nitrogen atmosphere. [emim][dca] and [emim][OTf] were obtained from Solvent Innovation and purified before use by stirring with activated charcoal, drying under vacuum at 40 and 60 °C, respectively, for 3−4 days, and finally stored over a molecular sieve. [emim][dca] had to be cleaned from Na[dca] that remained from the synthesis. This was achieved by addition of a 3-fold excess of dichloromethane to the liquid to precipitate Na[dca] and by subsequent filtration. The water content determined by Karl Fischer titration was 50 ppm for [emim][OTf] and 70 ppm for [emim][dca]. [emim][$EtSO_4$] was also obtained from Solvent Innovation and dried

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Table 1. Physical Properties of the ILs under Study[16]

	[emim][NTf_2]	[emim][dca]	[emim][$EtSO_4$]	[emim][tfa]	[emim][OTf]
color	colorless	slightly yellow	colorless	yellow	slightly yellow
miscibility with water	1.8 mass %	yes	yes	yes	yes
melting point [°C]	−17	−21	−65	−14	−12
viscosity (cP at 20 °C)	34	21 (at 25 °C)	120	35	35
density (g/cm^3 at 20 °C)	1.52	1.11	1.24	1.29	1.39

under vacuum at 40 °C for 10 days before use. The water content was 1800 ppm. [emim][NTf_2] and [emim][tfa] were synthesized according to an anion metathesis procedure described in the literature.[6] [emim]Br and Li[NTf_2] were obtained from Solvent Innovation and [emim]Br was purified twice by recrystallization prior to metathesis. The received [emim][NTf_2] was also stirred with activated charcoal and dried under vacuum at 40 °C, as described above. The water content was found to be 50−70 ppm. [emim]Cl was also obtained from Solvent Innovation, and Na[tfa] was purified by recrystallization prior to metathesis. The obtained [emim][tfa] was cleaned with activated charcoal, dried under vacuum at 60 °C, and stored over a molecular sieve. The water content was 400 ppm. [emim][BF_4] was synthesized as described in the literature.[19] [emim][$BuSO_4$], [emim][Et_2PO_4], [emim][Hex-OSO_3], and [emim][SCN] were obtained as small samples from the research group of Prof. Peter Wasserscheid, Department of Chemical and Bioengineering, University of Erlangen-Nürnberg.

Polarity of the ILs. All operations were performed under a nitrogen atmosphere. The polarity of the ILs using Reichardt's dye and phenol blue was measured according to a literature method.[20] Measurements at elevated pressure were done at 25 °C.

Density-Functional Theory (DFT)-Calculations. All structures were fully optimized using the B3LYP hybrid density functional[21–23] and the LANL2DZ basis set was augmented with polarization functions further denoted as LANL2DZp,[24–29] and characterized as minima or transition state structures by the computation of vibrational frequencies (for minima, all frequencies are positive, NImag = 0). All energies were corrected for zero point energies. The Gaussian 03 suite of programs was used throughout.[30]

Instrumentation and Measurements. Karl Fischer titrations were done on a 756 KF Coulometer (Metrohm). 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. pH measurements were performed with the aid of an inoLab pH Level 1 pH-meter. The UV−vis spectra of the studied ILs were recorded on a Varian Cary 1G spectrophotometer equipped with a thermostatted cell holder. Spectral measurements at elevated pressure (10 to 150 MPa) were performed on a Shimadzu UV-2101-PC spectrophotometer equipped with a laboratory-made high-pressure cell.[31,32] The high-pressure pump was purchased from NOVA SWISS;[33] it allows measurements in the selected pressure range. For kinetic measurements on fast reactions, a Durrum D110 (Dionex) stopped-flow instrument was used. The temperature of the instruments was controlled within an accuracy of ±0.1 K. Thiourea (TU) was selected as entering nucleophile since its high nucleophilicity prevents a possible back reaction.[34] The ligand-substitution reactions were studied under pseudo-first-order conditions by using at least a 10-fold excess of TU. All listed rate constants represent an average value of at least five kinetic runs under each experimental condition.

Results and Discussion

Polarity Measurements. We first report our results for the polarity of the ILs [emim][NTf_2], [emim][dca], and [emim][tfa] as a function of temperature and pressure. Solvent polarity reflects the influence of the solvent on physical and chemical processes within the solvent. It provides, for example, the overall solvation capability of the

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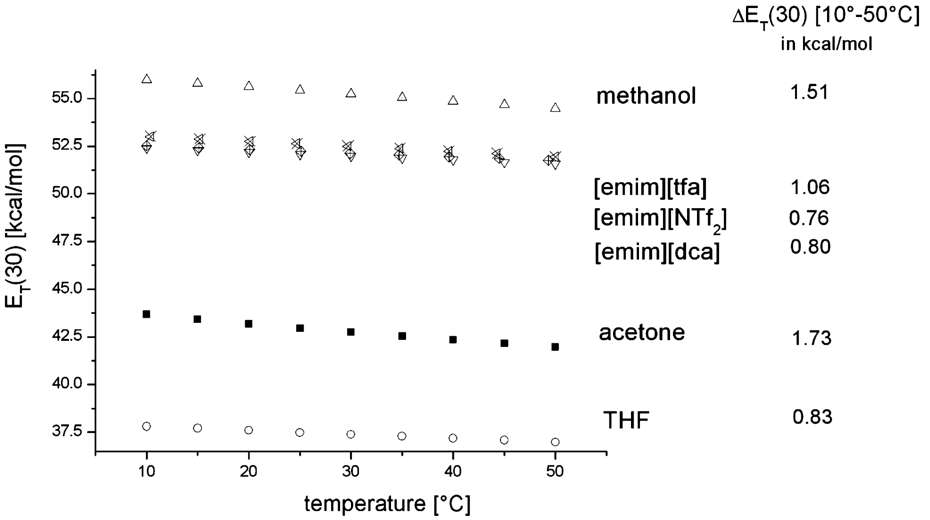

Figure 1. Temperature dependence of the solvent polarity determined at atmospheric pressure, using Reichardt's dye.

solvent for reactant and transition states, which controls the reaction rate.[35] Therefore, it is a very important property of a solvent that must be considered in mechanistic studies.

The polarity measurements were done using the solvatochromic behavior observed for well-known solvatochromic dyes such as Reichardt's dye[35] and phenol blue.[36] Depending on the solvent polarity, the long-wavelength absorption band of the dye is shifted to higher (bathochromic shift) or lower wavelength (hypsochromic shift) in the UV/vis/near-IR absorption spectrum. With these two dyes, even marginal changes in polarity can be detected and compared with reference values.

The $E_T(30)$ value defined as the molar transition energy of the standard betaine dye No. 30 in different solvents under standard conditions was introduced by Reichardt.[35] We used it in our work because it allows the quantitative prediction of solvent polarity. From a comparison of the two dyes in different solvents, a correlation could be made to convert the E_T values measured with phenol blue to the Reichardt's polarity scale[37] (Supporting Information, Figure S1).

It was possible to investigate the temperature dependence of the solvent polarity with both dyes equally well. The obtained results were completely reversible and showed the trends discussed below. The investigation of the pressure dependence of solvent polarity, however, turned out to be more complicated. We could not achieve any reasonable results with Reichardt's dye while working with conventional solvents (except for methanol) and ILs. The application of phenol blue yielded better results, which are discussed below. The conversion of the obtained data into $E_T(30)$ values on the basis of Supporting Information, Figure S1 allows an easy and coherent comparison and overview of the obtained results. For comparison with conventional molecular solvents, all polarity measurements were also done in acetone, methanol, and THF.

Figure 1 presents a comparison of the $E_T(30)$ values for the investigated solvents, measured over the temperature range 10 to 50 °C. The temperature dependence for all solvents shows a decrease in polarity with increasing temperature. The tested ILs show only very small changes in polarity on increasing temperature, which means that temperature variation has only a small influence on the polarity and therefore on the solubility of different species in these solvents. The polarity changes of the ILs are comparable to the changes measured for THF. The polarity values lie close to that for methanol, pointing to a similar polarity of these solvents. The three investigated ILs have only slightly different values for Reichardt's dye, which means that their polarities are very similar. It follows that temperature variation has only a small effect on the polarity of the ILs, and the changes are even smaller than for conventional molecular solvents. Both effects, namely, the similarity in the polarity of imidazolium-based ILs and those of short-chain alcohols[20,38–43] as indicated by the $E_T(30)$ values, and the polarity decrease with increasing temperature,[20,40] were also found by other research groups.

Figure 2 presents a comparison of the $E_T(30)$ values for the investigated solvents measured over the pressure range 100 to 1500 bar. The pressure dependence for all solvents shows an increase in polarity with increasing pressure. In general polarity changes induced by pressure are larger than those induced by temperature, pointing to a stronger influence of pressure variation on solvent polarity. Again, the ILs show only small changes in polarity as compared to the conventional solvents. However, there is a larger difference in their absolute polarity values as a consequence of the application

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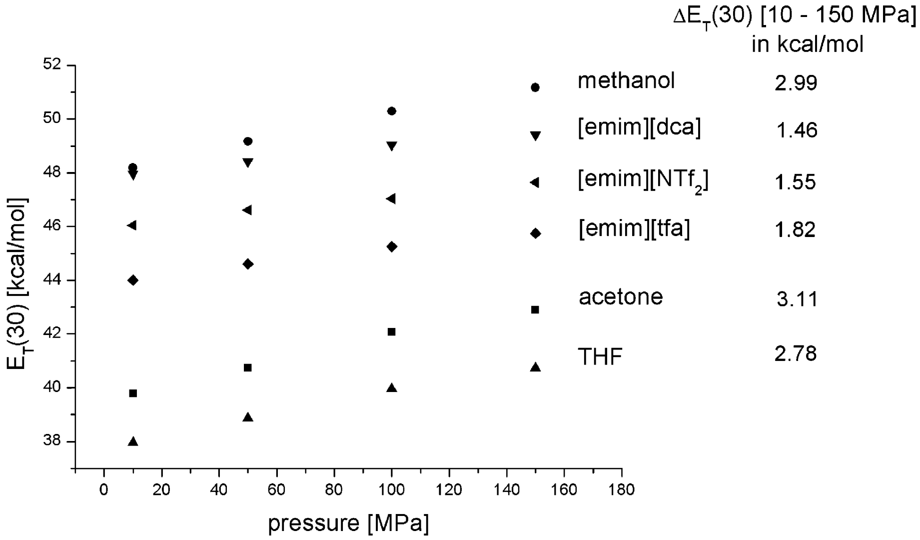

Figure 2. Pressure dependence of the solvent polarity determined at 25 °C using phenol blue.

of pressure. This could be related to different solvation and hydrogen bonding properties of the different ionic liquid anions, as phenol blue is known to be a polarity indicator that is responsive to hydrogen bonding.[44] [dca], suggested to be the strongest coordinating anion of the selected ILs, shows the highest polarity, followed by [NTf$_2$] and [tfa], which are known as weak coordinating or even noncoordinating anions.[38,45,46] Therefore, the absolute polarity values determined for phenol blue seem to be largely influenced by the coordinating ability of the ionic liquid anions. It seems to be important that the observed general opposite trend is that the polarity of the investigated ILs and conventional solvents increases not only with decreasing temperature but also with increasing pressure.

Besides the systematic study of solvent polarity using Reichardt's dye No. 30 and phenol blue, the solvent strength of ILs can also be quantified by Kamlet−Taft parameters.[47] The Kamlet−Taft linear solvation energy relationship breaks down solvent strength into dipolarity and polarizability (π^*), hydrogen bond donating acidity (α), and hydrogen bond accepting basicity (β). ILs have complex interaction forces between the anion and the cation such that a multiparameter solvatochromic correlation could be beneficial to understand the solvent strength. A recent publication[48] reports Kamlet−Taft parameters, especially β values, measured for a series of [bmim]-based ILs with different anions. These values were correlated with reaction rates and stabilization energies determined in this study, and they are presented here.

Interionic Interactions in ILs. To achieve a more detailed understanding at a molecular level, the experimental studies were extended by quantum chemical calculations. We studied ion-pair interactions in ILs containing the [emim]$^+$ cation. ILs represent an ionic medium such that the manner and magnitude of the interionic interactions between single ions in the neat state provide important information concerning the essential properties of IL as solvent and/or as reagent.

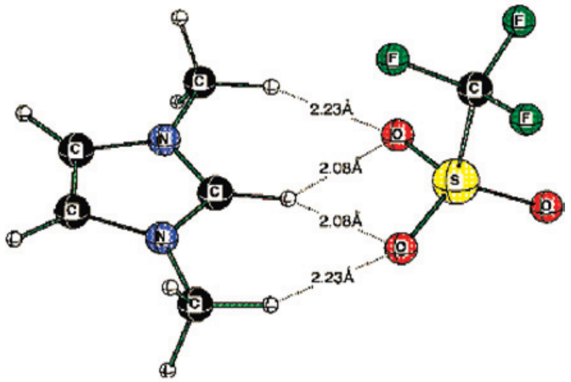

Figure 3. DFT calculated (RB3LYP/LANL2DZp) structure of [mmim]-[OTf].

The gas phase ion-pair stabilization energy was calculated for reaction (1) with [mmim]$^+$ as a working model for [emim]$^+$. Although the energies are surely biased because of the Coulomb attraction and the fact that the values do not include dispersion, we do find good correlations with experimental properties (see below). Figure 3 shows the calculated structure of the selected IL, where the C−H···anion interactions play an important role.

$$[\text{mmim}]^+ + [\text{IL anion}]^- \rightleftarrows [\text{mmim}][\text{IL anion}] \qquad (1)$$

At the same time we performed ^{1}H- and ^{13}C-NMR measurements that provided some interesting results. For ILs containing the [emim]$^+$ cation, one of the strongest interactions is the C−H···anion interaction via the proton in position 2 (Figure 3). Experimental ways to observe this are ^{1}H- or ^{13}C-NMR measurements that focus on the carbon atom to which the proton is bound. To exclude disturbing influences on the ion−ion interactions, all measurements were carried out in neat ILs, that is, in the absence of other deuterated solvents. To accomplish this, we used an NMR

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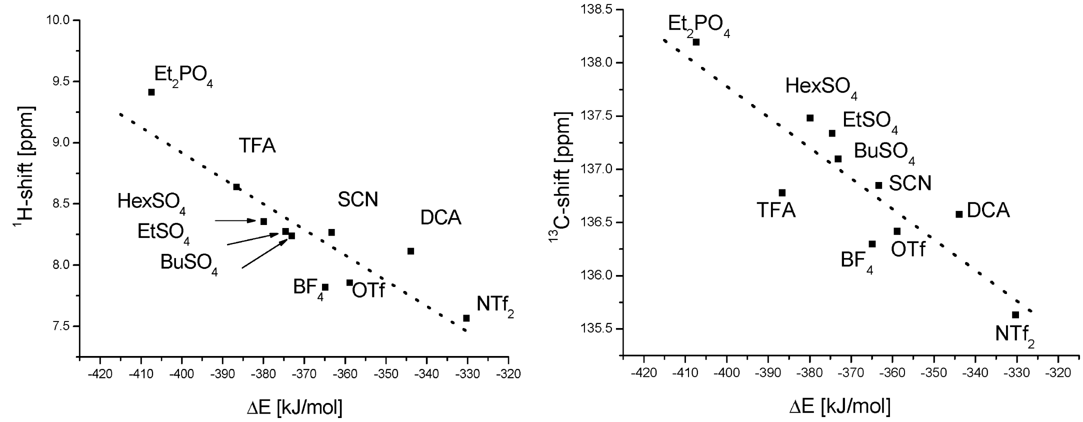


Figure 4. Correlation between calculated (RB3LYP/LANL2DZp) ion-pair stabilization energies and NMR-shifts for the proton and carbon at the C-2 position.

tube with a capillary filled with a 1:1 mixture of acetone-d$_6$ for the deuterium field-lock and TMS as standard. The NMR shifts obtained this way show a good correlation with the calculated ion-pair stabilization energies (Figure 4.)

The position of a single IL along the presented correlation is based on the magnitude of the interaction between its ionic components. Because the experiments and computations were done with ILs that possess the same cation, Figure 4 reflects the anion dependence of the cation−anion bond strength. The more the anions reside to the right side of the diagram, the weaker is the ion−ion interaction within the IL and the smaller is the possibility of a similar interaction with other types of cations, for example, positively charged metal centers.

The study of the properties of various ILs reported above revealed useful information that will assist the elucidation of the investigated reaction mechanisms that form the focus of our present report.

Mechanistic Studies on Ligand Substitution Reactions of [Pt(ppp)Cl]$^+$. A detailed kinetic study of the substitution reaction of the [Pt(ppp)Cl]Cl complex (Figure 5) with TU as entering nucleophile was performed in the ILs [emim][NTf$_2$], [emim][dca], [emim][OTf], and [emim][EtSO$_4$] as solvents. TU was selected as a neutral nucleophile to prevent complications in the interpretation of rate and activation parameters that result when anionic nucleophiles are used because of the effect of charge neutralization that then accompanies bond formation.

The investigated reaction is given in (eq 2)

$$[\mathrm{Pt(ppp)Cl}]^+ + \mathrm{TU} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Pt(ppp)TU}]^{2+} + \mathrm{Cl}^- \qquad (2)$$

The reaction was studied as a function of nucleophile (TU) concentration and temperature to determine the rate constants (k_2 and k_{-2}) and their activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$). The solvent dependence of reaction 2 was studied by dissolving the isolated complex and TU in the selected ILs and application of the stopped-flow technique to monitor the reaction. Typical examples of the observed spectral changes and kinetic traces are shown in Figures 6 and 7, respectively. The overall spectral changes were found to be rather similar, from which we concluded that the wavelengths suitable for stopped-flow measurements lay between 300 and 400 nm for all ILs under investigation.

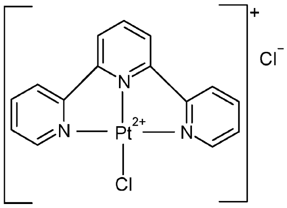
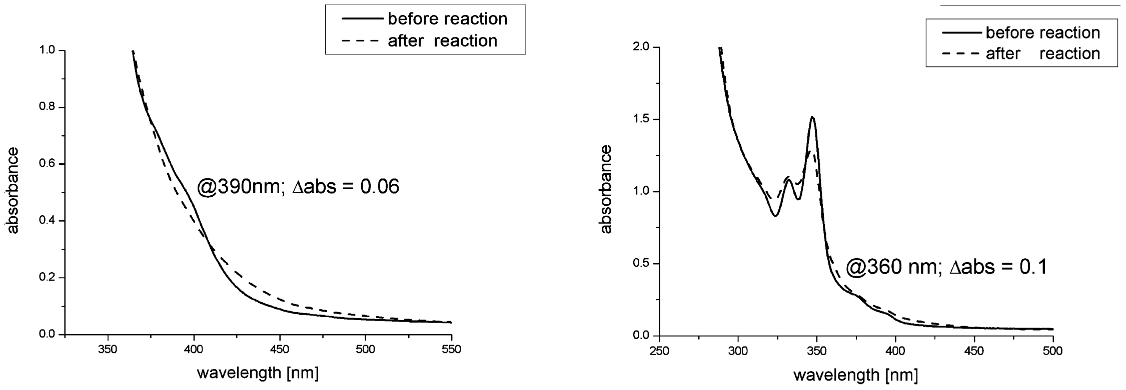


Figure 5. Schematic structure of chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride[17a].

Most of the recorded kinetic traces fitted a single-exponential function very well, in line with the pseudo-first-order behavior of reaction 2. Kinetic traces recorded in [emim][EtSO$_4$] showed a slow subsequent drift and had to be fitted with two exponential functions to correct for the slow drift. This seems to be related to the high viscosity of this IL that may cause inefficient mixing of the reactants in the stopped-flow instrument. The calculated pseudo-first-order rate constants, k_{obs}, were plotted against the TU concentration, and for all studied solvents a linear dependence with a negligible intercept was observed. Two typical plots are shown in Figure 8, from which it can be concluded that $k_{-2} \approx 0$.

The observed rate constant can be expressed as a function of the concentration of the entering ligand, namely, $k_{obs} = k_2[\mathrm{TU}]$, where k_2 is the second-order rate constant for the forward reaction in 2. The values of k_2 for the substitution of chloride by TU on the Pt^{II} complex in different ILs are summarized in Table 2. For comparison, this table also contains kinetic data for the investigated reaction in methanol and water, recently measured in our group.[14]

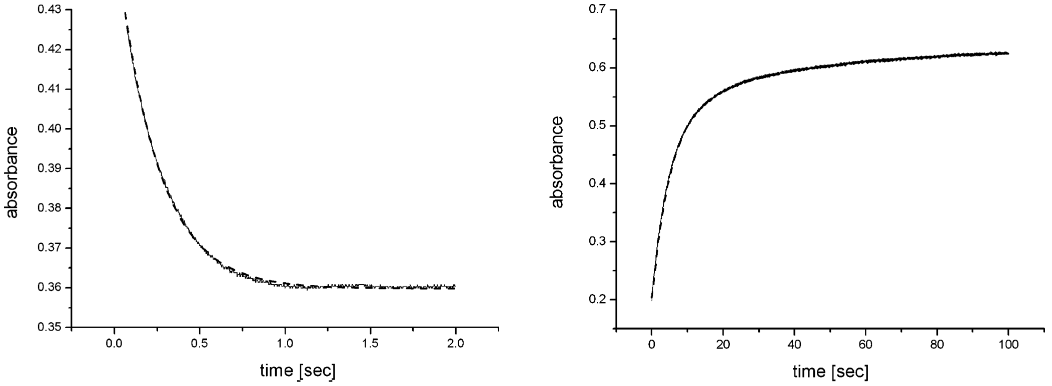
As the earlier work demonstrated,[14] the values of k_2 show that the substitution reaction of [Pt(ppp)Cl]$^+$ with TU depends significantly on the polarity of the solvent, and k_2 increases with increasing polarity, for example, k_2 (water) > k_2 (MeOH). A likely reason is the increase in dipole moment during the course of the reaction because of partial lengthening of the Pt−Cl bond in the five-coordinate trigonal bipyramidal transition state. In general, a decrease in solvent polarity results in a decrease in the rate of a reaction that involves an increase in dipole moment in going from the



(a): [emim][dca]

(b): [emim][EtSO4]

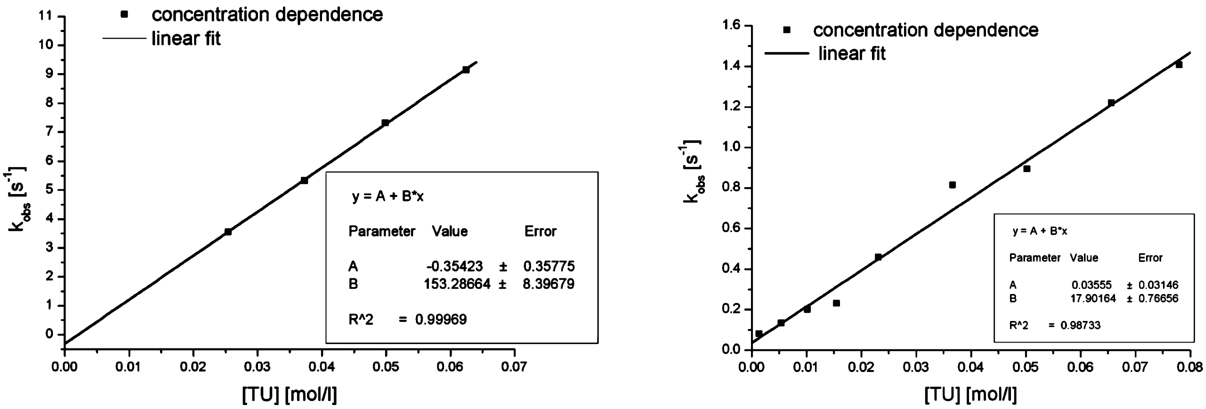
Figure 6. UV/vis spectral changes observed during the reaction between $[Pt(ppp)Cl]^+$ and TU in [emim][dca] and $[emim][EtSO_4]$ at 25 °C. The concentrations of the complex and TU are 0.2 and 150 mM (a), and 0.15 and 10.2 mM (b), respectively. The water content of the ILs was 70 ppm (a) and 1800 ppm (b). Optical path length = 0.88 cm.



(a): [emim][dca]

(b): [emim][EtSO4]

Figure 7. Typical kinetic traces recorded for the reaction between $[Pt(ppp)Cl]^+$ and TU in [emim][dca] and $[emim][EtSO_4]$ at 25 °C. Experimental conditions: (a) [complex] = 0.3 mM, [TU] = 50 mM, water content 70 ppm, λ = 390 nm; (b) [complex] = 0.15 mM, [TU] = 10.2 mM, water content 1800 ppm, λ = 360 nm. Optical path length = 2 cm.



(a): [emim][dca]

(b): [emim][EtSO4]

Figure 8. Plots of k_{obs} vs [TU] for reaction 2 in [emim][dca] and $[emim][EtSO_4]$ at 25 °C. Experimental conditions: (a) [complex] = 0.3 mM, water content 70 ppm, λ = 390 nm; (b) [complex] = 0.15 mM, water content 1800 ppm, λ = 360 nm.

Table 2. Summary of Rate and Activation Parameters for the Reaction between $[Pt(ppp)Cl]^+$ and TU in Different ILs and Other Solvents

solvent	k_2 [M^{-1} s^{-1}] at 25 °C	$\Delta H^\ddagger$ [kJ mol^{-1}]	$\Delta S^\ddagger$ [J K^{-1} mol^{-1}]
[emim][NTf_2]	500 ± 9	32.0 ± 0.3	−88 ± 1
[emim][dca]	153 ± 8	43 ± 1	−63 ± 4
[emim][$EtSO_4$]	17.6 ± 0.7	56 ± 2	−35 ± 7
[emim][OTf]	11.8 ± 0.5	41 ± 2	−80 ± 3
methanol	1344 ± 21	35 ± 1	−67 ± 3
water	2797 ± 42	29 ± 1	−82 ± 2

reactant to the transition state.[49] A decrease in solvent polarity also reduces the reaction free energy because the products are more ionic than the reactants.

The polarity of the ILs is similar to that of methanol, so one would expect similar k_2 values for these (if all other conditions are the same). The experimental data contradict this expectation. Table 2 shows that k_2 for the ILs lies considerably below the k_2 value found in methanol. The k_2 values also show large differences among the ILs, although their polarities were determined to be very similar. The reaction rate in [emim][dca] is nearly 3 times slower than in [emim][NTf_2], whereas the reaction in [emim][OTf] or [emim][$EtSO_4$] is more than 30 times slower than in [emim][NTf_2].

If we consider the polarity in terms of the Kamlet−Taft parameters and compare the determined k_2 with the corresponding β values,[48] we find a good correlation.

Figure 9 shows that the increase in β results in a decrease in the second-order rate constant. As shown in earlier work,[41] the β values for the ILs are dominated by the nature of the anion and demonstrate its ability to act as a hydrogen bond acceptor. The effect of ILs on a class of neutral nucleophiles is reported in the literature.[50] It was shown that the increase in nucleophilicity in ILs as compared to molecular solvents is due to stabilization of the activated complex of the investigated S_N2 reaction. A similar effect could occur in our case, but seems to be overcompensated by other effects, since we observed a decrease in rate constant with increasing β value. A possible increase in the nucleophilicity of TU with increasing β value because of a shift of electron density to the sulfur donor of the TU molecule seems also not to be the case according to the observed decrease in k_2 values. Thus, at first sight the k_2 values determined from our kinetic measurements contradict the trends observed in the literature.[50] It must, therefore, be concluded that other aspects that prevail over polarity effects must be important for the studied reaction in the different ILs.

The activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) were determined for reaction 2 and are included in Table 2. A representative plot showing a typical temperature dependence is given in Figure 10.

The negative $\Delta S^\ddagger$ values in Table 2 support the associative nature of the substitution mechanism, in general postulated for ligand substitution on square planar Pt^{II} complexes. The decrease in entropy is associated with a highly structured transition state, which is accompanied by a decrease in volume because of the compact nature of the transition state as a result of bond formation and an increase in solvation because of an increase in polarity of the transition state.[12] We found a continuous decrease in the activation entropy along the sequence [emim][$EtSO_4$], [emim][dca], [emim]-[OTf], and [emim][NTf_2] for the investigated substitution reaction 2. Comparison with the $\Delta S^\ddagger$ values for the same reaction in methanol and water indicates that the value for water is similar to that for [emim][OTf] and [emim][NTf_2], whereas the value for methanol is similar to that for [emim][dca] (see Table 2).

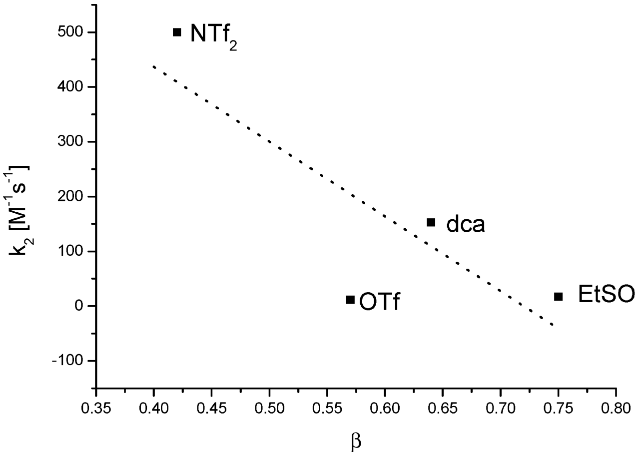


Figure 9. Correlation between rate constants k_2 (at 25 °C) and β values for the ILs.

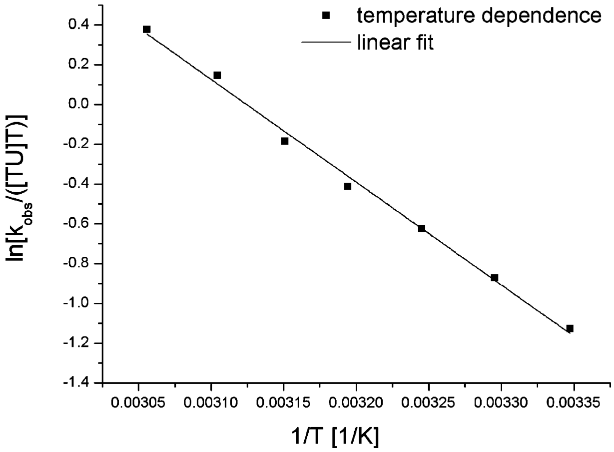


Figure 10. Temperature dependence of the reaction between $[Pt(ppp)Cl]^+$ and TU in [emim][dca] as solvent. Experimental conditions: [complex] = 0.3 mM, [TU] = 50 mM, water content 70 ppm, λ = 390 nm.

In the case of water as solvent we expect a large number of highly structured water molecules in the second coordination sphere of the transition state, in which hydrogen bonding plays a major role. A highly structured transition state can also be concluded for [emim][NTf_2] and [emim][OTf] since the three solvents show analogous $\Delta S^\ddagger$ values, where electrostatic interactions are most important in the case of the ILs. In the case of [emim][dca] and [emim][$EtSO_4$], as for methanol, a less structured transition state can be visualized in agreement with the less negative $\Delta S^\ddagger$ values. The increase in $\Delta S^\ddagger$ found for the ILs is in agreement with

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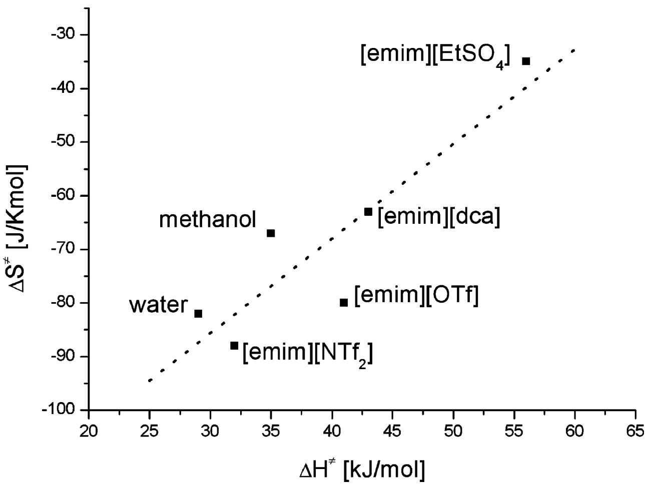

Figure 11. Correlation between the thermal activation parameters for the reaction between $[Pt(ppp)Cl]^+$ and TU in different ILs and conventional solvents.

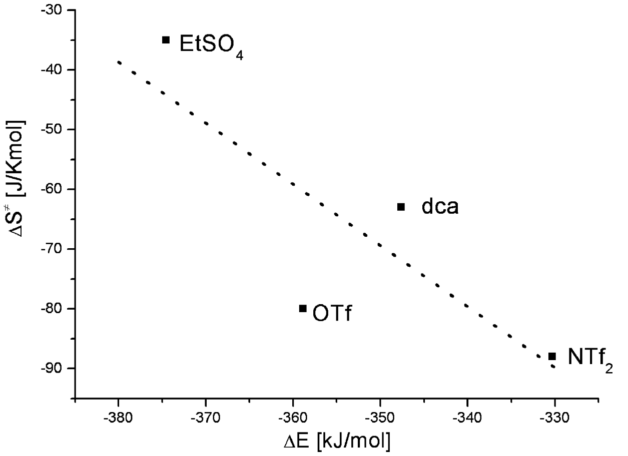

Figure 12. Correlation between ion-pair stabilization energies and activation entropies.

the increase in the values of $\Delta H^\ddagger$ as shown by the good compensation correlation between the activation parameters presented in Figure 11. The $\Delta H^\ddagger$ values reflect the ease of bond reorganization during the reaction. The lowest value was found for [emim][NTf_2] for which k_2 is the largest. The largest $\Delta H^\ddagger$ value was found for the reaction in [emim]-[$EtSO_4$] for which k_2 is very small.

The determined $\Delta S^\ddagger$ values show a good correlation with the calculated stabilization energies for the interaction between the ions of the ILs as shown in Figure 12. As the IL cation−anion attraction increases, the activation entropy for the reaction becomes less negative. This suggests that the loss in entropy as the starting materials come together is partly compensated by a concomitant disruption of the IL structure, with the importance of the effect increasing as the ions are more associated in the first place. Similar effects are known from the literature.[50] So the strongest ion−ion interaction within the IL was found for [emim][$EtSO_4$], in which the activation entropy has the lowest value among the studied ILs. Accordingly, the lowest calculated ΔE value for [emim][NTf_2] is accompanied by the highest $\Delta S^\ddagger$ value among the investigated systems. The values for [emim][OTf] and [emim][dca] lie in between.

Unexpected Results. The results of the investigated reactions described above allow the following conclusions to be made. The mechanism of the examined test reaction shows an associative substitution behavior in all studied ILs, similar to that found in conventional solvents, which is supported by the strongly negative $\Delta S^\ddagger$ values. However, some differences are apparent and indicate that the ILs themselves have a significant influence on the course of the reaction, which differs from that in conventional solvents. For example, it is not possible to correlate rate constants found for different ILs with their polarity as it is the case for conventional solvents.[14] Rate constants for the ligand substitution reaction 2 measured in ILs differ strongly from rate constants measured in conventional solvents (Table 2).

The significantly slower substitution reactions observed in the studied ILs may be due to an electronic interaction between the anion of the ILs and the positively charged Pt center, where electron density of the anion can shield the vacant p_z orbital of the Pt center and hinder nucleophilic attack by the entering nucleophile. This would then lead to a deceleration of the reaction and result in smaller values for k_2. This effect could be strengthened by the high electrophilicity of the metal center as a result of the π-acceptor properties of the terpyridine chelate.[13e] According to our calculations, $[EtSO_4]^-$ and $[OTf]^-$ show the best ability for such an interaction, whereas $[dca]^-$ and $[NTf_2]^-$ are less able to do this (see Figure 5). In agreement with this, the values of k_2 for reaction 2 are the lowest for $[EtSO_4]^-$ and $[OTf]^-$ and increase for $[dca]^-$ and $[NTf_2]^-$ (see Table 2).

Analogous to eq 1, we calculated the ion-pair interaction energies in the gas phase for the anions of the ILs and the Pt^{II} complex as shown in reaction 3.

$$[Pt(ppp)Cl]^+ + [IL\ anion]^- \rightleftarrows [Pt(ppp)Cl][IL\ anion] \quad (3)$$

The anions were those of the ILs used as reaction medium, namely, $[NTf_2]^-$, $[dca]^-$, $[OTf]^-$, and $[EtSO_4]^-$. The aim of these computations was to clarify whether there is some sort of interaction between the Pt center and the anion of the IL which would account for the observed deceleration in the reaction rate.

Figure 13 shows the computed structures of the [Pt(ppp)-Cl]$^+$ complex with the anions of the investigated ILs. The anions are found to occupy very different positions. $[NTf_2]^-$ sits on the side of the complex and leaves the metal center open for the nucleophilic attack, that is, the p_z orbital remains easily accessible. This can account for the largest k_2 value found in [emim][NTf_2]. $[dca]^-$ occupies a position above the complex but mostly over the plane formed by the pyridine rings of the ppp chelate. This means that the Pt center is more shielded than in the case of $[NTf_2]^-$ and the reaction rate decreases, but the approach of the nucleophile is still quite favorable so that the k_2 value is still significantly high.

The situation is different in the case of $[OTf]^-$ and $[EtSO_4]^-$. Both anions shift closer to the metal center as compared to $[dca]^-$ and $[NTf_2]^-$ and are partly positioned over the pyridine ring and partly over the five-membered ring formed by the Pt center and the ppp chelate. Furthermore, the distances between the anions and the metal center

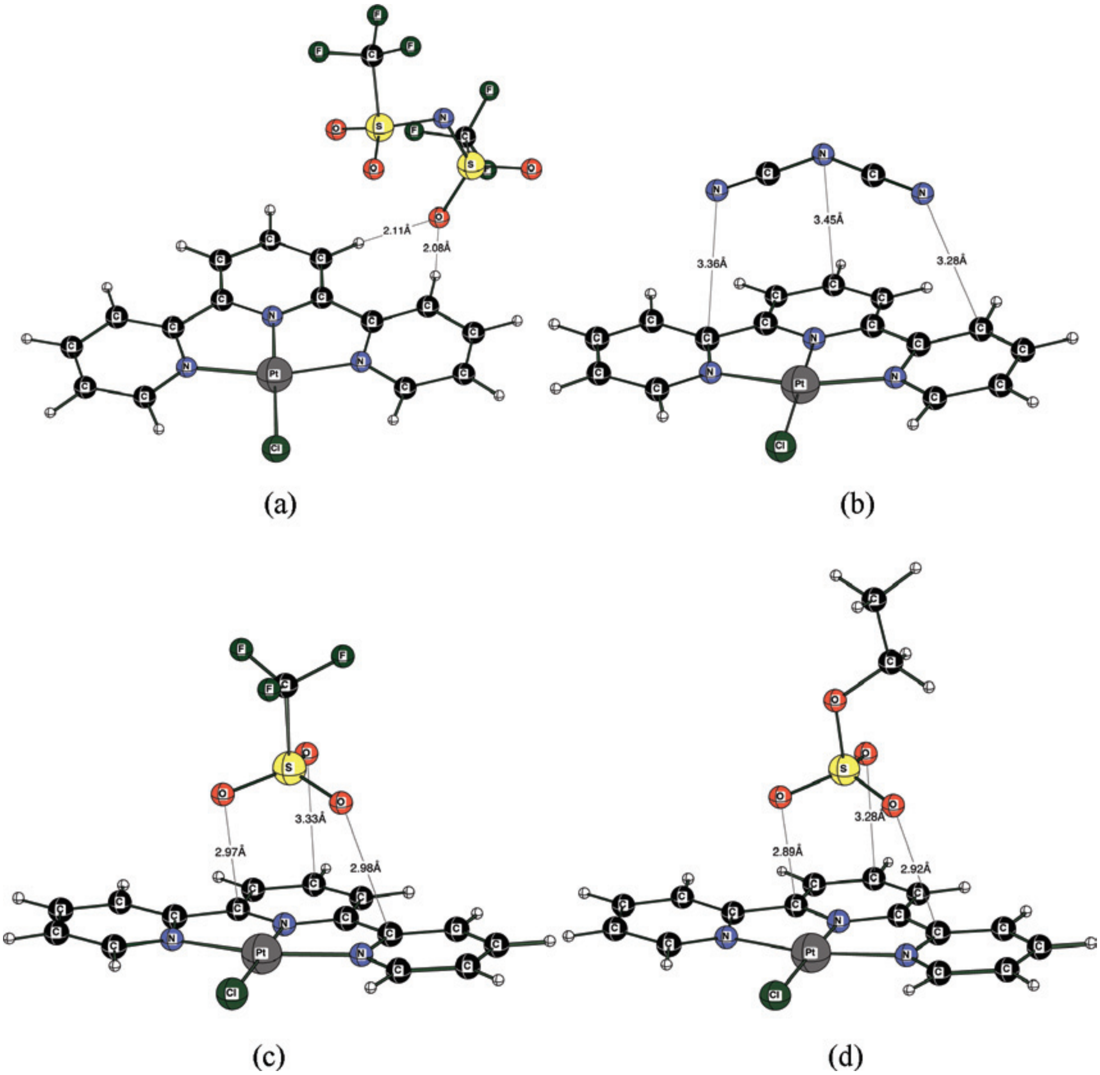

Figure 13. DFT calculated (RB3LYP/LANL2DZp) structures of the $[Pt(ppp)Cl]^+$ complex with the anions $[NTf_2]^-$ (a), $[dca]^-$ (b), $[OTf]^-$ (c), and $[EtSO_4]^-$ (d).

Table 3. Summary of Calculated (RB3LYP/LANL2DZp) Gas Phase Stabilization Energies between the Complex and Anions of the ILs

IL anion	$[NTf_2]^-$	$[dca]^-$	$[OTf]^-$	$[EtSO_4]^-$
ΔE, [kJ/mol]	−287.0	−293.3	−300.0	−315.5

become somewhat shorter, namely, they lie between 3.3 to 3.4 Å for $[dca]^-$ and between 2.9 to 3.3 Å for $[OTf]^-$ and $[EtSO_4]^-$. This means that the Pt center is more shielded and nucleophilic attack is more difficult, which leads to a further decrease in the k_2 values to reach the lowest values in the case of $[emim][EtSO_4]$ and [emim][OTf] according to the data in Table 2.

The calculated stabilization energies for the ion-pairs increase from $[NTf_2]^-$ and $[dca]^-$ to $[OTf]^-$ and $[EtSO_4]^-$ (see Table 3), and correlate with a substantial decrease in k_2 measured for the different ILs (see Figure 14).

The calculated stabilization energies for the interaction between the complex and the anions of the ILs also correlate well with the β values for the ILs (see Figure 15,) which are known to reflect the hydrogen bond acceptor abilities of the IL anions[48] and so their ability to provide electron density to the electrophilic center. In our case it results in an interaction between the IL anions and the Pt(II) center.

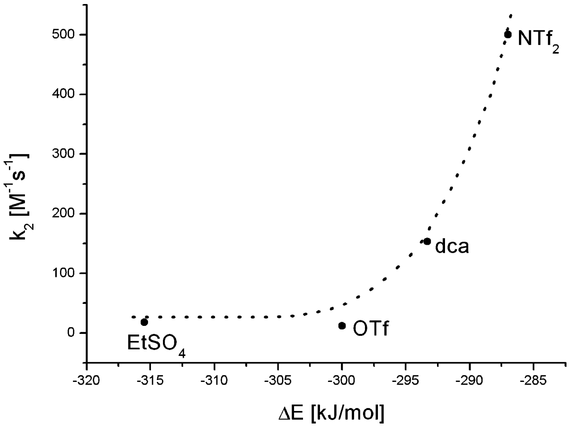

Figure 14. Correlation between rate constants k_2 and gas phase stabilization energies for the interaction between the complex and anions of the ILs.

The formation of “ion-pairs” in ILs is described in the literature.[51] Ions of the solute will be repelled by the ions of the IL bearing the same charge (cation−cation/anion−anion).

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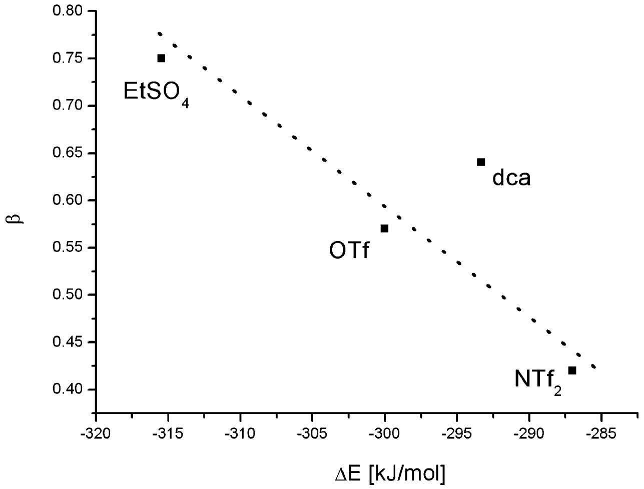

Figure 15. Correlation between β values and gas phase stabilization energies for the interaction between the complex and the anions of the ILs.

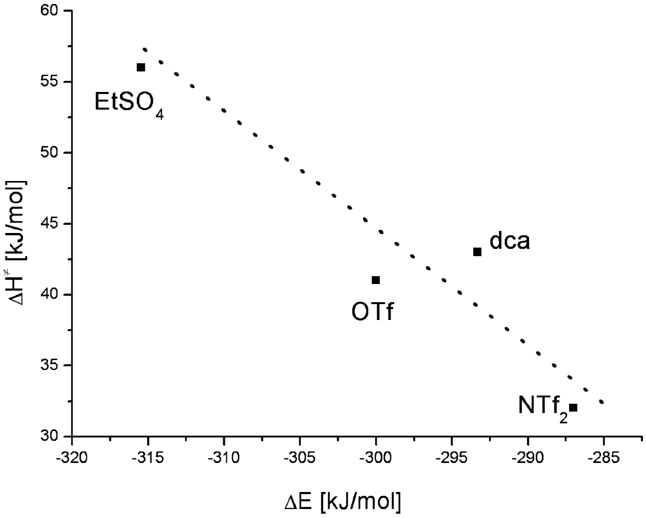

Figure 16. Correlation between calculated stabilization energies for the interaction between the complex and the anions of the ILs and the determined activation enthalpies.

We, therefore, suggest that in an IL a solute ion will always be closely associated with ions of opposite charge. This is not the same as an ion pair, but it is certainly not a free ion. We assume a similar situation in our case. Initially the cationic Pt complex is closely surrounded by a number of IL anions. Thus there is a need to remove an anion from the complex to liberate an active site for the substitution reaction. This process is supported by the good correlation between the calculated stabilization energies for the interaction between the complex and the anions of the ILs and the determined activation enthalpies as shown in Figure 16.

The highest value for ΔE calculated for [emim][$EtSO_4$] indicates the strongest interaction between the Pt complex and the IL anions, which results in the highest value for $\Delta H^{\ddagger}$, namely, the highest amount of energy required for bond formation. Accordingly, the lowest value is for [emim][NTf_2], and [emim][OTf] and [emim][dca] lie between these extremes. From our model calculations and kinetic measurements we conclude that ILs form an efficient solvent cage that can shield the metal center, hinder nucleophilic attack, and therefore lead to a significant decrease in reaction rate as compared to conventional molecular solvents.

Another possible explanation for the observed differences mentioned above could be the displacement of the leaving chloro ligand by the anion of the IL when the Pt(II) complex is dissolved in the appropriate IL. Our findings indicate that this can indeed be the case for an IL with an anionic component that is a strong nucleophile. For example, [emim][OTf] shows the largest and [emim][NTf_2] the smallest deviation in k_2 compared to methanol, although both anions are known to be weakly coordinating ligands.[38,45,52] If the chloro ligand of the complex is displaced by the anion of the IL, it should be possible to force this substitution process back to the chloro complex by using a large excess of chloride. To test this, we performed a series of experiments in water. The [Pt(ppp)Cl]Cl complex was dissolved, followed by rapid addition of a concentrated stock solution of sodium dicyanamide. The spectral changes shown in Supporting Information, Figure S2 clearly indicate the displacement of the chloro ligand by dicyanamide. To the solution of the formed $[Pt(ppp)(dca)]^+$ complex was added a concentrated stock solution of lithium chloride. The spectra reported in Supporting Information, Figure S3 indicate no significant changes on the addition of a large excess of chloride, from which we conclude that no reformation of the chloro complex from the formed $[Pt(ppp)(dca)]^+$ complex occurs. From these observations we conclude that $[Pt(ppp)Cl]^+$ must exist as $[Pt(ppp)(dca)]^+$ in the case when [emim][dca] is used as IL because the dca anion is expected to be the strongest nucleophile of the series of anionic components studied.

Nevertheless, the kinetic data for reaction 2 in [emim][dca] is well in line with the data for the other studied ILs that have much weaker anionic nucleophiles. The apparent reason for this is the fact that the studied substitution reactions all follow an associative reaction mode, in which the departing nucleophile (chloride or dca) plays a minor role as compared to the entering nucleophile. In addition, both the dca and chloro ligands are negatively charged, such that the overall charge on the Pt(II) complex does not change when Cl^- is displaced by dca^- in [emim][dca]. Further differences could arise from the size of the coordinated nucleophile, such that the substitution by TU is slower in the case of the sterically more demanding dicyanamide ion compared to the smaller chloro ligand. We, therefore, suggest that in [emim][dca] the observed substitution reaction must represent the displacement of the dicyanamide ligand by TU in a similar way as given for the chloro complex in reaction 2.

Conclusions

The results obtained demonstrate clearly that conventional research methods can be applied in the study of ILs as is done for conventional molecular solvents. Investigations based on solvatochromic dyes provide information about the polarity of ILs and accordingly about the solubility of different species in

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these solvents. The NMR investigations furnish information about the magnitude of the interaction between the ionic components of neat ILs. DFT calculations support this data as well. The UV−vis investigations based on stopped-flow kinetics can provide rate constants for reversible ligand substitution reactions and the corresponding activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for fast reactions in ILs. In the present case the numerical values indicate that there is no significant back reaction ($k_{-2} \approx 0$), and the forward reaction has an associative character ($\Delta S^{\ddagger} \ll 0$). We found evidence that certain processes in ILs differ considerably from those in conventional molecular solvents. A likely reason is that the influence of the IL itself can cause an interaction between the anionic component of the IL and the positively charged metal complex or even the displacement of the departing ligand through coordination of the IL anion as found in the case of [emim][dca].

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Supporting Information Available: Three figures presenting a correlation between E_T values for Reichardt's dye and phenol blue, and UV−vis spectral data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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