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Mechanistic Studies on Fast Ligand-Substitution Reactions of a Very Labile Pd^{II} Complex in Several Ionic Liquids

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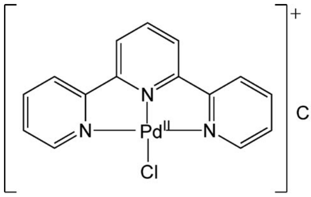
Keywords: Kinetics / Reaction mechanisms / Ionic liquids / Palladium / Ligand substitution

Detailed kinetic studies on the ligand-substitution reactions of the very labile [Pd(terpy)Cl]$^+$ (terpy = 2,2′:6′,2′′-terpyridine) complex have been performed for neutral and anionic nucleophiles in several imidazolium-based ionic liquids. The detailed substitution mechanisms derived from the obtained rate and activation parameters differ from those expected on the basis of data aquired in aqueous medium, since the selected ionic liquids significantly affect the nucleophilic attack of the entering ligand on the complex. The rate constant for the substitution reaction with thiourea as entering nucleophile is much larger in water, viz. $(7.8 \pm 0.2) \times 10^5$ $\text{M}^{-1}\,\text{s}^{-1}$, than in the ionic liquids [emim][NTf$_2$] and [emim][EtOSO$_3$], viz. $(2.5 \pm 0.1) \times 10^4$ and $(1.8 \pm 0.1) \times 10^3$ $\text{M}^{-1}\,\text{s}^{-1}$ at 25 °C, respectively, which can be accounted for in terms of the protective interaction of the anionic components of the ionic liquids with the electrophilic metal centre.

Introduction

The behaviour of transition metal catalysts in ionic liquids (ILs) represents an ever growing field of interest in inorganic chemistry and in their technical application.[1] In general, many industrial processes depend on the use of transition metal complexes as catalysts in the liquid phase. The use of ILs instead of conventional solvents in these processes can in some cases lead to a significant increase in the yield of a desired product. Furthermore, the lack of any significant vapor pressure can lead to a reduction of costs and an increase in environmental-friendliness of the overall process.[2–4] Over the past 10 years, several small, niche applications of ILs have found their way into the market, as well as a few selective large-scale industrial applications.[5] However, the origin of the effect of ILs on these processes is still not well understood. More specific, the question whether the reaction mechanisms underlying the observed processes are influenced or even changed by the ILs, stands at the centre of our interest, especially for fast reactions on a time scale of seconds or minutes, as most mechanistic studies to date have been performed on relatively slow reactions in ILs.[6,7]

Earlier work from our group in this field involved ligand-substitution reactions of inert and labile Pt^{II} complexes with thiourea (TU) or thiocyanate (SCN$^-$) as entering nucleophiles.[8–10] The results indicate that the nature of the underlying substitution mechanism, in this case associative (A) or associative-interchange (I$_a$), remains the same on switching from conventional solvents to ILs, even though reaction rates can be slowed down by several orders of magnitude on switching to ILs. The results presented here show that ILs can even have more significant effects when the metal ion is changed from the relatively inert Pt^{II} to the very labile Pd^{II}. In general, Pd^{II} complexes are in many cases selected as models for the more inert Pt^{II} complexes since they usually react in the same way but up to 6 orders of magnitude faster.[11] With this report we complete a series of detailed kinetic studies that investigated the influence of several ILs on the ligand-substitution reaction of the very labile Pd^{II} complex [Pd(terpy)Cl]Cl (**I**) (Scheme 1), where terpy = 2,2′:6′,2′′-terpyridine.



I

Scheme 1. Schematic structure of [Pd(terpy)Cl]Cl (**I**).

Several nucleophiles that can displace the chloride ligand of complex **I** were investigated; among them are neutral and anionic nucleophiles, viz. thiourea (TU), thiocyanate (SCN$^-$) and iodide (I$^-$). Depending on the charge of the nucleophile and the ILs used, the overall nature of the substitution mechanism can change significantly. These effects are presented and discussed in this report. As the complex in question has until now only been investigated in a water/methanol mixture,[11] we also studied by way of comparison some of the reactions in aqueous solution to be able to make a direct comparison with the results in ILs.

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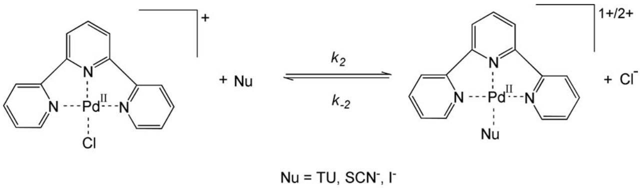
The high lability of complex **I**, which originates partly from the π-back bonding by the in-plane terpyridine chelate that significantly increases the electrophilicity of the Pt^{II} or Pd^{II} centre,[12,13] can complicate the study of such reactions in ILs since stopped-flow techniques exhibit a much longer dead time when solvents of higher viscosity than water are used. Under such conditions the employed experimental technique is pushed to its limits by the combination of a very labile complex and viscous solvents that slow down all micro-flow processes. It was, therefore, a further aim of this work to evaluate the physical limits of stopped-flow techniques in terms of the maximum rate constants measurable with viscous ILs. For this purpose, dead times of the stopped-flow apparatus were correlated with the viscosity of the ILs employed.

The ILs employed as solvents in the ligand-substitution reactions studied, all consist of the [emim] cation combined with different anions as shown in the Exp. Section. A summary of the physical properties of the ILs used has already been given in our earlier report.[8]

Results and Discussion

Preliminary Observations

In this section we summarize all preliminary measurements performed and observations made prior to a systematic study of the reactions outlined in Scheme 2 in water and in the ILs summarized in the Exp. Section. Thiourea (TU) was selected as a neutral nucleophile in order to prevent complications in the interpretation of rate and activation parameters that result when anionic nucleophiles such as SCN^- and I^- are used. In the latter case charge neutralization that accompanies the ligand substitution process will cause a significant decrease in electrostriction, which in turn will affect observed activation entropy.



Scheme 2. Substitution reactions of $[Pd(terpy)Cl]^+$ with neutral and charged entering nucleophiles.

In general the substitution reactions were studied as a function of the nucleophile concentration and temperature, in order to determine the rate constants (viz. k_2 and k_{-2}) and the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$. This was done by dissolving the complex and nucleophile in the selected ILs and applying the stopped-flow technique to monitor the reaction. In order to determine the wavelength at which the reaction can be monitored best, UV/Vis-spectra were recorded before and after the reaction in the different ILs. Typical spectral changes that accompany the reaction are shown in Figure 1. The wavelengths suitable for stopped-flow detection lie between 350 and 400 nm depending on the solvent and the nucleophile used.

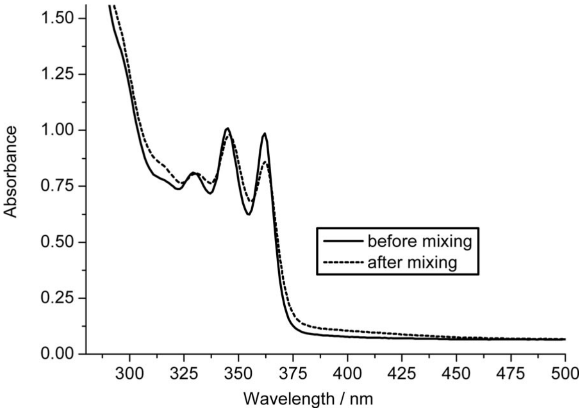


Figure 1. Typical UV/Vis spectral changes that accompany the reaction of **I** with TU in $[emim][NTf_2]$ at room temperature.

We have recently demonstrated how low concentrations of impurities in ILs can have a drastic affect on the outcome of mechanistic studies in ILs.[14] Therefore, special care was taken to control the level of water, chloride and methylimidazole in the employed ILs as outlined in the Exp. Section. In addition, the viscosity of the selected ILs, which is 20 to 120 times higher than that of water (see Table 1), had a drastic influence on the experimental ability to study the very fast substitution reactions outlined in Scheme 2. The relative high viscosity of the ILs affects the mixing and flow rate within the stopped-flow instrument and so causes a drastic increase in dead time with increasing viscosity. In most cases the first part of the observed kinetic trace had to be deleted since the solutions were not completely mixed. For instance in $[emim][NTf_2]$ a maximum k_{obs} value of 120 s^{-1} could be measured, and reactions faster than 120 s^{-1} could not be fitted because too much of the reaction was lost during the dead time of the instrument. Figure 2 shows a typical kinetic trace for the reaction of complex **I** with TU in $[emim][NTf_2]$, including a dead time of 20 ms that has to be cut off. Furthermore, in the case of $[NTf_2]$ the resulting absorbance change could become very small under which condition the ripple of the Xenon lamp could lead to further deviations. Other examples are given in Figure S1 (Supporting Information).

Table 1. Viscosity and corresponding stopped-flow dead time for different ILs.

Ionic liquid	Viscosity [cP]	Dead time [ms]	Comments
[emim][dca]	21	20–25	
$[emim][NTf_2]$	34	18–25	relatively large absorbance changes allow higher rate constants to be observed
[emim][OTf]	45	70–80	first reaction step is not observable
$[emim][EtOSO_3]$	120	20–50	dead time is highly dependent on temperature and water content

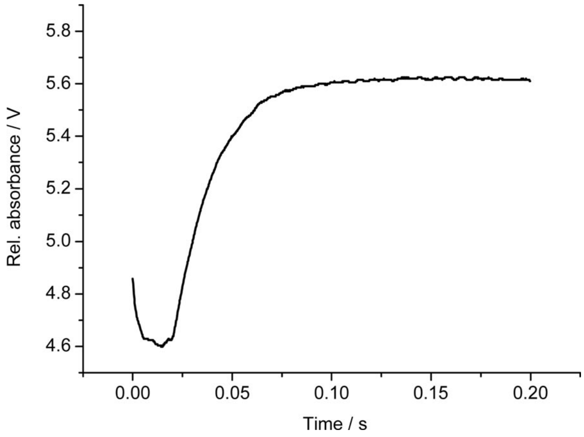


Figure 2. Representative kinetic trace for the reaction of complex **I** with TU in [emim][NTf$_2$] including a dead time of 20 ms. Experimental conditions: [**I**] = 0.08 mM, [TU] = 1.2 mM, T = 25 °C.

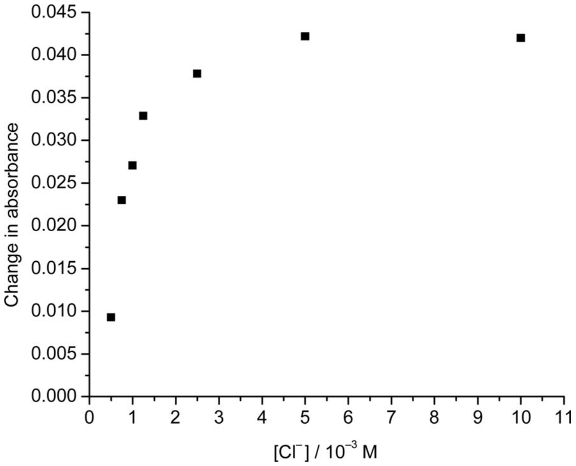


Figure 3. Change in absorbance of complex **I** (0.08 mM) at 240 nm as a function of chloride concentration in 0.01 M CF$_3$SO$_3$H at room temperature.

Table 1 summarizes the viscosity of the ILs and the corresponding dead time of the instrument. In general a higher viscosity increases the dead time and reduces the maximum observable rate constant for a specific IL. Thus dead time could become a serious problem when rapid reactions are to be studied in highly viscous ILs. Also, during temperature dependence measurements, the dead time decreased with increasing temperature due to a decrease in viscosity, i.e. increase in fluidity. Some of the ILs used in this study show quite a large background absorbance in the spectral range where complex **I** shows characteristic absorbance changes when it undergoes a ligand-substitution reaction. This limits the complex concentration that can be used and also the maximum observable rate constant. Keeping all the above-mentioned complications in mind, we now turn to the presentation of the kinetic measurements performed in water and the selected ILs.

Water as Solvent

To be able to compare the results on Pd^{II} with our earlier work on the analogous Pt^{II} complex,[8,10] some reactions had to be studied in water since only a few selected reactions in water/methanol mixtures have been studied before.[11] When complex **I** is dissolved in a water/CF$_3$SO$_3$H mixture, it undergoes spontaneous aquation to form the corresponding aqua complex. Such aqua complexes are known to be orders of magnitude more labile than the corresponding chloro complexes. This aquation process can be suppressed by addition of chloride to the complex solution. The absorbance measurements reported in Figure 3 show that the minimum concentration of chloride needed for the complex to remain in the chloro form is ca. 5 mM. To assure that the complex in water does not undergo undesired aquation, 0.01 M HCl was used to prepare all solutions. In this way aquation of the chloro complex and possible formation of hydroxo complexes could be prevented.

Several nucleophiles, charged and uncharged (e.g. Br$^-$, I$^-$, dimethyl sulfide), were selected and tested, but for most of them it was not possible to observe a kinetic trace, i.e. to measure k_{obs}. This was mostly due to the reaction of **I** with the selected nucleophile being too fast to be observed by conventional stopped-flow techniques, or the change in absorbance accompanying the reaction was too small to be observed on a fast time scale. This was, however, not the case for TU and SCN$^-$ as entering nucleophiles, for which it was possible to measure the concentration and temperature dependence for the reaction with complex **I**. Absorbance changes characteristic for the reactions were followed at 350 nm for both nucleophiles. The recorded kinetic traces fitted nicely to a single exponential function and the observed rate constants (k_{obs}) showed a linear dependence on the concentration of TU with no significant intercept (see Figure S2, Supporting Information). The studied reaction nicely follows the reaction Scheme outlined in Scheme 2, where TU displaces chloride in an irreversible manner and the reaction follows the simple rate law $k_{obs} = k_2[\text{TU}]$. The maximum k_{obs} value that could be measured was found to be 400 s^{-1} for the reaction with 0.5 mM TU, which corresponds to a half-life of the reaction of 2.5 ms, i.e. close to the dead-time of the stopped-flow instrument when using water as solvent, and higher concentrations of TU could not be measured accurately anymore. The resulting k_2 value is $(7.8 \pm 0.2) \times 10^5$ M^{-1} s^{-1} at 25 °C, i. e. indeed a very fast substitution reaction.

The temperature dependence of k_2 was also measured for which the Eyring plot is given in Figure S3 (Supporting Information). The low activation enthalpy $\Delta H^{\#}$ of 18.5 ± 0.9 kJ mol^{-1} contributes to an overall low activation barrier that can be ascribed to the high electrophilicity of the Pd^{II} centre that causes rapid binding of TU. The negative activation entropy $\Delta S^{\#}$ of -69 ± 3 J K^{-1} mol^{-1} supports the assignment of an associative (A) or associative interchange (I$_a$) mechanism, characteristic for substitution reactions of square-planar complexes.[8–10,15]

In the case of $SCN^–$ as entering nucleophile, the concentration dependence of k_{obs} exhibits a significant intercept (see Figure 4), indicating the participation of a back or parallel reaction as shown in Scheme 3, for which $k_{obs} = k_2[SCN^–] + k_{–2}[Cl]$ (or $k_S[H_2O]$). The value of k_2 is $(16.6 \pm 0.4) \times 10^3\ \text{M}^{-1}\,\text{s}^{-1}$ at 25 °C, which is 50 times slower than for the reaction with TU. On this basis we suggest that the intercept of $13.1 \pm 0.5\ \text{s}^{-1}$ is due to a back reaction in the presence of the added chloride (10 mM HCl), i.e. $k_{–2} = (13.1 \pm 0.5) \times 10^2\ \text{M}^{-1}\,\text{s}^{-1}$. The ratio $k_2/k_{–2} = 10$ appears rather small; we attribute this to the fact that the very electrophilic centre of **I** lessens the influence of incoming ligands and thus the difference in rates.[16]

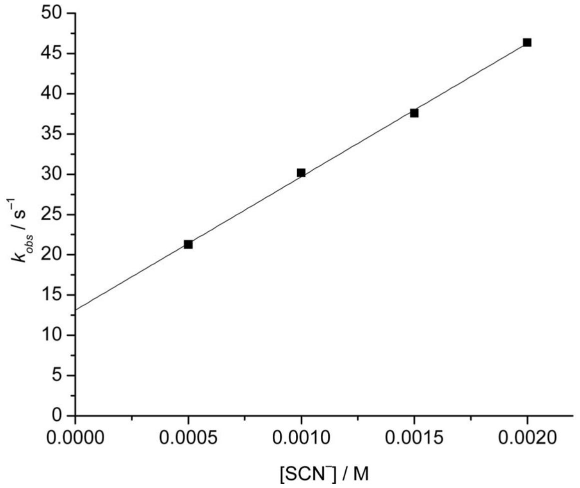
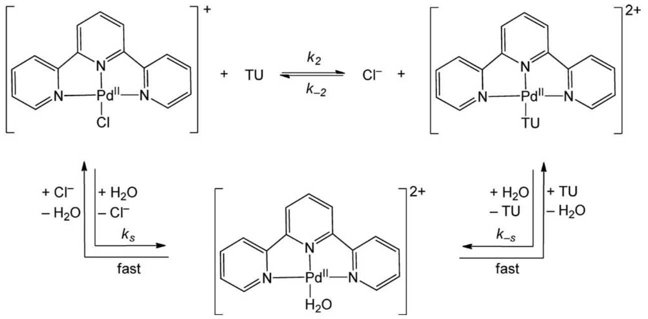


Figure 4. Concentration dependence of k_{obs} for the reaction of complex **I** with $SCN^–$ in water at room temperature.



Scheme 3. Substitution pathways for complex **I** including parallel aquation and reversible reactions in water as solvent.

[emim][NTf_2] as Solvent

The substitution reactions of complex **I** were studied in [emim][NTf_2] as solvent. Absorbance changes were followed at 361, 352 and 354 nm for TU, $SCN^–$ and $I^–$, respectively, and the kinetic traces could be fitted with a single exponential function. Since these reactions are very fast even for stopped-flow measurements, a very low nucleophile concentration had to be selected in order to be able to follow the reaction, viz. in the case of TU between 1 and 4 mM. Lower nucleophile concentrations could not be studied as the pseudo-first-order condition restricted the complex concentration to one tenth of the nucleophile concentration.

In the case of TU the calculated pseudo-first-order rate constants k_{obs} were plotted against the nucleophile concentration and resulted in a linear dependence with a significant intercept (see Figure 5). Since TU is a much stronger nucleophile than chloride, the back reaction ($k_{–2}$) is not expected to appear, and the intercept is ascribed to the contribution of a parallel aquation pathway (k_S) since the overall absorbance change observed during the reaction does not depend on the nucleophile concentration. The observed rate constant can then be expressed as $k_{obs} = k_2[TU] + k_S$ (see Scheme 3).

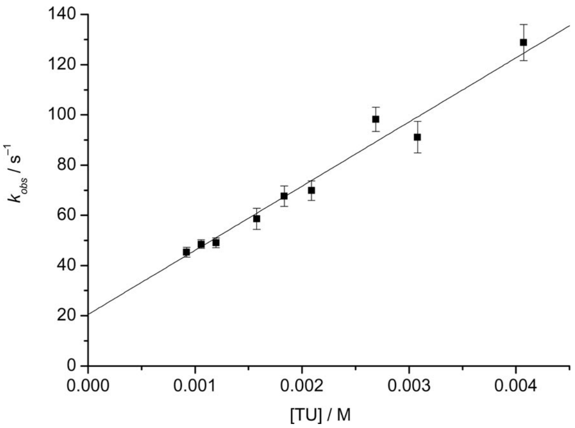


Figure 5. Concentration dependence of k_{obs} for the reaction of complex **I** with TU in [emim][NTf_2] monitored at 352 nm at room temperature.

The intercept of Figure 5 ($k_S = 20 \pm 2\ \text{s}^{-1}$) represents the parallel aquation reaction with the water present in [emim][NTF_2], which was found to be ca. 60 ppm or 5 mM. The value of $k_2 = (2.5 \pm 0.1) \times 10^4\ \text{M}^{-1}\,\text{s}^{-1}$ obtained from the slope of the plot, is ca. 30 times smaller than that observed for the same reaction in water at 25 °C. The temperature dependence of the reaction was studied for several TU concentrations to determine the activation parameters for k_2. The intercepts of the corresponding plots were not accurate enough to determine reliable activation parameters for k_S. According to the Eyring plot given in Figure S4 (Supporting Information) $\Delta H^{\#} = 22 \pm 2\ \text{kJ}\,\text{mol}^{-1}$ and $\Delta S^{\#} = –82 \pm 6\ \text{J}\ \text{K}^{-1}\,\text{mol}^{-1}$ for k_2. These values are very close to those reported above for the same reaction in water and support the associative nature of the substitution process.

The nucleophile concentration dependences for the reaction of complex **I** with $SCN^–$ and $I^–$, however, show a different behaviour. For both charged nucleophiles, saturation kinetics is observed with no significant intercept (see Figure 6). This suggests the participation of a pre-equilibrium, where the complex and entering nucleophile form an ion-pair intermediate prior to the ligand exchange process typical for an interchange mechanism. Scheme 4 summarizes the proposed mechanism in which K_1 is the ion-pair formation constant and k_1 is the interchange rate constant.

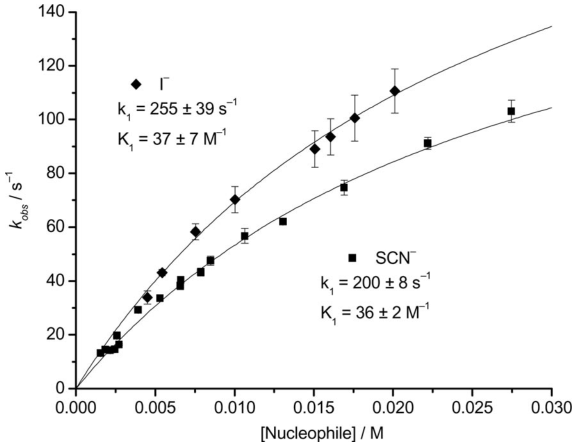
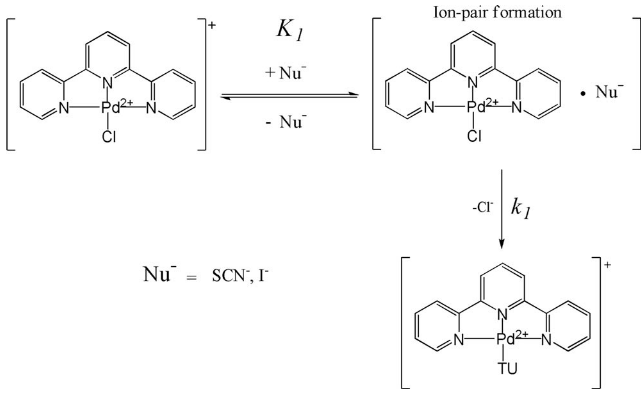


Figure 6. Concentration dependence for the reaction of **I** with SCN^- and I^- in $[emim][NTf_2]$ at room temperature.



Scheme 4. Proposed substitution mechanism for the reaction of complex **I** with charged nucleophiles involving ion-pair formation.

The rate law for the inclusion of the ion-pair pre-equilibrium is given by:

$$k_{obs} = \frac{k_1 \cdot K_1 \cdot [Nu]}{1 + K_1 \cdot [Nu]}$$

The reactions with the charged nucleophiles were found to be slightly slower than with TU, but still remarkably fast. As in the case with TU, the maximum observable value of k_{obs} was ca. 120 s^{-1} due to the longer dead time of the instrument when $[emim][NTf_2]$ is used as solvent. The reaction with I^- is slightly faster than the reaction with SCN^-, in line with the reactivity already known from substitution reactions with Pt^{II}.[17,18] The ion-pair formation constants found for both reactions are almost the same (see Table 2), which confirms the establishment of a similar pre-equilibrium prior to the substitution process in both cases. Since both ions are equally charged and have nearly the same size, a similar ion-pair formation constant can be expected for both processes. The values of the pre-equilibrium constants are in line with related ion-pair formation constants reported in the literature.[19]

In the absence of significant curvature, i.e. a smaller K_1 value, the rate law simplifies to $k_{obs} = k_1K_1[\text{Nu}]$, where k_1K_1 represents the second-order rate constant for the overall process. Table 2 summarizes the available rate and equilibrium constants, and activation parameters for the reactions of complex **I** with TU, SCN^- and I^- in $[emim][NTf_2]$. From a comparison of the overall second-order rate constants (k_1K_1 or k_2) for the reactions with the selected nucleophiles, it follows that the anionic nucleophiles react ca. 3 times slower than the neutral nucleophile in this IL.

[emim][EtOSO$_3$] as Solvent

The substitution reactions of complex **I** were also studied in the significantly more viscous IL $[emim][EtOSO_3]$ as solvent. The reaction with TU was measurable, but the long dead time (ranging from 30 to 60 ms, depending on the water content and temperature) in the stopped flow instrument as a result of the high viscosity of this IL, prevented the determination of k_{obs} values larger than 55 s^{-1}. In addition the observed kinetic traces tended to show a subsequent slow drift that most likely originated from slow diffusion processes due to the high viscosity of the ionic liquid. In some cases the kinetic traces had to be fitted with a two-exponential function in order to correct for this complication. The concentration dependence of k_{obs} for the reaction with TU is shown in Figure S5 (Supporting Information). The reaction follows the simple rate law as found for the same reaction in water as solvent. The k_2 value is $(1.79 \pm 0.08) \times 10^3$ $M^{-1} s^{-1}$ at 25 °C which is 440 times slower than in water, which can be ascribed to an ionic interaction of the ethylsulfate anion with the electrophilic Pd^{II} center that blocks the active site and slows down the nucleophilic attack by TU. A similar effects was especially noted for this IL in our earlier studies for the corresponding Pt^{II} complex.[8]

In comparison to the reaction in $[emim][NTf_2]$ where the intercept of the concentration dependence was attributed to an aquation reaction, there is no indication of a parallel or back reaction in $[emim][EtOSO_3]$ although the water content of this IL was much higher. This is most likely due to the high chloride content of $[emim][EtOSO_3]$, viz. 340 ppm or 12 mM, which in turn will stabilize the chloro complex

Table 2. Summary of rate and equilibrium constants along with activation parameters for the reaction of complex **I** with different nucleophiles in $[emim][NTf_2]$ at 25 °C.[a]

Nucleophile	K_1 [M^{-1}]	k_1 [s^{-1}]	k_1K_1 or k_2 [$M^{-1} s^{-1}$]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1}, mol^{-1}]
TU			$(2.5 \pm 0.1) \times 10^4$	22 ± 2	-82 ± 6
SCN^-	36 ± 2	200 ± 8	$(7.2 \pm 0.7) \times 10^3$		
I^-	37 ± 7	255 ± 39	$(9 \pm 3) \times 10^3$		

[a] Preliminary data for the reaction with TU as nucleophile were reported earlier.[9]

and prevent the parallel aquation reaction. As in the case of the measurements in water, chloride serves to stabilize the palladium complex by preventing aquation and subsequently suppresses the parallel reaction. The activation parameters were obtained from a temperature dependence study (see Figure S6, Supporting Information) and the values $\Delta H^{\neq} = 35 \pm 1$ kJ mol^{-1} and $\Delta S^{\neq} = -62 \pm 4$ J K^{-1} mol^{-1} are once again in line with an associative or associative interchange mechanism as expected.

The reactions with SCN$^-$ as nucleophile were difficult to follow as this reaction seemed to be very sensitive to the purity of the IL. Also the spectral changes were very small and at wavelengths where the absorbance of the IL itself was already quite high. The measured concentration dependence shows an extremely slow reaction for the Pd^{II} complex, viz. a linear dependence of the observed rate constant on the SCN$^-$ concentration, and a significant intercept (see Figure 7). Also, the absorbance change associated with the reaction increases with increasing nucleophile concentration, which points to an equilibrium process, i.e. a significant back reaction. The temperature dependence of the reaction was not studied since the results were not very reproducible, especially at higher temperatures.

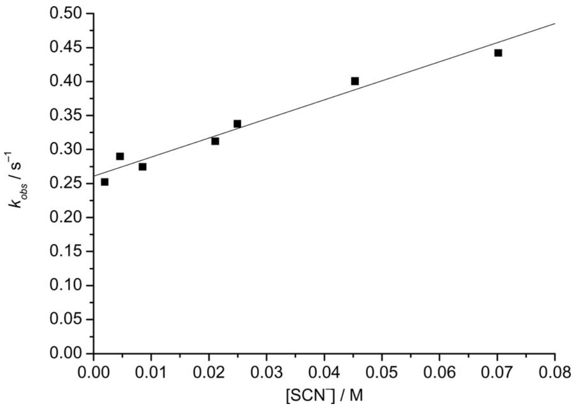
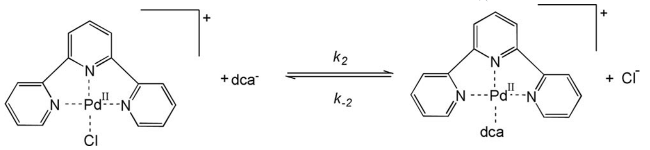


Figure 7. Concentration dependence of k_{obs} for the reaction of complex **I** with SCN$^-$ in [emim][EtOSO$_3$] at 25 °C.

[emim][dca] as Solvent

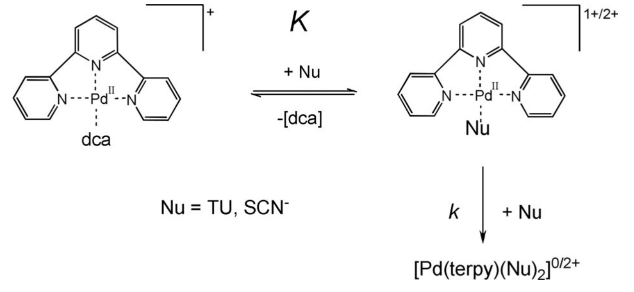
This IL presents a special case amidst the selected ILs for this study. The dicyanamide anion can act as a nucleophile and coordinate to the metal centre. It is therefore reasonable to expect on dissolving complex **I** in this IL that a spontaneous substitution reaction will cause the displacement of the chloride ligand by the dca anion as shown in Scheme 5 as a result of its high concentration. On addition of sodium dicyanamide to a solution of **I** in water, changes in the UV/Vis spectrum clearly indicated a reaction of dca$^-$ with the complex (see Figure S7). Due to the very high concentration of [dca] present in the IL, the equilibrium in Scheme 5 is expected to lie completely on the right side when complex **I** is dissolved in [emim][dca].



Scheme 5. Possible displacement of Cl$^-$ by dca$^-$ in complex **I**.

Thus, for the reaction of TU or SCN$^-$ with **I** in [emim][dca] it must be taken into account that apparently dca$^-$ and not chloride will be displaced by the entering nucleophile from the Pd^{II} complex present in solution. Another drawback of this IL is its quite intense yellow color that can interfere with the spectral changes observed during the substitution process. The UV/Vis-spectrum of [emim][dca] shows a strong absorbance band starting at 400 nm and increasing into the UV range. Even after thorough cleaning procedures,[21] the absorbance was still too high to be able to measure any kinetic traces below 350 nm (see Figure S8, Supporting Information). In addition, the [Pd(terpy)dca]$^+$ complex proved to be very labile such that the ligand-substitution reaction with the entering nucleophiles was too fast to be observed on the stopped-flow time scale.

Because of these complications, the simple ligand-substitution reaction between the [Pd(terpy)dca]$^+$ complex and TU or SCN$^-$ could not be studied. However, on increasing the nucleophile concentration a slower subsequent reaction could be observed. On the basis of Scheme 6 it is suggested that the entering nucleophile is able to displace one of the coordinated nitrogen donors from the terpyridine ligand to undergo partial dechelation during a second slower reaction step. This is also known from the literature, where N-donor chelate ligands are partially or even completely displaced by strong sulfur donor nucleophiles such as TU and SCN$^-$.[20]



Scheme 6. Possible reaction pathway for the dechelation of the terpyridine ligand by TU or SCN$^-$ in [emim][dca].

The first reaction is very fast due to the rapid substitution of the weakly coordinated dca$^-$ and can be treated as pre-equilibrium step (K) which is followed by the second, rate-determining dechelation step (k). The rate law for this reaction sequence is given below, and can be simplified when $K\cdot[\mathrm{NU}] \ll 1$. Under such conditions the rate law suggests a quadratic dependence of k_{obs} on the nucleophile concentration. The kinetic data for the reaction with TU indeed seem to fit this suggested behavior as shown in Figure 8. The values of kK, a third-order rate constant, were found to be 82 ± 3 and $(3.8 \pm 0.1) \times 10^{-2}$ M^{-2} s^{-1} at 25 °C for the reactions with TU and SCN$^-$, respectively. Once again the reactions with TU are significantly faster than with SCN^- presumably due to competition with the excess dca^- present that will especially affect the reaction with SCN^- also being an anion.

$$k_{obs} = \frac{K \cdot [Nu]}{1 + K \cdot [Nu]} k \cdot [Nu]$$

and for $K\cdot[Nu] << 1$, $k_{obs} = K \cdot k \cdot [Nu]^2$

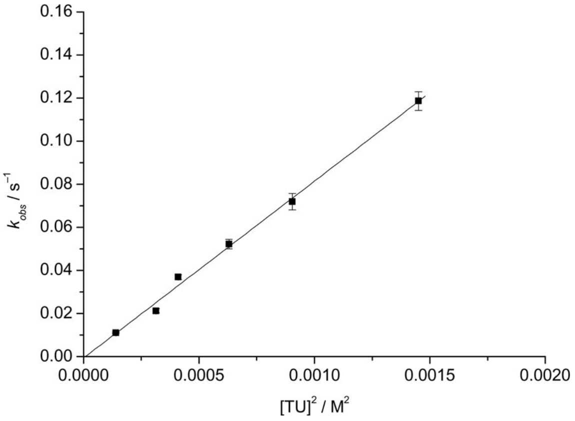


Figure 8. Quadratic dependence of k_{obs} on the concentration of TU for the reaction of TU with $[Pd(terpy)(dca)]^+$ in [emim][dca] at room temperature.

[emim][OTf] as Solvent

This IL also exhibits a relatively high viscosity (45 cP[22]) which increases the dead time of the stopped-flow instrument. Since this IL showed the largest deceleration of ligand-substitution reactions in the case of the analogous Pt^{II} complex,[8] we were confident that even the very fast reaction expected for the corresponding Pd^{II} complex would be slowed down significantly to allow it to be observed on the stopped-flow time scale. Figure S9 (Supporting Information) shows a typical kinetic trace apparently recorded for the reaction of complex **I** with TU in this IL. The observed reaction unfortunately turned out to be caused by the long dead time of the stopped-flow apparatus and remained the same throughout all measurements. The dead time for [emim][OTf] solutions in the stopped-flow instrument is at least 70 ms and we were not able to find any other suitable nucleophile that would react slowly enough with complex **I** to allow a systematic study; the reactions were either too fast, or the absorbance changes were too small to be measured.

We then turned to the second reaction step, where TU partially dechelates the terpyridine ligand in a slow subsequent dechelation reaction following the rapid substitution of chloride. Figure 9 reports the quadratic concentration dependence of k_{obs} for the reaction of complex **I** with TU at higher concentrations in [emim][OTf]. A possibly reaction pathway is given in Scheme 7.

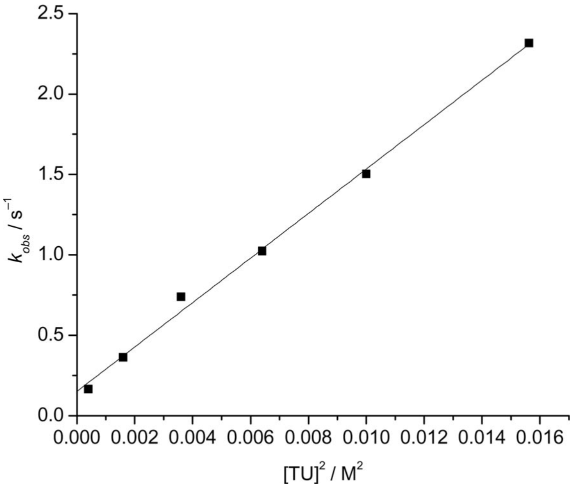
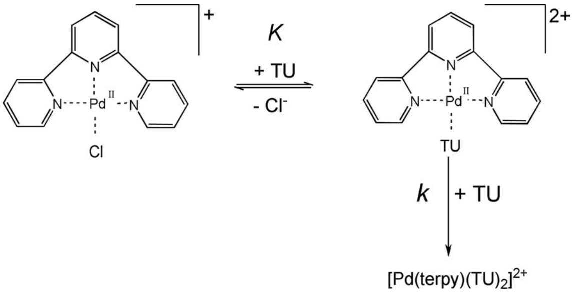


Figure 9. Quadratic concentration dependence of k_{obs} for the reaction of complex I with TU in [emim][OTf] at 25 °C.



Scheme 7. Possible reaction pathway for the partial dechelation of the terpyridine ligand by TU in [emim][OTf].

The rate law follows the same pattern as in the case of [emim][dca] and presents itself as a quadratic dependence of k_{obs} on the nucleophile concentration. The third-order rate constant $kK = 138 \pm 4\ \text{M}^{-2}\,\text{s}^{-1}$. To ensure that **I** was not aquated in the IL, a tandem cuvette experiment showed no evidence for a reaction when sodium chloride (50 mM) was added to **I** dissolved in [emim][OTf].

Conclusions

The substitution reactions of complex **I** were studied for different nucleophiles in water and several ionic liquids. The reaction of the Pd^{II} complex with TU in water is 260 times faster than for the corresponding Pt^{II} complex studied in our earlier work.[8] The significantly higher lability of the Pd^{II} complex caused severe complications in terms of the dead time of the stopped-flow method in dealing with such viscous ILs. The study therefore demonstrated the limits of this method and to what extent such reactions can indeed be studied. Table 3 summarizes the resulting rate constants and activation parameters for the cases where a linear dependence on the TU concentration was observed.

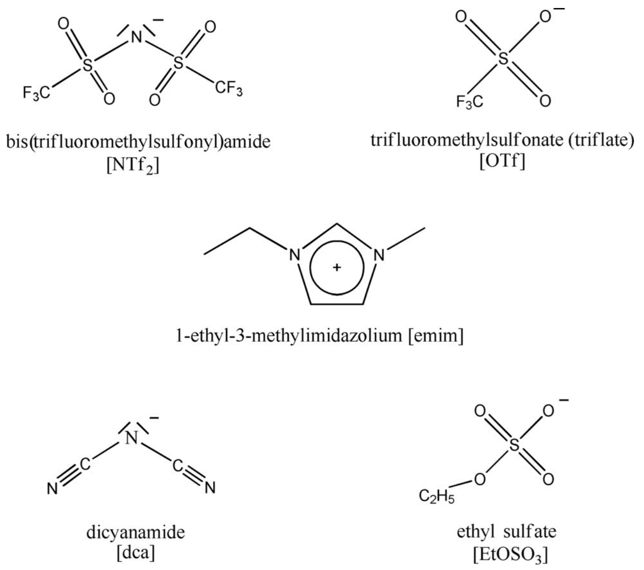
The rate constants in Table 3 follow the same pattern as in the case of the corresponding Pt^{II} complex, where the reaction was found to be 6 times slower in $[emim][NTf_2]$

Table 3. Summary of the second-order rate constants and activation parameters for the reaction of complex **I** with TU as nucleophile in water and two ILs at 25 °C.

Solvent	k_2 [M^{-1} s^{-1}]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]
water	$(7.8 \pm 0.2) \times 10^5$	18.5 ± 0.9	-69 ± 3
[emim][NTf$_2$]	$(2.5 \pm 0.1) \times 10^4$	22 ± 2	-82 ± 6
[emim][EtOSO$_3$]	$(1.79 \pm 0.08) \times 10^3$	35 ± 1	-62 ± 4

and 150 times slower in [emim][EtOSO$_3$] as compared to the reaction in water. The trend in the present case is much stronger in that the reaction of the Pd^{II} complex in [emim][NTf$_2$] was slowed down by a factor of 30 and in [emim]-[EtOSO$_3$] by a factor of 440. The activation enthalpy for the reaction is about 10 kJ mol^{-1} lower in water and [emim][NTf$_2$], and about 20 kJ mol^{-1} lower in [emim][EtOSO$_3$] than in the case of the Pt^{II} complex, which is attributed to the higher electrophilicity of the Pd^{II} complex that in turn reduces the activation barrier. Activation entropies remained roughly the same and all support the operation of an associatively activated substitution mechanism. In the case of SCN$^-$ as entering nucleophile only water and [emim][EtOSO$_3$] show a linear concentration dependence, where the reaction in the IL is slowed down significantly by a factor of 6000 (for SCN$^-$: k_2(water) = $(16.6 \pm 0.4) \times 10^3$ M^{-1} s^{-1}, k_2([emim][EtOSO$_3$]) = 2.8 ± 0.2 M^{-1} s^{-1}). This can be ascribed to an effective shielding of the electrophilic metal center by the anionic component of the IL, which will retard the attack by the anionic nucleophile. The results for the other ILs vary in terms of the nature of their reaction mechanisms, which makes a direct comparison less fruitful.

Our work has demonstrated that mechanistic studies on fast reactions in ionic liquids can be performed with conventional methods like stopped-flow kinetics and UV/Vis spectroscopy. However, the viscosity and inherent colour of the ILs often hinder detailed investigations and limit the accessible concentration ranges. Impurities like water, halides or organic residues can also have a significant effect on the outcome of the reactions in IL. Furthermore, the reported results clearly demonstrate that ILs are far from being “innocent” solvents for transition metal chemistry. Their influence on the reaction rate and mechanism, especially for labile complexes like the one studied, is versatile and difficult to predict. As a final remark it should be said that ILs are to be checked individually with respect to their influence on the kinetics and mechanism of reactions performed in ILs.



Scheme 8. The [emim] cation and various anions used for the ILs in this study.

Experimental Section

Materials: All chemicals used were of analytical reagent grade and of the highest purity commercially available. The [Pd(terpy)Cl]Cl complex was synthesized as described in the literature.[11] The organic solvents used for the preparation of the ILs were dried as described in the literature.[21] The water used was double-distilled and deionized. The Ils used in this study are outlined in Scheme 8.

Synthesis and Purification of ILs: All operations were performed under nitrogen atmosphere. [emim][dca] was obtained from Solvent Innovation GmbH and purified before use by stirring with activated charcoal, drying under vacuum at 40 °C for 3–4 d, and finally storing over molecular sieves. It had to be cleaned from Na[dca] that remained from the synthesis of this IL. This was achieved by addition of a threefold excess of dichloromethane to the liquid to precipitate Na[dca], followed by filtration. Following the proposed cleaning procedure from the literature, [emim][dca] was filtered through a specially designed column to remove colouring impurities.[22] [emim][OTf] was obtained from IoLiTec GmbH and purified before use by stirring with activated charcoal, drying under vacuum at 65 °C for 3–4 d, and finally storing over molecular sieve. The synthetic route used by IoLiTec GmbH ensured that no chloride was present in the IL. An ion chromatographic measurement showed that the IL also contained no methylimidazole. The water content determined by Karl-Fischer titration was 270 ppm for [emim][OTf] and 70 ppm for [emim][dca]. [emim][EtOSO$_3$] was also obtained from Solvent Innovation and purified before use. The IL was dissolved in an equal amount of water and extracted three times with distilled chloroform to ensure removal of organic residues (viz. methylimidazole) that remained from the synthesis. Chloroform was removed by decantation and water by slow evaporation, functioning as steam distillation. Activated charcoal was added and the suspension was stirred for several days. After filtration the liquid was dried under vacuum at 40 to 50 °C for several days before use. The water content was then adjusted to 1800 ppm to reduce the high viscosity of this IL and to increase the solubility of the substrates. The resulting IL was colourless. [emim][NTf$_2$] was synthesized according to an anion metathesis procedure described in the literature.[23] [emim]Br and Li[NTf$_2$] were obtained from Solvent Innovation GmbH, [emim]Br was purified twice by recrystallization before metathesis, and was obtained as a white solid. The obtained [emim][NTf$_2$] was washed at least eight times with water to remove the remaining halide residues. The IL was then stirred with activated charcoal, filtered and dried under vacuum at 40 to 50 °C for 3–4 d. The resulting liquid was colorless and had a water content of 50–70 ppm as determined by Karl Fischer titration.

Instrumentation and Measurements: Karl-Fischer titrations were performed on a 756 KF Coulometer (Metrohm). Elemental analysis [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 characterization, respectively. Ion chromatography was performed on an Ion Chromatography System ICS-3000 (Dionex) IonPac AS20 with a GS20 guard column. The UV/Vis spectra of the studied ILs were recorded on a Varian Cary 1G spectrophotometer equipped with a thermostatted cell holder. Fast UV/Vis spectral changes were observed using tandem cuvettes with an optical pathway of 0.88 mm. For kinetic measurements on the substitution reactions in ILs a Durrum D110 (Dionex) stopped-flow instrument was used. This instrument had several advantages: the complete sample syringes could be inspected for the presence of undesired gas bubbles; a 2 cm optical path; the possibility to trigger the optical detector prior to completion of the flow process, i.e. prior to filling the stop syringe. For kinetic measurements in water as solvent, an Applied Photophysics Spectra Kinetic stopped-flow instrument was used, since this apparatus has a shorter dead-time than the Durrum instrument and allows the measurement of rate constants up to 500 s^{-1}, depending on the size of the observed spectral changes. The temperature of the instruments was controlled within an accuracy of 25.0 ± 0.1 °C for all measurements, except where the temperature dependence was studied. The ligand-substitution reactions were studied under pseudo-first-order conditions by using at least a tenfold excess of the entering nucleophile. All listed rate constants represent an average value of at least five kinetic runs under each experimental condition.

Preparation of Solutions and Analysis of Data: All solutions of complex **I** and the nucleophiles in the ILs (or water) were prepared under nitrogen atmosphere. The Pd^{II} complex was added to the ILs (or water) and stirred overnight for all ILs, except for [emim][OTf] where all complex solutions were prepared and measured on the same day as the complex slowly decomposed in this IL. All nucleophile solutions were prepared in advance, as they turned out to be stable in all ILs and water over a longer period of time. The complex concentration was kept between 0.01 and 0.3 mM in all ILs, depending on the observation wavelength and nucleophile concentration. All solutions of the complex and nucleophiles in water were prepared in 0.01 M hydrochloric acid in order to prevent spontaneous aquation of the chloro complex. Since the ILs consist entirely of cations and anions, no ionic strength adjustment was made. The kinetic traces obtained were fitted with Origin 7. Nearly all kinetic traces were fitted with a single-exponential function; exceptions are mentioned in the corresponding sections.

Supporting Information (see also the footnote on the first page of this article): Figures S1–S9 (showing kinetic traces and UV/Vis spectra).

Acknowledgments

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