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Transition-State Effects of Ionic Liquids in Substitution Reactions of Pt^{II} Complexes**

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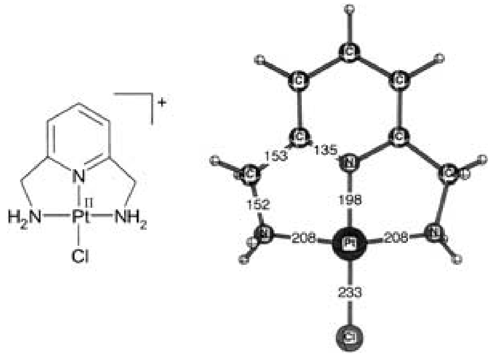
Ligand-substitution reactions of square-planar complexes of d^8 metal ions such as Pt^{II} and Pd^{II} play a fundamental role in many chemical processes, for instance, in the treatment of tumors and in homogeneous catalysis.[1,2] Detailed mechanistic studies have demonstrated that such complexes usually undergo associative ligand-substitution reactions as a result of the 16-valence-electron structure of the square-planar complex.[3] The transition state has either a semi-five-coordinate character in the case of an associative interchange (I_a) mechanism, or forms a short-lived, five-coordinate intermediate in the case of a limiting associative (A) mechanism. Exceptions are found in cases in which two neighboring spectator ligands form metal–carbon bonds with the metal center and induce a dissociative mechanism.[4]

In terms of the biological or catalytic application of such metal complexes, the fundamental understanding of the ligand-substitution mechanisms enables a systematic tuning of the lability of the metal center, that is, the efficiency of the chemical process. A distinction between the three mechanisms can usually be made on the basis of activation parameters derived from the temperature and pressure dependence of the reaction, that is, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta V^{\neq}$.[3,5,6] In recent work performed in our laboratories, the lability of Pt^{II} complexes could be systematically tuned through the introduction of σ-donor and π-acceptor spectator chelates.[7,8] Rate and activation parameters clearly supported the associative nature of the underlying substitution mechanism.

In recent years, ionic liquids have become a popular research area that is expected to grow as a result of their potential industrial application.[9] Not only are such liquids interesting in terms of applications in separation techniques but also they may be used to improve the solubility of weakly soluble gases and enhance the catalytic activity of metal complexes.[10] The first industrial process based on the application of ionic liquids has been launched.[11]

Mechanistic studies on chemical reactions in ionic liquids have only been performed to a limited degree. Skrzypczak and Neta determined the rate constants for the reaction of 1,2-dimethylimidazole with benzyl bromide (Menschutkin reaction) in a series of ionic liquids and organic solvents. The rate constants in the ionic liquids are comparable with those for polar aprotic solvents, but much larger than those for weakly polar organic solvents and alcohols.[12] Chiappe and Pieraccini determined rate constants and activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) for the reactions of Br_3^- and ICl_2^- ions with some alkenes and alkynes in a series of ionic liquids and in 1,2-dichloroethane.[13] McLean and co-workers[14] studied the effect of ionic liquids on bimolecular rate constants for the displacement of solvent from $[(C_6H_6)Cr(CO)_2(solv)]$. Inhibition of the catalytic activity of a Ru^{II} catalyst in ionic liquids was recently reported by Daguenet and Dyson for a reaction system in which chloride dissociation is a crucial step.[15] More recently, work in our laboratory demonstrated that this inhibition could be related to the selected anionic component of the employed ionic liquids, since other anions in our hands clearly lead to a faster chloride dissociation step from a Pt^{II} complex in the catalytic process studied.[16] Following the submission of this work, Shaughnessy and co-workers reported kinetic data for oxidative-addition and ligand-substitution reactions in ionic liquids.[17,18]

A fundamental question, however, does remain: Do ionic liquids really behave as "normal" solvents, or are there unknown aspects that could affect the substitution behavior of square-planar Pt^{II} complexes? We report herein a detailed kinetic study of the substitution reactions of the $[Pt^{II}(apa)Cl]^+$ complex **1** (apa = 2,6-bis(aminomethyl)pyridine; Scheme 1) with thiourea and iodide as nucleophiles, in water, methanol, and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluor-



Scheme 1. Chemical formula and DFT structure of complex **1**; distances in pm.

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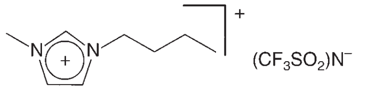
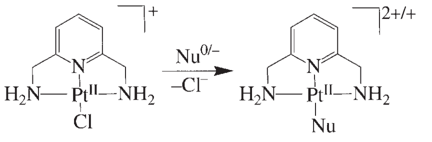
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

omethylsulfonyl)amide ([BMIM]BTA) as solvents. This ionic liquid has a melting point of $-4\,^{\circ}C$[19] and a polarity close to that of ethanol.[9d] We studied the reaction as a function of the concentration of the entering ligand, the temperature, and the pressure to determine all the rate and activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta V^{\neq}$). This is, as far as we know, the first time that a systematic pressure-dependence study was undertaken for a chemical reaction in an ionic liquid. The reported rate and activation parameters show a rather "normal" behavior for the employed ionic liquid and demonstrate some unique properties of the ionic liquid as medium for the investigated substitution reactions.



[BMIM]BTA

The solvent dependence of the ligand-substitution reactions of **1** with thiourea (TU) and iodide (Scheme 2) were studied by dissolving the isolated complex **1**-Cl in the selected solvents followed by rapid mixing with a stock solution of the nucleophile. Typical examples of the observed spectral changes and kinetic traces are shown in Figure 1. The overall spectral changes were found to be rather similar for the studied solvents, with the exception of [BMIM]BTA due to the absorption of this liquid in the wavelength range $\lambda <$ 350 nm (see Figure 1c). All kinetic traces (Figure 1b,d) showed excellent fits to a single-exponential function, in line with pseudo-first-order behavior. The calculated pseudo-first-order rate constants, k_{obs}, were plotted against the concentration of the entering nucleophiles, TU and iodide, and are linear with a zero intercept under all conditions (see typical examples given in the Supporting Information). The rate constant k_{obs} can be expressed as a function of the concentration of the entering ligand, namely, $k_{obs} = k_2[Nu]$, in which k_2 is the second-order rate constant.



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Scheme 2. The investigated substitution reaction for thiourea (Nu^0) and iodide ion (Nu$^-$).

We also studied the effect of the water content of the ionic liquid on the second-order rate constant for the reaction of **1** with TU in [BMIM]BTA. The following k_2 values were obtained at 25 °C (water content in ppm in brackets): 0.260 (23), 0.245 (100), and 0.259 $M^{-1}s^{-1}$ (200). It follows that the water content has no significant effect on the rate constant in the investigated concentration range.

The activation parameters were determined from the effect of temperature and pressure on k_2. Spectral changes observed for the reaction in [BMIM]BTA at 100 MPa (see Supporting Information) are in excellent agreement with those observed at ambient pressure. The thermal activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were obtained from Eyring plots (see example in the Supporting Information), whereas $\Delta V^{\neq}$ was calculated from the gradient ($-\Delta V^{\neq}/RT$) of the plot of $\ln k$ versus pressure (see Supporting Information). Table 1 summarizes the values of the dielectric constants (ε), E_T^N, k_2, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta V^{\neq}$ for the studied reactions in the three selected solvents. It should be noted that the reactions in the ionic liquid showed the same behavior as that found for other more conventional solvents as a function of the experimental variables.

The reaction of **1** with TU, a strong nucleophile, is considerably faster than the reaction with iodide in the same solvent. The k_2 values show that the substitution reactions depend significantly on the polarity of the solvent, namely, $k_2(H_2O) \gg k_2(MeOH) \approx k_2(\text{ionic liquid})$. A likely reason is an increase in the dipole moment during the course of the reaction due to 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 reactant to the transition state.[22] The trend in the values of k_2 clearly indicates that the ionic liquid behaves like methanol and that no drastic acceleration or deceleration of the substitution of chloride, as reported for other Pt^{II} complexes in this and closely related ionic liquids, can be observed.[15,16]

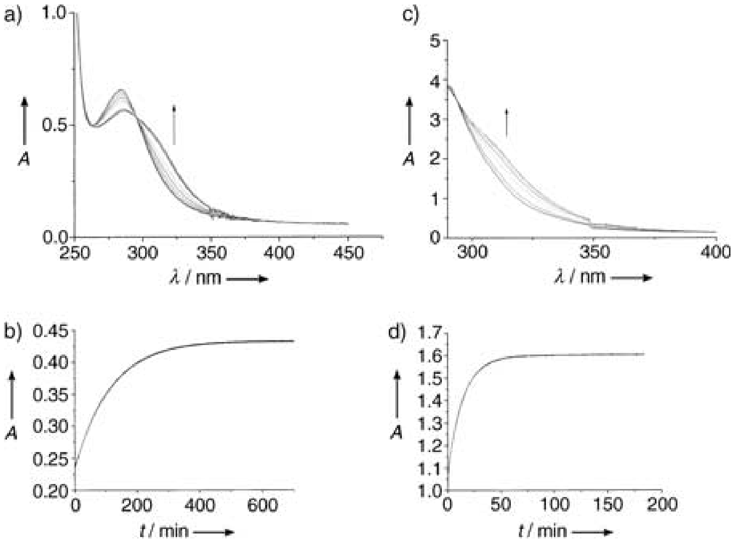

Figure 1. UV/Vis spectra (a,c) and typical kinetic traces at 320 nm (b,d) recorded for the reaction of **1** with iodide in methanol (a,b) and [BMIM]BTA (c,d). The experimental kinetic traces can be perfectly fitted with a single-exponential function. Experimental conditions: a) $[Pt^{II}] = 9.5\times10^{-5}$ M, LiCl (0.002 M), $[I^-] = 0.015$ M, ionic strength = 0.2 M ($LiClO_4$), pH 2 (0.01 M trifluoromethanesulfonic acid), $T = 25\,^{\circ}C$, optical path length = 10 mm. b) $[Pt^{II}] = 9.5\times10^{-5}$ M, LiCl (0.002 M), $[I^-] = 0.0090$ M, ionic strength = 0.2 M ($LiClO_4$), pH 2 (0.01 M trifluoromethanesulfonic acid), $T = 25\,^{\circ}C$. c,d) $[Pt^{II}] = 3.3\times10^{-4}$ M, $[I^-] = 0.0392$ M, $T = 25\,^{\circ}C$, optical path length = 5 mm.

Table 1: Summary of second-order rate constants and activation parameters[a] for the displacement of chloride by iodide and thiourea in **1** in different solvents.

	Solvent	ε(298 K), E_T^N[b]	$10^3 k_2$ at 25 °C [$\mathrm{M^{-1}\,s^{-1}}$]	$\Delta H^{\neq}$ [$\mathrm{kJ\,mol^{-1}}$]	$\Delta S^{\neq}$ [$\mathrm{J\,K^{-1}\,mol^{-1}}$]	$\Delta V^{\neq}$ [$\mathrm{cm^3\,mol^{-1}}$]
I^-	water	78.30, 1.000	253 ± 2	58 ± 1	−62 ± 3	−6.9 ± 0.3
I^-	methanol	32.66, 0.762	15.3 ± 0.2	69 ± 1	−51 ± 4	−10.0 ± 0.2
I^-	[BMIM]BTA	–, 0.642	32.1 ± 0.2	66 ± 1	−53 ± 5	−14.1 ± 0.4
TU	water	78.30, 1.000	1620 ± 10	49 ± 1	−77 ± 4	−10.4 ± 0.5
TU	methanol	32.66, 0.762	385 ± 2	63 ± 1	−42 ± 4	−6.6 ± 0.1
TU	[BMIM]BTA	–, 0.642	277 ± 3	49 ± 1	−92 ± 2	−13.9 ± 0.2

[a] Activation parameters were calculated from the temperature and pressure dependence of the second-order rate constant in the usual way. No corrections were made for changes in solvent density[20] or viscosity[21] as a function of temperature and pressure. [b] Dielectric constant (ε) of the solvent and its polarity (E_T^N).

The activation parameters summarized in Table 1 show some interesting trends. Throughout the series of reactions studied, the negative activation entropy and volume data clearly support the operation of a compact transition state in terms of an associative mechanism.[3] For the reaction between complex **1** and TU, significantly more negative activation entropies and volumes are found for water and [BMIM]BTA as the solvent irrespective of their significant difference in polarity. This finding suggests that reorganization in the transition state is not controlled by solvent electrostriction. The less negative activation entropies and volumes for the reaction in methanol once again illustrate that solvent electrostriction does not contribute significantly to the transition state, otherwise the opposite effect would occur. In this case, TU is a neutral entering nucleophile and the mentioned activation parameters mainly correspond to intrinsic entropy and volume changes.

In the case of iodide as the entering nucleophile, the values of the activation entropy are almost the same for the different solvents, whereas the activation volumes are significantly more negative in the case of methanol and [BMIM]BTA as solvents. This result suggests that charge neutralization in the five-coordinate transition state leads to a decrease in electrostriction—that is, a less negative activation volume—in the more polar solvents (water and methanol). This trend, however, does not show up in the values of the activation entropy, which is probably related to the usually larger error limits of this parameter. Nevertheless, the trend in the activation volumes for the different solvents is quite convincing.

The activation volumes for the reactions with TU and iodide in [BMIM]BTA are indeed very similar, which suggests that volume changes in this ionic liquid do not respond to changes in the overall charge of the transition state. We suggest that this lack of response is due to strong hydrogen bonding and possibly also van der Waals forces in ionic liquids, which result in specific solvent structures that consist of well aligned cation–anion aggregates. The formation of such aggregates in ionic liquids has recently been investigated by using microcalorimetry.[23] The stability of such aggregates will show a resistance towards solvent structural changes (electrostriction/solvation) as a result of charge neutralization or charge creation. The value of about $-14\,\mathrm{cm^3\,mol^{-1}}$ for $\Delta V^{\neq}$ is close to that expected for an associative ligand-substitution mechanism and represents the intrinsic volume collapse associated with the formation of a five-coordinate transition state.[5,6]

To gain further insight into the details of the ligand-substitution mechanism, in particular, the question of associative interchange (I_a) versus associative (A), we calculated the pathways for the reactions of **1** with chloride (chloride exchange), iodide, and thiourea by using B3LYP hybrid density functional theory[24] and the LANL2DZ ECP basis set augmented with polarization functions.[25,26] We have employed this theoretical level in previous work.[16,27]

The first step in the reaction is the formation of a precursor complex between the platinum complex **1** and the incoming ligand. As **1** bears a positive charge, interaction energies in the gas phase are dominated by electrostatics and exaggerated interaction energies are calculated, particularly for the complexes with the anionic nucleophiles chloride and iodide. Nevertheless, the structures of the precursor complexes for all incoming ligands indicate rather weak bonding. The main contact consists of a hydrogen bond to one of the amine hydrogen atoms (202, 249, and 221 pm for Cl^-, I^-, and S, respectively). On the other hand, the platinum–halide distances, 386 (chloride) and 437 pm (iodide), and the platinum–sulfur separation (for the reaction with thiourea), 458 pm, are very long. The other bonds around platinum differ only to a minor extent from those in **1**.

Hydrogen bonds to an amine hydrogen atom are well known in the solid state,[28] but may be unrealistic in the gas phase. Therefore, we also studied the reactions for the dimethylamino derivative, [Pt{2,6-bis(dimethylaminomethyl)pyridine}Cl]$^+$ ([Pt^{II}(mapa)Cl]$^+$, **2**). As expected, the platinum–ligand bonds are shorter in the absence of the hydrogen bonds, but only modestly: Pt−Cl 346, Pt−I 409, Pt−S 378 pm.

All reactions proceed through a single transition-state structure. Despite extensive searches along the reaction coordinate, no stationary points other than the precursor and product complexes could be located. Thus, the reactions clearly proceed by an interchange-type mechanism. The calculated activation barriers range from 64 to $89\,\mathrm{kJ\,mol^{-1}}$ and show that the nucleophile has a remarkably small influence (Table 2). Due to the presence of the hydrogen bond in the precursor complex, the barriers for the reactions of **1** are somewhat higher than for the reactions of **2**. The influence of *N*-methylation on the coordination sphere around the platinum center appears to be negligible.

The transition-state structures are compact, with relatively short bonds to the ligands that are being exchanged (Figure 2). This compactness is best seen in the reaction of **1** with Cl^-: the Pt−Cl bonds of the transition state are 259 pm, only 26 pm longer than the Pt−Cl bond in **1** itself and 23 pm longer than the Pt−Cl bond in the precursor complex. The situation in the other transition-state structures is very similar.

Table 2: Computational results for the reactions **1**+X and **2**+X (X = Cl^-, I^-, TU).

Reaction	Relative energies [kJ mol^{-1}][a]			Distances [pm] (Pt–Cl/Pt–X)		
	E_{cpx}	E_{react}	E_{act}	precursor	transition state	product
1+Cl^-	451	0	89	236/386	259/259	386/236
1+I^-	364	3	77	235/437	259/287	385/266
1+TU	86	13	72	235/458	259/268	298/238
2+Cl^-	415	0	66	237/346	260/260	346/237
2+I^-	334	21	75	237/409	262/291	345/269
2+TU	59	13	64	237/378	265/268	318/239

[a] E_{cpx}: complexation energy released on the formation of the precursor complex; E_{react}: reaction energy for the formation of the product complex; E_{act}: activation energy for the formation of the transition state relative to the precursor complex.

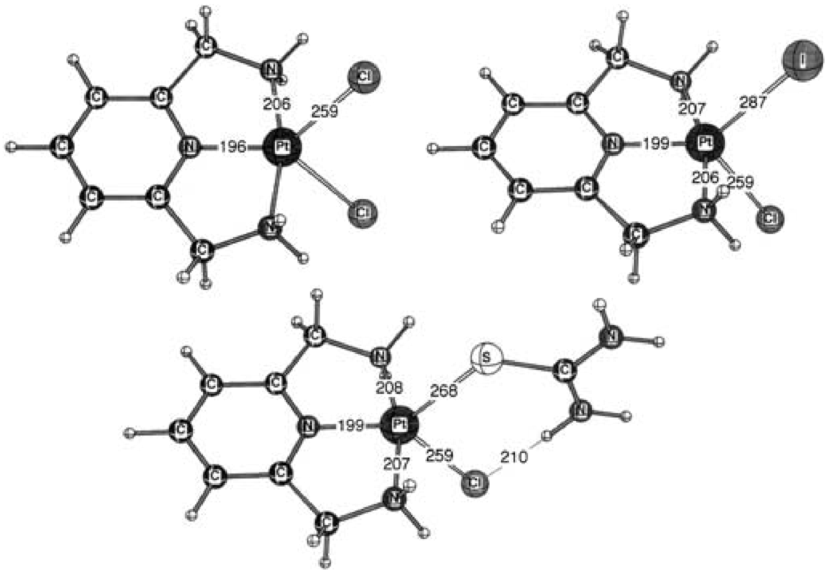

Figure 2. Calculated transition-state structures for the reaction of **1** with Cl^-, I^-, and thiourea. Distances are given in pm.

Hence, the reactions are best characterized as proceeding by an associative interchange, I_a, mechanism. In addition, in the reactions with thiourea, a hydrogen bond between chloride and one of the thiourea hydrogen atoms is preserved throughout the reaction.

The reactions of **1** with I^- and TU are both calculated to be mildly endothermic (+3 and +13 kJ mol^{-1}, respectively) in the gas phase. This is due to the lack of stabilizing solvation of the leaving chloride ion. For the reaction of **1** with iodide, inclusion of the influence of the bulk solvent through the isodensity polarizable continuum model (IPCM) gives a reaction energy of -7 kJ mol^{-1}.[29]

In conclusion, the studied substitution reaction was selected as a test system to investigate the behavior of ionic liquids as reaction medium for ligand-substitution reactions in comparison to conventional solvents. The observed spectral changes, kinetic traces, rate, and activation parameters clearly demonstrate the "normal" behavior and innocence of the selected ionic liquid in ligand-substitution reactions of Pt^{II} complexes. The kinetic data can be treated according to the transition-state theory as for any other solvent. No deviations whatsoever were observed. For the first time it has been possible to determine the activation volume for a ligand-substitution reaction on a metal complex in an ionic liquid. An analysis of the thermal and pressure activation parameters indicates that the ionic liquid exhibits rather unique properties in terms of electrostriction/solvation of transition states that involve different degrees of polarity as reflected by similar activation parameters in conventional solvents. The apparent insensitivity of the ionic liquid towards changes in polarity on going to the transition state can be ascribed to its tendency to form well-structured cation–anion aggregates. As a result of the apparent absence of solvent reorganization due to changes in electrostriction in this medium, the observed activation volume can be directly correlated with intrinsic volume changes that result from changes in bond lengths and bond angles on going to the transition state. This factor can, in principle, considerably simplify the accurate assignment of intimate mechanisms in cases in which changes in the polarity of the transition state cause large solvent effects in terms of electrostriction/solvation in conventional solvents and complicate the mechanistic assignment on the basis of activation parameters, especially activation entropy and volume data. This unique property of ionic liquids may come in very handy to resolve mechanistic discrepancies in conventional solvents.

Experimental Section

All chemicals used were of analytical reagent grade and of the highest purity commercially available. $K_2[PtCl_4]$ was obtained from Strem Chemical Co.; [BMIM]Cl and lithium bis(trifluoromethylsulfonyl)amide were obtained from Solvent Innovation. Ultrapure water was used for the spectroscopic and kinetic measurements. The solvatochromic Reichardt's dye, (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate hydrate, was obtained from Aldrich.

The complex **1**-Cl·H_2O, was synthesized following a reported procedure.[7] The ligand, 2,6-bis(aminomethyl)pyridine, was prepared according to a method used to synthesize 6-(aminomethyl)-2,2′-bipyridine[30] by using 2,6-bis(bromomethyl)pyridine[31] as the starting material. The corresponding platinum complex was prepared as described previously and was obtained in the same quality (see Supporting Information).[7]

The ionic liquid [BMIM]BTA was synthesized by using a reported procedure.[32,33] A solution of [BMIM]Cl (705 g, 4.04 mol) in H_2O (200 mL) was added to a solution of Li(bis(trifluoromethylsulfonyl)amide) (1.054 kg, 3.67 mol) in H_2O (200 mL; 1.1:1 molar ratio). The reaction media was mixed whereupon two phases formed: the bottom, slightly yellow phase was [BMIM]BTA; the top phase was aqueous LiCl. The reaction mixture was stirred overnight at room temperature and the top phase was decanted off. CH_2Cl_2 (200 mL) was then added and the mixture was washed three times with H_2O (500 mL). The addition of CH_2Cl_2 led to an improved separation of the phases. After removal of CH_2Cl_2 and addition of activated carbon, the mixture was stirred for over 48 h at room temperature. Filtration of the mixture through a normal frit followed by Millipore filtration (pore size 0.22 μm) afforded a colorless liquid, which was washed with water once more, dried at 50–60 °C under vacuum for 48 h and filtered through a Millipore filter (pore size 0.22 μm). The product, [BMIM]BTA, was a clear colorless liquid; its NMR data are in close agreement with those reported for an acetone solution (see Supporting Information).[33] The water content of [BMIM]BTA was determined by a Karl–Fischer titration by using a Metrohm 756 KF coulometer and found to be 23 ppm.

Instrumentation and measurements: [BMIM]BTA was dried and degassed before use. Its polarity was determined by using the solvatochromic Reichardt's dye (see the Supporting Information). The dimensionless normalized E_T^N values of the solvent were calculated according to reference [34].

Carlo Erba Elemental Analysers 1106 and 1108, and Bruker Avance DPX 300 and DRX 400 NMR spectrometers were used for chemical analysis and compound characterization, respectively. The UV/Vis spectra for the study of slow reactions were recorded on a Varian Cary 1G spectrophotometer equipped with a cell holder and thermostat. For the kinetic measurements on fast reactions an Applied Photophysics SX 18MV stopped-flow instrument was used. The wavelengths used are listed in the Supporting Information. Kinetic experiments at elevated pressure (1 to 130 MPa) were performed in a laboratory-made high-pressure stopped-flow instrument[35] or a Shimadzu UV-2101-PC spectrophotometer equipped with a high-pressure cell designed for the study of slow reactions.[36] The temperature of the instruments was controlled within an accuracy of ±0.1 K. TU and I^- (as LiI) were used as entering nucleophiles. Their high nucleophilicity prevents the back reaction. The starting complex was dissolved in water and methanol that contained LiCl (0.002 M) to avoid its solvolysis. Trifluoromethanesulfonic acid (0.01 M) was added to avoid formation of hydroxo or alcoholate ions, which could compete in the chloride displacement. In the case of iodide as nucleophile and methanol and water as solvent, the ionic strength was kept at 0.2 M ($LiClO_4$). The reactions were studied under pseudo-first-order conditions by using at least a tenfold excess of the nucleophiles. All listed rate constants represent an average value of at least five kinetic runs for each experimental condition.

Calculations: Structures were fully optimized at B3LYP/LANL2DZp[24–26] and characterized by calculation of vibrational frequencies. Relative energies include corrections for zero-point vibrational energy differences. Solvent effects were probed with IPCM single-point energy calculations by using the default parameters, that is, water as solvent.[29] The Gaussian program was used.[37]

Supporting Information available: Yields, elemental analyses, and ^1H NMR data for synthesized compounds; plots showing the concentration, temperature, and pressure dependence of the observed rate constants for the reactions between complex **1** and thiourea or iodide.

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