Experimental Section

General:
All chemicals used were of analytical reagent grade and of the highest purity commercially available. Thiourea and the chelate 2,2’:6’,2’’-terpyridine were purchased from Aldrich and used as received. K₂PtCl₄ and K₂PdCl₄ were obtained from Strem and used as received. Li[btb] and [emim]Br were purchased from Solvent Innovations. [emim]Br was recrystallized twice from methanol/acetone prior to use. [Pt(terpy)Cl]Cl and [Pd(terpy)Cl]Cl were synthesized according to known procedures.¹²³

[emim][btb] was synthesized according the synthetic route described elsewhere⁴ with some slight modifications. To obtain a really optical pure liquid suitable for spectrophotometric investigations down to wavelengths below 350 nm, the liquid resulting from the metathesis reaction was washed 8 times with ultrapure water, dried under high vacuum and then stirred for at least one week with activated charcoal purchased from Acros: Norit CN1 and Norit A SUPRA. After filtration over a millipore filter with Ø = 0.2 µm it was dried again. The water content of [emim][btb] was determined by Karl–Fischer titration using a Metrohm 756 KF coulometer and found to be in the range 55 to 70 ppm. The resulting UV/vis-spectrum of the purified liquid is given in Figure S1.

Instrumentation and Measurements:
UV/Vis spectra were recorded with Varian Cary 1G and Varian Cary 500 spectrophotometers, equipped with thermostatted cell holders. The absorbance maxima of the two used complexes were between 280 and 400 nm. Addition of an excess of thiourea causes clear changes in the absorbance spectrum (see Figures S2 and S4). The substitution of chloride by thiourea was monitored at 360 nm in case of [Pt(terpy)Cl]⁺ and at 352 nm in case of [Pd(terpy)Cl]⁺.

Kinetic measurements of the reactions were studied with a Dionex Durrum D-110 stopped-flow spectrophotometer with an optical pathway of 2 cm and a Xenon lamp as
light source. The minimum mixing time with [emim][bta] as solvent was about 18 ms. A pneumatic flow actuator operating with a pressure of 5 bar was used to ensure complete mixing of the relatively viscous solutions.

The solutions were all prepared in small volumetric flasks with nitrogen lines to prevent water contamination. The complex and the nucleophile had to be stirred over night to ensure complete dissolution. The solutions were filled into glass syringes and closed with three-way valves. Prior to filling the solutions into the stopped-flow instrument, it was flushed with water, acetone, air and a small amount of clean ionic liquid, to get rid of traces of water.

The temperature of the instruments was controlled with an accuracy of ± 0.1 °C. Thiourea (TU) was selected as entering ligand since its high nucleophilicity prevents the back reaction. The ligand substitution reactions were studied under pseudo-first-order conditions by using at least a ten-fold excess of TU. All listed rate constants represent an average value of at least five kinetic runs under each experimental condition.

References

Figures

Figure S1: UV-Vis spectrum of [emim][bta] recorded in a 1 cm quartz cell following all purification steps
Figure S2: Spectral changes observed for the reaction of [Pt(terpy)Cl]^+ with thiourea in [emim][bta]
Figure S3: Influence of the water content of the ionic liquid on the observed rate constant
Figure S4: Spectral changes observed for the reaction of [Pd(terpy)Cl]+ with thiourea in [emim][bta]