Electronic Supplementary Information (ESI)

Tuning the reactivity of chelated dinuclear Pt(II) complexes through a flexible diamine linker. A detailed kinetic and mechanistic study

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Table SI 1 Summary of the wavelengths (nm) used for monitoring the reactions between a series of Pt(II) complexes with bis(2-pyridylmethyl)amine chelates and thiourea nucleophiles.

Complex	nu	Wavelength (λ), nm
En	tu dmtu tmtu I^-	325 327 330 308
Prop	tu dmtu tmtu I^-	318 324 318
But	tu dmtu tmtu I^-	315 325 327 310
Hex	tu dmtu tmtu I^-	315 324 330 300
Oct	tu dmtu tmtu	312 324 327
Dec	tu dmtu tmtu	330 324 335
bpma	tu dmtu tmtu	276 276 300

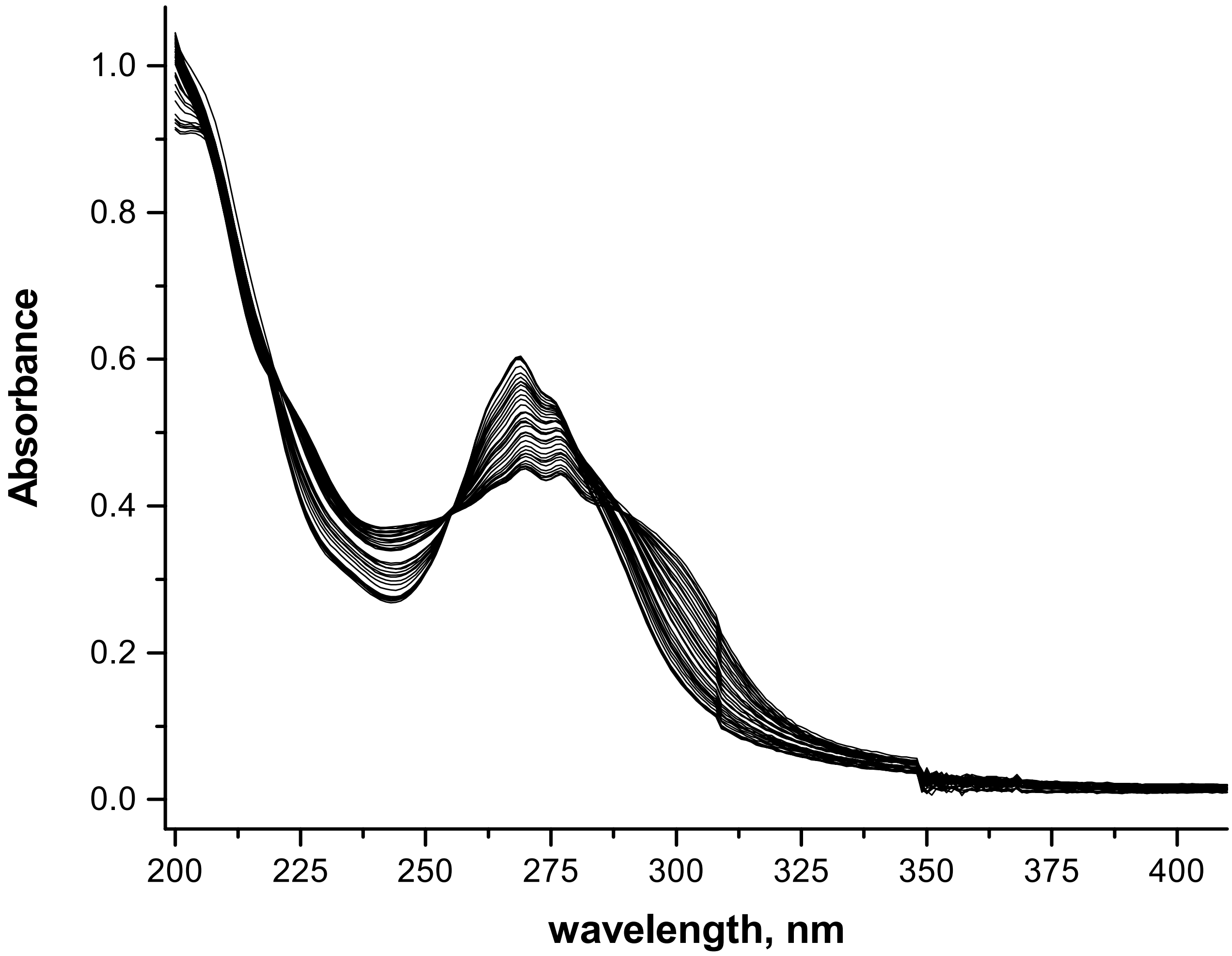


Fig. SI 1 UV-visible spectra for the titration of **Oct** (0.1 mM) with NaOH, pH range 2- 9, T = 298 K.

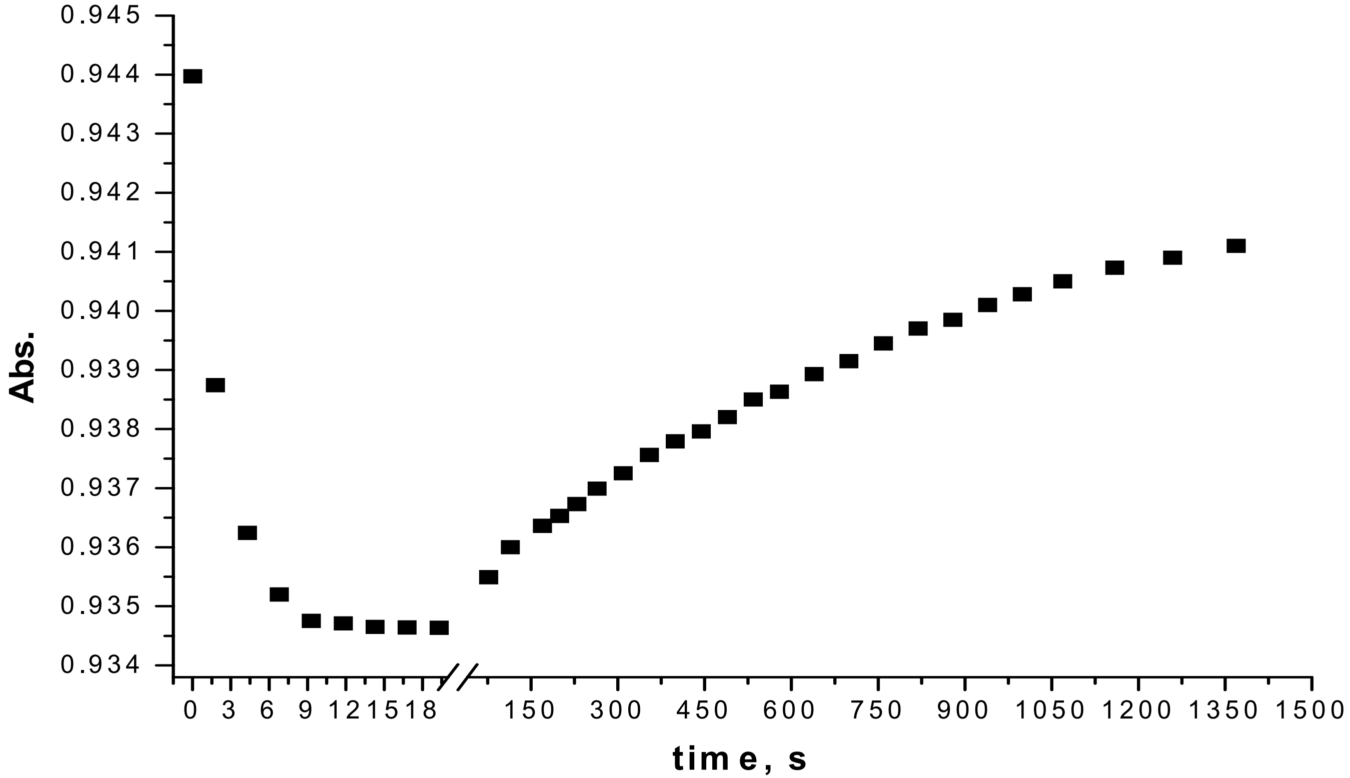
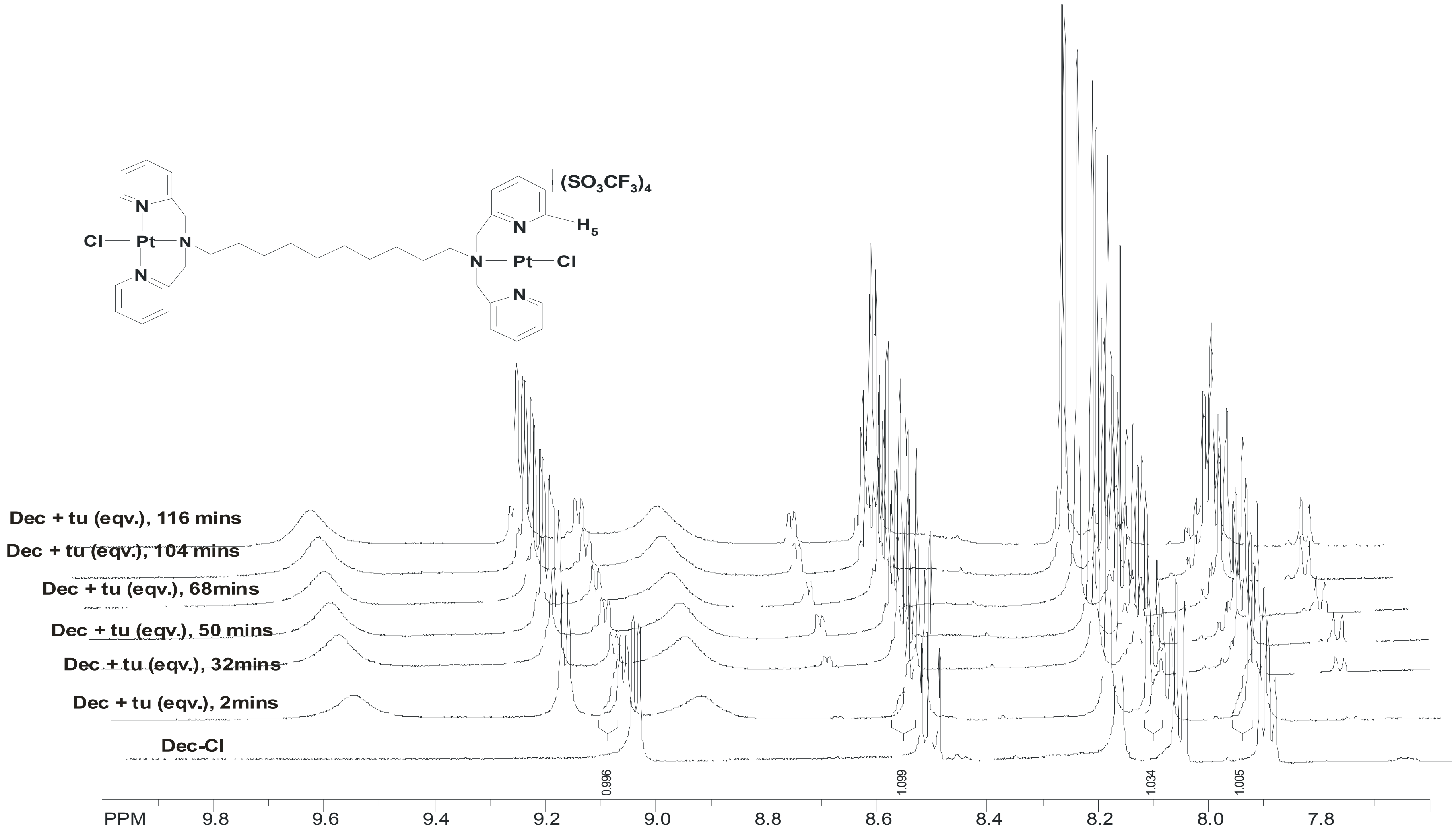


Fig. SI 2a A typical kinetic trace for the two-steps reaction between **bpma** (0.1 mM) and tu (3 mM) recorded at 276 nm, T = 298 K, pH = 2.0, I = 0.02 M {CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.



Proton NMR (aromatic region) for Dec-Cl and tu in DMF-d7

Fig. **SI 2b** ^{1}H NMR spectral array of **Dec-Cl** (showing only the aromatic region) acquired during its reaction with three equivalents of thiourea (tu) in DMF-*d*7.

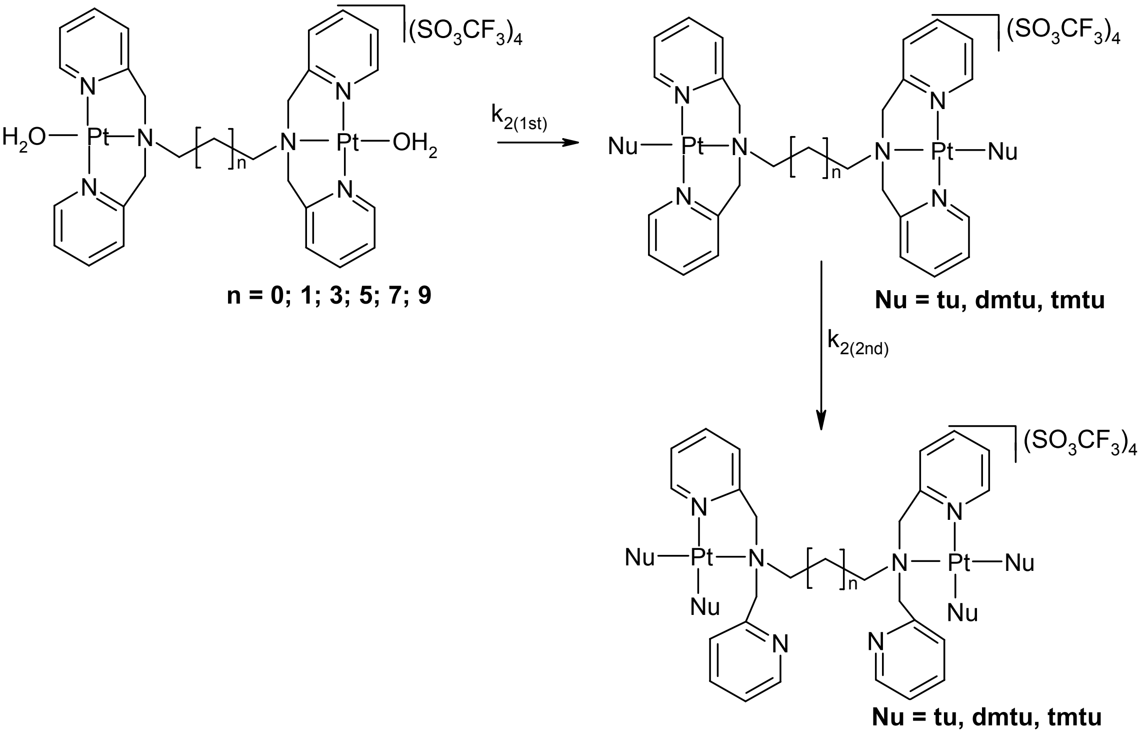


Fig. SI 2c Proposed[14c] mechanism of substitution of the aqua leaving groups in the clelated Pt(II) dinuclear complexes and **bpma**.

Table SI 2a. Average observed rate constants, $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **Prop** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu (λ = 318 nm)		**dmtu** (λ = 324 nm)		**tmtu** (λ = 318 nm)	
Conc., M	$k_{obs,}$ s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	1.091	9.996E-4	0.7499	0.001	0.3084
0.002	2.104	0.002	1.47	0.002	0.6344
0.003	3.051	0.003	2.201	0.003	0.918
0.004	4.197	0.004	2.874	0.004	1.208
0.005	5.135	0.005	3.633	0.005	1.522

Table SI 2b Average observed rate constants, $k_{obs(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **Prop** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
Conc., M	$k_{obs,}$ s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	0.0042	0.001	0.0064	0.001	0.0026
0.002	0.0096	0.002	0.0107	0.002	0.0067
0.003	0.0136	0.003	0.0156	0.003	0.0095
0.004	0.0180	0.004	0.0208	0.004	0.0126
		0.005	0.0260	0.005	0.0155

Table SI 2c Average observed rate constants, $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **Oct** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu (λ = 312 nm)		**dmtu** (λ = 324 nm)		**tmtu** (λ = 327 nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	0.559	0.00102	0.522	0.00100	0.191
0.002	1.142	0.00204	1.064	0.00201	0.422
0.003	1.741	0.00306	1.673	0.00301	0.629
0.004	2.318	0.00408	2.195	0.00401	0.838
0.005	2.829	0.00510	2.755	0.00501	1.020

Table SI 2d Average observed rate constants, $k_{obs(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **Oct** thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	0.0065	0.00101	0.0051	0.00100	0.0026
0.002	0.0123	0.00202	0.0112	0.00201	0.0055
0.003	0.0184	0.00302	0.0162	0.00301	0.0084
0.004	0.0249	0.00403	0.0221	0.00401	0.0109
0.005	0.0315	0.00504	0.0267	0.00501	0.0139

Table SI 2e Average observed rate constants, $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **En**, **Prop**, **But** and **Hex** by iodide, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

En		**Prop**		**But**		**Hex**	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	0.673	0.001	28.83	0.001	14.71	0.001	9.576
0.002	1.180	0.002	59.89	0.002	30.39	0.002	21.18
0.003	1.973	0.003	91.57	0.003	43.86	0.003	31.87
0.004	2.708	0.004	115.3	0.004	59.61	0.004	43.71
0.005	3.359	0.005	149.7	0.005	73.00	0.005	56.15

Table SI 2f Average observed rate constants, $k_{obs(2^{nd})}$, s^{-1}, for the simultaneous displacement of the aqua igands in **En**, **Prop**, **But** and **Hex** by iodide, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

En		**Prop**		**But**		**Hex**	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.001	0.556	0.001	5.039	0.001	7.250	0.001	7.199
0.002	1.180	0.002	8.726	0.002	11.99	0.002	14.09
0.003	1.973	0.003	13.23	0.003	18.87	0.003	19.03
0.004	2.708	0.004	18.18	0.004	23.81	0.004	26.47
0.005	3.359	0.005	22.83	0.005	29.29	0.005	33.50

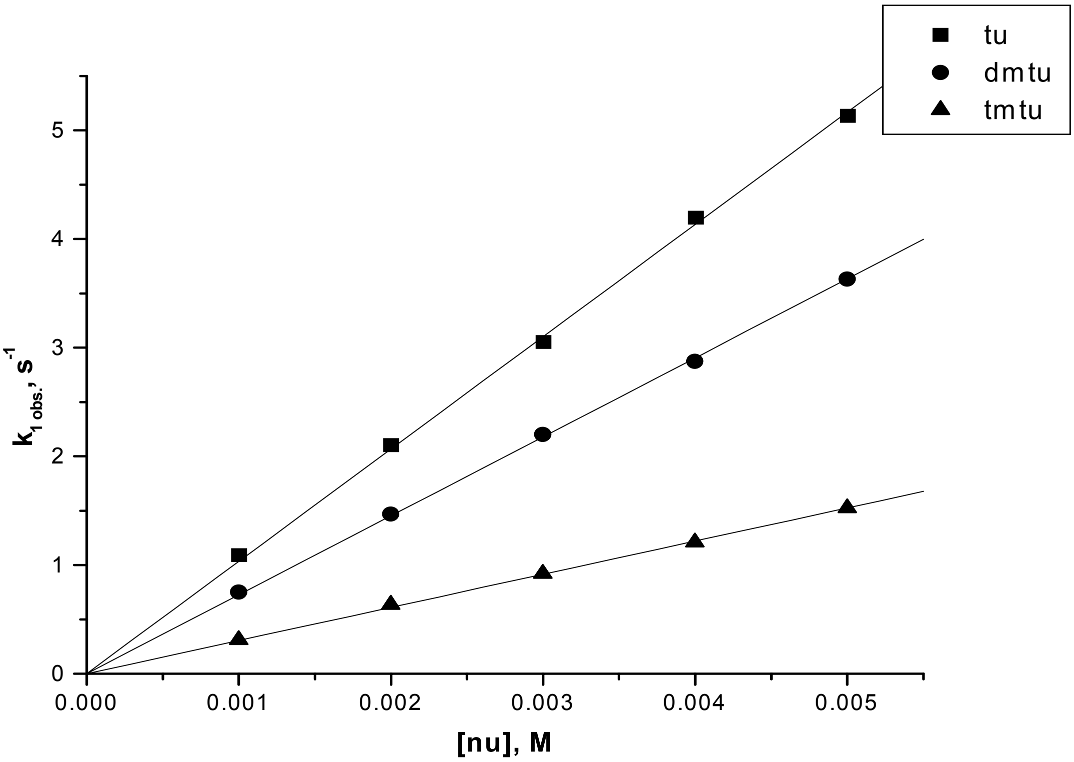


Fig. SI 3a Concentration dependence of $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **Prop** thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

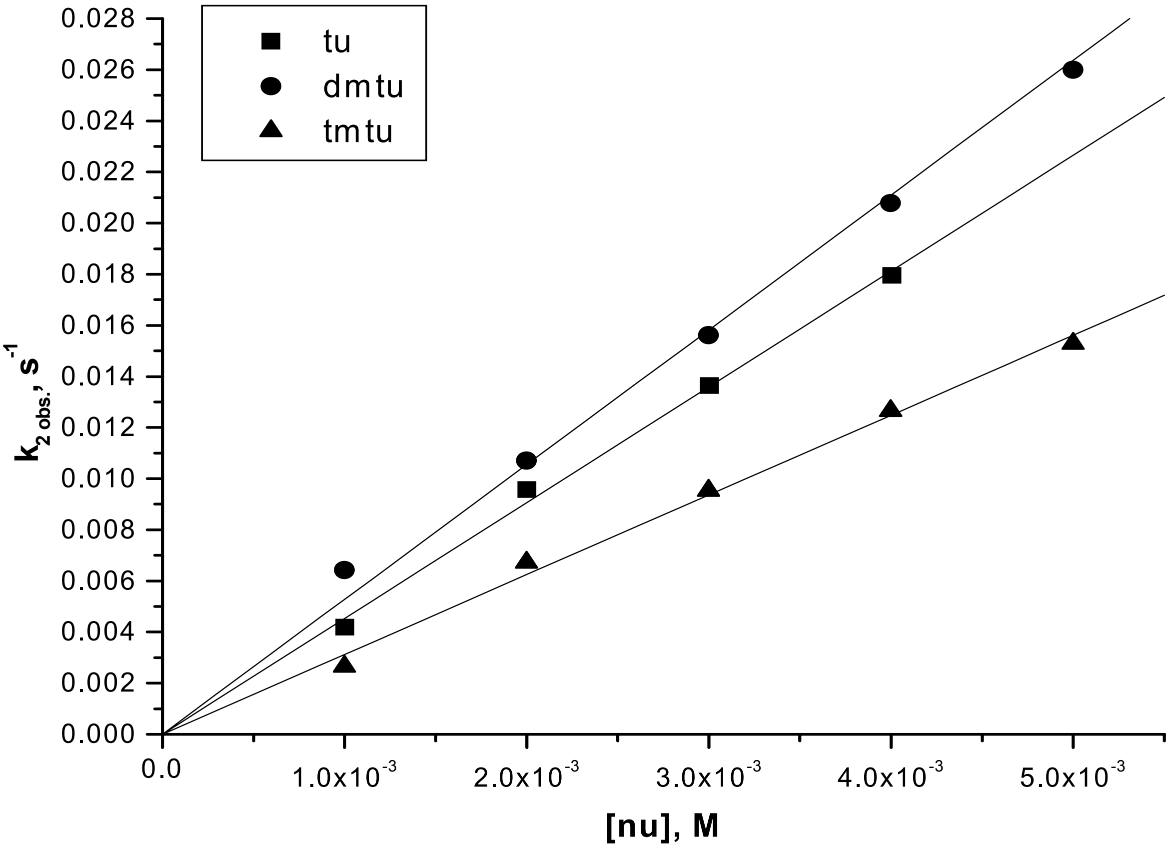


Fig. SI 3b Concentration dependence of $k_{obs(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **Prop** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

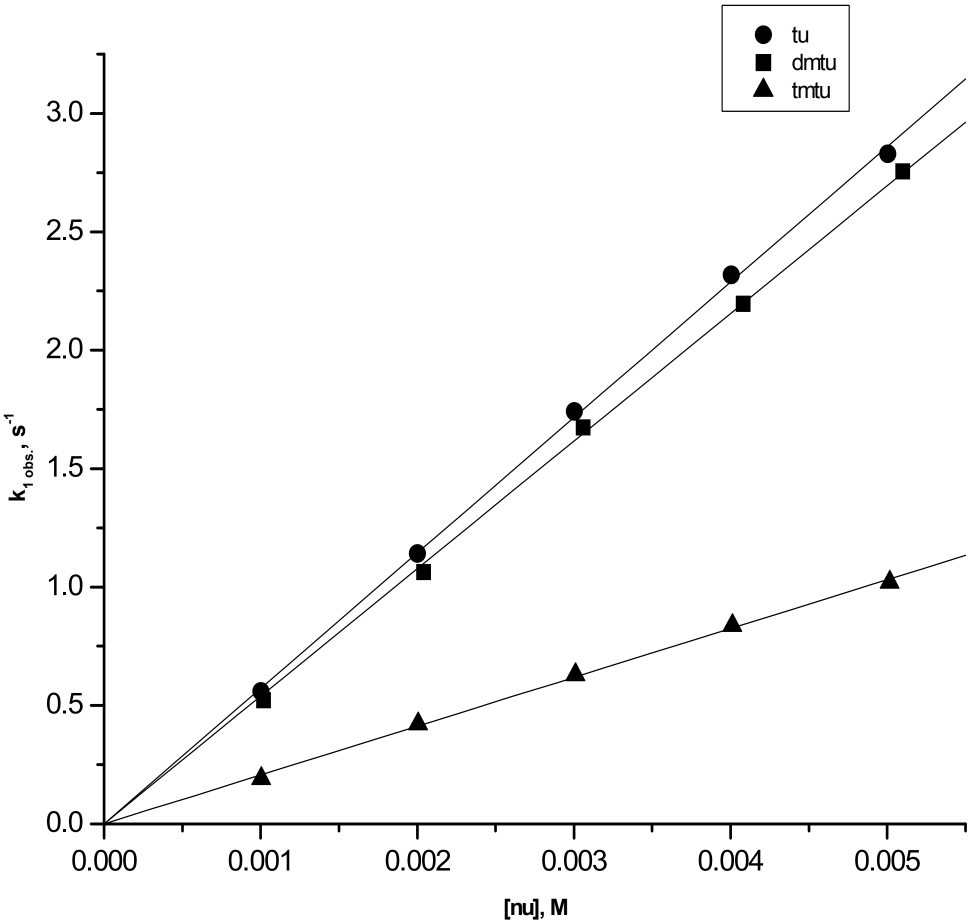


Fig. SI 3c Concentration dependence of $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **Oct** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

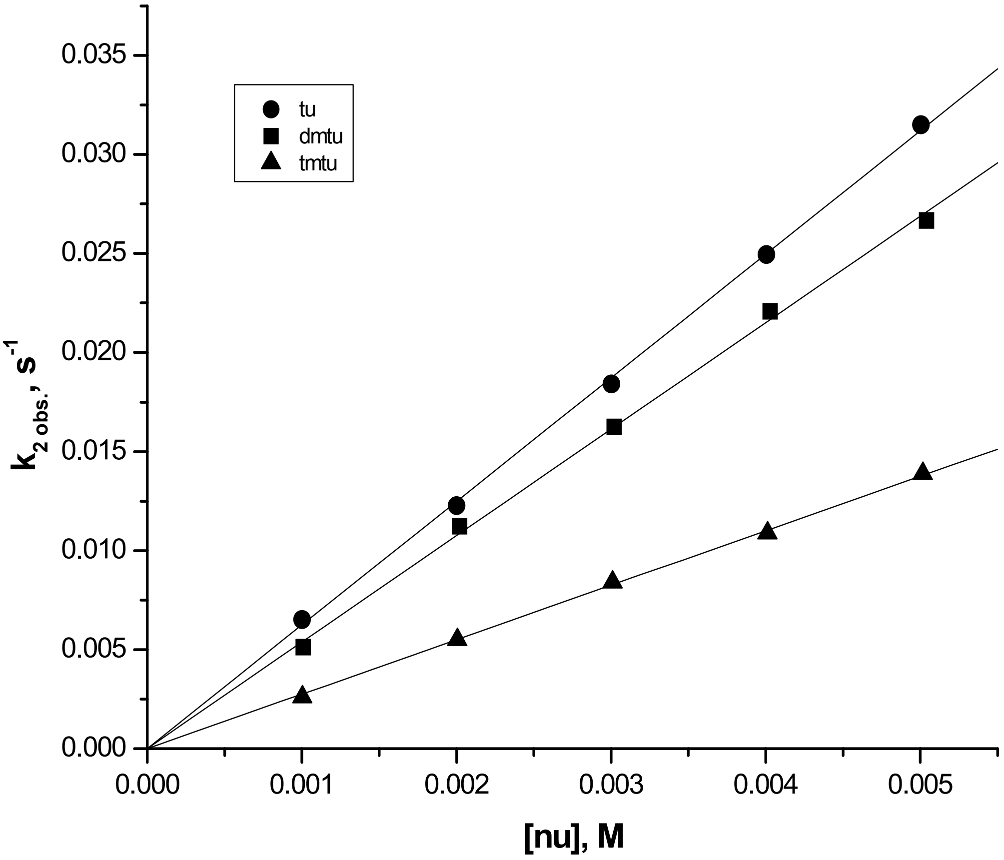


Fig SI 3d Concentration dependence of $k_{obs(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **Oct** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

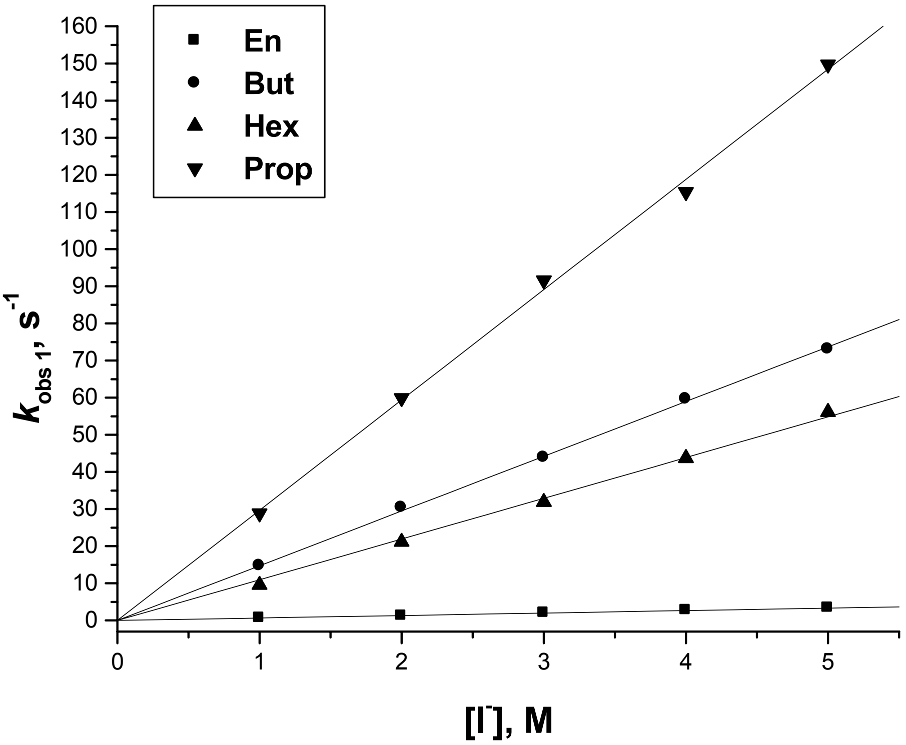


Fig. SI 3e Plots of concentration dependence of $k_{obs(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **En**, **Prop**, **But** and **Hex** by iodide, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

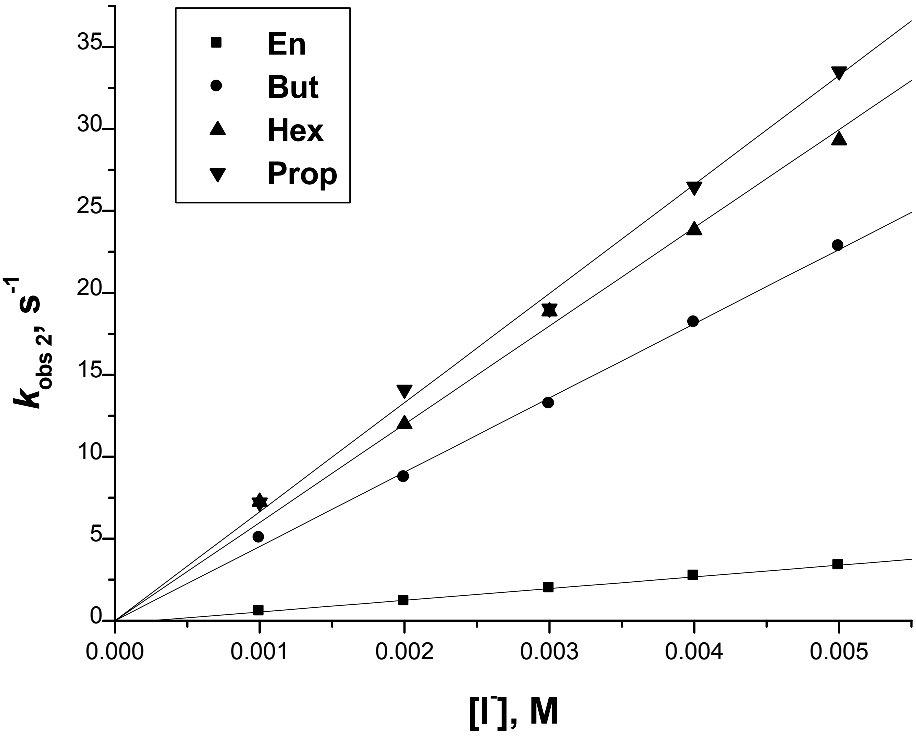


Fig. SI 3f Plots of concentration dependence of $k_{2(2^{nd})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **En**, **Prop**, **But** and **Hex** by iodide, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

Table SI 3a Temperature dependence of $k_{2(1^{st})}$, M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **Prop** by thiourea nucleophiles ([nu] at 60-fold excess over [metal complex]) , pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)
		0.00325	1.353	0.00325	0.669
0.0033	1.397	0.00330	1.164	0.00330	0.409
0.00335	1.243	0.00335	0.904	0.00335	0.145
0.00341	1.060	0.00341	0.672	0.00341	-0.108
0.00347	0.899	0.00347	0.436	0.00347	-0.408

Table SI 3b Temperature dependence of $k_{2(2^{nd})}$, M^{-1} s^{-1}, for the dechelation of the pyridyl units in **Prop** by thiourea nucleophiles ([nu] at 60 fold excess of [metal complex]}, pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)
				0.00325	-3.942
0.0033	-3.778	0.0033	3.594	0.0033	-4.143
0.00335	-3.919	0.00335	3.771	0.00335	-4.420
0.00341	-4.072	0.00341	3.976	0.00341	-4.750
0.00347	-4.204	0.00347	4.159	0.00347	-5.020

Table SI 3c Temperature dependence of $k_{2(1^{st})}$, M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **Oct** by thiourea nucleophiles ([nu] at 60-fold excess over [metal complex]) , pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)	1/T, K^{-1}	ln(k_2/T)
0.00325	1.099	0.00325	1.090	0.00325	0.074
0.00330	0.883	0.00330	0.890	0.00330	-0.183
0.00335	0.692	0.00335	0.711	0.00335	-0.505
0.00341	0.482	0.00341	0.472	0.00341	-0.853
0.00347	0.261	0.00347	0.237	0.00347	-1.175

Table SI 3d Temperature dependence of $k_{2(2^{nd})}$, M^{-1} s^{-1}, for the dechelation of the pyridyl units in **Oct** by thiourea nucleophiles ([nu] at 60 fold excess of [metal complex]}, pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

nucleophiles					
tu		**dmtu**		**tmtu**	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00325	-3.495	0.00325	-3.514	0.00325	-4.096
0.00330	-3.660	0.00330	-3.694	0.00330	-4.378
0.00335	-3.804	0.00335	-3.874	0.00335	-4.671
0.00341	-3.976	0.00341	-4.051	0.00341	-5.033
0.00347	-4.166	0.00347	-4.267	0.00347	-5.354

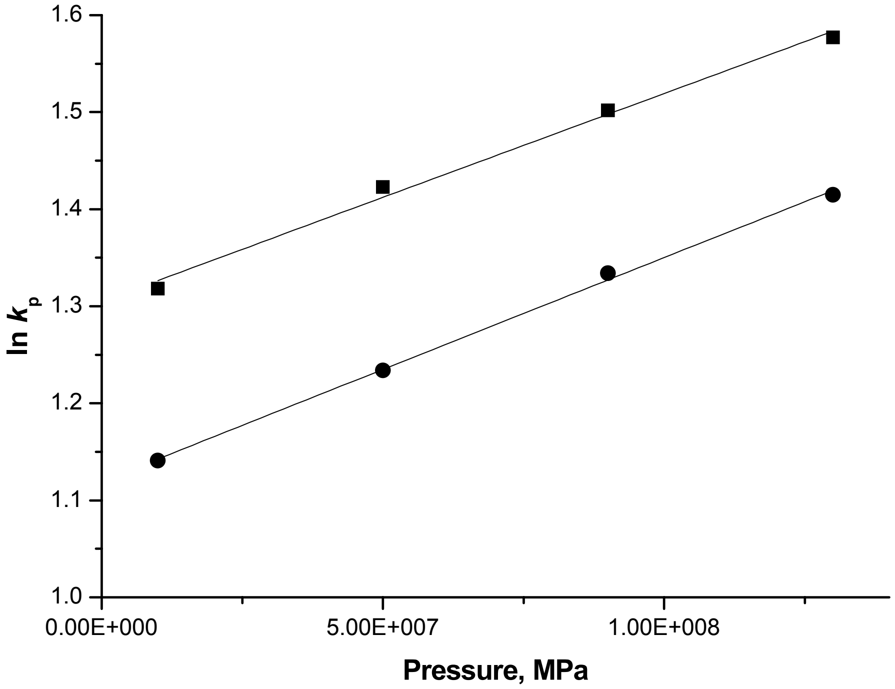


Fig. SI 4a Dependence of lnk_{obs} (repeated twice) on pressure for the reaction between **Prop** and tu recorded at 320 nm for the simultaneous displacement of the aqua ligands, ([tu] maintained at a 60-fold excess concentration over the complex) at 298 K, pH = 2.0, I = 0.02 M {CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

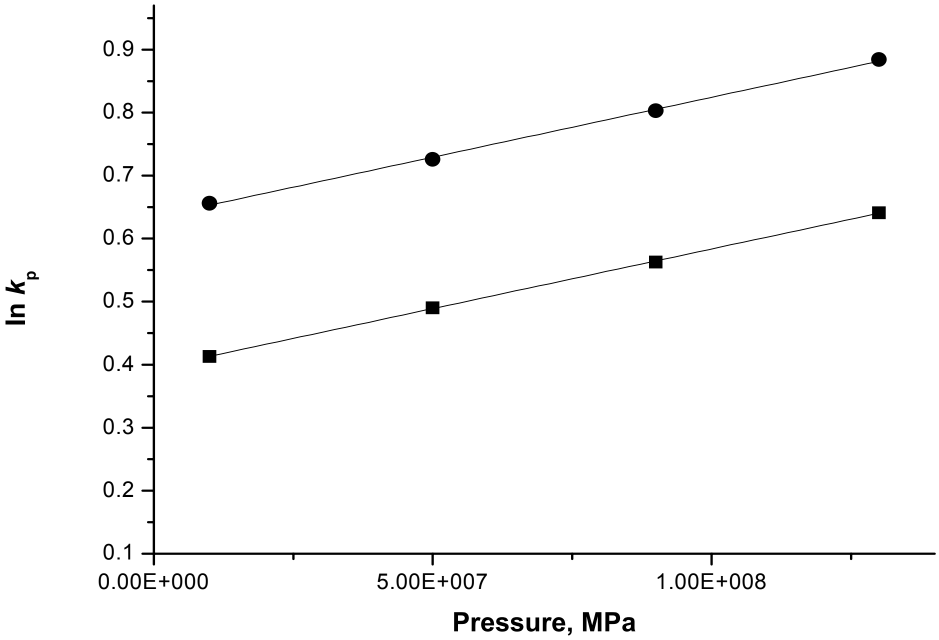
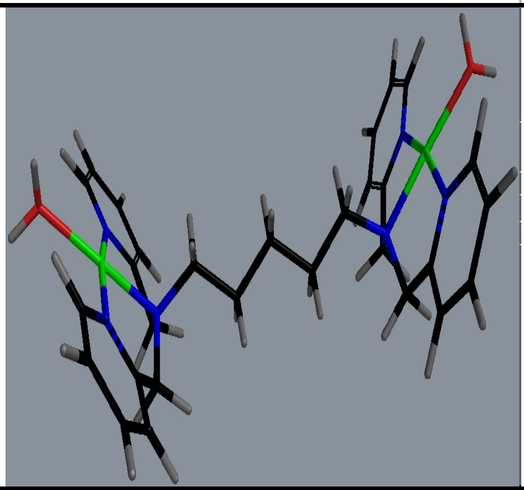
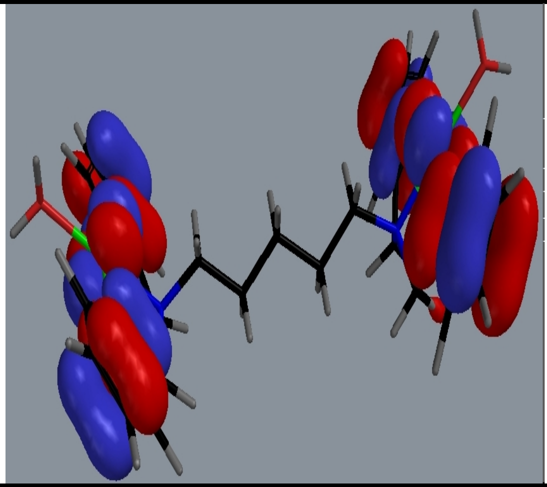
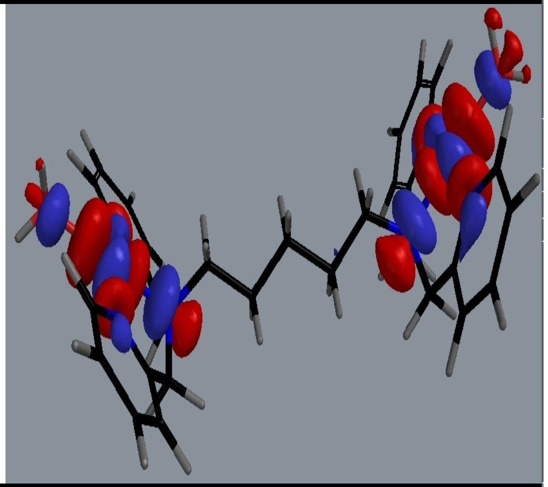


Fig. SI 4b Dependence of lnk_{obs} (repeated twice) on pressure for the reaction between **Oct** and tu recorded at 320 nm for the simultaneous displacement of the aqua ligands, ([tu] maintained at a 60-fold excess concentration over the complex) at 298 K, pH = 2.0, I = 0.02 M {CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}

Table SI 5 Density functional theoretical (DFT)[26] minimum energy structures, HOMO and LUMO frontier molecular orbitals for **Pen** and **Hep**. The calculations were performed with the Spartan '04 for Windows quantum chemical package[27] using the B3LYP hybrid functional method[28] and the LACVP+**[29] pseudo-potentials basis set.

Complex	Structure	HOMO Map	LUMO Map
Pen			
Hep