Electronic Supplementary Information

A kinetics and Mechanistic study on the role of the structural rigidity of the linker on the substitution reactions of chelated dinuclear Pt(II) complexes.

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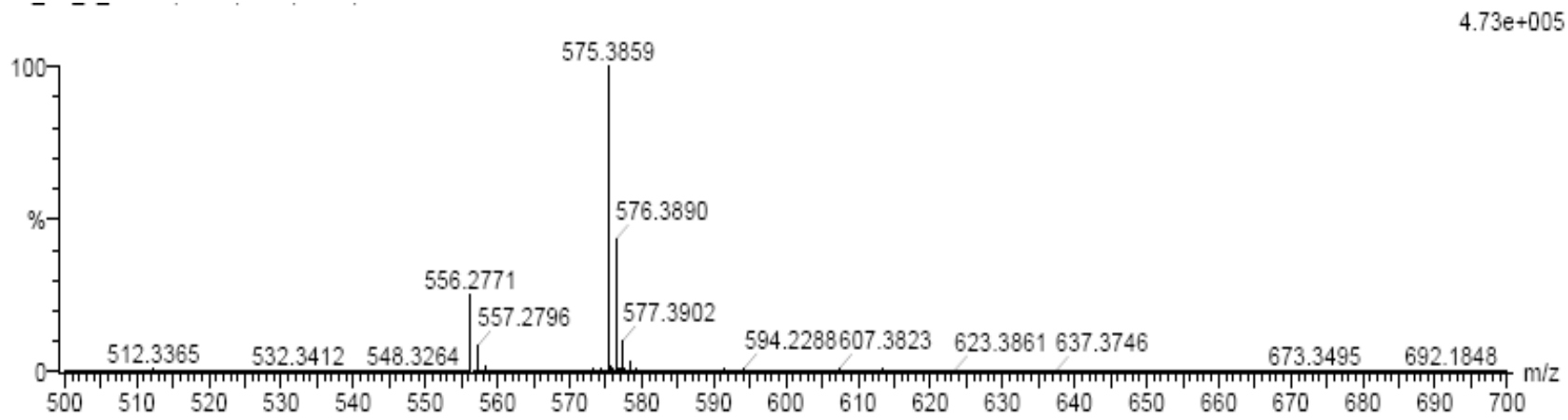
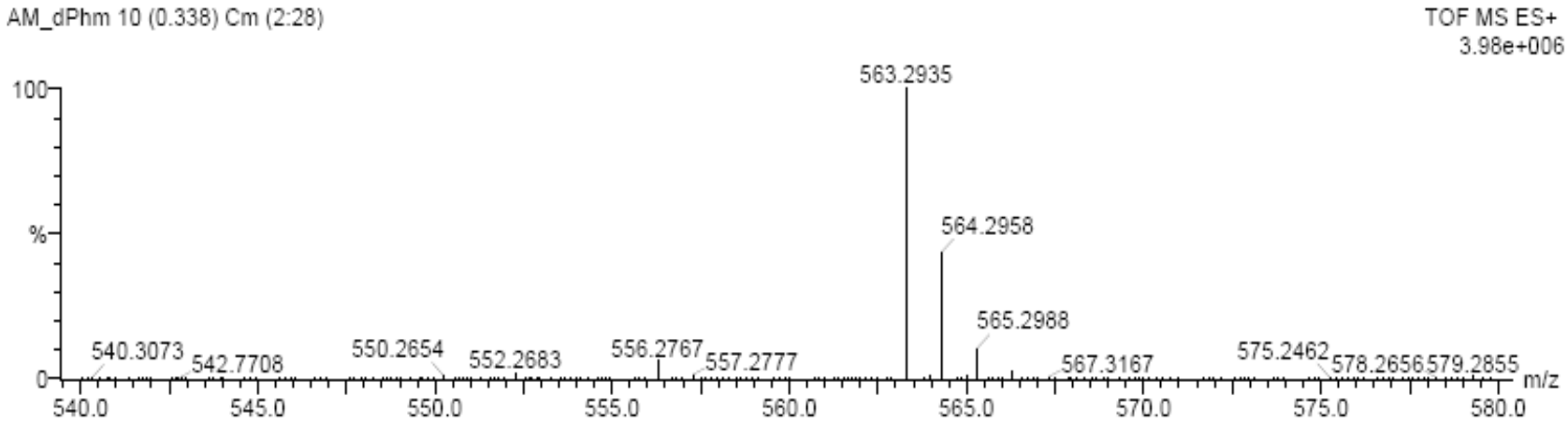
Table SI 1 Summary of the wavelengths (nm) used for monitoring the reactions between a series of Pt(II) complexes with bis(2-pyridylmethyl)amine chelates and thiourea nucleophiles.

Complex	nu	Wavelength (λ), nm
bpPha	tu dmtu tmtu	310 286 312
mPh	tu dmtu tmtu	312 325 335
pPh	tu dmtu tmtu	315 325 330
dPhm	tu dmtu tmtu	315 318 335
bpcHna	tu dmtu tmtu	283 284 315
cHn	tu dmtu tmtu	324 325 318
dcHnm	tu dmtu tmtu	325 325 327



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
575.3859	575.3862	-0.3	-0.5	17.5	115611.8	12C37 1H47 N6

Figure SI 1a Mass spectrum (TOF-MS$^+$) for *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-4,4'-diclohexylmethanediamine (**L3**).



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
563.2935	563.2923	1.2	2.1	23.5	51.8	12C37 1H35 14N6
	563.2906	2.9	5.1	10.5	298.5	12C3 1H23 14N36
	563.2973	-3.8	-6.7	13.5	530.6	12C12 1H27 14N28

Figure SI 1b Mass spectrum (TOF-MS$^+$) for *N,N,N′,N′*-tetrakis(2-pyridylmethyl)- 4,4'-diphenylmethanediamine (**L7**).

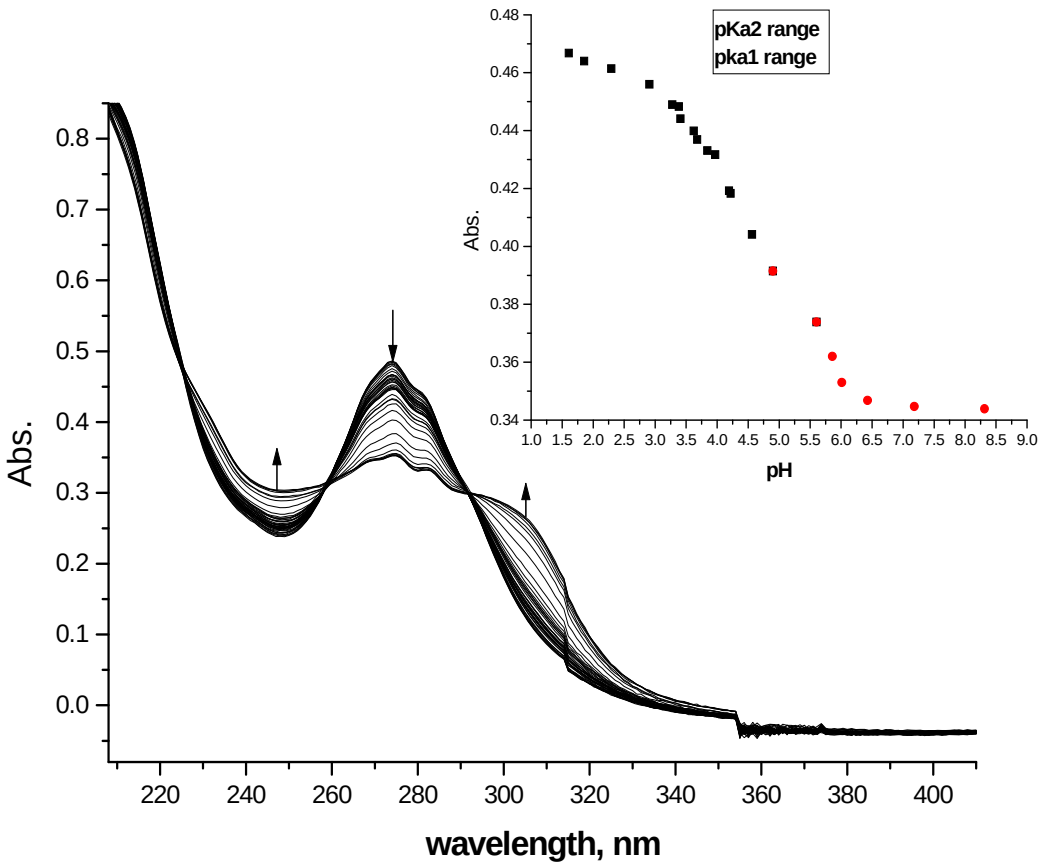


Figure SI 2 UV-visible spectra for the titration of 0.11 mM **dcHnm** with NaOH, pH range 2-9, T = 298K. Inset is the titration curve at 268 nm.

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

[tu], M	$k_{obs\ 1}$, s^{-1}	[dmtu], M	$k_{obs\ 1}$, s^{-1}	[tmtu], M	$k_{obs\ 1}$, s^{-1}
5.33E-4	0.4819	5.33E-4	0.5256	5.34E-4	0.1166
0.0011	1.018	0.0011	1.081	0.0011	0.228
0.0016	1.525	0.0016	1.616	0.0016	0.3343
0.0021	2.012	0.0021	2.194	0.0021	0.4503
0.0027	2.496	0.0027	2.779	0.0027	0.5506

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

[tu], M	$k_{obs\ 2}$, s^{-1}	[dmtu], M	$k_{obs\ 2}$, s^{-1}	[tmtu], M	$k_{obs\ 2}$, s^{-1}
5.33E-4	0.00409	5.3E-4	0.0048	5.33E-4	0.00128
0.0011	0.00794	0.0011	0.0095	0.0011	0.00216
0.0016	0.01064	0.0016	0.0147	0.0016	0.00374
0.0021	0.01464	0.0021	0.0198	0.0021	0.0046
0.0027	0.01864	0.0027	0.0266	0.0027	0.00573

Table SI 2c Temperature dependence of $k_{2(1^{st}),}$ M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **bpcHna** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	1.654	0.00325	1.758	0.00325	0.1939
0.0033	1.412	0.0033	1.502	0.0033	-0.07
0.00335	1.204	0.00335	1.253	0.00335	-0.368
0.00341	0.9062	0.00341	0.9781	0.00341	-0.608
0.00347	0.6515	0.00347	0.6894	0.00347	-0.974

Table SI 2d Temperature dependence of $k_{2\ (2^{nd}),}$ M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bpcHna** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	-3.142	0.00325	-3.013	0.00325	-4.258
0.0033	-3.364	0.0033	-3.294	0.0033	-4.563
0.00335	-3.658	0.00335	-3.498	0.00335	-4.898
0.00341	-4.002	0.00341	-3.858	0.00341	-5.281
0.00347	-4.231	0.00347	-4.217	0.00347	-5.675

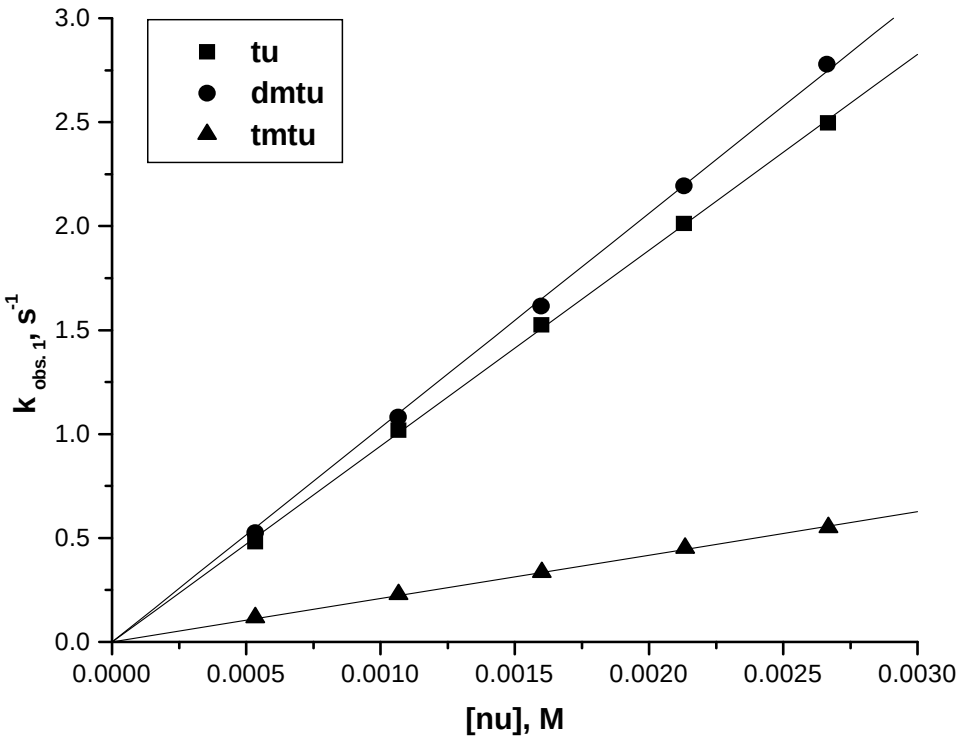


Figure SI 3a Concentration dependence of $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **bpcHna** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

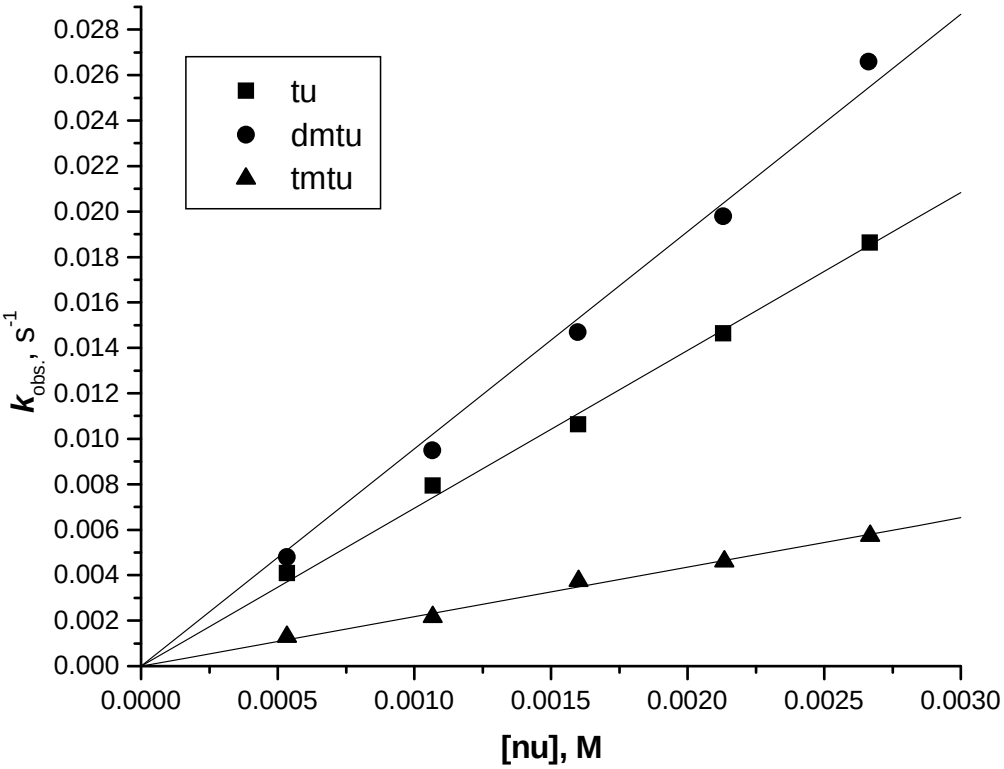


Figure SI 3b Concentration dependence of $k_{obs.(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **bpcHna** by thiourea, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

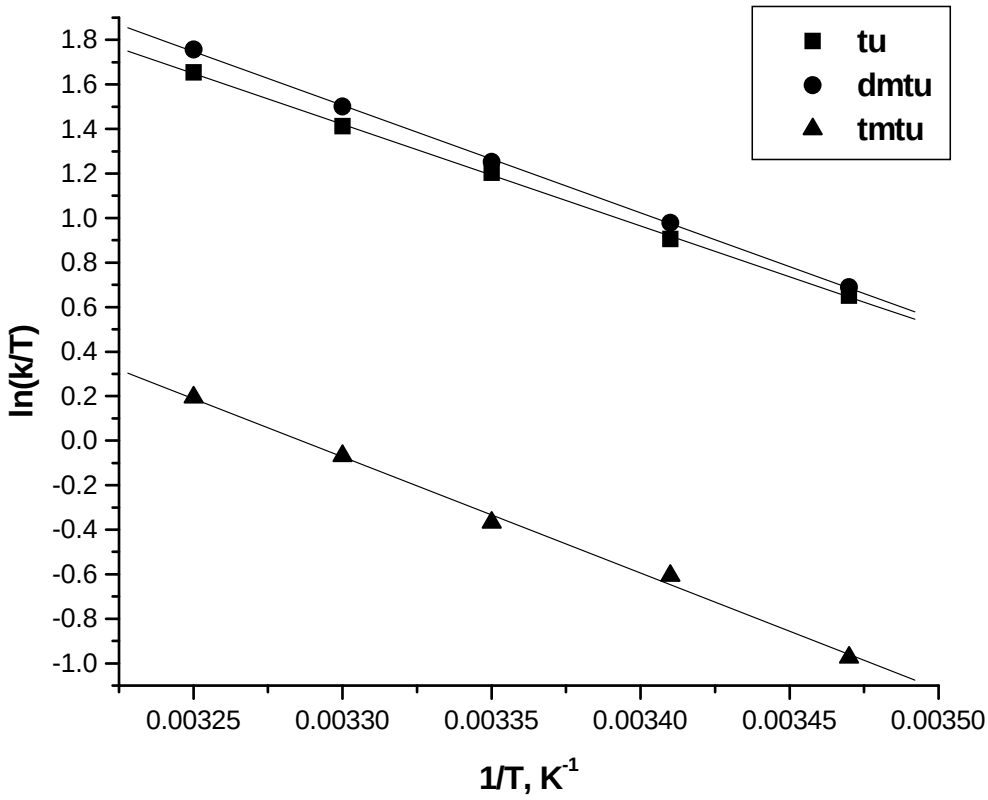


Figure SI 4a Temperature dependence of $k_{2(1^{st})}$, M^{-1} s^{-1}, for the simultaneous displacement of the first aqua ligand in **bpcHna** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

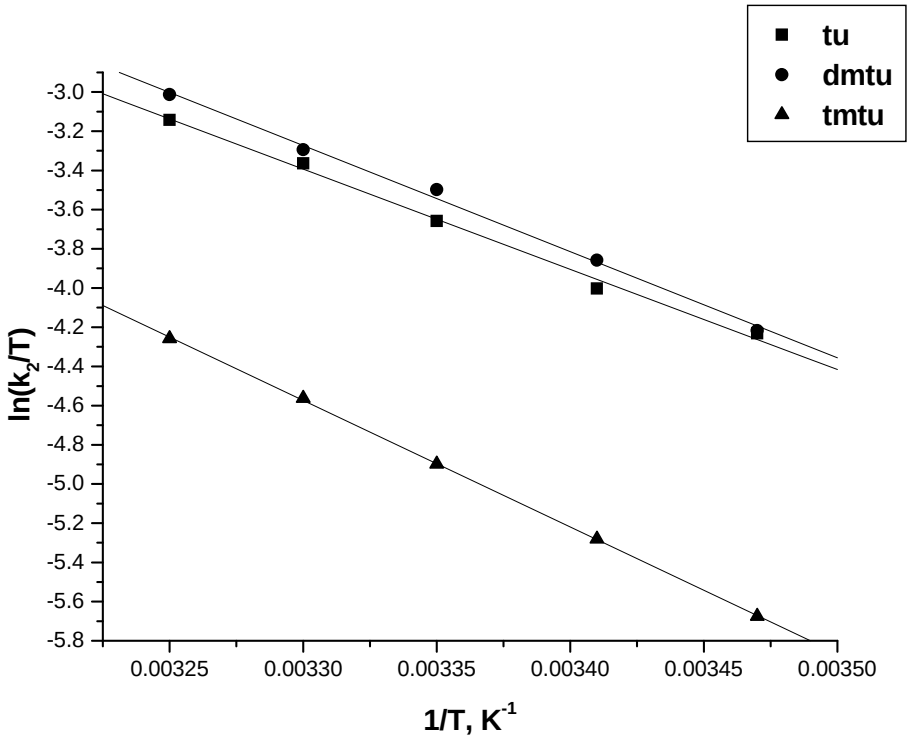


Figure SI 4b Temperature dependence of $k_{2\,(2^{nd}),}$ M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bpcHna** by thiourea, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

Table SI 3a Average observed rate constants, $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **dcHnm** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	**[dmtu], M**	$k_{obs\ 1}$, s^{-1}	**[tmtu] ,M**	$k_{obs\ 1}$, s^{-1}
0.00106	0.821	0.00107	0.9916	0.00107	0.224
0.00213	1.637	0.00213	1.983	0.00213	0.4554
0.00319	2.439	0.0032	2.965	0.0032	0.6678
0.00426	3.279	0.00426	4.001	0.00426	0.8921
0.00532	4.155	0.00533	5.016	0.00533	1.135

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

[tu], M	$k_{obs\ 1}$, s^{-1}	[dmtu], M	$k_{obs\ 1}$, s^{-1}	[tmtu] ,M	$k_{obs\ 1}$, s^{-1}
0.00107	0.00826	0.00107	0.00925	0.00107	0.00259
0.00214	0.0176	0.00214	0.01971	0.00214	0.00551
0.0032	0.0249	0.0032	0.02789	0.0032	0.0078
0.00426	0.0325	0.00426	0.0364	0.00426	0.01017
0.00532	0.0413	0.00532	0.04626	0.00532	0.01293

Table SI 3c Temperature dependence of $k_{2(1^{st}),}$ M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **dcHnm** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	1.452	0.00325	1.604	0.00325	0.2837
0.0033	1.203	0.0033	1.4265	0.0033	-0.0318
0.00335	0.963	0.00335	1.149	0.00335	-0.3366
0.00341	0.7257	0.00341	0.8833	0.00341	-0.6413
0.00347	0.4208	0.00347	0.5258	0.00347	-0.9573

Table SI 3d Temperature dependence of $k_{2\ (2^{nd}),}$ M^{-1} s^{-1}, for the dechelation of the pyridyl units in **dcHnm** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	-3.078	0.00325	-3.005	0.00325	-4.104
0.0033	-3.356	0.0033	-3.264	0.0033	-4.449
0.00335	-3.643	0.00335	-3.53	0.00335	-4.8
0.00341	-3.939	0.00341	-3.805	0.00341	-5.172
0.00347	-4.244	0.00347	-4.088	0.00347	-5.549

Table SI 4a Average observed rate constants, $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **pPh** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	[dmtu], M	$k_{obs\ 1}$, s^{-1}	[tmtu], M	$k_{obs\ 1}$, s^{-1}
5.3366E-4	0.4904	5.3366E-4	0.397	5.3366E-4	0.1197
0.00107	0.9981	0.00107	0.7997	0.00107	0.2355
0.0016	1.495	0.0016	1.183	0.0016	0.3578
0.00213	2.03	0.00213	1.561	0.00213	0.4847
0.00267	2.498	0.00267	1.988	0.00267	0.588

Table SI 4b Average observed rate constants, $k_{obs.(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **pPh** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 2}$, s^{-1}	[dmtu], M	$k_{obs\ 2}$, s^{-1}	[tmtu], M	$k_{obs\ 2}$, s^{-1}
5.3366E-4	0.00307	5.3366E-4	0.00336	5.3366E-4	0.00185
0.00107	0.0061	0.00107	0.00674	0.00107	0.0037
0.0016	0.01013	0.0016	0.01016	0.0016	0.00524
0.00213	0.01305	0.00213	0.01354	0.00213	0.00705
0.00267	0.01698	0.00267	0.01684	0.00267	0.00888

Table SI 4c Temperature dependence of $k_{2(1^{st}),}$ M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **pPh** by thiourea nucleophiles, pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	1.379	0.00325	1.558	0.00325	0.207
0.0033	1.131	0.0033	1.354	0.0033	-0.049
0.00335	0.927	0.00335	1.146	0.00335	-0.319
0.00341	0.655	0.00341	0.9108	0.00341	-0.6345
0.00347	0.315	0.00347	0.7042	0.00347	-0.8789

Table SI 4d Temperature dependence of $k_{2\ (2^{nd}),}$ M^{-1} s^{-1}, for the dechelation of the pyridyl units in **pPh** by thiourea nucleophiles, pH = 2.0, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	-3.253	0.00325	-3.258	0.00325	-3.511
0.0033	-3.546	0.0033	-3.494	0.0033	-3.859
0.00335	-3.852	0.00335	-3.781	0.00335	-4.195
0.00341	-4.148	0.00341	-4.057	0.00341	-4.601
0.00347	-4.465	0.00347	-4.386	0.00347	-5.018