Supplementary Support Information

The Role of Extended π-Acceptor Effect in the Substitution Reactions of Tridentate *N*-Donor Ligand Complexes of Platinum(II): A Detailed Kinetic and Mechanistic study

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Table S1 1.0: Summary of the wavelengths (nm) used for monitoring the reactions between a series of Pt(II) complexes with tridentate ligands and neutral S-donor and ionic nucleophiles.

Complex	Nucleophiles	Wavelength, λ (nm)
CH_3PhisoqPtCl	TU	363
	DMTU	363
	TMTU	386
	I^-	448
	SCN^-	412
	Br^-	412
pyPhenPtCl	TU	308
	DMTU	313
	TMTU	339
	I^-	309
	SCN^-	415
	Br^-	302

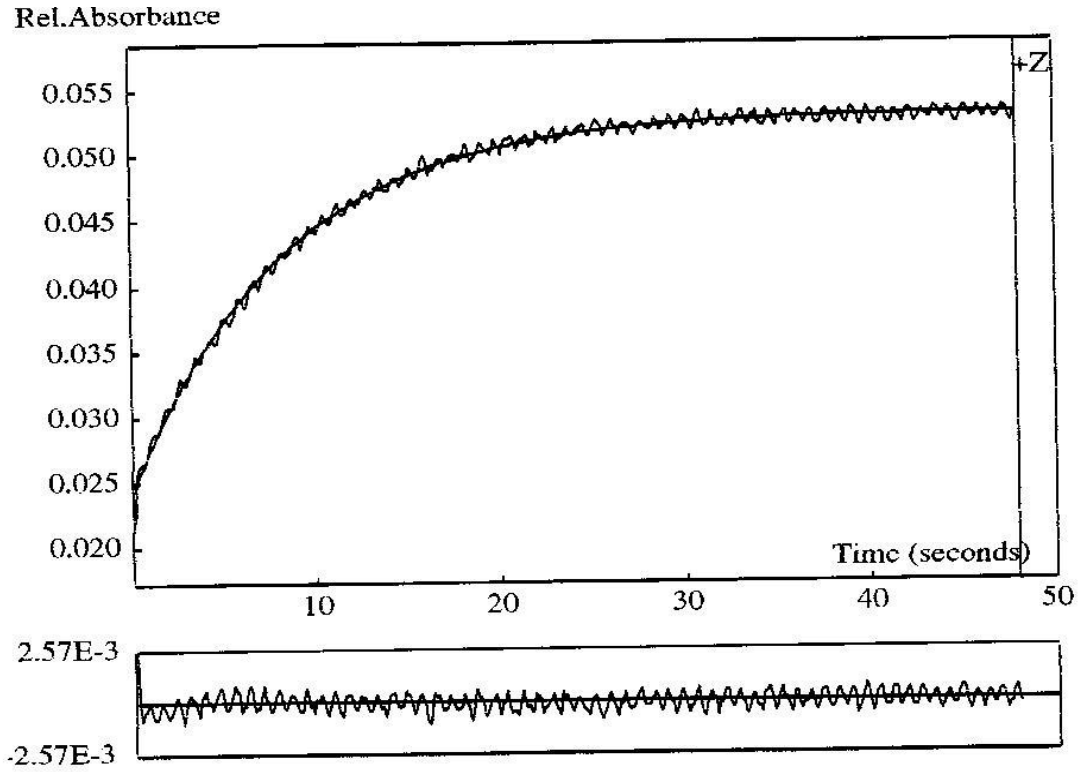


Figure SI 1.0: Kinetic trace at 448 nm for the substitution reaction between **CH_3PhisoqPtCl** (0.054 mM) and I^- (6.06 mM) at 298 K, I = 0.1 M Li(SO_3CF_3) in methanol.

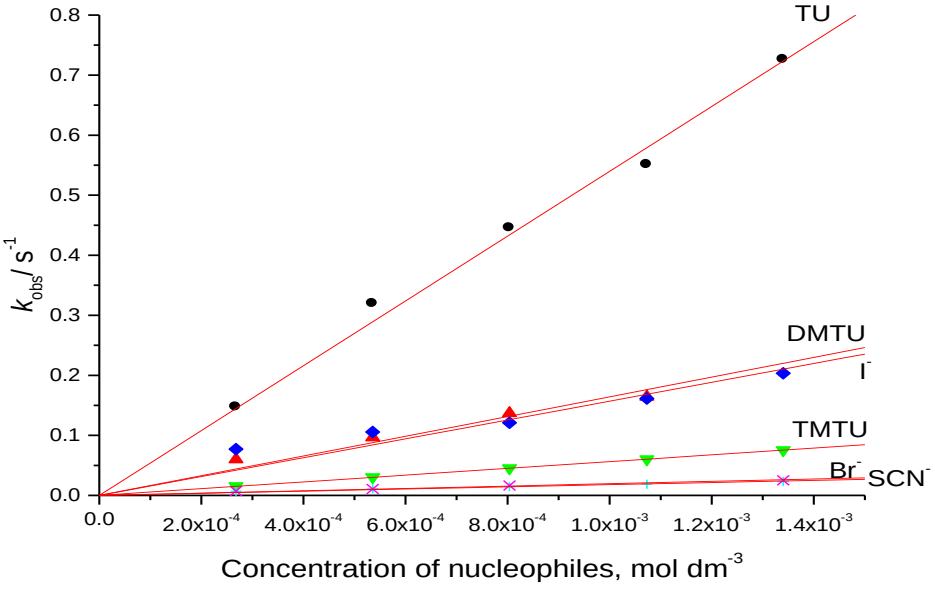
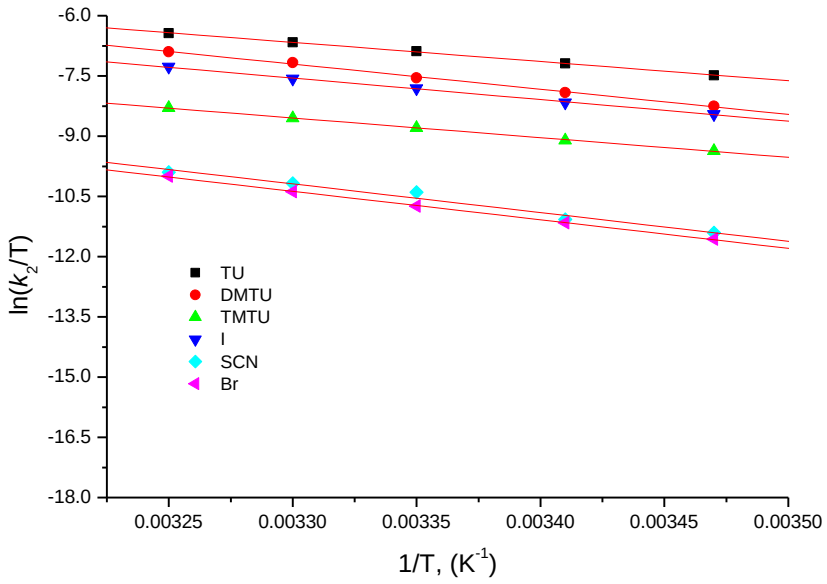


Figure SI 1.2: Concentration dependence of $k_{obs/}$ s^{-1}, for the substitution of the chloride ligand in **CH_3PhisoqPtCl** by a series of nucleophiles, T = 298 K, I = 0.1 M ($LiSO_3CF_3$) in methanol.



Figures SI 1.3: Temperature dependence of k_2, $M^{-1}s^{-1}$, for the substitution of the chloride from **CH_3PhisoqPtCl**, by thiourea nucleophiles I = 0.1 M ($LiSO_3CF_3$) in methanol.

Table SI 1.1a: Average observed rate constants, k_{obs}, s^{-1}, for substitution of chloride from **pyPhenPtCl** by thiourea nucleophiles, T = 298 K, I = 0.1 M ($LiSO_3CF_3$)

TU (λ = 308 nm)		**DMTU** (λ =370 nm)		**TMTU** (λ = 339 nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.0005	1.4628	6.88×10^{-4}	0.5415	6.88×10^{-4}	0.1032
0.001	3.3150	0.00138	1.1255	0.00138	0.1995
0.0015	5.2825	0.00206	1.7128	0.00206	0.2821
0.002	6.8256	0.00275	2.3766	0.00275	0.3885
0.0025	8.5872	0.00344	2.9588	0.00344	0.475

Table SI 1.1b: Average observed rate constants, k_{obs}, s^{-1}, for substitution of chloride from **pyPhenPtCl** by ionic nucleophiles, T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

I^- (λ = 308 nm)		**SCN^-** (λ =415 nm)		**Br^-** (λ = 339 nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
3.675×10^{-4}	0.454	3.675×10^{-4}	0.06798	3.675×10^{-4}	0.0108
7.350×10^{-4}	0.946	7.350×10^{-4}	0.12574	7.350×10^{-4}	0.0216
0.00110	1.350	0.00110	0.18135	0.00110	0.0326
0.00147	1.708	0.00147	0.25052	0.00147	0.0432
0.00184	2.260	0.00184	0.30788	0.00184	0.0493

Table SI 1.2a: Average observed rate constants, k_{obs}, s^{-1}, for substitution of chloride from **CH_3PhisoqPtCl** by thiourea nucleophiles, T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

TU (λ = 363 nm)		**DMTU**(λ = 363 nm)		**TMTU** (λ = 386 nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
2.679×10^{-4}	0.1094	2.859×10^{-4}	0.03674	5.5×10^{-4}	0. 01532
5.358×10^{-4}	0.2054	5.718×10^{-4}	0.07474	1.0×10^{-3}	0.03022
8.037×10^{-4}	0.3053	8.577×10^{-4}	0.01100	1.5×10^{-3}	0.04530
1.070×10^{-3}	0.4003	1.140×10^{-3}	0.14510	2.0×10^{-3}	0.06022
1.340×10^{-3}	0.5003	1.430×10^{-3}	0.18010	2.5×10^{-3}	0.07541

Table SI 1.2b: Average observed rate constants, k_{obs}, s^{-1}, for substitution of chloride from **CH_3PhisoqPtCl** by ionic nucleophiles, T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

I^- (λ = 448 nm)		**SCN^-**(λ = 412 nm)		**Br^-** (λ = 412 nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.00101	0.07716	0.00101	0.00680	0.00200	0. 00740
0.00127	0.10554	0.00127	0.01085	0.00250	0.01069
0.00152	0.12108	0.00152	0.01463	0.00300	0.01638
0.00202	0.16142	0.00202	0.01872	0.00375	-
0.00253	0.20340	0.00253	0.02330	0.00500	0.02508

Table SI 1.3a: Temperature dependence of k_2, M^{-1} s^{-1}, for substitution of chloride from **pyPhenPtCl** by thiourea nucleophiles at 30-fold excess of [metal complex], T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

TU (λ = 308 nm)		**DMTU** (λ = 313 nm)		**TMTU** (λ = 386 nm)	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00347	-4.5802	0.00347	-5.6746	0.00347	-7.5524
0.00341	-4.2442	0.00341	-5.3850	0.00341	-7.2611
0.00335	-4.0327	0.00335	-5.1589	0.00335	-6.9626
0.00330	-3.7067	0.00330	-4.8711	0.00330	-6.7590
0.00325	-3.4966	0.00325	-4.6417	0.00325	-6.5508

Table SI 1.3b: Temperature dependence of k_2, M^{-1} s^{-1}, for substitution of chloride from **pyPhenPtCl** by ionic nucleophiles at 30-fold excess of [metal complex], T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

I^- (λ = 309 nm)		**SCN^-**(λ = 415 nm)		**Br^-** (λ = 302 nm)	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00347	-6.0403	0.00347	-5.8971	0.00347	-9.9127
0.00341	-	0.00341	-5.5947	0.00341	-9.3691
0.00335	-5.7060	0.00335	-5.2524	0.00335	-8.7501
0.00330	-5.0057	0.00330	-5.0685	0.00330	-8.6466
0.00325	-4.6598	0.00325	-4.8690	0.00325	-8.2166

Table SI 1.4a: Temperature dependence of k_2, M^{-1} s^{-1}, for substitution of chloride from **CH_3PhisoqPtCl** by thiourea nucleophiles at 30-fold excess of [metal complex], T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

TU (λ = 363 nm)		**DMTU**(λ = 363 nm)		**TMTU** (λ = 386 nm)	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00347	-7.4827	0.00347	-8.2511	0.00347	-9.3656
0.00341	-7.1918	0.00341	-7.9115	0.00341	-9.1025
0.00335	-6.8836	0.00335	-7.5483	0.00335	-8.7915
0.00330	-6.6624	0.00330	-7.1682	0.00330	-8.5540
0.00325	-6.4338	0.00325	-6.8974	0.00325	-8.2937

Table SI 1.4b: Temperature dependence of k_2, M^{-1} s^{-1}, for substitution of chloride from **CH_3PhisoqPtCl** by ionic nucleophiles at 30-fold excess of [metal complex], T = 298 K, I = 0.1 M ($LiSO_3CF_3$).

I^- (λ = 448 nm)		**SCN^-** (λ = 423 nm)		**Br^-** (λ = 412 nm)	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00347	-8.4525	0.00347	-11.4029	0.00347	-11.567
0.00341	-8.1633	0.00341	-11.0728	0.00341	-11.157
0.00335	-7.8082	0.00335	-10.3975	0.00335	-10.745
0.00330	-7.5678	0.00330	-10.1735	0.00330	-10.385
0.00325	-7.2753	0.00325	-9.8964	0.00325	-9.997

Table SI 1.5: Average observed rate constants, k_{obs} [a], at varied temperatures for the reactions of **CH_3PhisoqPtCl** (0.054 mM) with a series of different nucleophiles whilst maintaining nucleophile concentrations at ≈ 30x [metal complex].

	Observed rate constant/ k_{obs} s^{-1}					
T (K)	TU	DMTU	TMTU	I^-	SCN^-	Br^-
288.15	0.3196	0.07512	0.0261	0.0615	0.00404	0.00273
293.15	0.4200	0.1074	0.0323	0.0835	0.00455	0.00400
298.15	0.5578	0.1447	0.0450	0.1211	0.00909	0.00649
303.15	0.7950	0.2343	0.0566	0.1566	0.01157	0.0133
308.15	1.1067	0.3084	0.0771	0.2133	0.01551	-

[a] Taken as an average of at least five kinetic runs with a SD between 0.1 and 2%.

Table SI 1.6: Average observed rate constants, k_{obs} [a], at varied temperatures for the reactions of **pyPhenPtCl** (0.054 mM) with a series of different nucleophiles whilst maintaining nucleophile concentrations at ≈ 30x [metal complex].

Observed rate constant/ k_{obs} s^{-1}						
T (K)	TU	T (K)	TU	T (K)	TU	T (K)
288.15	2.863	0.9886	0.1534	0.7140	0.7890	0.0143
293.15	4.350	1.3429	0.2095	1.0408	1.0862	0.0250
298.15	5.278	1.6759	0.2748	1.3496	1.4857	0.0324
303.15	8.916	2.3807	0.3459	2.0383	1.9349	0.0533
308.15	12.723	3.1928	0.4346	2.9314	2.4492	0.8470

[a] Taken as an average of at least five kinetic runs with a SD between 0.1 and 2%.

Table SI 1.7: DFT calculated electrostatic potential surfaces (EPS) of the chloro Pt(II) complexes with tridentate ligands. The blue region indicates the most electropositive areas and the red area indicates the most electronegative areas.

Complex	**CH_3PhPtCl**	**CH_3PhisoqPtCl**	**PtCl**	**pyPhenPtCl**
EPS