A Kinetic and Mechanistic Study of Analogous Bifunctional Dialkylamine Platinum(II) Complexes

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Electronic Supporting Information (ESI)

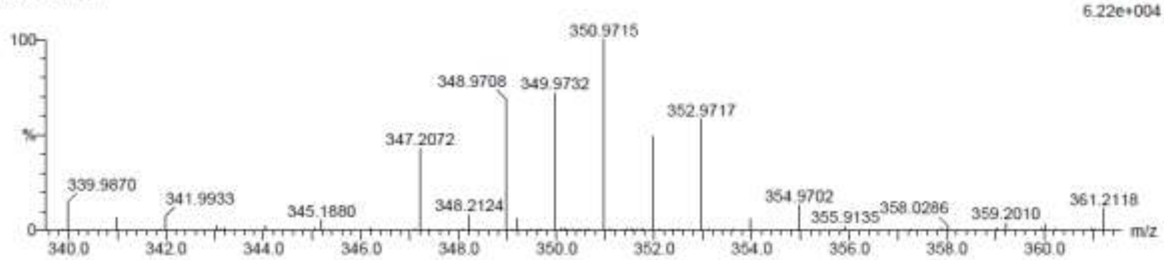
The available ESI includes several Mass and NMR spectra, elemental analysis, wavelengths for kinetic measurements, concentration dependence and Eyring plots for determination of second order rate constant and activation parameters.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-5 H: 5-10 N: 0-3 Na: 1-1 35Cl: 0-1 37Cl: 0-1 194Pt: 0-1

cPtMa 2711 54 (1.787) Cm (1:61)
TOF MS ES+



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
350.9715	350.9716	-0.1	-0.3	-1.5	135.4	0.0	C2 H10 N2 Na 35Cl 37Cl 194Pt

Fig. S1 Mass spectrum of cPtM

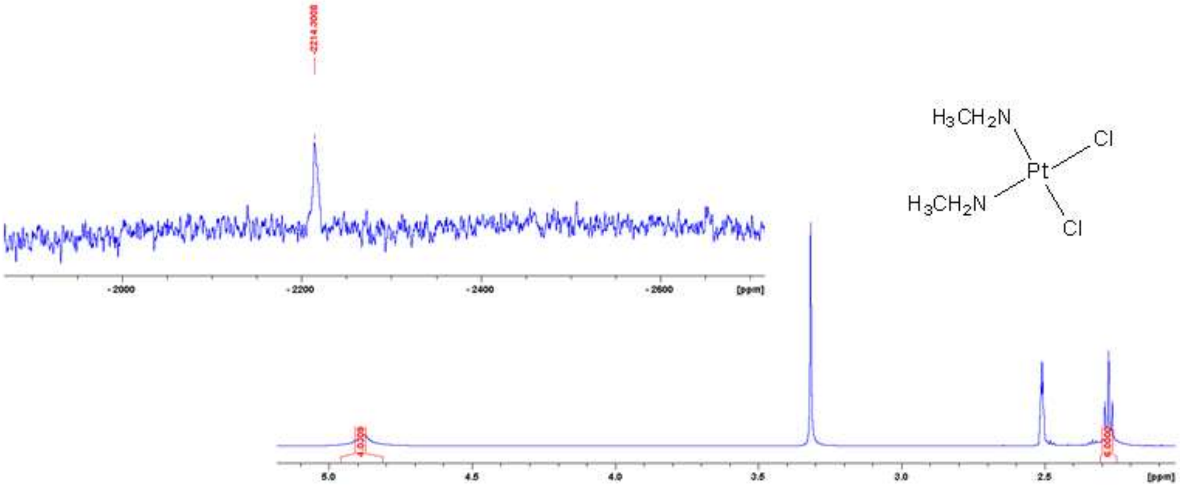
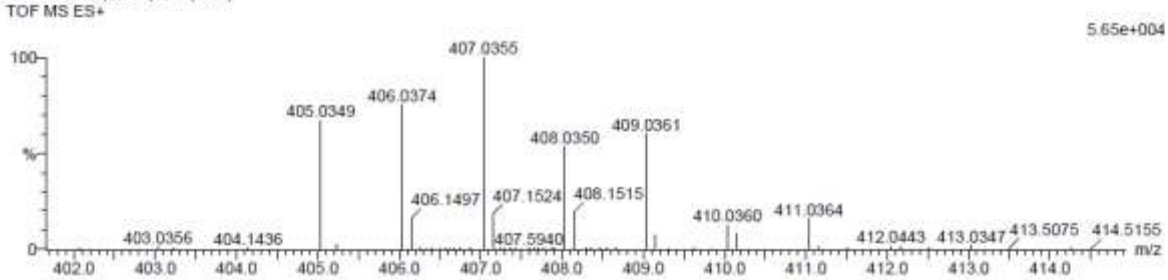


Fig. S2 [1]HNMR and [195]PtNMR of cPtM

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
60 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 6-6 H: 15-20 N: 0-5 Na: 1-1 35Cl: 0-2 37Cl: 1-2 194Pt: 0-1
cPtR 2711 2 (0.034) Cm (1:61)
TOF MS ES+



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
407.0355	407.0342	1.3	3.2	-1.5	214.5	0.0	C6 H18 N2 Na 35Cl 37Cl 194Pt

Fig. S3 Mass spectrum for cPtR

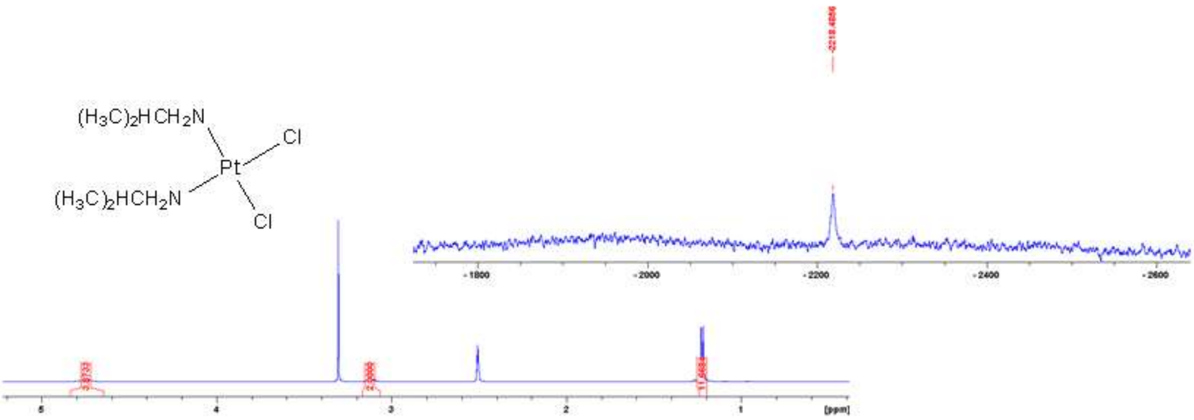


Fig. S4 [1]HNMR and [195]PtNMR of cPtR

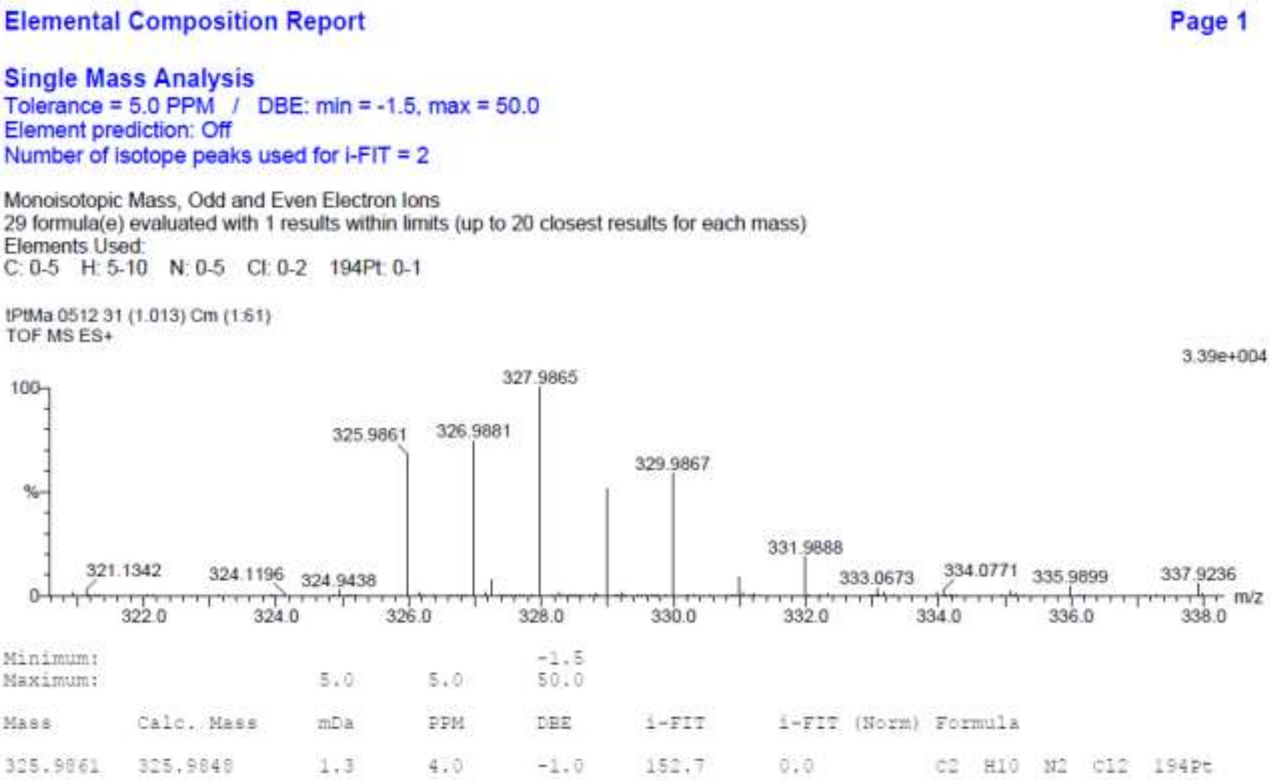


Fig. S5 Mass spectrum for tPtM

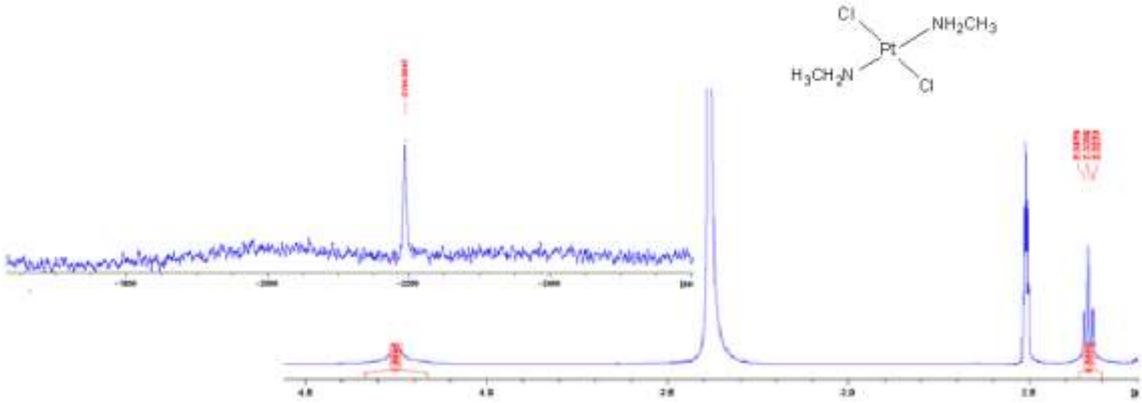


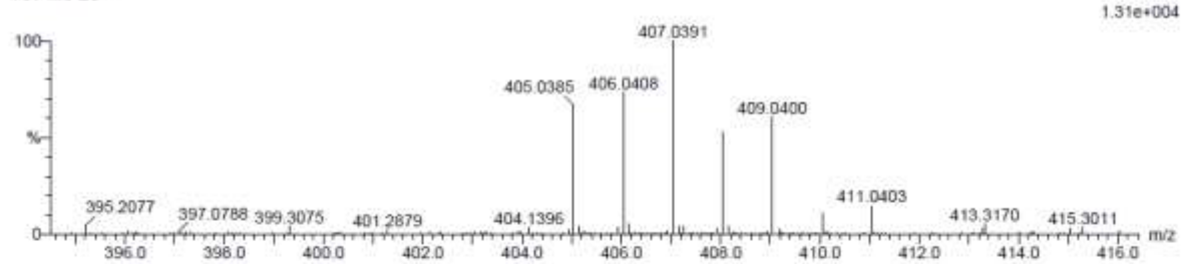
Fig. S6 ^{1}HNMR and ^{195}PtNMR of tPtM

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 5-10 H: 15-20 N: 0-5 Na: 1-1 Cl: 0-2 194Pt: 0-1

tPtR 0512 60 (1.990) Cm (1:61)
TOF MS ES+



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
405.0385	405.0372	1.3	3.2	-1.5	181.5	0.0	C6 H18 N2 Na Cl2 194Pt

Fig. S7 Mass spectrum for tPtR

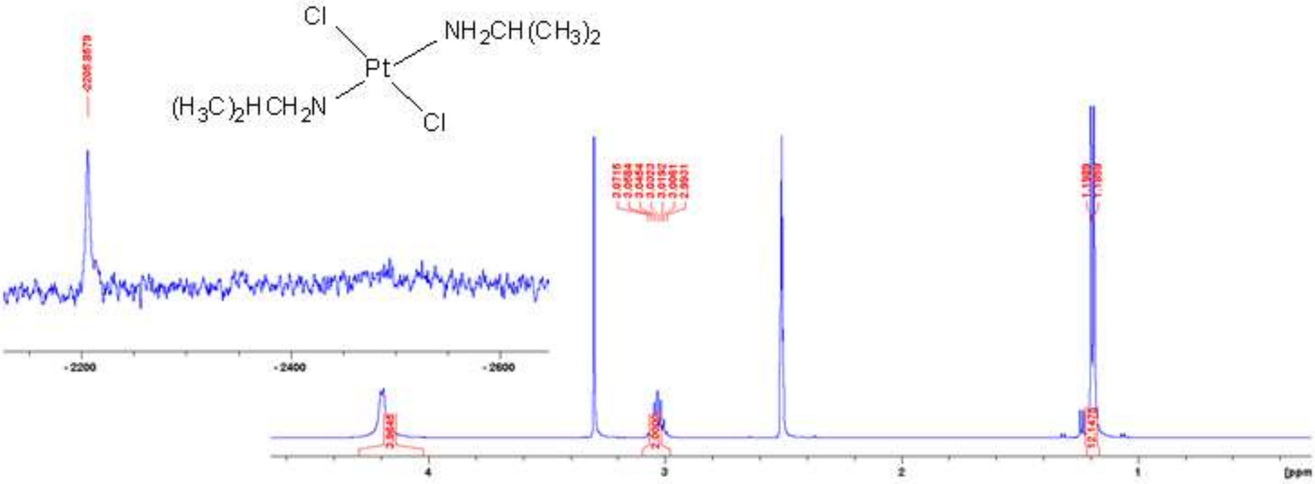
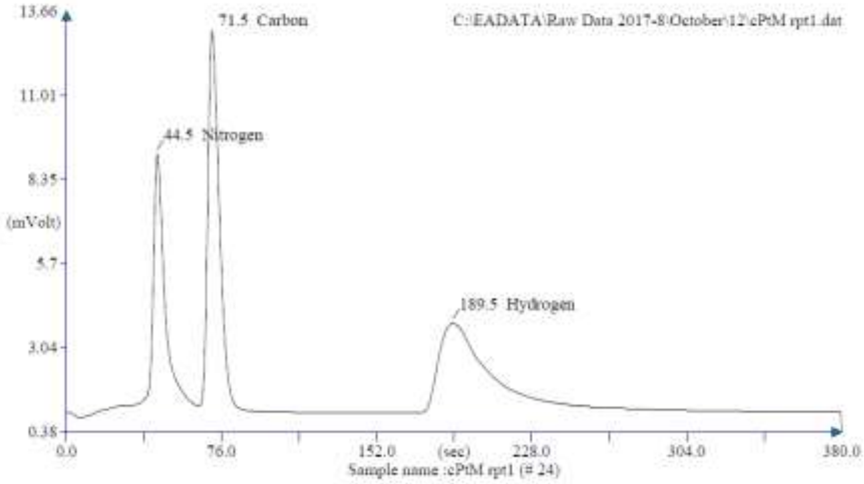
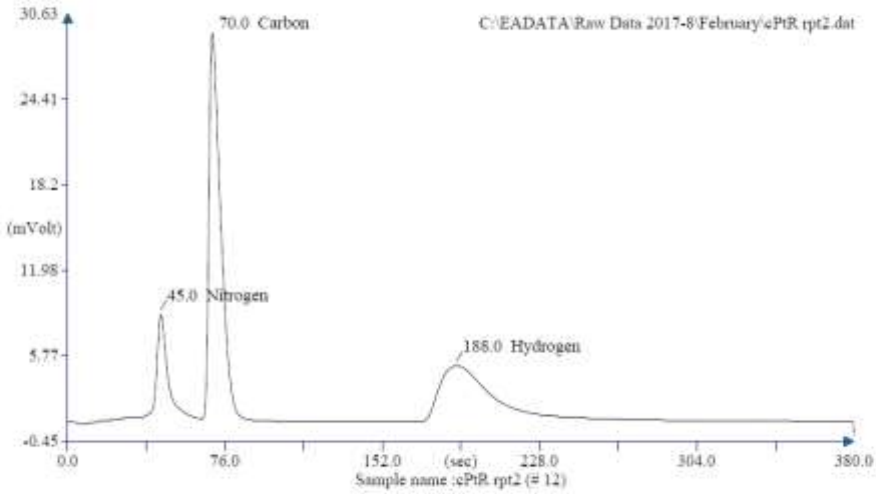


Fig. S8 ^{1}HNMR and ^{195}PtNMR of tPtR



Retention Time (min)	Element Name	Element %
0.742	Nitrogen	5.294
1.192	Carbon	7.270
3.158	Hydrogen	2.795
		15.359

Fig. S9 Elemental analysis of cPtM



Retention Time (min)	Element Name	Element %
0.750	Nitrogen	7.615
1.167	Carbon	18.542
3.133	Hydrogen	4.444
		30.601

Fig. S10 Elemental analysis of cPtR

Table S1 Wavelengths for kinetic measurements used in the study

Complex	Nucleophile	Wavelength (λ) Stopped-flow(nm)
cPt	TU	340
	DMTU	340
	TMTU	-
cPtM	TU	340
	DMTU	340
		-
cPtR	TU	340
	DMTU	340
tPt	TU	330
	DMTU	330
	TMTU	345
tPtM	TU	330
	DMTU	330
	TMTU	345
tPtR	TU	330
	DMTU	330
	TMTU	360

Supplementary Tables and Figures for the *cis* complexes

Table S2 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **cPt** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.15	0.01499	0.15	0.00670
0.30	0.02933	0.30	0.01340
0.45	0.04452	0.45	0.01958
0.60	0.05835	0.60	0.02653
0.75	0.07286	0.75	0.03320

Table S3 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the ammine ligands in **cPt** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.15	0.00325	0.15	0.00134
0.30	0.00652	0.30	0.00264
0.45	0.00960	0.45	0.00386
0.60	0.01283	0.60	0.00515
0.75	0.01598	0.75	0.00647

Table S4 Temperature dependence of k_2/$M^{-1}s^{-1}$, for the displacement of the aqua ligands in **cPt** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

TU		DMTU	
1/T (K^{-1})	ln(k_2/T)	1/T (K^{-1})	ln(k_2/T)
0.00341	-8.1305	0.00341	-9.1597
0.00336	-8.0104	0.00336	-8.8318
0.00330	-7.8947	0.00330	-8.5148
0.00325	-7.7830	0.00325	-8.2083
0.00319	-7.6751	0.00319	-7.9118

Table S5 Temperature dependence of k_2/$M^{-1}s^{-1}$, for the displacement of the ammine ligands in **cPt** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

TU		DMTU	
1/T (K^{-1})	ln(k_2/T)	1/T (K^{-1})	ln(k_2/T)
0.00341	-9.9427	0.00341	-10.8448
0.00336	-9.5446	0.00336	-10.4549
0.00330	-9.1598	0.00330	-10.0780
0.00325	-8.7900	0.00325	-9.71380
0.00319	-8.4279	0.00319	-9.36140

Table S6 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **cPtM** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.15	0.00895	0.15	0.00590
0.30	0.01729	0.30	0.01199
0.45	0.02593	0.45	0.01809
0.60	0.03505	0.60	0.02379
0.75	0.04385	0.75	0.02993

Table S7 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the amine ligands in **cPtM** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.15	0.00122	0.15	5.40E-4
0.30	0.00243	0.30	0.00113
0.45	0.00364	0.45	0.00171
0.60	0.00488	0.60	0.00225
0.75	0.00615	0.75	0.00281

Table S8 Temperature dependence of k_2/$M^{-1}s^{-1}$, for the displacement of the aqua ligands in **cPtM** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

TU		DMTU	
1/T (K^{-1})	ln(k_2/T)	1/T (K^{-1})	ln(k_2/T)
0.00341	-8.8020	0.00341	-9.3005
0.00336	-8.3909	0.00336	-8.9110
0.00330	-7.9640	0.00330	-8.5312
0.00325	-7.5864	0.00325	-8.1324
0.00319	-7.2285	0.00319	-7.8063

Table S9 Temperature dependence of k_2/$M^{-1}s^{-1}$, for the displacement of the amine ligands in **cPtM** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

TU		DMTU	
1/T (K^{-1})	ln(k_2/T)	1/T (K^{-1})	ln(k_2/T)
0.00341	-10.9030	0.00341	-11.7030
0.00336	-10.3744	0.00336	-11.2698
0.00330	-9.87140	0.00330	-10.8223
0.00325	-9.39450	0.00325	-10.3786
0.00319	-9.01460	0.00319	-10.0246

Table S10 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **cPtR** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.15	4.13E-4	0.15	2.9965E-4
0.30	8.26E-4	0.30	5.9930E-4
0.45	0.00130	0.45	8.8401E-4
0.60	0.00173	0.60	0.0011202
0.75	0.00210	0.75	0.0014010

Table S11 Temperature dependence of k_2/$M^{-1}s^{-1}$, for the displacement of the aqua ligands in **cPtR** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

TU		DMTU	
1/T (K^{-1})	ln(k_2/T)	1/T (K^{-1})	ln(k_2/T)
0.00341	-11.9710	0.00341	-12.3101
0.00336	-11.5880	0.00336	-11.9296
0.00330	-11.2390	0.00330	-11.5530
0.00325	-10.8831	0.00325	-11.1736
0.00319	-10.5320	0.00319	-10.8420

Fig. S11 Dependence of the *pseudo* first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the aqua and ammine substitution for **cPt** in $NaClO_4$ (I = 0.1 M) at 298.15 K.

Fig. S12 Eyring plots obtained for **cPt** with the nucleophiles for the substitution reactions over the temperature range 293.15 – 313.15 K in $NaClO_4$ (I = 0.1 M).

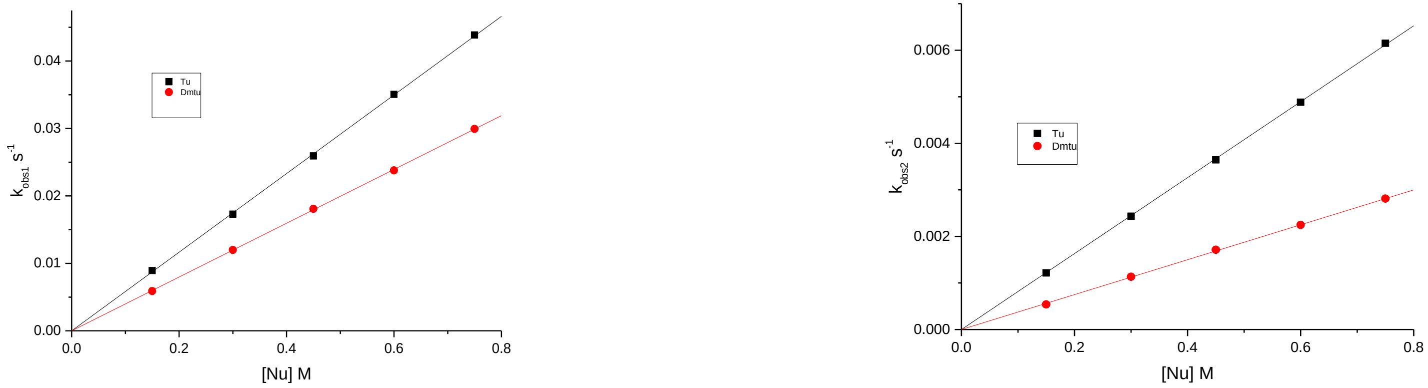


Fig. S13 Dependence of the *pseudo* first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the aqua and ammine substitution for **cPtM** in $NaClO_4$ (I = 0.1 M) at 298.15 K.

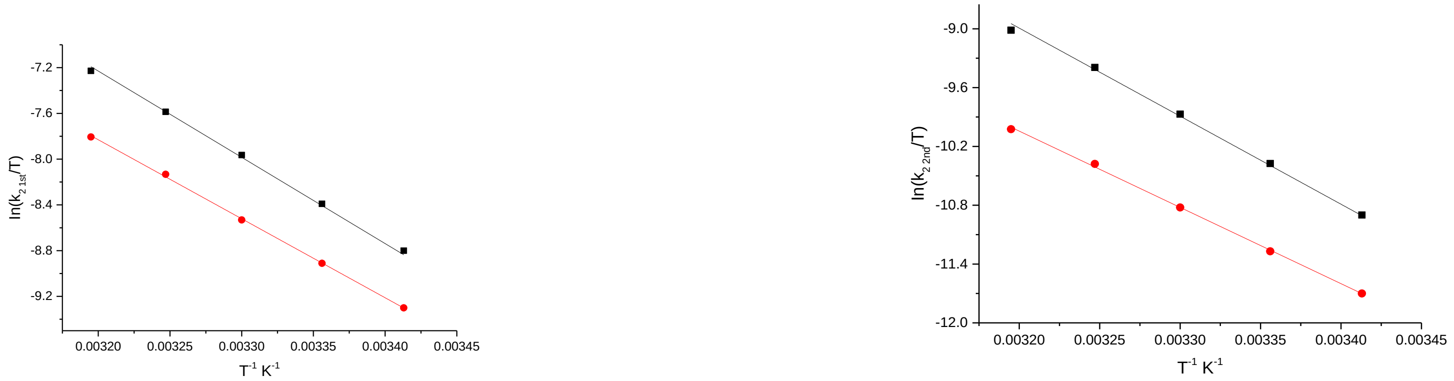


Fig. S14 Eyring plots obtained for **cPtM** with the nucleophiles for the substitution reactions over the temperature range 293.15 – 313.15 K in $NaClO_4$ (I = 0.1 M).

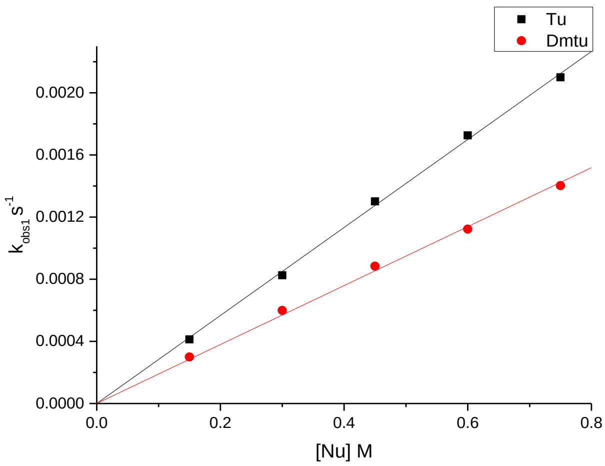


Fig. S15 Dependence of the *pseudo* first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the aqua substitution for **cPtR** in $NaClO_4$ (I = 0.1 M) at 298.15 K.

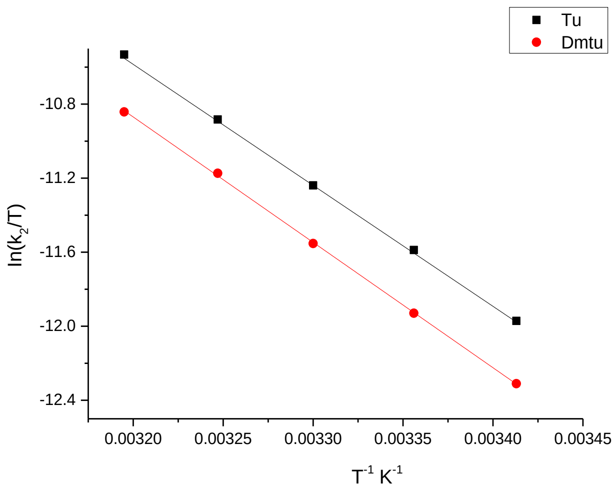


Fig. S16 Eyring plots obtained for **cPtR** with the nucleophiles for the substitution reactions over the temperature range 293.15 – 313.15 K in $NaClO_4$ (I = 0.1 M)

Supplementary Tables and Figures for the *trans* complexes

Table S12 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **tPt** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU		TMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.02	0.88570	0.02	0.44470	0.02	0.11560
0.04	1.76139	0.04	0.88944	0.04	0.22301
0.06	2.65197	0.06	1.36503	0.06	0.33463
0.08	3.54107	0.08	1.83272	0.08	0.44624
0.10	4.42689	0.10	2.30257	0.10	0.55780

Table 13 Temperature dependence of k_2/M^{-1}s^{-1}, for the displacement of the aqua ligands in **tPt** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

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)
0.00341	-5.3765	0.00341	-5.9580	0.00341	-7.5010
0.00336	-4.9525	0.00336	-5.5682	0.00336	-7.0386
0.00330	-4.4827	0.00330	-5.2301	0.00330	-6.5803
0.00325	-4.1163	0.00325	-4.8681	0.00325	-6.1379
0.00319	-3.7560	0.00319	-4.5157	0.00319	-5.7141

Table S14 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **tPtM** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU		TMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.02	0.70761	0.02	0.35958	0.02	0.07501
0.04	1.38197	0.04	0.72830	0.04	0.15287
0.06	2.12432	0.06	1.09171	0.06	0.21985
0.08	2.83238	0.08	1.45619	0.08	0.30406
0.10	3.54455	0.10	1.81803	0.10	0.38153

Table S15 Temperature dependence of k_2/M^{-1}s^{-1}, for the displacement of the aqua ligands in **tPtM** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

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)
0.00341	-5.50310	0.00341	-6.40301	0.00341	-7.49021
0.00336	-5.16405	0.00336	-5.98240	0.00336	-7.18778
0.00330	-4.81410	0.00330	-5.60226	0.00330	-6.79401
0.00325	-4.30090	0.00325	-5.20010	0.00325	-6.39420
0.00319	-3.90790	0.00319	-4.78801	0.00319	-5.99961

Table S16 Average observed rate constants, k_{obs}, s^{-1}, for the displacement of the aqua ligands in **tPtR** with the nucleophiles, at pH = 2.0, T = 298.15 K, I = 0.1 M $NaClO_4$.

TU		DMTU		TMTU	
Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})	Conc., M	k_{obs} (s^{-1})
0.02	0.37915	0.02	0.20575	0.02	0.04475
0.04	0.75827	0.04	0.41151	0.04	0.08950
0.06	1.13741	0.06	0.61726	0.06	0.13218
0.08	1.51701	0.08	0.82302	0.08	0.17771
0.10	1.89550	0.10	1.02877	0.10	0.22382

Table S17 Temperature dependence of k_2/M^{-1}s^{-1}, for the displacement of the aqua ligands in **tPtR** by the nucleophiles at 60-fold at pH = 2.0, I = 0.1 M $NaClO_4$

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)
0.00341	-3.10426	0.00341	-3.72431	0.00341	-5.31546
0.00336	-2.75497	0.00336	-3.36618	0.00336	-4.90727
0.00330	-2.31217	0.00330	-2.97527	0.00330	-4.54127
0.00325	-2.01889	0.00325	-2.69267	0.00325	-4.14127
0.00319	-1.56808	0.00319	-2.28466	0.00319	-3.82437

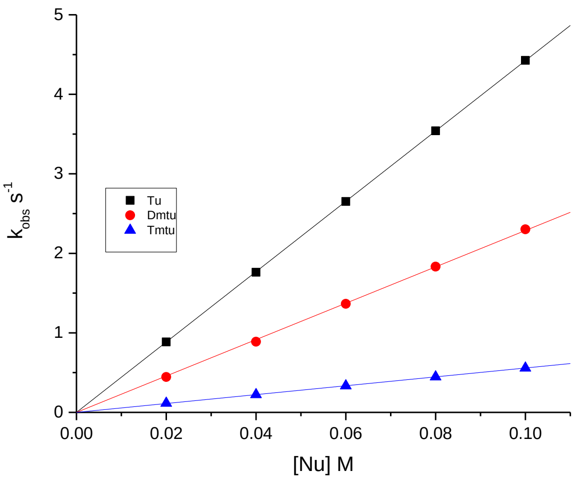


Fig. S17 Dependence of the *pseudo* first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the aqua substitution for **tPt** in $NaClO_4$ (I = 0.1 M) at 298.15 K.

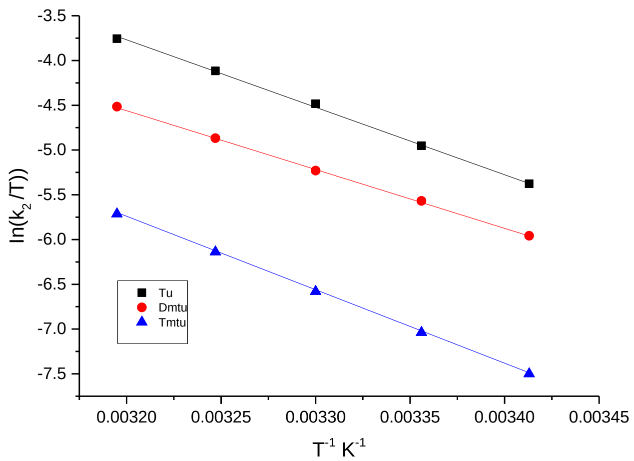


Fig. S18 Eyring plots obtained for t**Pt** with the nucleophiles for the substitution reactions over the temperature range 293.15 – 313.15 K in $NaClO_4$ (I = 0.1 M)

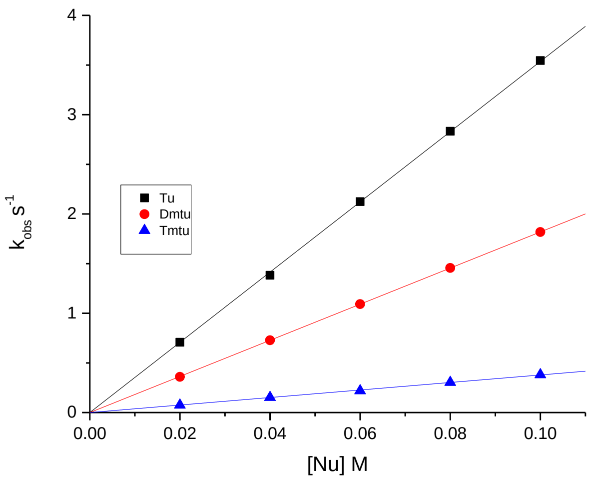


Fig. S19 Dependence of the *pseudo* first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the aqua substitution for **tPtM** in $NaClO_4$ (I = 0.1 M) at 298.15 K.

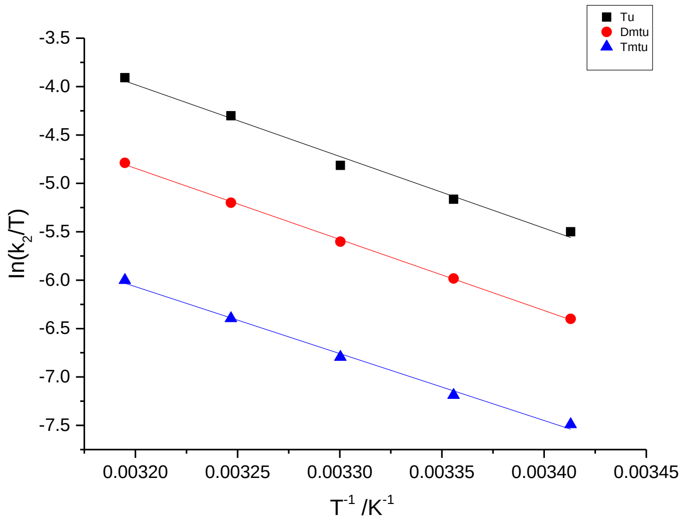


Fig. S20 Eyring plots obtained for t**PtM** with the nucleophiles for the substitution reactions over the temperature range 293.15 – 313.15 K in $NaClO_4$ (I = 0.1 M)

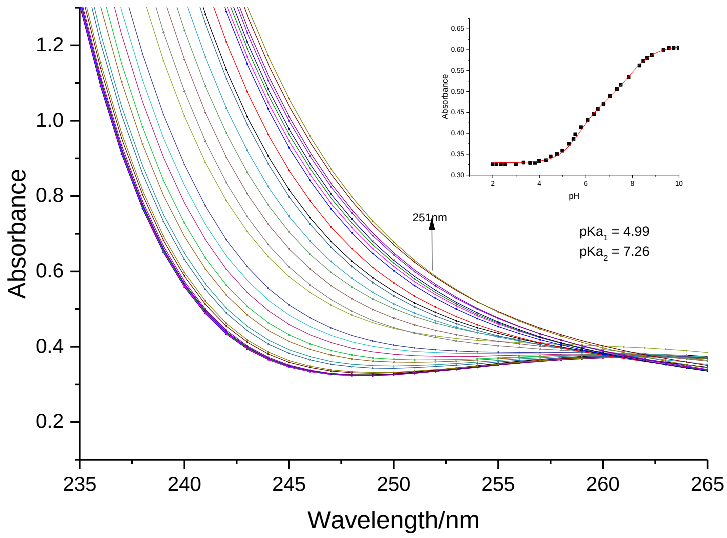


Fig. S21 Determination of pK_a values for **cPt** using Boltzmann equation from the sigmoid curve at the inflection point

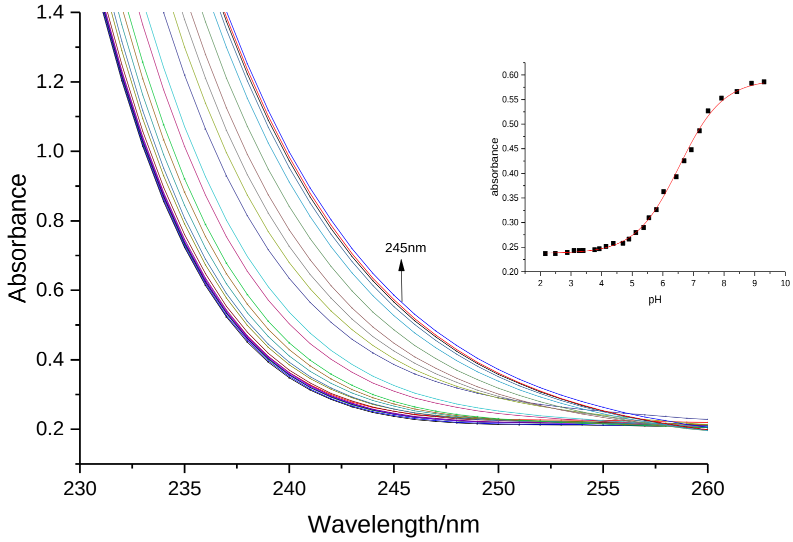


Fig. S22 Determination of pK_a values for **cPtM** using Boltzmann equation from the sigmoid curve at the inflection point