Electronic Supplementary Information

Thermodynamic and Kinetic Behaviour of [Pt(2-methylthiomethylpyridine)$(OH_2)_2$]$^{2+}$

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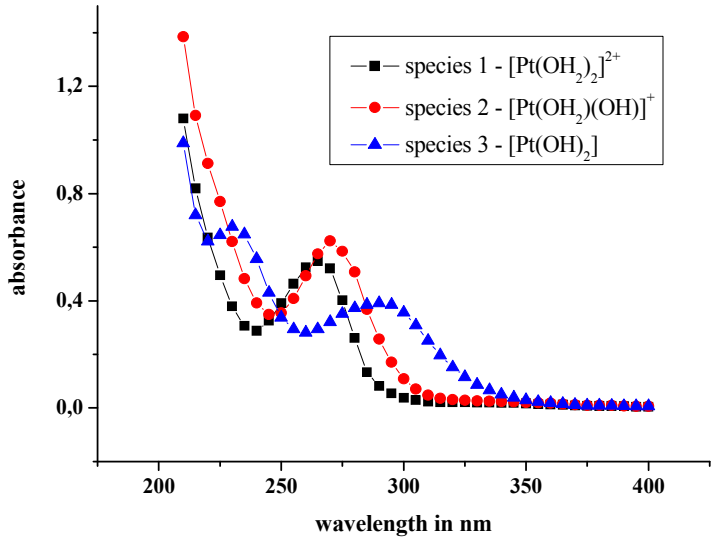

Fig. SI 1 Calculated absorbance traces for the species 1 – 3 for the **Pt(mtp)** complex as a function of pH.

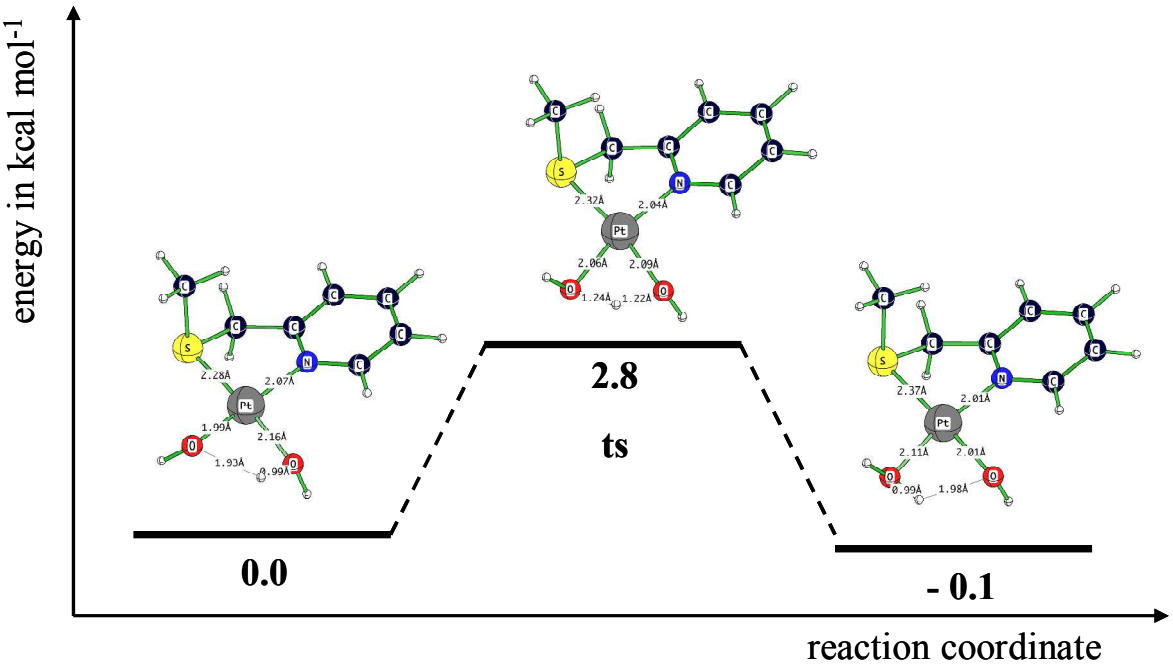

Fig. SI 2 Calculated energy (B3LYP/LANL2DZp) profile for intramolecular proton transfer of the mono-deprotonated **Pt(mtp)** complex with the transition state (ts).

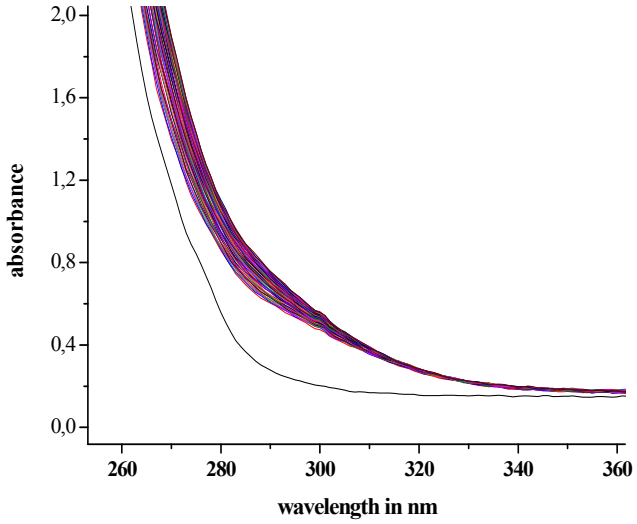

Fig. SI 3 UV-vis spectra recorded for the reaction of 0.125 mM **Pt(mtp)** with 5 mM dmtu at pH 2 (I = 0.01 M triflic acid) and 25 °C.

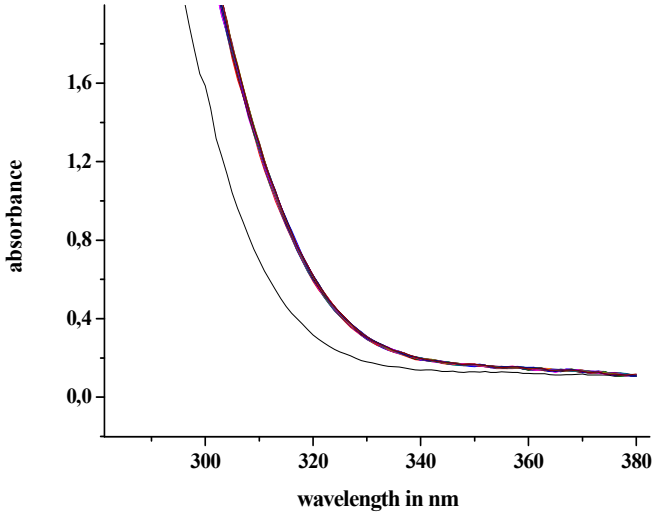

Fig. SI 4 UV-vis spectra recorded for the reaction of 0.125 mM **Pt(mtp)** with 5 mM tmtu at pH 2 (I = 0.01 M triflic acid) and 25 °C.

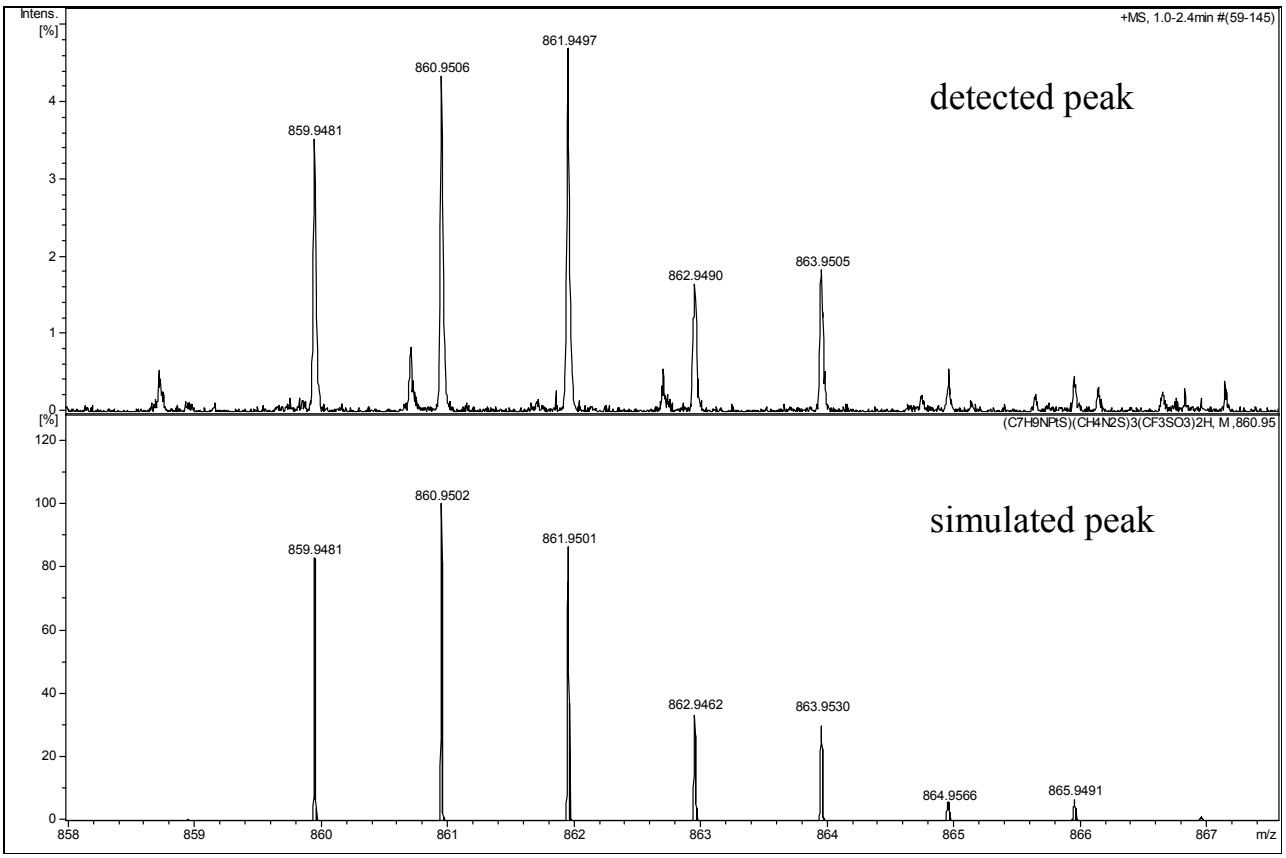

Fig. SI 5 Isotopic pattern and simulation of the peak around m/z = 861 (M = 860.95 g mol^{-1}), which belongs to the **Pt(mtp)** complex that includes three thiourea ligands (at pH 2).

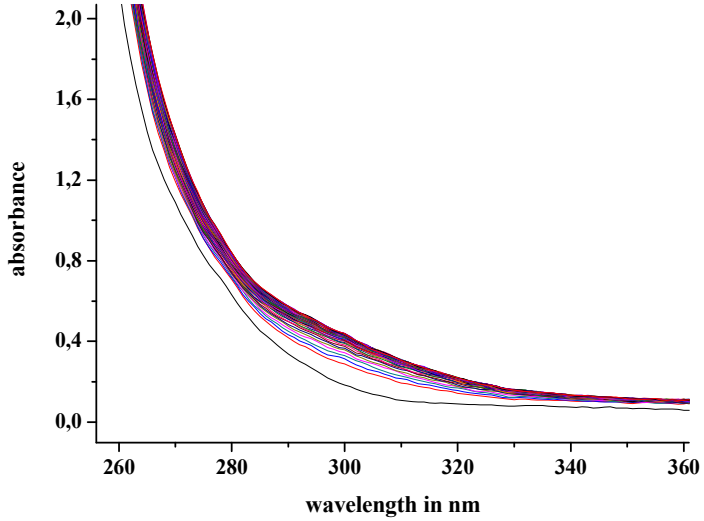

Fig. SI 6 UV-vis spectra recorded for the reaction of 0.125 mM **Pt(mtp)** with 5 mM dmtu at pH 4.75 (I = 0.1 M acetate buffer solution) and 25 °C.

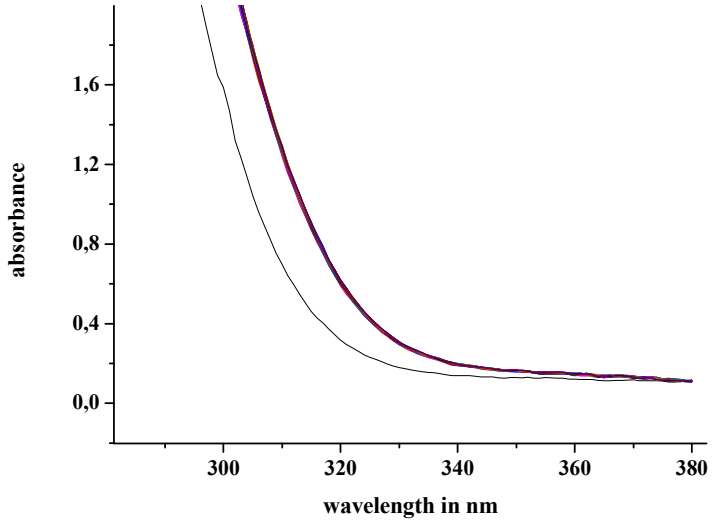

Fig. SI 7 UV-vis spectra recorded for the reaction of 0.125 mM **Pt(mtp)** with 5 mM tmtu at pH 4.75 (I = 0.1 M acetate buffer solution) and 25 °C.

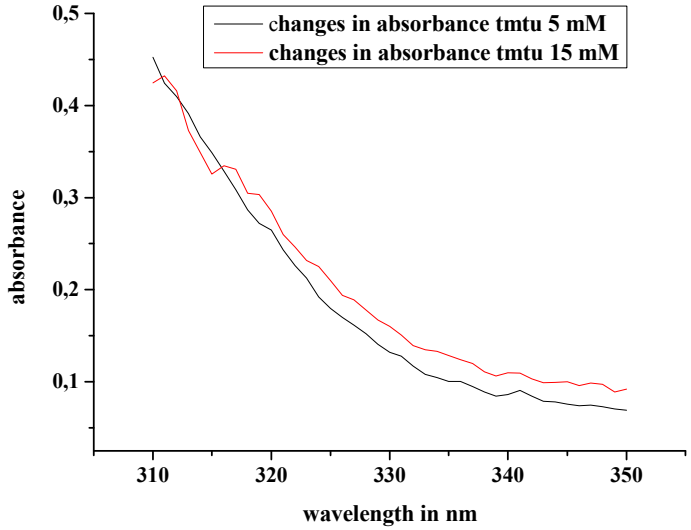

Fig. SI 8 Changes in absorbance during the reaction of 0.125 mM **Pt(mtp)** with 5 mM tu (black) and 15 mM tu (red).

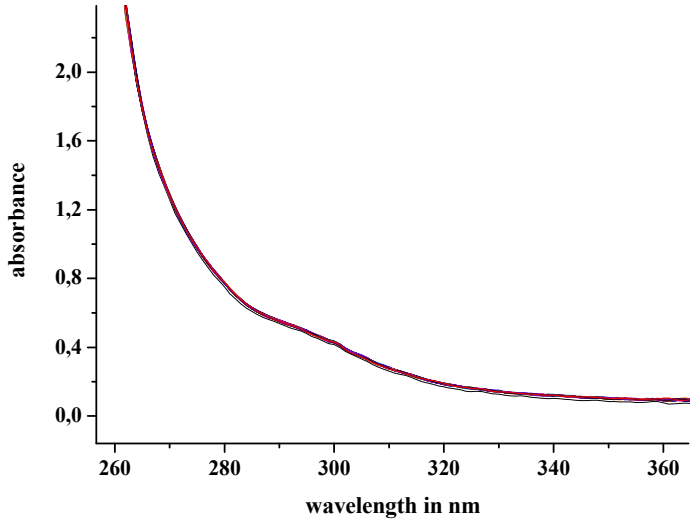

Fig. SI 9 UV-vis spectra recorded for the reaction of 0.125 mM **Pt(mtp)** with 5 mM tu at pH 7.4 (*I* = 0.1 M TRIS buffer) and 25 °C.

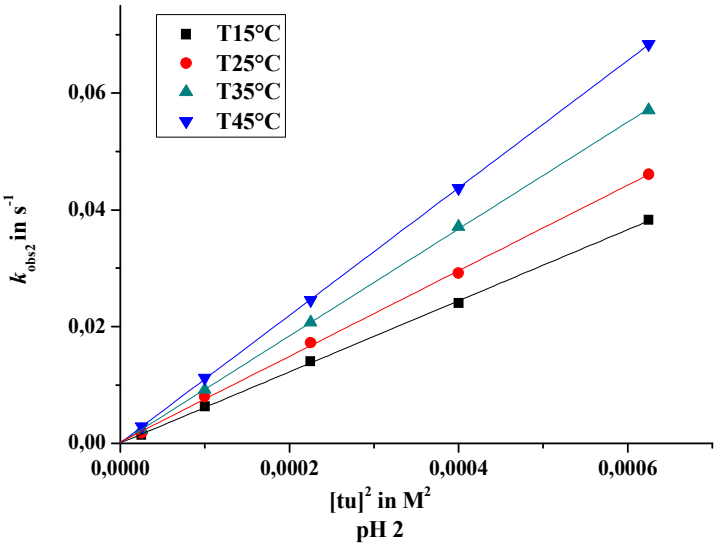

Fig. SI 10 Plots of k_{obs2} vs $[tu]^2$ for different temperatures at pH 2 (I = 0.01 M triflic acid).

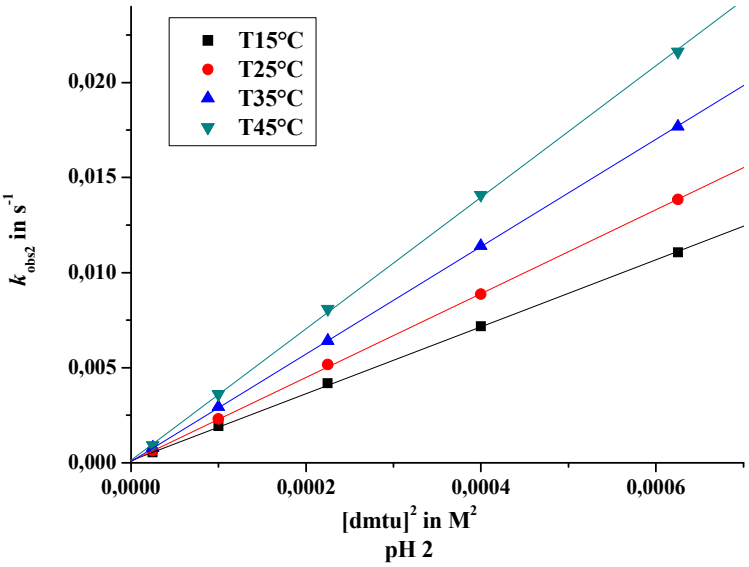

Fig. SI 11 Plots of k_{obs2} vs $[dmtu]^2$ for different temperatures at pH 2 (I = 0.01 M triflic acid).

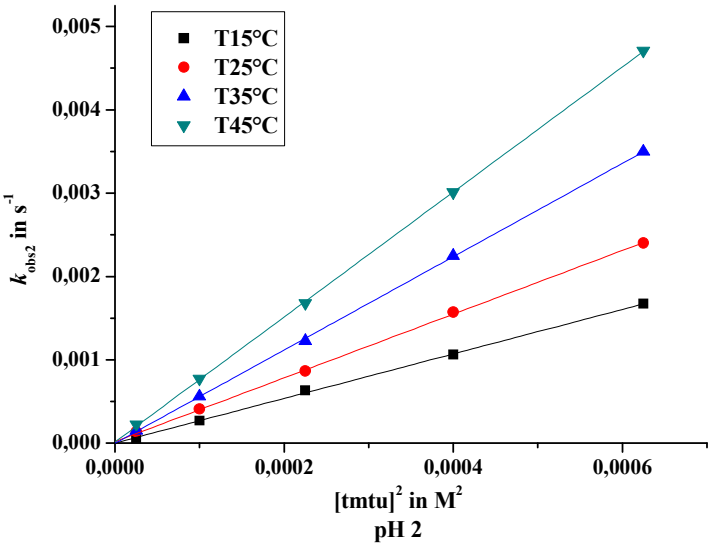

Fig. SI 12 Plots of k_{obs2} vs $[tmtu]^2$ for different temperatures at pH 2 (I = 0.01 M triflic acid).

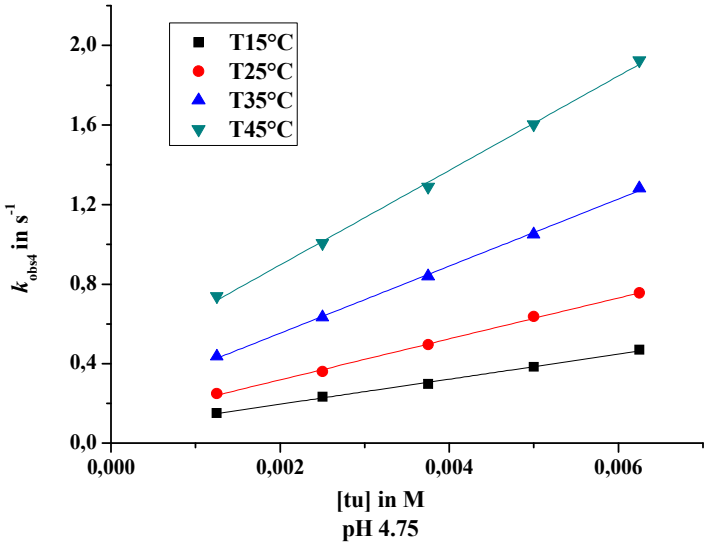

Fig. SI 13 Plots of k_{obs4} vs tu concentration for different temperatures at pH 4.75 (I = 0.1 M acetate buffer).

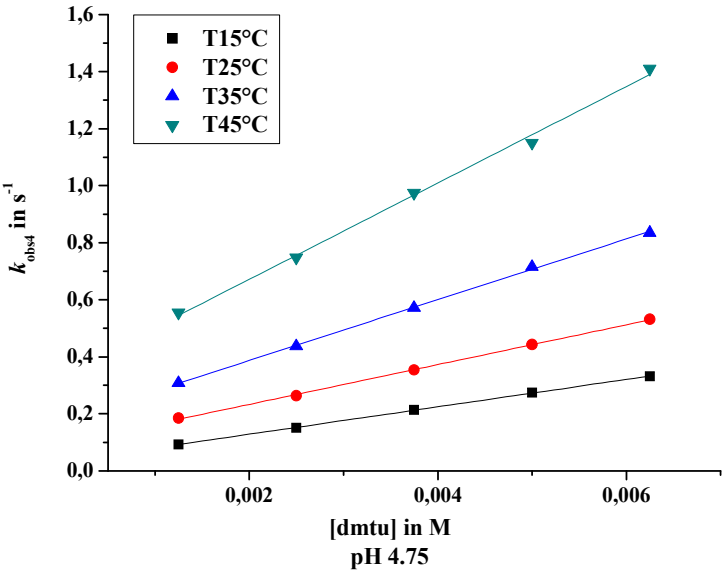

Fig. SI 14 Plots of k_{obs4} vs dmtu concentration for different temperatures at pH 4.75 (I = 0.1 M acetate buffer).

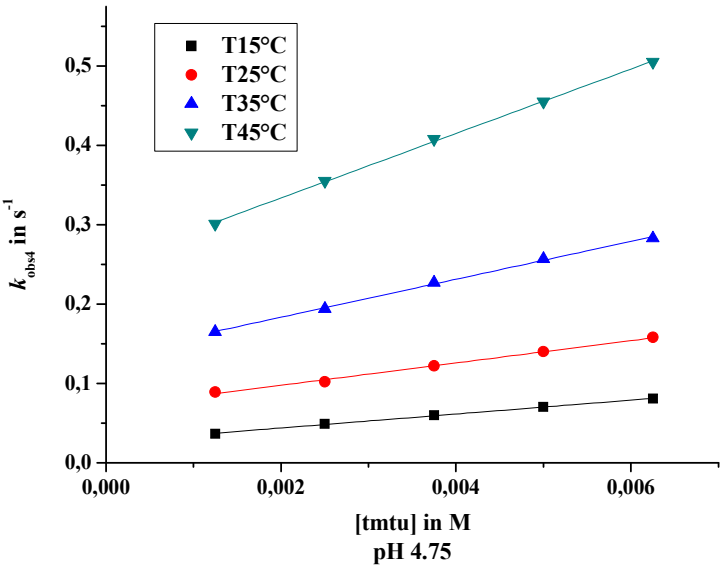

Fig. SI 15 Plots of k_{obs4} vs tmtu concentration for different temperatures at pH 4.75 (I = 0.1 M acetate buffer).

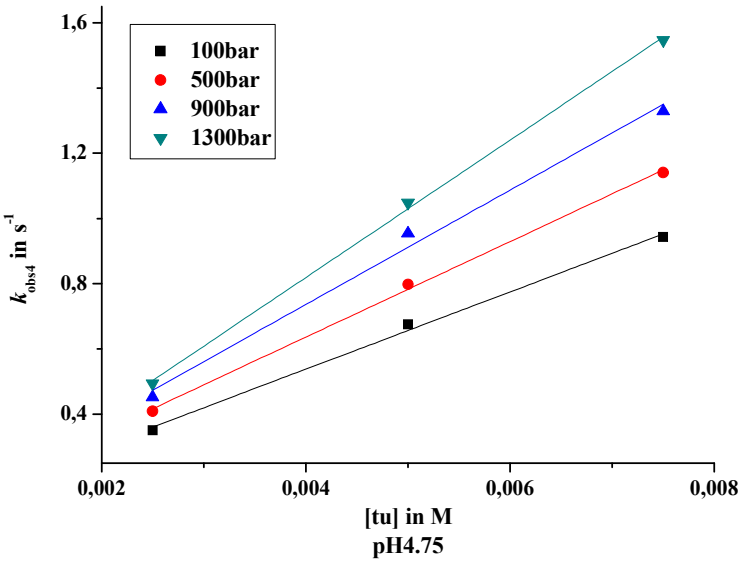

Fig. SI 16 Plots of k_{obs4} vs tu concentration for different pressures at pH 4.75 (I = 0.1 M acetate buffer) and 25 °C.

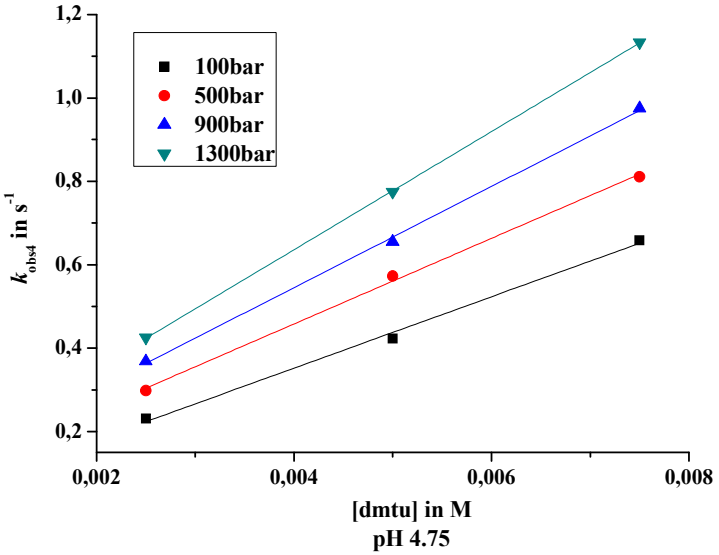

Fig. SI 17 Plots of k_{obs4} vs dmtu concentration for different pressures at pH 4.75 (I = 0.1 M acetate buffer) and 25 °C.

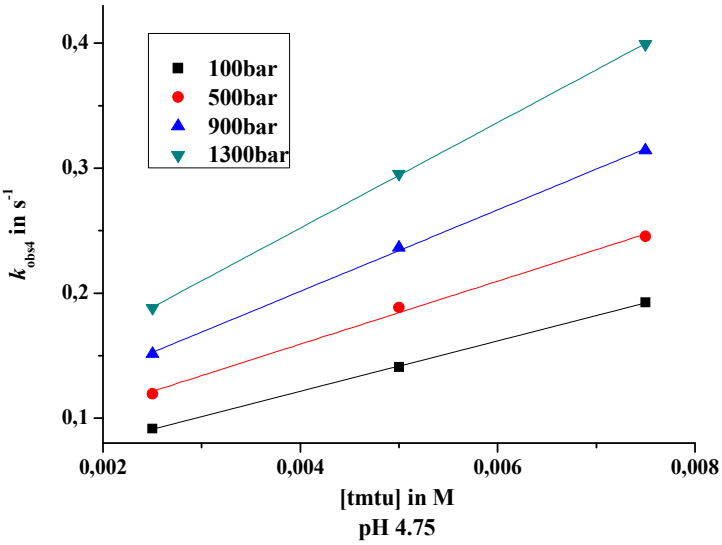

Fig. SI 18 Plots of k_{obs4} vs tmtu concentration for different pressures at pH 4.75 (I = 0.1 M acetate buffer) and 25 °C.

Table SI 1 Selected wavelengths for the successive substitution reactions of all three nucleophiles and different pH values.

	pH	tu	dmtu	tmtu
1st step	2	310 nm	310 nm	310 nm
	4.75	310 nm	310 nm	320 nm
2nd step	2	290 nm	290 nm	320 nm
	4.75	310 nm	310 nm	320 nm

Table SI 2 Average observed rate constants, k_{obs1}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at pH 2 (I = 0.01 M triflic acid) and 25 °C.

Nucleophile	**tu**	**dmtu**	**tmtu**
[Nu] in mM		k_{obs1} in s^{-1}	
1.25	0.764 ± 0.008	0.613 ± 0.006	0.184 ± 0.006
2.50	1.62 ± 0.03	1.246 ± 0.008	0.405 ± 0.004
3.75	2.47 ± 0.03	1.93 ± 0.05	0.63 ± 0.02
5.00	3.20 ± 0.02	2.56 ± 0.04	0.80 ± 0.02
6.25	3.92 ± 0.02	3.13 ± 0.02	1.03 ± 0.03

Table SI 3 Average observed rate constants, k_{obs2}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at pH 2 (I = 0.01 M triflic acid) and 25 °C.

Nucleophile	**tu**	**dmtu**	**tmtu**
[Nu] in mM		$10^2\ k_{obs2}$ in s^{-1}	
5.00	0.18 ± 0.03	0.064 ± 0.006	0.013 ± 0.007
10.00	0.802 ± 0.009	0.230 ± 0.002	0.041 ± 0.004
15.00	1.724 ± 0.005	0.516 ± 0.003	0.086 ± 0.006
20.00	2.919 ± 0.003	0.886 ± 0.005	0.16 ± 0.01
25.00	4.608 ± 0.005	1.385 ± 0.002	0.240 ± 0.005

Table SI 4 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at pH 4.75 (I = 0.1 M acetate buffer) and 25 °C.

Nucleophile	**tu**	**dmtu**	**tmtu**
[Nu] in mM		k_{obs4} in s^{-1}	
1.25	0.231 ± 0.003	0.18 ± 0.02	0.089 ± 0.006
2.50	0.359 ± 0.003	0.263 ± 0.002	0.102 ± 0.008
3.75	0.495 ± 0.001	0.353 ± 0.005	0.122 ± 0.002
5.00	0.636 ± 0.007	0.442 ± 0.005	0.140 ± 0.002
6.25	0.755 ± 0.002	0.53 ± 0.01	0.16 ± 0.01

Table SI 5 Average observed rate constants, k_{obs5}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at pH 4.75 (I = 0.1 M acetate buffer) and 25 °C.

Nucleophile	**tu**	**dmtu**	**tmtu**
[Nu] in mM	$10^2\ k_{obs5}$ in s^{-1}		
1.25	0.231 ± 0.002	0.141 ± 0.006	0.011 ± 0.002
2.50	0.461 ± 0.003	0.293 ± 0.002	0.023 ± 0.008
3.75	0.73 ± 0.03	0.436 ± 0.003	0.036 ± 0.002
5.00	0.961 ± 0.002	0.586 ± 0.009	0.050 ± 0.001
6.25	1.191 ± 0.001	0.747 ± 0.001	0.061 ± 0.003

Table SI 6 Average observed rate constants, k_{obs1}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (3.75 mM) at different temperatures and pH 2 (I = 0.01 M triflic acid).

Nucleophile	**tu**	**dmtu**	**tmtu**
T in K		k_{obs1} in s^{-1}	
288.15	1.39 ± 0.01	1.197 ± 0.006	0.32 ± 0.01
298.15	2.468 ± 0.007	1.928 ± 0.004	0.63 ± 0.04
308.15	3.607 ± 0.006	2.96 ± 0.03	1.023 ± 0.006
318.15	5.79 ± 0.02	4.81 ± 0.05	1.679 ± 0.009

Table SI 7 Average observed rate constants, k_{obs2}, for the reaction of 0.125 mM **Pt(mtp)** with different **tu** concentrations at different temperatures and pH 2 (I = 0.01 M triflic acid).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[tu] in mM	$10^2\ k_{obs2}$ in s^{-1}			
5.00	0.146 ± 0.005	0.18 ± 0.03	0.237 ± 0.008	0.290 ± 0.006
10.00	0.636 ± 0.007	0.802 ± 0.009	0.92 ± 0.04	1.124 ± 0.009
15.00	1.408 ± 0.008	1.724 ± 0.005	2.07 ± 0.03	2.45 ± 0.02
20.00	2.40 ± 0.01	2.919 ± 0.003	3.71 ± 0.07	4.37 ± 0.02
25.00	3.82 ± 0.05	4.608 ± 0.005	5.71 ± 0.03	6.84 ± 0.01

Table SI 8 Average observed rate constants, k_{obs2}, for the reaction of 0.125 mM **Pt(mtp)** with different **dmtu** concentrations at different temperatures and pH 2 (I = 0.01 M triflic acid).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[dmtu] in mM	$10^2\ k_{obs2}$ in s^{-1}			
5.00	0.053 ± 0.005	0.064 ± 0.006	0.079 ± 0.008	0.092 ± 0.006
10.00	0.193 ± 0.007	0.230 ± 0.002	0.293 ± 0.04	0.361 ± 0.005
15.00	0.42 ± 0.04	0.516 ± 0.003	0.641 ± 0.03	0.81 ± 0.01
20.00	0.718 ± 0.006	0.886 ± 0.005	1.140 ± 0.07	1.41 ± 0.02
25.00	1.385 ± 0.009	1.385 ± 0.002	1.769 ± 0.03	2.161 ± 0.009

Table SI 9 Average observed rate constants, k_{obs2}, for the reaction of 0.125 mM **Pt(mtp)** with different **tmtu** concentrations at different temperatures and pH 2 (I = 0.01 M triflic acid).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[tmtu] in mM	$10^2\ k_{obs2}$ in s^{-1}			
5.00	0.006 ± 0.0001	0.013 ± 0.007	0.015 ± 0.008	0.022 ± 0.006
10.00	0.027 ± 0.007	0.041 ± 0.004	0.056 ± 0.004	0.077 ± 0.005
15.00	0.063 ± 0.004	0.086 ± 0.006	0.12 ± 0.01	0.168 ± 0.006
20.00	0.106 ± 0.006	0.16 ± 0.01	0.225 ± 0.007	0.301 ± 0.008
25.00	0.167 ± 0.009	0.240 ± 0.005	0.35 ± 0.01	0.47 ± 0.01

Table SI 10 Summary of the third-order rate constants, k_3K_2, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at different temperatures and pH 2 (I = 0.01 M triflic acid).

Nucleophile	**tu**	**dmtu**	**tmtu**
T in K		k_3K_2 in M^{-2} s^{-1}	
288.15	60.9 ± 0.1	17.6 ± 0.1	2.87 ± 0.08
298.15	73.3 ± 0.4	22.1 ± 0.4	3.82 ± 0.04
308.15	91.5 ± 0.2	28.2 ± 0.3	4.84 ± 0.06
318.15	109.1 ± 0.1	34.6 ± 0.1	6.2 ± 0.1

Table SI 11 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different **tu** concentrations at different temperatures and pH 4.75 (I = 0.1 M acetate buffer).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[tu] in mM	k_{obs4} in s^{-1}			
1.25	0.151 ± 0.01	0.249 ± 0.003	0.43 ± 0.01	0.739 ± 0.006
2.50	0.232 ± 0.007	0.36 ± 0.01	0.633 ± 0.004	1.01 ± 0.02
3.75	0.296 ± 0.004	0.495 ± 0.004	0.84 ± 0.01	1.29 ± 0.01
5.00	0.383 ± 0.006	0.636 ± 0.007	1.051 ± 0.007	1.60 ± 0.008
6.25	0.469 ± 0.009	0.755 ± 0.002	1.28 ± 0.01	1.92 ± 0.03

Table SI 12 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different **dmtu** concentrations at different temperatures and pH 4.75 (I = 0.1 M acetate buffer).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[dmtu] in mM	k_{obs4} in s^{-1}			
1.25	0.092 ± 0.005	0.18 ± 0.02	0.308 ± 0.008	0.555 ± 0.003
2.50	0.151 ± 0.002	0.263 ± 0.002	0.44 ± 0.01	0.748 ± 0.009
3.75	0.21 ± 0.01	0.353 ± 0.005	0.572 ± 0.009	0.974 ± 0.002
5.00	0.274 ± 0.002	0.442 ± 0.005	0.72 ± 0.02	1.15 ± 0.01
6.25	0.331 ± 0.006	0.53 ± 0.01	0.83 ± 0.01	1.41 ± 0.01

Table SI 13 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different **tmtu** concentrations at different temperatures and pH 4.75 (I = 0.1 M acetate buffer).

T in K	**288.15**	**298.15**	**308.15**	**318.15**
[tmtu] in mM	k_{obs4} in s^{-1}			
1.25	0.036 ± 0.003	0.089 ± 0.006	0.165 ± 0.004	0.30 ± 0.03
2.50	0.049 ± 0.002	0.102 ± 0.008	0.194 ± 0.004	0.35 ± 0.01
3.75	0.060 ± 0.008	0.122 ± 0.002	0.227 ± 0.08	0.41 ± 0.01
5.00	0.070 ± 0.003	0.140 ± 0.002	0.26 ± 0.001	0.455 ± 0.008
6.25	0.081 ± 0.003	0.16 ± 0.01	0.283 ± 0.009	0.505 ± 0.005

Table SI 14 Summary of the second-order rate constants, k_4, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at different temperatures and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
T in K		k_4 in M^{-1} s^{-1}	
288.15	69.7 ± 0.6	48.0 ± 0.4	8.8 ± 0.2
298.15	106 ± 2	70 ± 1	14.1 ± 0.5
308.15	164 ± 5	107 ± 2	23.9 ± 0.5
318.15	260 ± 7	169 ± 5	41 ± 1

Table SI 15 Average observed rate constants, k_{obs5}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (3.75 mM) at different temperatures and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
T in K		$10^2\ k_{obs5}$ in s^{-1}	
288.15	0.38 ± 0.01	0.23 ± 0.02	0.155 ± 0.005
298.15	0.70 ± 0.01	0.41 ± 0.01	0.262 ± 0.004
308.15	1.13 ± 0.03	0.72 ± 0.02	0.55 ± 0.01
318.15	1.79 ± 0.02	1.15 ± 0.05	0.102 ± 0.002

Table SI 16 Average observed rate constants, k_{obs1}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (5 mM) at different pressures, 25°C and pH 2 (I = 0.01 M triflic acid).

Nucleophile	**tu**	**dmtu**	**tmtu**
p in MPa		k_{obs1} in s^{-1}	
10	2.78 ± 0.01	2.42 ± 0.02	0.789 ± 0.009
50	3.056 ± 0.008	2.753 ± 0.009	1.004 ± 0.006
90	3.32 ± 0.01	3.08 ± 0.01	1.25 ± 0.02
130	3.58 ± 0.02	3.48 ± 0.02	1.556 ± 0.007

Table SI 17 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (2.5 mM) at different pressures, 25°C and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
p in MPa		k_{obs4} in s^{-1}	
10	0.35 ± 0.01	0.23 ± 0.01	0.094 ± 0.007
50	0.41 ± 0.01	0.298 ± 0.009	0.11 ± 0.02
90	0.45 ± 0.02	0.37 ± 0.01	0.14 ± 0.01
130	0.49 ± 0.01	0.42 ± 0.01	0.17 ± 0.02

Table SI 18 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (5 mM) at different pressures, 25°C and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
p in MPa		k_{obs4} in s^{-1}	
10	0.67 ± 0.01	0.42 ± 0.01	0.14 ± 0.01
50	0.798 ± 0.008	0.57 ± 0.02	0.18 ± 0.02
90	0.95 ± 0.01	0.65 ± 0.04	0.22 ± 0.01
130	1.05 ± 0.02	0.77 ± 0.02	0.275 ± 0.006

Table SI 19 Average observed rate constants, k_{obs4}, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles (7.5 mM) at different pressures, 25°C and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
p in MPa		k_{obs4} in s^{-1}	
10	0.943 ± 0.007	0.659 ± 0.006	0.192 ± 0.006
50	1.14 ± 0.01	0.811 ± 0.009	0.24 ± 0.01
90	1.33 ± 0.01	0.97 ± 0.01	0.298 ± 0.004
130	1.547 ± 0.009	1.13 ± 0.02	0.37 ± 0.01

Table SI 20 Summary of the second-order rate constants, k_4, for the reaction of 0.125 mM **Pt(mtp)** with different nucleophiles at different pressures and pH 4.75 (I = 0.1 M acetate buffer).

Nucleophile	**tu**	**dmtu**	**tmtu**
p in MPa		k_4 in M^{-1} s^{-1}	
10	121 ± 3	86 ± 2	20 ± 1
50	146 ± 6	103 ± 4	25.2 ± 0.4
90	175 ± 5	121 ± 4	32.1 ± 0.3
130	208 ± 6	142 ± 1	41 ± 1