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Platinum(II) complexes with hybrid amine-imidazolin-2-imine ligands and their reactivity toward bio-molecules

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[(DACH(Im^*iPr*H)₂)(AuCl₂)₂]:

¹H NMR (300 MHz; CDCl₃): δ = 5.65 (bs, 2H, NH), 4.98 (sept, 4H, J_{HH} 7.0 Hz, C*H*Me₂), 3.40 (bs, 2H, CH₂C*H*(NH)C*H*(NH)CH₂), 2.22 (s, 12H, CC*H*₃), 1.79 - 1.60 (m, 6H, C*H*₂), 1.60 (d, 12H, J_{HH} 7.0 Hz, CH(C*H*₃)₂), 1.52 (d, 12H, J_{HH} 7.0 Hz, CH(C*H*₃)₂), 1.23 - 1.18 (m, 2H, C*H*₂) ppm.

¹³C NMR (100 MHz; CDCl₃): δ = 147.5 (N₂*C*NH), 124.3 (*C*Me), 63.4 (CH₂*C*H(NHC)*C*H(NHC)CH₂), 50.4 (*C*HMe₂), 35.6 (*C*H₂), 25.5 (*C*H₂), 22.6 (CH(*C*H₃)₂), 20.8 (CH(*C*H₃)₂), 11.7 (C*C*H₃) ppm.
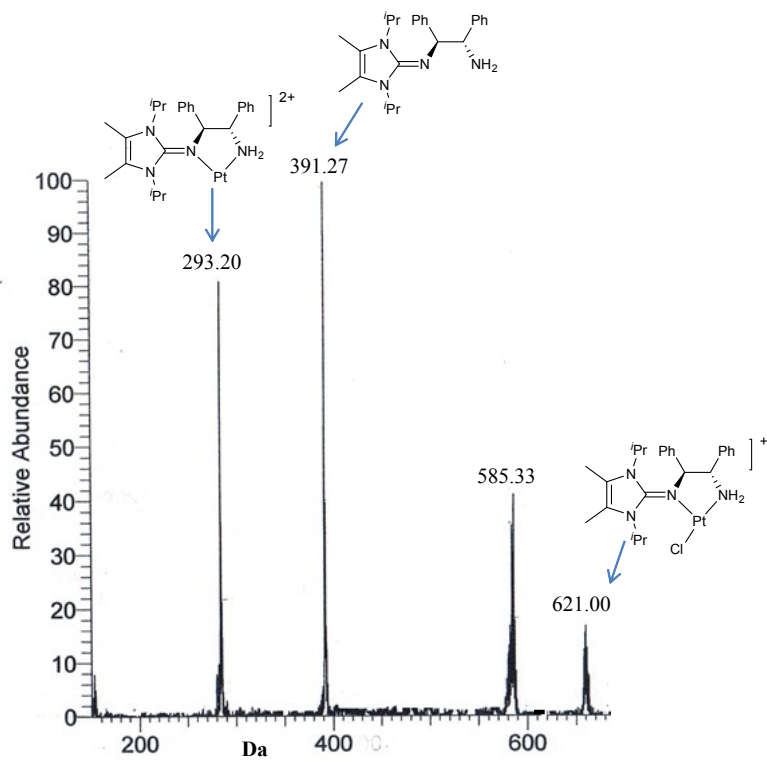
Figure S1. Mass spectrum of the [Pt(DPENIm$^{i\text{Pr}}$)Cl$_2$] complex.
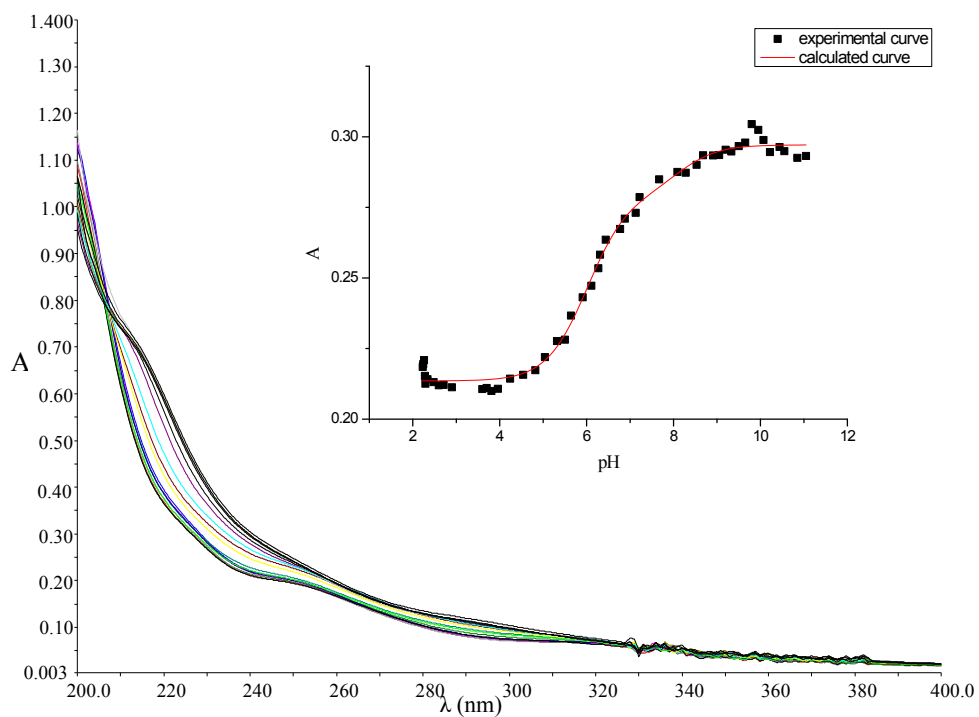
Figure S2. UV-vis spectra recorded for 0.1 mM [Pt(DPENIm$^{i\text{Pr}}$)(H$_2$O)$_2$]$^{2+}$ in the pH range 2 to 12 at 25 °C. Insert: Plot of absorbance *vs* pH at 262 nm.
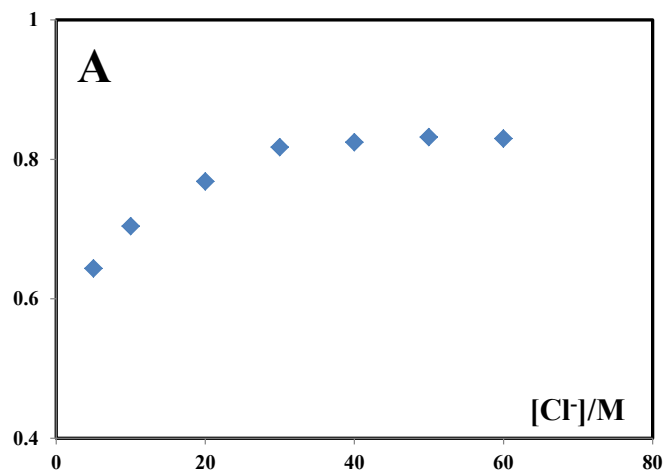
Figure S3. The effect of different concentrations of chloride ions on the change in absorbance in the solution of the complex $[Pt(DPENIm^{iPr})Cl_2]$ in 25 mM Hepes buffer (pH $\approx$ 7,2) at 245 nm.
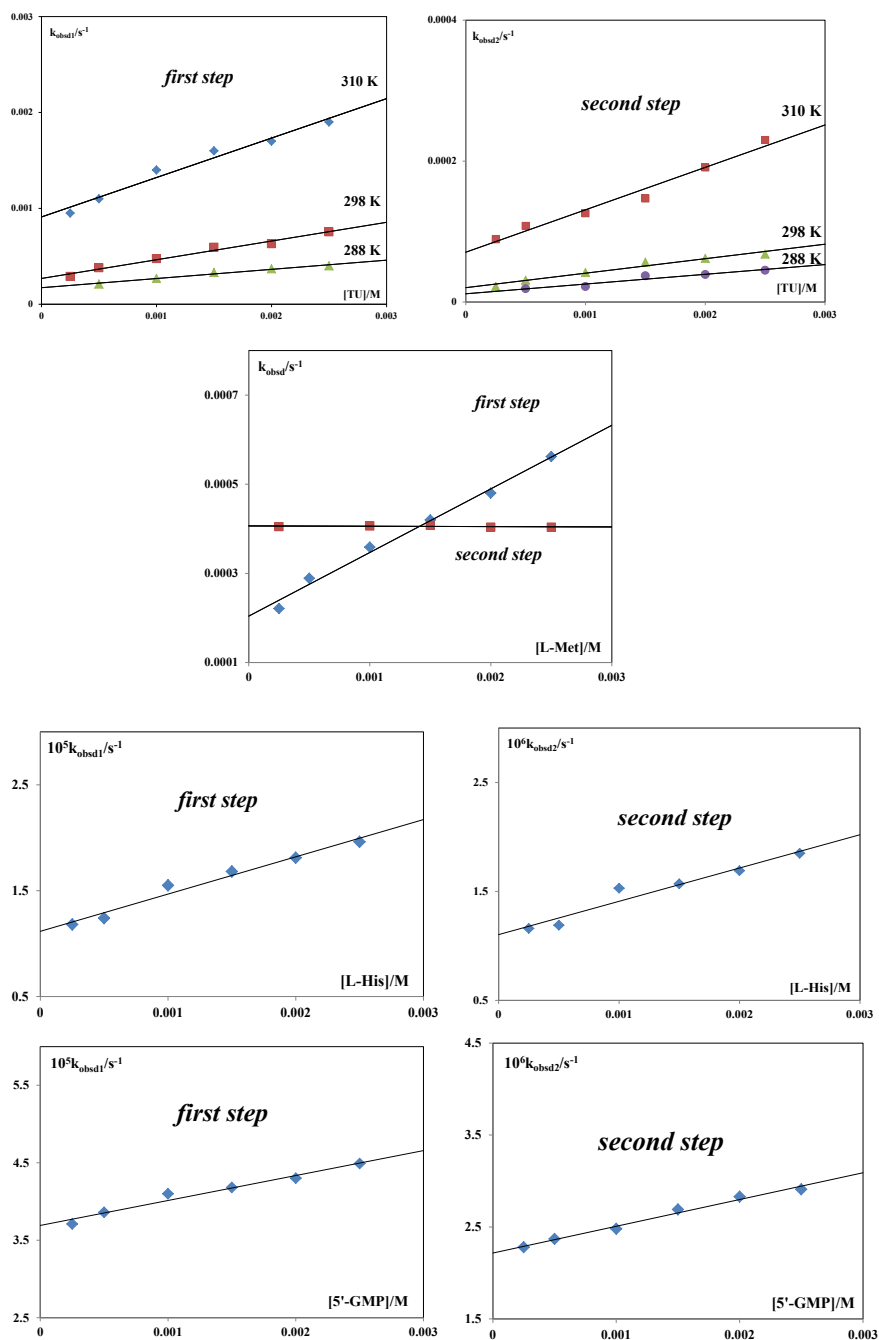
Figure S4. *Pseudo*-first-order rate constants plotted as a function of nucleophile concentration for the first and second step of the substitution reactions of the [Pt(DMEAIm$^{i\text{Pr}}$)Cl$_2$] complexes with TU, L-Met, L-His and 5'-GMP at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.
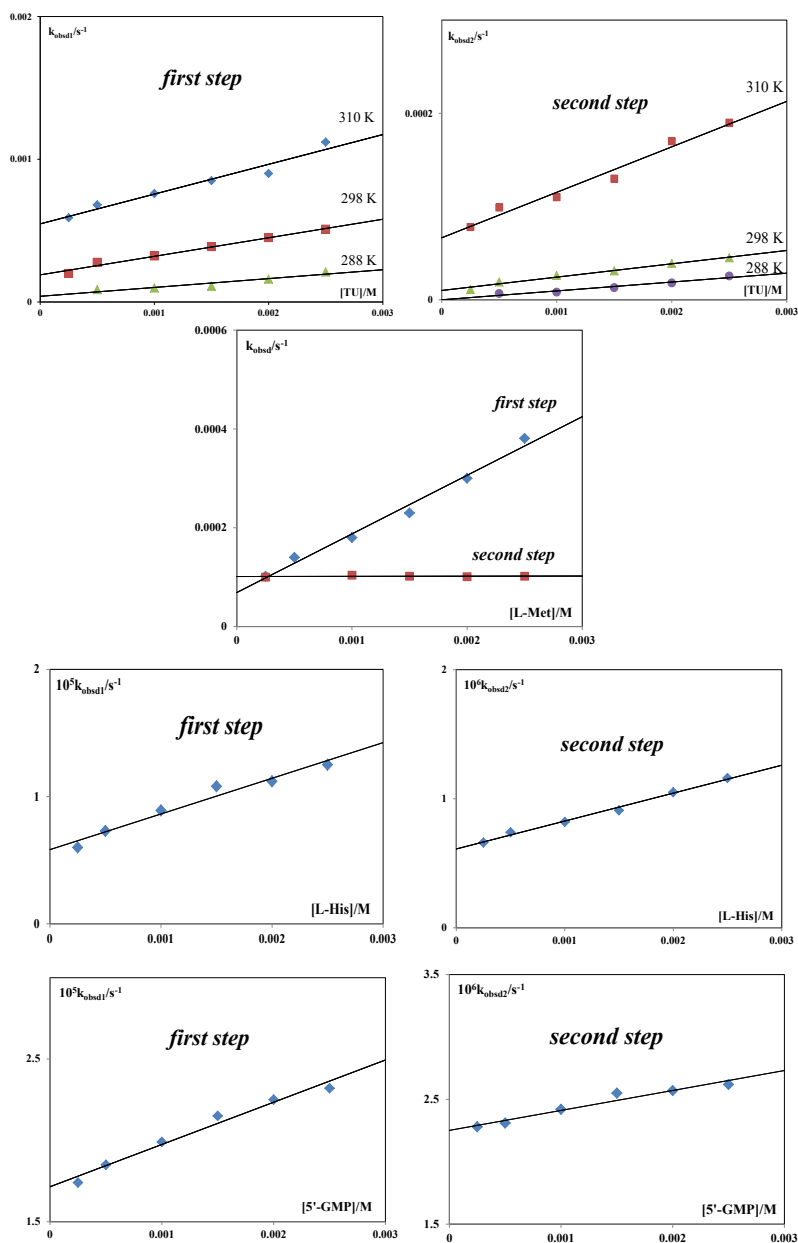
Figure S5. *Pseudo*-first-order rate constants plotted as a function of nucleophile concentration for the first and second step of the substitution reactions of the $[Pt(DPENIm^{iPr})Cl_2]$ complexes with TU, L-Met, L-His and 5'-GMP at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.
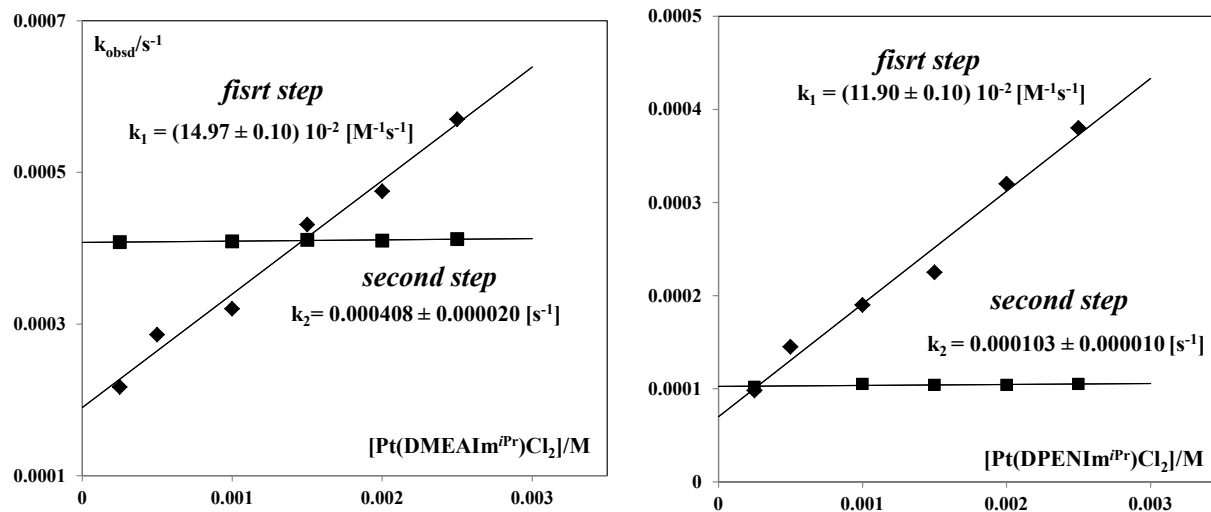
Figure S6. *Pseudo*-first-order rate constants plotted as a function of complex concentration for the first and second step of the substitution reactions of the [Pt(DMEAIm^{iPr})Cl$_2$] and [Pd(DPENIm^{iPr})Cl$_2$] complexes with L-Met at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.

Table S1. Activation parameters for the first and the second reaction steps between investigated Pt(II) complexes and TU at pH = 7.2, 25 mM Hepes buffer and 30 mM NaCl.

	first step		*second step*	
	$\Delta H_1^{\neq}$ [kJ mol^{-1}]	$\Delta S_1^{\neq}$ [JK^{-1} mol^{-1}]	$\Delta H_2^{\neq}$ [kJ mol^{-1}]	$\Delta S_2^{\neq}$ [JK^{-1} mol^{-1}]
[Pt(DMEAIm$^{i\text{Pr}}$)Cl$_2$]	47 ± 1	-115 ± 4	47 ± 1	-131 ± 4
[Pt(DPENIm$^{i\text{Pr}}$)Cl$_2$]	38 ± 6	-149 ± 18	53 ± 1	-115 ± 5

Table S2. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first and second reaction step between complex $[Pt(DMEAIm^{iPr})Cl_2]$ and TU at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310, 298 and 288 K.

T(K)	C_{TU}/M	first step k_{obsd1}/s^{-1}	second step k_{obsd2}/s^{-1}
288.0	0.0025	0.00040(3)	0.000045(3)
	0.0020	0.00037(3)	0.000039(3)
	0.0015	0.00033(3)	0.000037(3)
	0.0010	0.00027(3)	0.000022(3)
	0.0005	0.00021(3)	0.000019(3)
	0.0002	/	/
298.0	0.0025	0.00075(2)	0.000068(2)
	0.0020	0.00063(3)	0.000062(3)
	0.0015	0.00059(3)	0.000057(3)
	0.0010	0.00047(3)	0.000042(3)
	0.0005	0.00038(3)	0.000031(3)
	0.0002	0.00029(4)	0.000022(3)
310.0	0.0025	0.0019(4)	0.00023(4)
	0.0020	0.0017(3)	0.00019(3)
	0.0015	0.0016(3)	0.00015(3)
	0.0010	0.0014(3)	0.00013(3)
	0.0005	0.0011(4)	0.00011(4)
	0.0002	0.0009(4)	0.00009(4)

Table S3. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex $[Pt(DMEAIm^{iPr})Cl_2]$ and L-Met at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C_{L-Met}/M	first step k_{obsd1}/s^{-1}	second step k_{obsd2}/s^{-1}
310.0	0.0025	0.00056(3)	0.000404(3)
	0.0020	0.00048(3)	0.000404(3)
	0.0015	0.00042(3)	0.000408(3)
	0.0010	0.00036(3)	0.000406(3)
	0.0005	0.00029(3)	/
	0.0002	0.00022(3)	0.000405(3)

Table S4. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex $[Pt(DMEAIm^{iPr})Cl_2]$ and L-His at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C_{L-His}/M	first step $10^5\ k_{obsd1}$/s^{-1}	second step $10^6\ k_{obsd2}$/s^{-1}
310.0	0.0025	1.96(2)	1.85(3)
	0.0020	1.81(3)	1.69(3)
	0.0015	1.68(3)	1.57(3)
	0.0010	1.55(3)	1.53(3)
	0.0005	1.24(4)	1.19(3)
	0.0002	1.18(3)	1.16(3)

Table S5. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DMEAIm^{iPr})Cl$_2$] and 5'-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C$_{5'-GMP}$/M	first step $10^5 \, k_{obsd1}/s^{-1}$	second step $10^6 \, k_{obsd2}/s^{-1}$
310.0	0.0025	4.49(4)	2.91(3)
	0.0020	4.30(3)	2.83(3)
	0.0015	4.18(3)	2.69(3)
	0.0010	4.10(3)	2.48(3)
	0.0005	3.86(3)	2.37(3)
	0.0002	3.71(3)	2.28(3)

Table S6. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first and second reaction step between complex [Pt(DPENIm$^{i\text{Pr}}$)Cl$_2$] and TU at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310, 298 and 288 K.

T(K)	C_{TU}/M	first step k_{obsd1}/s^{-1}	second step k_{obsd2}/s^{-1}
288.0	0.0025	0.00021(3)	0.000025(3)
	0.0020	0.00016(3)	0.000018(3)
	0.0015	0.00011(3)	0.000013(3)
	0.0010	0.00009(3)	0.000008(3)
	0.0005	0.00008(3)	0.000007(3)
	0.0002	/	/
298.0	0.0025	0.00051(3)	0.000045(3)
	0.0020	0.00045(3)	0.000039(3)
	0.0015	0.00039(3)	0.000031(3)
	0.0010	0.00032(3)	0.000026(3)
	0.0005	0.00028(3)	0.000019(3)
	0.0002	0.00020(4)	0.000011(4)
310.0	0.0025	0.00112(4)	0.00019(4)
	0.0020	0.00090(3)	0.00017(3)
	0.0015	0.00085(3)	0.00013(3)
	0.0010	0.00076(3)	0.00011(3)
	0.0005	0.00068(4)	0.00009(4)
	0.0002	0.00059(4)	0.00008(4)

Table S7. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex $[Pt(DPENIm^{iPr})Cl_2]$ and L-Met at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C_{L-Met}/M	first step k_{obsd1}/s^{-1}	second step k_{obsd2}/s^{-1}
310.0	0.0025	0.00038(3)	0.000102(3)
	0.0020	0.00030(3)	0.000101(3)
	0.0015	0.00023(3)	0.000102(3)
	0.0010	0.00018(4)	0.000104(3)
	0.0005	0.00014(3)	/
	0.0002	0.00010(3)	0.000100(3)

Table S8. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex $[Pt(DPENIm^{iPr})Cl_2]$ and L-His at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C_{L-His}/M	first step $10^5 k_{obsd}$/s^{-1}	second step $10^6 k_{obsd}$/s^{-1}
310.0	0.0025	1.25(4)	1.16(3)
	0.0020	1.12(3)	1.05(3)
	0.0015	1.08(3)	0.91(3)
	0.0010	0.89(3)	0.82(3)
	0.0005	0.73(3)	0.74(3)
	0.0002	0.60(3)	0.66(3)

Table S9. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pd(DPENIm^{iPr})Cl$_2$] and 5'-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

T(K)	C$_{Gly}$/M	first step $10^5 k_{obsd1}/s^{-1}$	second step $10^6 k_{obsd2}/s^{-1}$
310.0	0.0025	2.32(3)	2.62(6)
	0.0020	2.25(4)	2.57(6)
	0.0015	2.15(3)	2.55(6)
	0.0010	1.99(3)	2.42(6)
	0.0005	1.85(3)	2.31(6)
	0.0002	1.74(3)	2.28(6)

Table S10. The rate constants for the back reactions of the first and the second reaction step of the substitution reactions of the Pt(II) complexes with TU, L-Met, L-His and 5'-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

| | [Pt(DMEAIm$^{i\text{Pr}}$)Cl$_2$] | | [Pt(DPENIm$^{i\text{Pr}}$)Cl$_2$] | |
	first step $k_{-1}[\text{Cl}^-][\text{M}^{-1}\,\text{s}^{-1}]$	second step $k_{-2}[\text{Cl}^-][\text{M}^{-1}\,\text{s}^{-1}]$	first step $k_{-1}[\text{Cl}^-][\text{M}^{-1}\,\text{s}^{-1}]$	second step $k_{-2}[\text{Cl}^-][\text{M}^{-1}\,\text{s}^{-1}]$
TU	$(9.0 \pm 0.2)\ 10^{-4}$	$(7.0 \pm 0.2)\ 10^{-5}$	$(6.7 \pm 0.2)\ 10^{-4}$	$(6.7 \pm 0.2)\ 10^{-5}$
L-Met	$(2.0 \pm 0.1)\ 10^{-4}$	/	$(6.9 \pm 0.2)\ 10^{-5}$	/
L-His	$(1.0 \pm 0.1)\ 10^{-5}$	$(1.1 \pm 0.1)\ 10^{-6}$	$(5.8 \pm 0.1)\ 10^{-5}$	$(6.1 \pm 0.1)\ 10^{-6}$
5'-GMP	$(3.7 \pm 0.2)\ 10^{-5}$	$(2.2 \pm 0.1)\ 10^{-6}$	$(1.7 \pm 0.2)\ 10^{-5}$	$(2.3 \pm 0.1)\ 10^{-6}$