Supporting Information

Kinetics and mechanism of the substitution behaviour of Pd(II) piperazine complexes with different biologically relevant nucleophiles

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Table S1. Summary of the rate constans at various temperature and activation parameters for the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with 5'-GMP, L-Met and tu, $I = 0.1$ M.

| Nu	T/°C	k_1 x 10^{-3} / $M^{-1}s^{-1}$	k_{-1} / s^{-1}	k_2 / $M^{-1}s^{-1}$	k_{-2} / s^{-1}	k_3 / $M^{-1}s^{-1}$	k_{-3} / s^{-1}
5'-GMP	10	1.0 ± 0.1					
	15	1.6 ± 0.1					
	20	2.6 ± 0.1		0.19 ± 0.02			
	25	3.7 ± 0.1		0.28 ± 0.01			
	30	4.7 ± 0.6		0.40 ± 0.01			
	$\Delta H^{\neq}$ / kJ mol^{-1}	51 ± 3		52 ± 4			
	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}	−7 ± 9		−80 ± 14			
L-Met	5	35 ± 3	23 ± 11	81 ± 19	1.8 ± 0.1		
	10	40 ± 5	45 ± 30	112 ± 42	2.1 ± 0.4		
	15	50 ± 2	56 ± 17	132 ± 19	2.8 ± 0.1		
	20	62 ± 5	80 ± 31	168 ± 21	3.3 ± 0.1		
	$\Delta H^{\neq}$ / kJ mol^{-1}	21 ± 3	–	30 ± 3	33 ± 5		
	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}	−78 ± 11	–	−99 ± 11	−122 ± 18		
tu	5	73 ± 8					
	20			84 ± 5	0.12 ± 0.07	6.4 ± 0.9	0.034 ± 0.008
	25			106 ± 2	0.35 ± 0.03	7.8 ± 0.5	0.038 ± 0.005
	30			146 ± 5	0.43 ± 0.08	8.2 ± 0.9	0.041 ± 0.008
	35			193 ± 8	0.92 ± 0.12	8.8 ± 0.9	0.048 ± 0.007
	$\Delta H^{\neq}$ / kJ mol^{-1}	–		39 ± 3	–	13 ± 3	15 ± 3
	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}	–		−75 ± 9	–	−185 ± 9	−223 ± 9
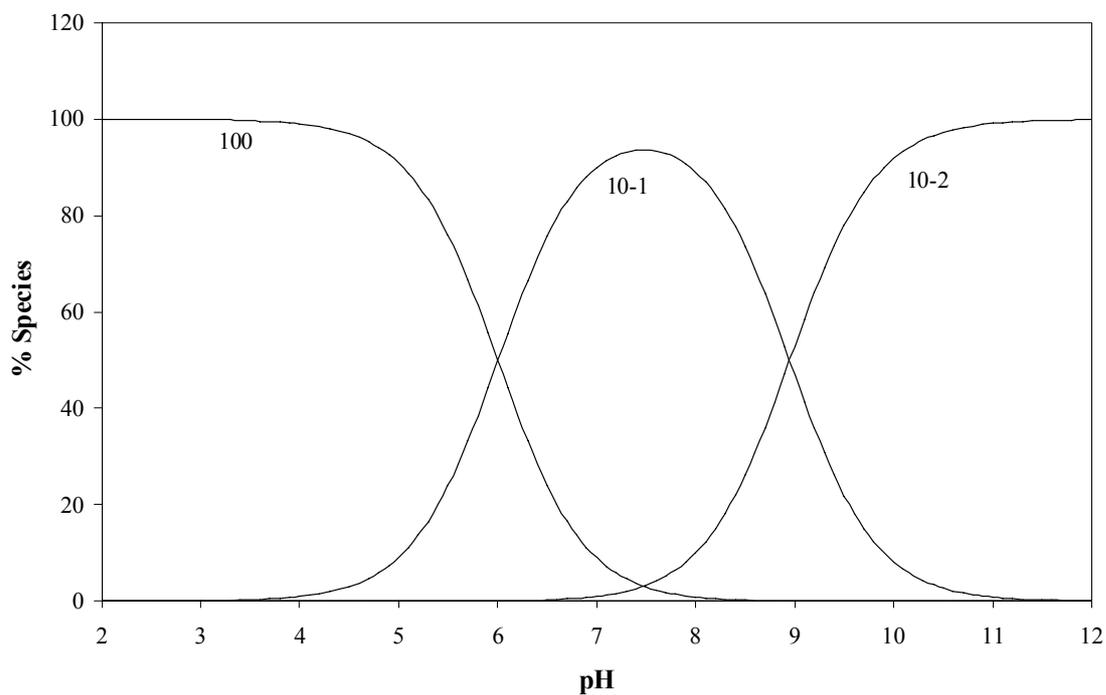
**Figure S1.** Concentration distribution of various species for $[Pd(Pip)(H_2O)_2]^{2+}$ as a function of pH.
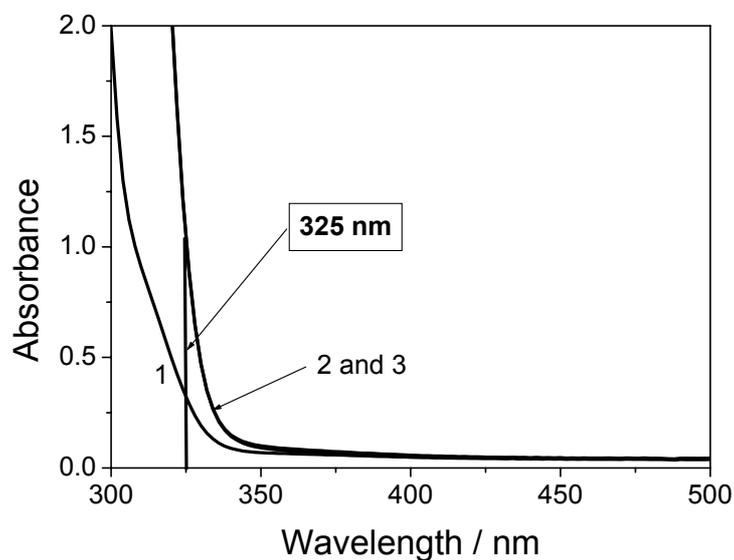
Figure S2 . UV-Vis spectra for the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with 5′-GMP⁻ recorded before (1) and after 0.25 (2) and 30 min (3) following mixing of the reactants. Experimental conditions: $[Pd(II)] = 0.5$ mM, $[5′\text{-GMP}]_{Tot} = 0.01$ M, I = 0.1 M, T = 25 °C.
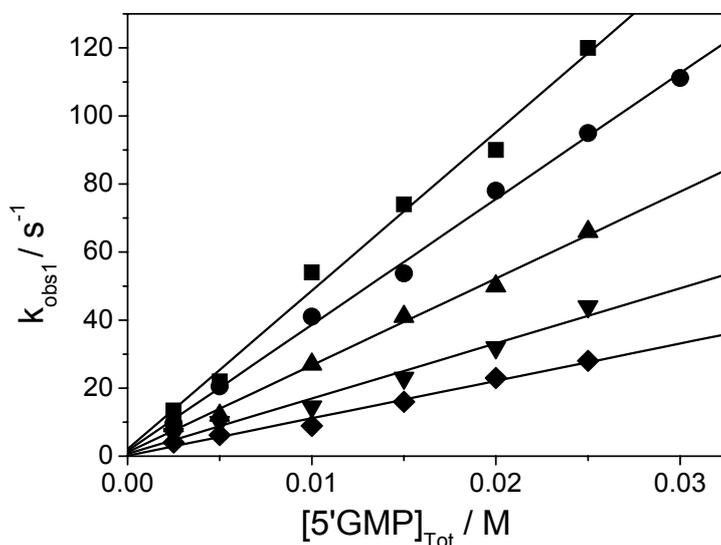
Figure S3. Concentration and temperature dependence for the first step of the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with 5′-GMP⁻. Experimental conditions: $[Pd(II)]$ = 0.25 mM, $[5′\text{-}GMP]_{Tot}$ = 2.5 – 25 mM, I = 0.1 M, pH = 5.3-5.6, T = 10 – 30 °C (every 5°C).
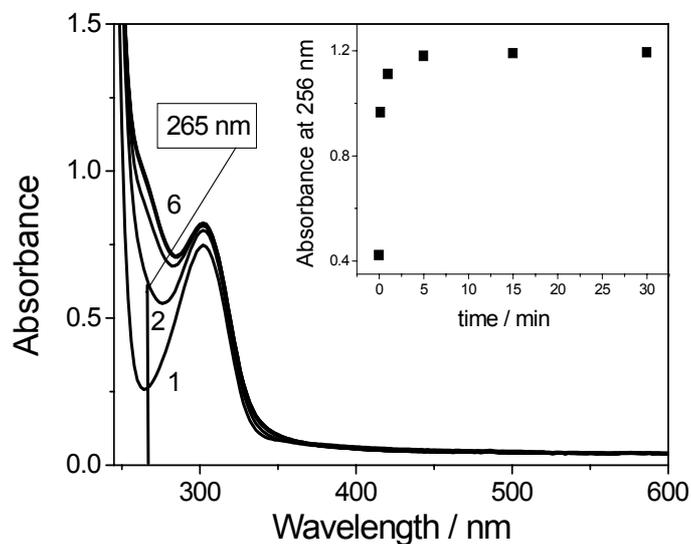
Figure S4. UV-Vis spectra for the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with L-Met recorded before (1) and after 0.25 (2), 1 (3), 5 (4) 15 (5) and 30 min (6) following mixing of the reactants. Experimental conditions: $[Pd(II)]$ = 0.5 mM, [L-Met] = 0.01 M, I = 0.1 M, T = 25 °C.
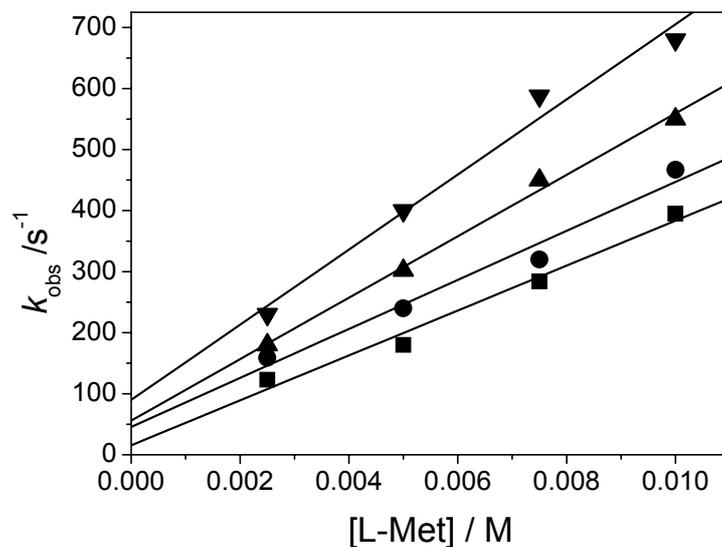
**Figure S5**. Concentration and temperature dependence for the first step of the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with L-Met. Experimental conditions: $[Pd(II)] = 0.25$ mM, $[L-Met] = 2.5 – 10$ mM, $I = 0.1$ M, pH = 3.5, T = 5 – 20 °C (every 5°C).
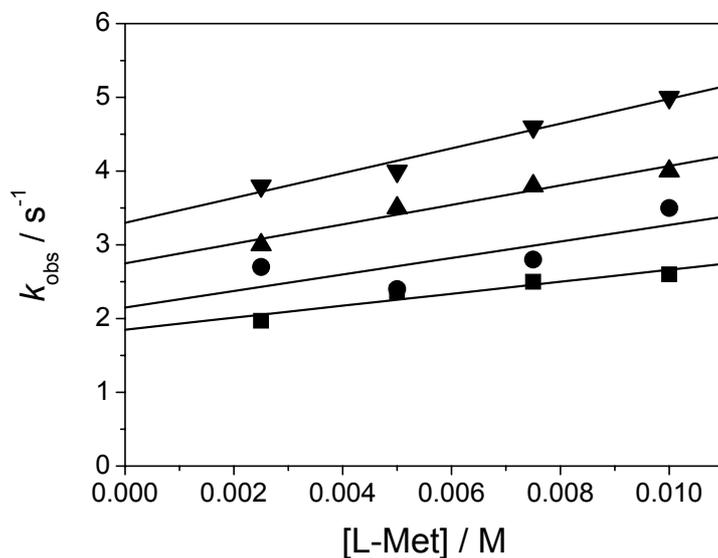

Figure S6. Concentration and temperature dependence for the second step of the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with L-Met. Experimental conditions: $[Pd(II)] = 0.25$ mM, $[L-Met] = 2.5 – 10$ mM, $I = 0.1$ M, pH = 3.5, T = 5 – 20 °C (every 5°C).
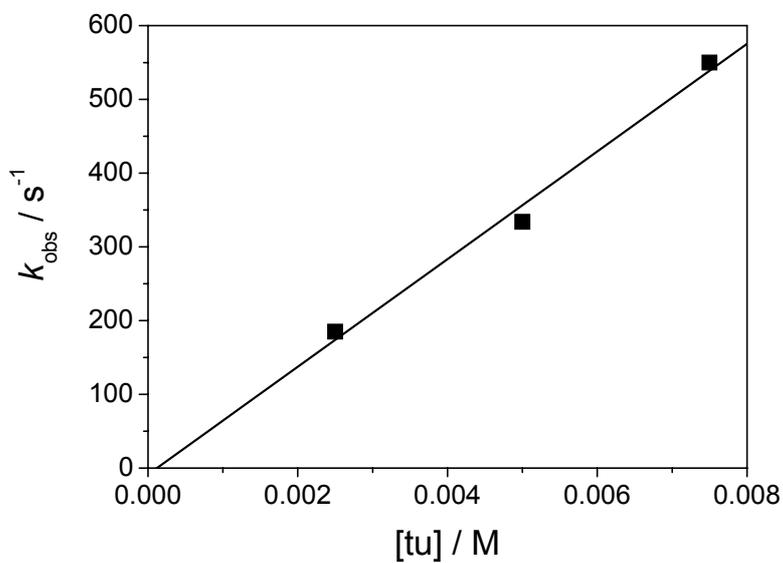
**Figure S7**. Concentration dependence for the first step of the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with tu. Experimental conditions: $[Pd(II)] = 0.25$ mM, $[L\text{-Met}] = 5 - 30$ mM, $I = 0.1$ M, pH $= 3.7$, T $= 5\ °C$.
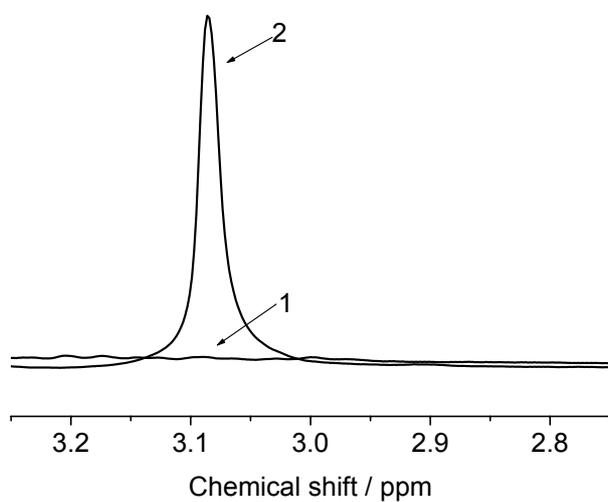
**Figure S8.** Selected region of the ^1H NMR spectrum of $[Pd(Pip)(D_2O)_2]^{2+}$ (D_2O solution) before (1) and after (2) addition of tu. The new resonance at 3.08 ppm is attributed to CH_2 groups of free piperazine. Experimental conditions: $[Pd(II)] = 0.017$ M, $[tu] = 0.07$ M, T $= 25\ °C$.
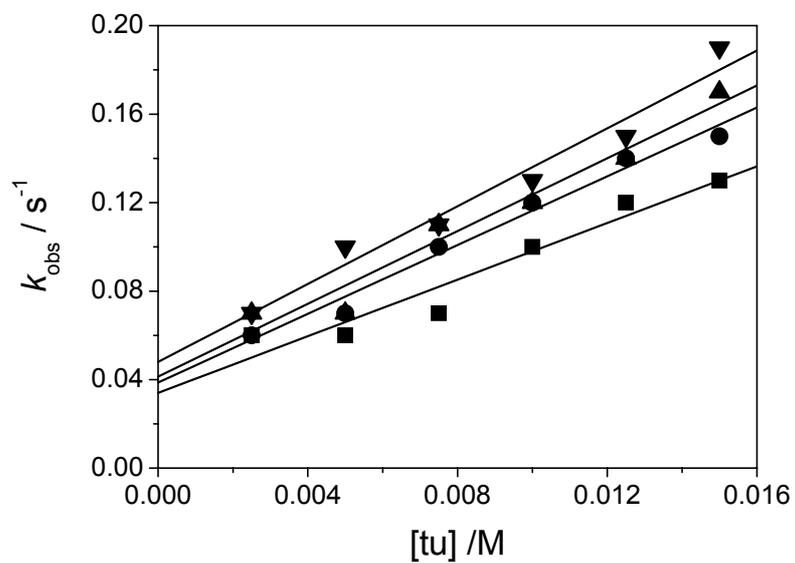
**Figure S9**. Concentration and temperature dependence for the third step of the reaction of $[Pd(Pip)(H_2O)_2]^{2+}$ with tu. $[Pd(II)] = 0.25$ mM, $[tu] = 2.5 – 30$ mM, $I = 0.1$ M, pH = 3.7, T = 20 – 35 °C (every 5°C).