

Electronic Supplementary Information for Dalton Transactions
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Supplementary Information

Influence of the chloride concentration on ligand substitution reactions of [Pt(SMC)Cl₂] with biologically relevant nucleophiles

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Table S1. Summary of the selected wavelengths (nm) used in the kinetic measurements.

Nucleophile	pH	reaction step	Wavelength, nm
L-met	2.5	1	260
	7.2		
GSH	2.5	1	252
INO	2.5	1	312
5'-GMP	2.5	1	300
	7.2		

Table S2. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with L-methionine in the presence of various chloride concentrations. I = 0.10 M NaClO₄ at pH = 2.5 and 37 °C.

C/M	k _{obsd} /s ⁻¹	k _{obsd} /s ⁻¹ 1.25 mM NaCl	k _{obsd} /s ⁻¹ 2.50 mM NaCl	k _{obsd} /s ⁻¹ 5 mM NaCl	k _{obsd} /s ⁻¹ 10 mM NaCl	k _{obsd} /s ⁻¹ 30 mM NaCl	k _{obsd} /s ⁻¹ 50 mM NaCl
0.003	0.0879	0.1591	0.1316	0.1230	0.1125	0.1499	0.1359
0.006	0.1886	0.1974	0.1720	0.1402	0.1267	0.1695	0.1403
0.009	0.2998	0.2739	0.1946	0.1598	0.1499	0.1803	0.1546
0.012	0.3717	0.3537	0.2421	0.1984	0.1669	0.1988	0.1606
0.015	0.4484	0.4028	0.2822	0.2184	0.1783	0.2181	0.1754

Table S3. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with L-methionine in the presence of various chloride concentrations. I = 0.25 M Hepes buffer at pH = 7.2 and 37 °C.

C/M	$k_{\text{obsd}}/\text{s}^{-1}$	$k_{\text{obsd}}/\text{s}^{-1}$ 1.25 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 2.50 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 5 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 10 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 30 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 50 mM NaCl
0.003	0.1186	0.1355	0.1439	0.1438	0.1411	0.1434	0.1442
0.006	0.2400	0.2177	0.1836	0.1789	0.1551	0.1530	0.1517
0.009	0.3690	0.2992	0.2452	0.1972	0.1865	0.1789	0.1643
0.012	0.4592	0.4369	0.3003	0.2495	0.2222	0.1960	0.1808
0.015	0.6012	0.5294	0.3779	0.2844	0.2439	0.2063	0.1987

Table S4. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with glutathione in the presence of various chloride concentrations. I = 0.10 M NaClO₄ at pH = 2.5 and 37 °C.

C/M	$k_{\text{obsd}}/\text{s}^{-1}$	$k_{\text{obsd}}/\text{s}^{-1}$ 1.25 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 2.50 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 5 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 10 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 30 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 50 mM NaCl
0.003	0.0258	0.0435	0.0399	0.0359	0.0362	0.0352	0.0380
0.006	0.0418	0.0514	0.0455	0.0381	0.0373	0.0387	0.0385
0.009	0.0767	0.0654	0.0527	0.0421	0.0414	0.0407	0.0407
0.012	0.0901	0.0780	0.0589	0.0455	0.0420	0.0429	0.0420
0.015	0.1204	0.0899	0.0694	0.0491	0.0481	0.0430	0.0464

Table S5. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with inosine in the presence of various chloride concentrations. I = 0.10 M NaClO₄ at pH = 2.5 and 37 °C.

C/M	k _{obsd} /s ⁻¹	k _{obsd} /s ⁻¹ 1.25 mM NaCl	k _{obsd} /s ⁻¹ 2.50 mM NaCl	k _{obsd} /s ⁻¹ 5 mM NaCl	k _{obsd} /s ⁻¹ 10 mM NaCl	k _{obsd} /s ⁻¹ 30 mM NaCl	k _{obsd} /s ⁻¹ 50 mM NaCl
0.003	0.0313	0.0347	0.0265	0.0320	0.0274	0.0302	0.0300
0.006	0.0453	0.0429	0.0371	0.0370	0.0297	0.0306	0.0301
0.009	0.0584	0.0562	0.0447	0.0403	0.0335	0.0308	0.0304
0.012	0.0823	0.0738	0.0597	0.0460	0.0350	0.0310	0.0305
0.015	0.0993	0.0896	0.0633	0.0524	0.0390	0.0312	0.0307

C/M	k _{obsd} /s ⁻¹ 70 mM NaCl	k _{obsd} /s ⁻¹ 100 mM NaCl
0.003	0.0248	0.0247
0.006	0.0250	0.0248
0.009	0.0251	0.0249
0.012	0.0253	0.0250
0.015	0.0254	0.02502

Table S6. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with guanosine-5'-monophosphate in the presence of various chloride concentrations. I = 0.10 M NaClO₄ at pH = 2.5 and 37 °C.

C/M	k _{obsd} /s ⁻¹	k _{obsd} /s ⁻¹ 1.25 mM NaCl	k _{obsd} /s ⁻¹ 2.50 mM NaCl	k _{obsd} /s ⁻¹ 5 mM NaCl	k _{obsd} /s ⁻¹ 10 mM NaCl	k _{obsd} /s ⁻¹ 30 mM NaCl	k _{obsd} /s ⁻¹ 50 mM NaCl
0.003	0.0082	0.0118	0.0111	0.0107	0.0099	0.0092	0.0110
0.006	0.0127	0.0135	0.0124	0.0113	0.0101	0.00996	0.0113
0.009	0.0192	0.0170	0.0144	0.0121	0.0109	0.0101	0.0117
0.012	0.0246	0.0196	0.0168	0.0124	0.0112	0.0105	0.0121
0.015	0.0321	0.0229	0.0182	0.0132	0.0119	0.0109	0.0124

Table S7. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pt(SMC)Cl₂] with guanosine-5'-monophosphate in the presence of various chloride concentrations. I = 0.25 M Hepes buffer at pH = 7.2 and 37 °C.

C/M	$k_{\text{obsd}}/\text{s}^{-1}$	$k_{\text{obsd}}/\text{s}^{-1}$ 1.25 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 2.50 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 5 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 10 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 30 mM NaCl	$k_{\text{obsd}}/\text{s}^{-1}$ 50 mM NaCl
0.003	0.0032	0.0034	0.0032	0.0025	0.0026	0.0024	0.0025
0.006	0.0057	0.0053	0.0047	0.0033	0.0033	0.0028	0.00268
0.009	0.0097	0.0078	0.0060	0.0037	0.0035	0.0029	0.00272
0.012	0.0118	0.0096	0.0073	0.0043	0.0038	0.0032	0.0029
0.015	0.0150	0.0111	0.0095	0.0051	0.00398	0.0033	0.0029

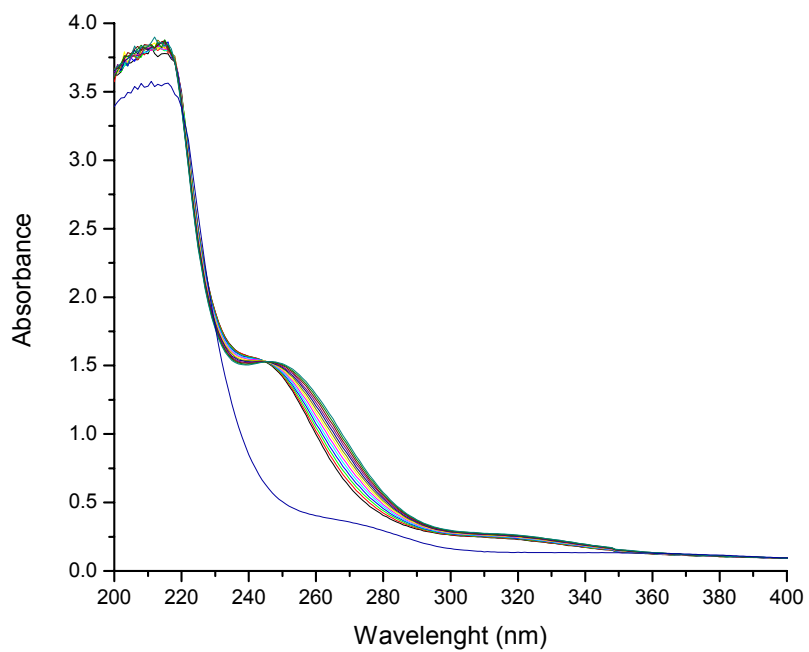


Figure S1. Rapid-scan spectra recorded for the reaction of $[\text{Pt}(\text{SMC})\text{Cl}_2]$ with L-methionine at time intervals of 1 s after mixing at $\text{pH} = 2.5$. $I = 0.10 \text{ M NaClO}_4$.

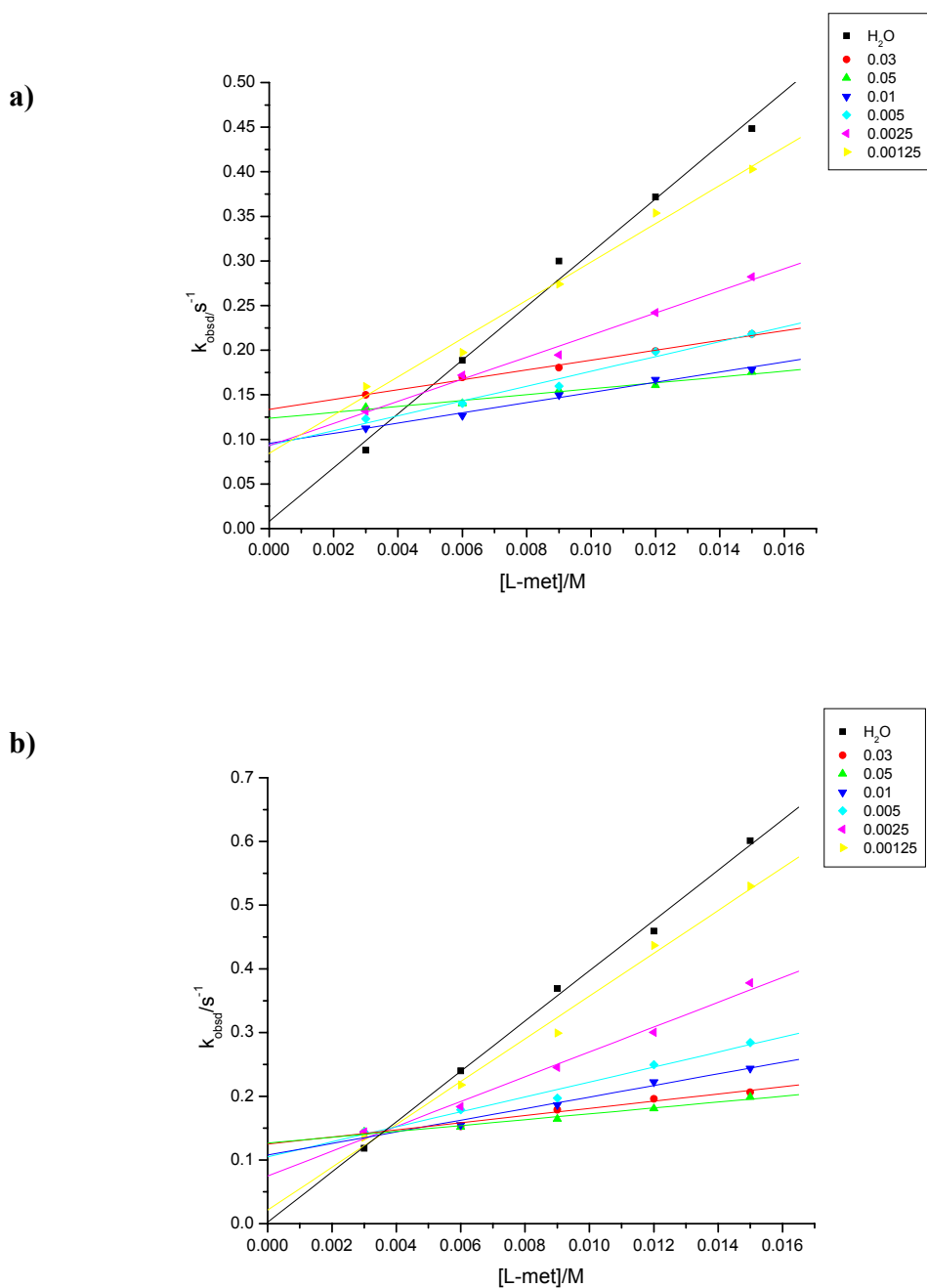
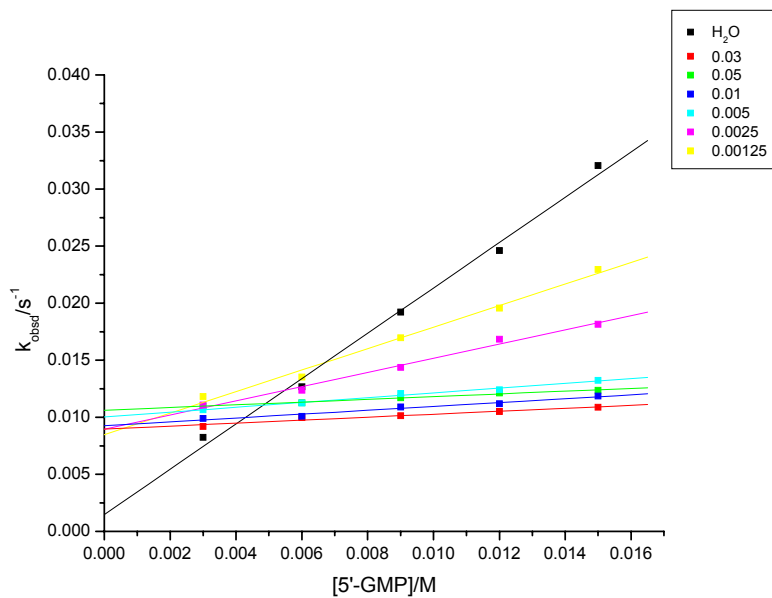


Figure S2. Pseudo-first order rate constants as a function of nucleophile concentration for the substitution reaction of $[\text{Pt}(\text{SMC})\text{Cl}_2]$ by L-methionine in the presence of various chloride concentrations at pH = 2.5, 0.1 M NaClO_4 (a) and pH = 7.2, 0.25 M Hepes buffer (b) and 37 °C.

a)



b)

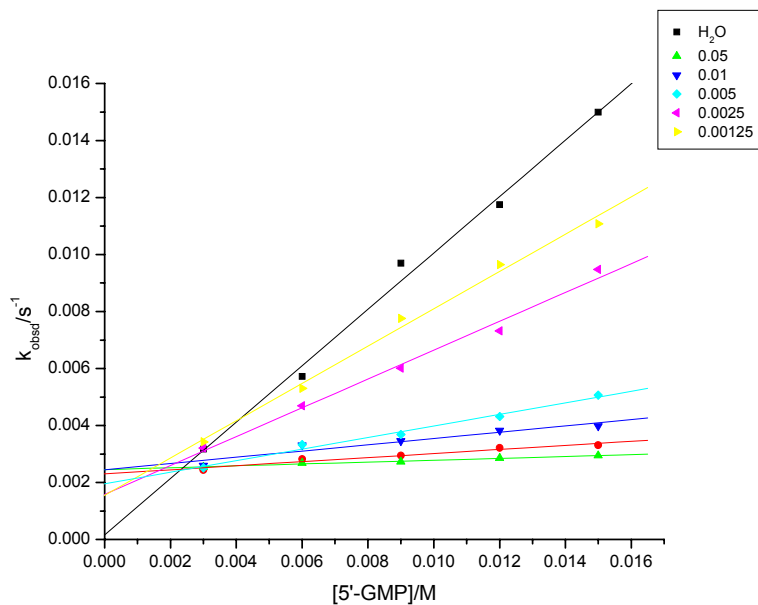


Figure S3. Pseudo-first order rate constants as a function of nucleophile concentration for the substitution reaction of $[\text{Pt}(\text{SMC})\text{Cl}_2]$ by guanosine-5'-monophosphate in the

presence of various chloride concentrations at pH = 2.5, 0.1 M NaClO₄ (a) and pH = 7.2, 0.25 M Hepes buffer (b) and 37 °C.

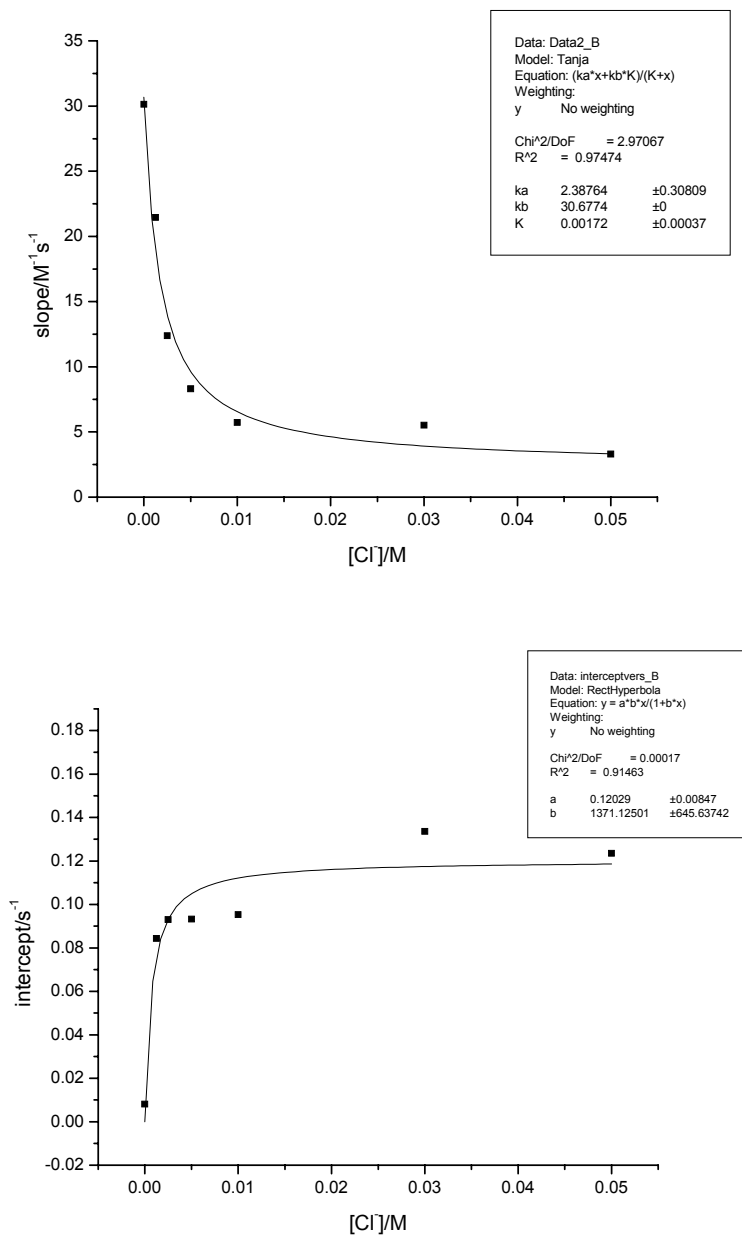


Figure S4. Dependence of slope and intercept on the chloride concentration for substitution of [Pt(SMC)Cl₂] by L-methionine at pH = 2.5, I = 0.1 M NaClO₄ and 37 °C.

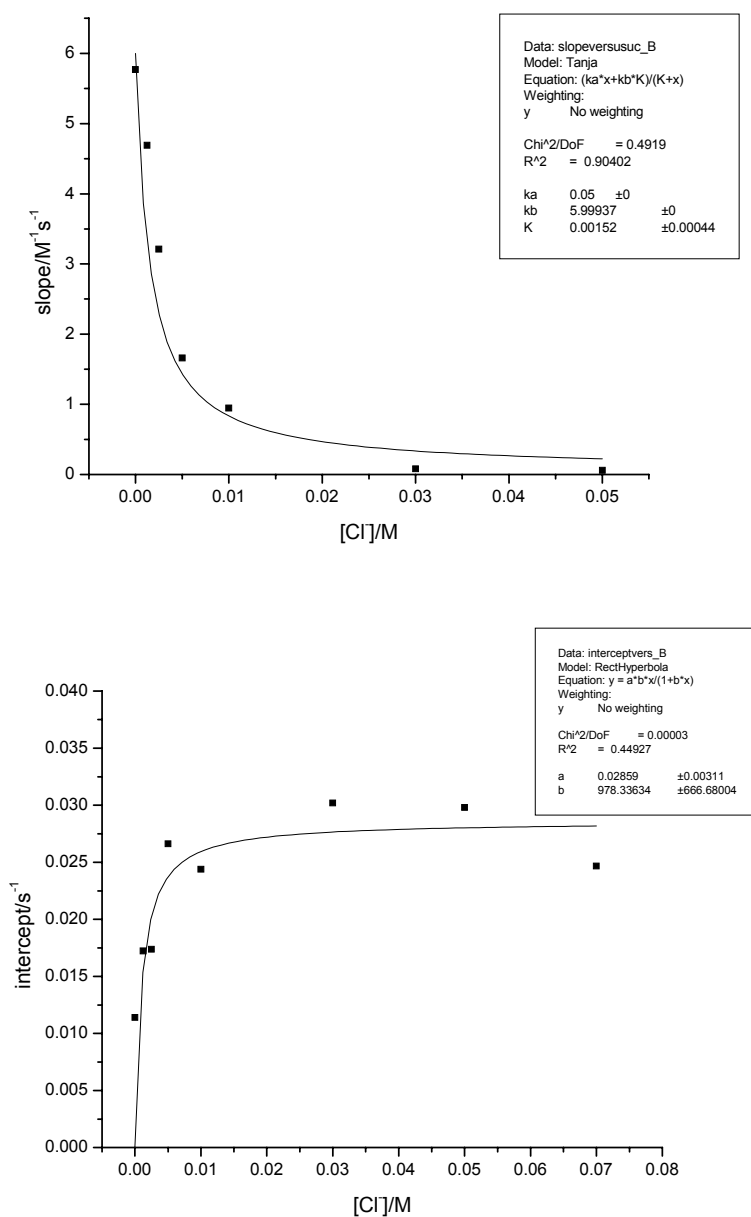


Figure S5. Dependence of slope and intercept on the chloride concentration for substitution of [Pt(SMC)Cl₂] by inosine at pH = 2.5, I = 0.1 M NaClO₄ and 37 °C.

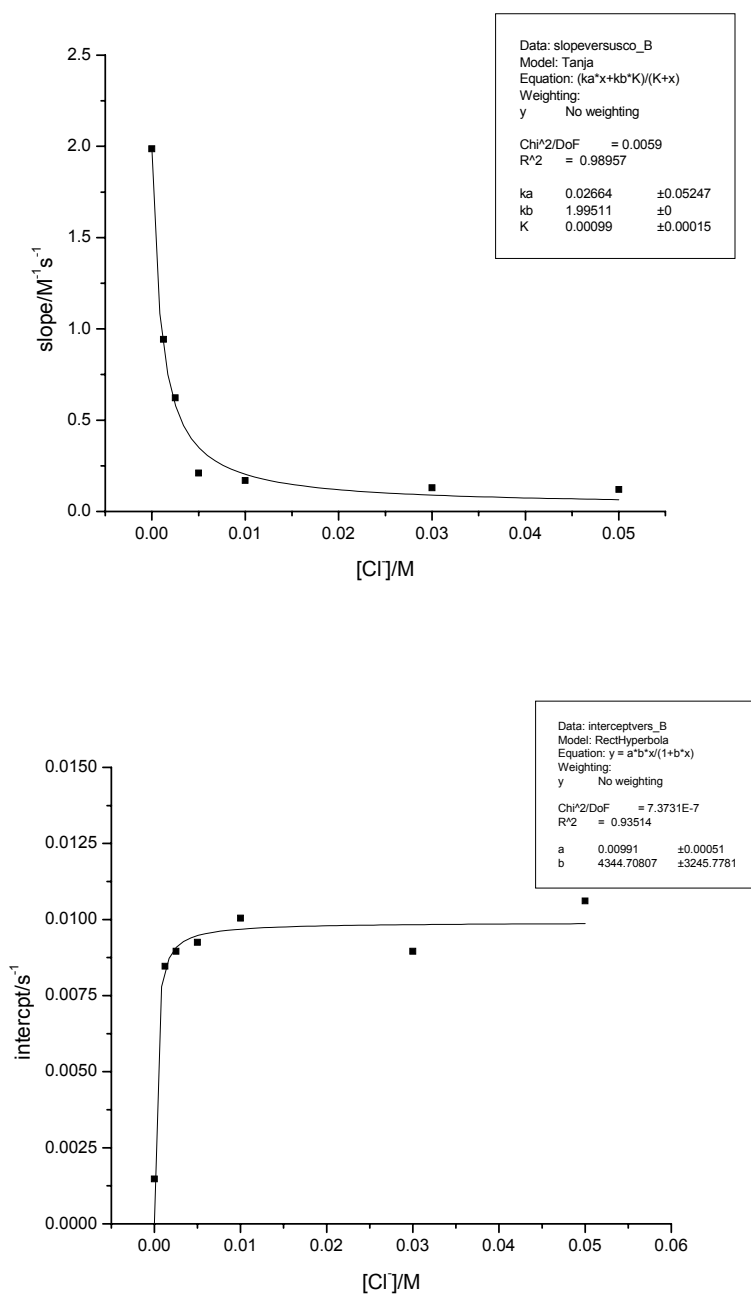


Figure S6. Dependence of slope and intercept on the chloride concentration for substitution of [Pt(SMC)Cl₂] by guanosine-5'-monophosphate at pH = 2.5, I = 0.1 M NaClO₄ and 37 °C.

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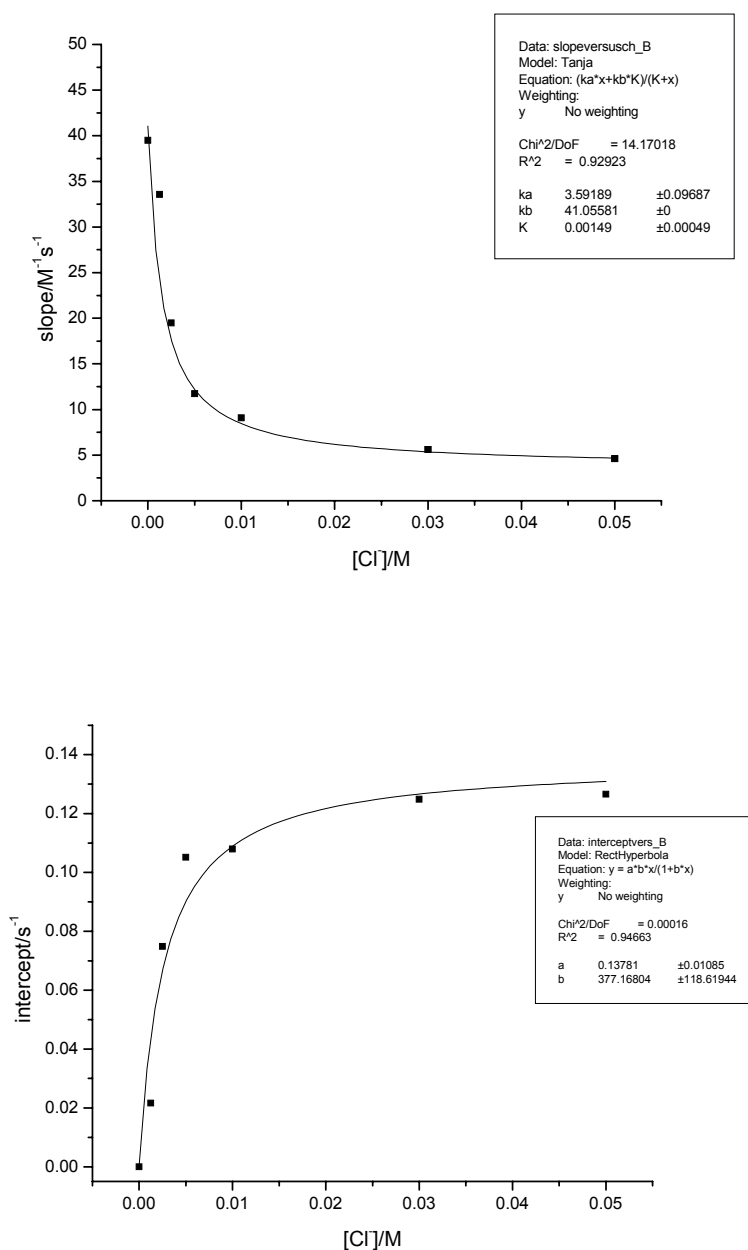


Figure S7. Dependence of slope and intercept on the chloride concentration for substitution of $[\text{Pt}(\text{SMC})\text{Cl}_2]$ by L-methionine at $\text{pH} = 7.2$, 0.25 M HEPES buffer and 37°C .

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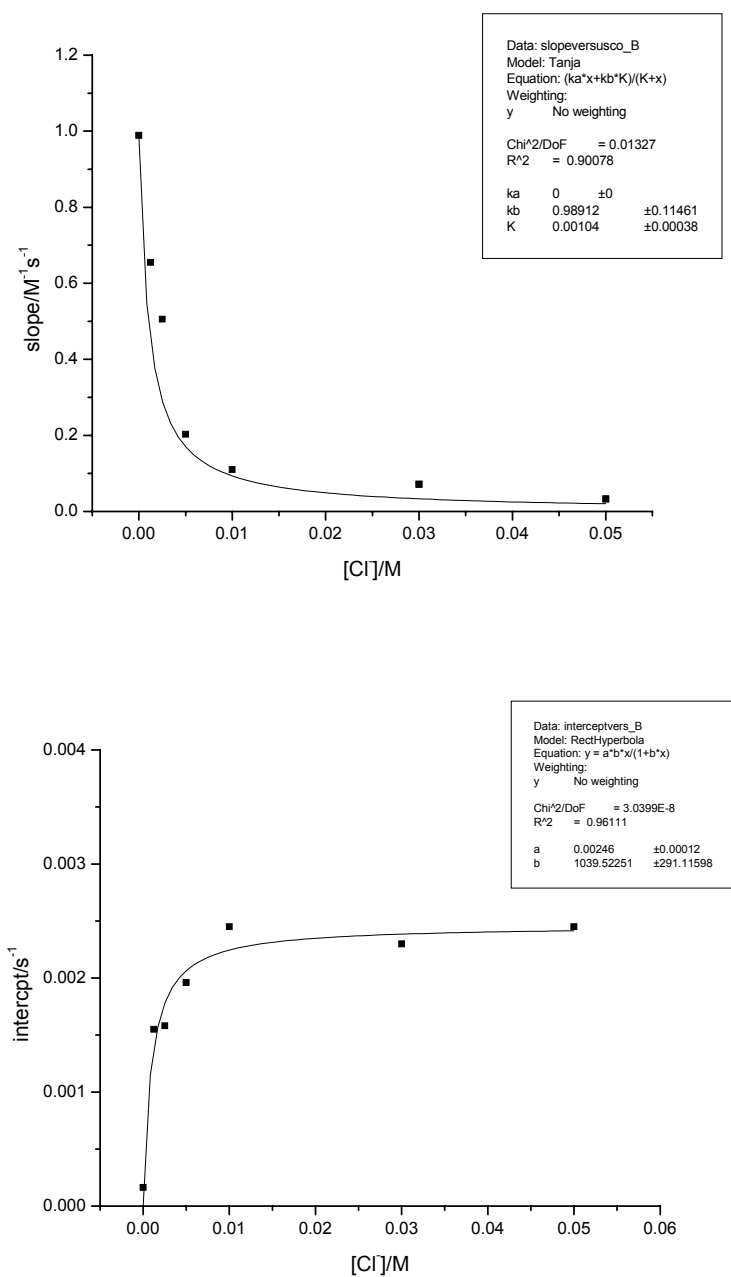


Figure S8. Dependence of slope and intercept on the chloride concentration for substitution of $[\text{Pt}(\text{SMC})\text{Cl}_2]$ by guanosine-5'-monophosphate at $\text{pH} = 7.2$, 0.25 M HEPES buffer and 37 °C.