

Supporting Information

Kinetic studies on the reactions of [Pd(dach)(X-Y)] complexes with some DNA constituents

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Table S1 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(H₂O)₂]²⁺ and inosine in 0.10 M NaClO₄, pH = 2.5, λ = 325 nm.

	T/K	10 ⁻³ C _{Ino} /M	k _{obsd} /s ⁻¹
First step	298.1	1.5	2.96(9)
		2.0	4.47(8)
		3.0	11.5(9)
		4.0	8.22(7)
		5.0	10.1(8)
Second step	298.1	1.5	0.119(9)
		2.0	0.129(8)
		3.0	0.149(8)
		4.0	0.162(7)
		5.0	0.188(7)

Table S2 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(\text{H}_2\text{O})_2]^{2+}$ and 5'-IMP in 0.10 M NaClO_4 , $\text{pH} = 2.5$, $\lambda = 330$ nm.

	T/K	$10^{-3} C_{5'\text{-IMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.3	1.0	1.10(9)
		1.5	1.52(7)
		2.0	2.00(8)
		3.0	2.77(8)
		4.0	3.49(7)
		5.0	4.52(8)
Second step	298.3	1.5	0.073(7)
		2.0	0.085(7)
		3.0	0.095(7)
		4.0	0.109(6)
		5.0	0.127(7)

Table S3 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(\text{H}_2\text{O})_2]^{2+}$ and 5'-GMP in 0.10 M NaClO_4 , $\text{pH} = 2.5$, $\lambda = 320$ nm.

	T/K	$10^{-3} C_{5'\text{-GMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.2	1.0	1.13(9)
		1.5	1.55(8)
		2.0	2.04(7)
		3.0	2.81(7)
		4.0	3.77(8)
		5.0	4.67(8)
Second step	298.2	1.5	0.124(8)
		2.0	0.138(7)
		3.0	0.156(7)
		4.0	0.170(8)
		5.0	0.178(7)

Table S4 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-cbdca)] and inosine in 25 mM Hepes, pH = 7.2, $\lambda = 305$ nm.

	T/K	$10^{-3} C_{\text{Ino}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	297.9	1.0	0.72(8)
		1.5	0.98(7)
		2.0	1.33(7)
		3.0	2.01(8)
		4.0	2.64(6)
		5.0	3.26(8)
Second step	297.9	1.5	0.064(7)
		2.0	0.068(7)
		3.0	0.074(7)
		4.0	0.085(6)
		5.0	0.093(8)

Table S5 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-cbdca)] and 5'-IMP in 25 mM Hepes, pH = 7.2, $\lambda = 335$ nm.

	T/K	$10^{-3} C_{5'-IMP}/M$	k_{obsd}/s^{-1}
First step	298.0	1.0	0.196(7)
		1.5	0.245(7)
		2.0	0.322(8)
		3.0	0.389(7)
		4.0	0.488(8)
		5.0	0.619(9)
Second step	298.0	1.5	0.027(7)
		2.0	0.031(7)
		3.0	0.036(7)
		4.0	0.039(8)
		5.0	0.044(8)

Table S6 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-cbdca)] and 5'-GMP in 25 mM HEPES, pH = 7.2, $\lambda = 325$ nm.

	T/K	$10^{-3} C_{5'-GMP}/M$	k_{obsd}/s^{-1}
First step	298.0	1.0	0.211(8)
		1.5	0.313(7)
		2.0	0.392(7)
		3.0	0.580(6)
		4.0	0.727(7)
		5.0	0.892(7)
Second step	298.0	1.5	0.046(7)
		2.0	0.051(6)
		3.0	0.057(6)
		4.0	0.061(7)
		5.0	0.066(6)

Table S7 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-ox)] and inosine in 25 mM Hepes, pH = 7.2, $\lambda = 320$ nm.

	T/K	$10^{-3} C_{\text{Ino}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.1	1.0	1.57(7)
		1.5	2.45(6)
		2.0	3.38(6)
		3.0	4.95(7)
		4.0	6.45(8)
		5.0	8.13(7)
Second step	298.1	1.5	0.049(6)
		2.0	0.062(6)
		3.0	0.082(6)
		4.0	0.098(7)
		5.0	0.110(7)

Table S8 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-ox)] and 5'-IMP in 25 mM Hepes, pH = 7.2, $\lambda = 320$ nm.

	T/K	$10^{-3} C_{5'-IMP}/M$	k_{obsd}/s^{-1}
First step	298.0	1.0	0.98(8)
		1.5	1.55(7)
		2.0	1.88(7)
		3.0	2.64(6)
		4.0	3.34(7)
		5.0	4.25(6)
Second step	298.0	1.5	0.056(6)
		2.0	0.062(7)
		3.0	0.069(6)
		4.0	0.081(6)
		5.0	0.092(6)

Table S9 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)(*O,O*-ox)] and 5'-GMP in 25 mM Hepes, pH = 7.2, $\lambda = 325$ nm.

	T/K	$10^{-3} C_{5'-\text{GMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.0	1.0	1.04(7)
		1.5	1.43(7)
		2.0	2.02(6)
		3.0	2.88(8)
		4.0	3.68(6)
		5.0	4.42(9)
Second step	298.0	1.5	0.01(7)
		2.0	0.065(6)
		3.0	0.077(7)
		4.0	0.091(6)
		5.0	0.101(8)

Table S10 Observed *pseudo*-first order rate constants as a function of ligand concentration and temperature for the reaction between $[\text{Pd}(\text{dach})(N,O\text{-gly})]^+$ and inosine in 25 mM Hepes, pH = 7.2, $\lambda = 305$ nm.

	T/K	$10^{-3} C_{\text{Ino}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	288.3	1.0	1.13(8)
		1.5	1.78(8)
		2.0	2.32(8)
		3.0	3.42(7)
		4.0	4.45(8)
		5.0	5.81(7)
	298.0	1.0	1.51(7)
		1.5	2.23(8)
		2.0	2.89(8)
		3.0	4.34(7)
		4.0	5.99(8)
		5.0	7.24(9)
	308.0	1.0	1.95(7)
		1.5	2.75(6)
		2.0	3.37(7)
3.0		5.17(6)	
4.0		6.85(7)	
5.0		8.83(8)	
Second step	288.3	1.5	0.020(8)
		2.0	0.027(7)
		3.0	0.034(7)
		4.0	0.046(8)
		5.0	0.056(7)
	298.0	1.5	0.027(8)
		2.0	0.039(7)
		3.0	0.049(7)
		4.0	0.063(8)
		5.0	0.078(8)
	308.0	1.5	0.038(7)
		2.0	0.046(6)
		3.0	0.065(6)
		4.0	0.082(6)
		5.0	0.101(8)

Table S11 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(N,O\text{-gly})]^+$ and 5'-IMP in 25 mM Hepes, pH = 7.2, $\lambda = 320$ nm.

	T/K	$10^{-3} C_{5'\text{-IMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.3	1.0	0.98(7)
		1.5	1.43(7)
		2.0	1.88(7)
		3.0	2.76(6)
		4.0	3.36(7)
		5.0	4.00(8)
Second step	298.3	1.5	0.041(7)
		2.0	0.047(6)
		3.0	0.057(6)
		4.0	0.065(7)
		5.0	0.070(7)

Table S12 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(N,O\text{-gly})]^+$ and 5'-GMP in 25 mM Hepes, pH = 7.2, $\lambda = 318$ nm.

	T/K	$10^{-3} C_{5'\text{-GMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.3	1.0	0.99(8)
		1.5	1.58(7)
		2.0	2.04(6)
		3.0	2.83(6)
		4.0	3.62(7)
		5.0	4.22(7)
Second step	298.3	1.5	0.042(7)
		2.0	0.046(6)
		3.0	0.060(6)
		4.0	0.068(6)
		5.0	0.078(7)

Table S13 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(N,S\text{-met})]^+$ and inosine in 25 mM Hepes, pH = 7.2, $\lambda = 315$ nm.

	T/K	$10^{-3} C_{\text{Ino}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.0	1.0	0.018(7)
		1.5	0.028(7)
		2.0	0.038(6)
		3.0	0.052(7)
		4.0	0.072(6)
		5.0	0.090(8)
Second step	298.0	1.5	0.00019(7)
		2.0	0.00025(6)
		3.0	0.00038(6)
		4.0	0.00052(6)
		5.0	0.00063(8)

Table S14 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(N,S\text{-met})]^+$ and 5'-IMP in 25 mM Hepes, pH = 7.2, $\lambda = 328$ nm.

	T/K	$10^{-3} C_{5'\text{-IMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.0	1.0	0.016(7)
		1.5	0.020(7)
		2.0	0.022(6)
		3.0	0.032(7)
		4.0	0.043(8)
		5.0	0.050(7)
Second step	298.0	1.5	0.00023(7)
		2.0	0.00027(5)
		3.0	0.00034(6)
		4.0	0.00039(7)
		5.0	0.00044(7)

Table S15 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between $[\text{Pd}(\text{dach})(N,S\text{-met})]^+$ and 5'-GMP in 25 mM Hepes, pH = 7.2, $\lambda = 330$ nm.

	T/K	$10^{-3} C_{5'\text{-GMP}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
First step	298.0	1.0	0.016(7)
		1.5	0.020(7)
		2.0	0.027(7)
		3.0	0.034(6)
		4.0	0.044(6)
		5.0	0.056(7)
Second step	298.0	1.5	0.00023(7)
		2.0	0.00028(6)
		3.0	0.00034(6)
		4.0	0.00041(6)
		5.0	0.00049(7)

Table S16 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)Cl₂] and inosine in 25 mM Hepes, pH = 7.2, λ = 310 nm.

	T/K	10 ⁻³ C _{Ino} /M	k _{obsd} /s ⁻¹
First step	298.0	1.0	1.42(8)
		1.5	1.91(7)
		2.0	2.64(7)
		3.0	4.15(7)
		4.0	5.64(6)
		5.0	6.58(7)
Second step	298.0	1.5	0.023(7)
		2.0	0.031(6)
		3.0	0.041(7)
		4.0	0.058(6)
		5.0	0.076(7)

Table S17 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)Cl₂] and 5'-IMP in 25 mM Hepes, pH = 7.2, λ = 335 nm.

	T/K	10 ⁻³ C _{5'-IMP} /M	k _{obsd} /s ⁻¹
First step	298.0	1.0	1.22(7)
		1.5	1.69(7)
		2.0	2.14(6)
		3.0	2.75(6)
		4.0	3.26(6)
		5.0	3.96(7)
Second step	298.0	1.5	0.015(7)
		2.0	0.020(6)
		3.0	0.027(6)
		4.0	0.040(6)
		5.0	0.048(6)

Table S18 Observed *pseudo*-first order rate constants as a function of ligand concentration for the reaction between [Pd(dach)Cl₂] and 5'-GMP in 25 mM Hepes, pH = 7.2, λ = 330 nm.

	T/K	10 ⁻³ C _{5'-GMP} /M	k _{obsd} /s ⁻¹
First step	298.0	1.0	1.41(8)
		1.5	1.72(7)
		2.0	2.11(6)
		3.0	2.87(7)
		4.0	3.43(7)
		5.0	4.31(7)
Second step	298.0	1.5	0.017(7)
		2.0	0.022(6)
		3.0	0.030(6)
		4.0	0.043(6)
		5.0	0.052(7)

Table S19 Observed *pseudo*-first order rate constants as a function of pressure for the reaction between $[\text{Pd}(\text{dach})(\text{H}_2\text{O})_2]^{2+}$ and inosine (2 mM) in 0.10 M NaClO_4 , pH = 2.5. The first reaction step.

T/K	P/MPa	$k_{\text{obsd}}/\text{s}^{-1}$
283.1	10	1.984(5)
	50	2.060(4)
	90	2.290(5)
	130	2.410(4)

First Step

Second step

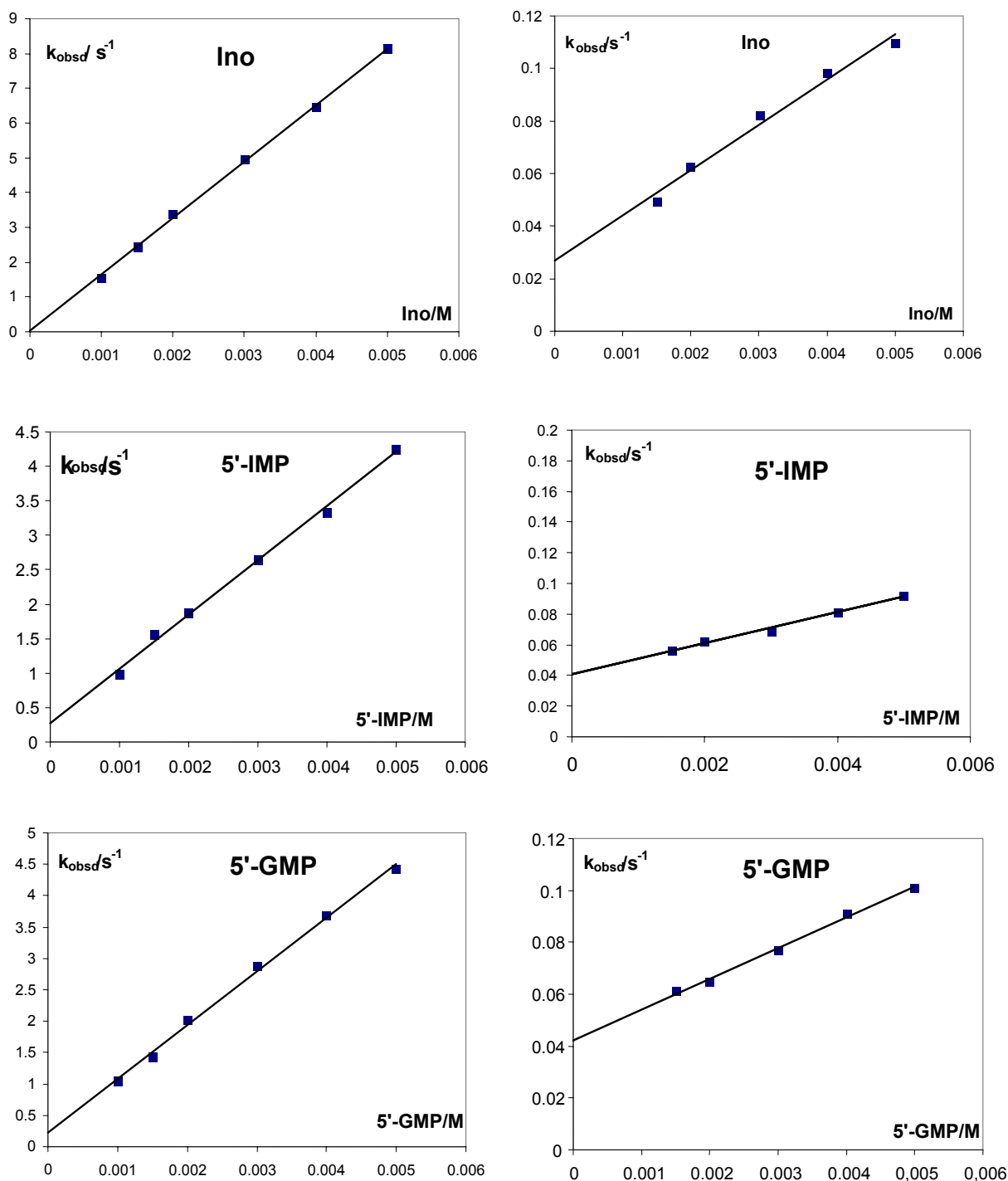


Fig. S1 Pseudo-first order rate constants as a function of nucleophile concentration for the first and second steps of the substitution reactions of $[Pd(dach)(O,O-ox)]$ at pH = 7.2, 25 mM Hepes, T = 298 K.

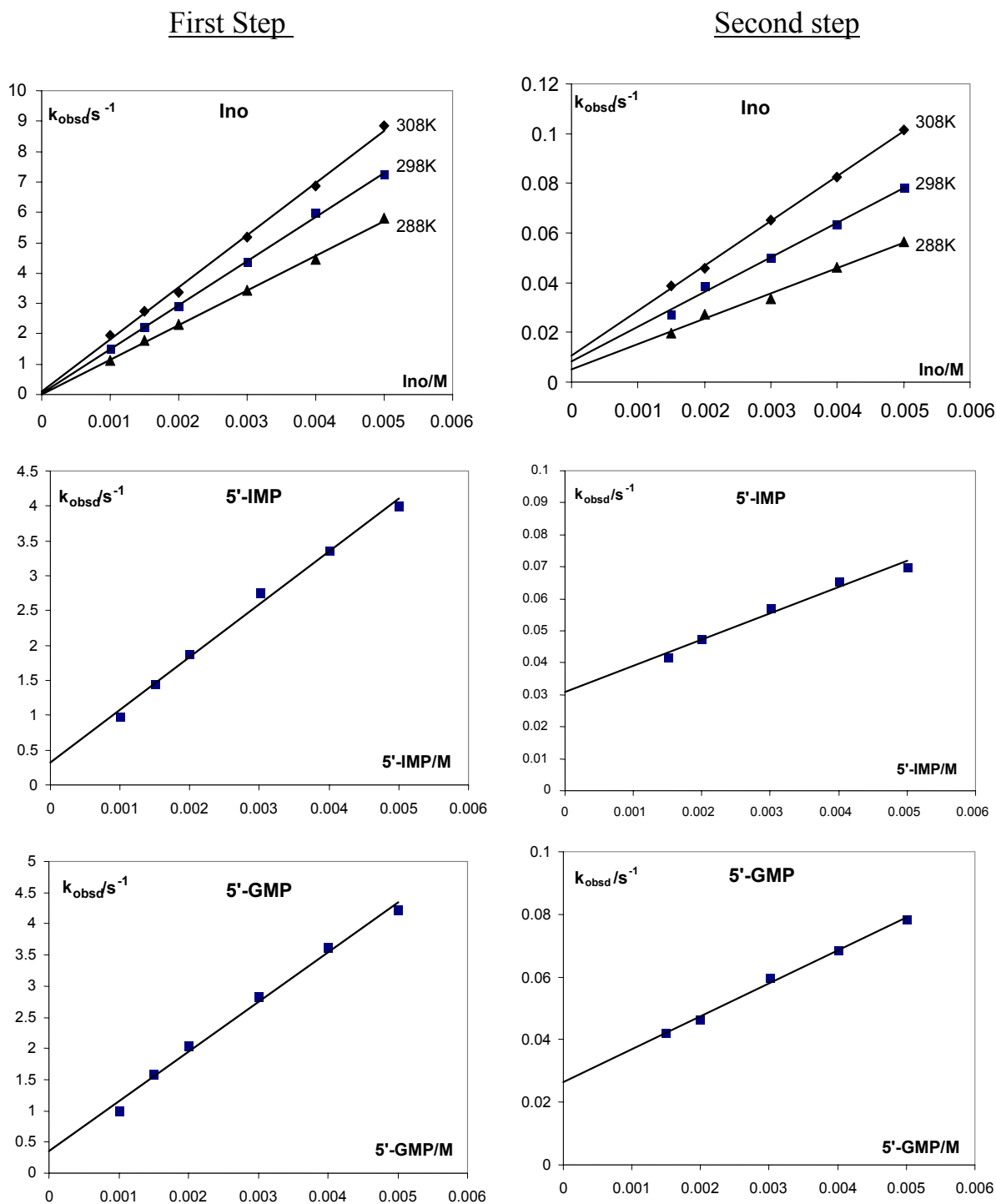


Fig. S2 Pseudo-first order rate constants as a function of nucleophile concentration for the first and second step of the substitution reaction of $[\text{Pd}(\text{dach})(N,O\text{-gly})]^+$ at pH = 7.2, 25 mM Hepes, T = 298 K

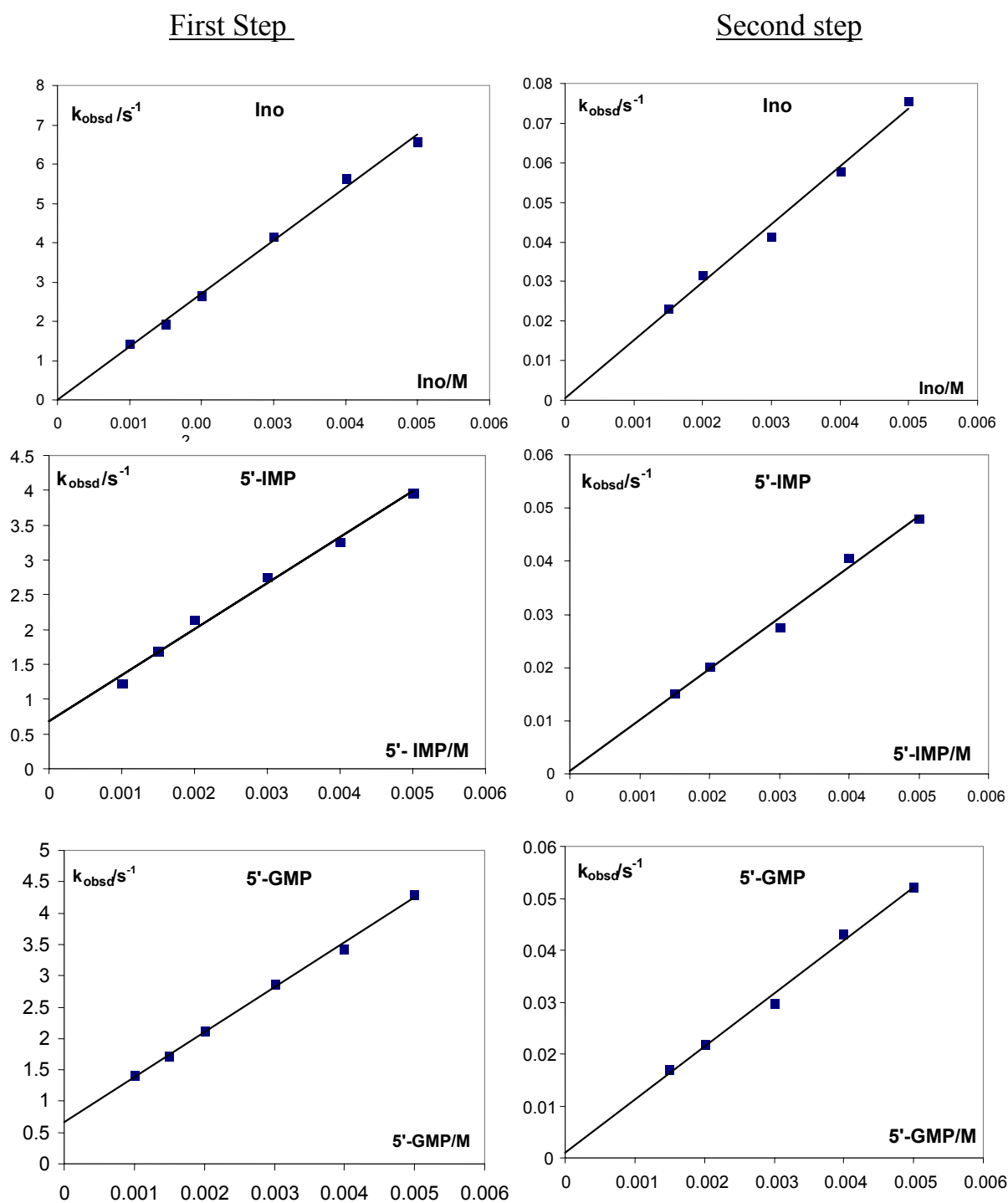


Fig. S3 Pseudo-first order rate constants as a function of nucleophile concentration for the first and second steps of the substitution reactions of $[\text{Pd}(\text{dach})\text{Cl}_2]$ at $\text{pH} = 7.2$, 25 mM Hepes, $T = 298 \text{ K}$.

First Step

Second step

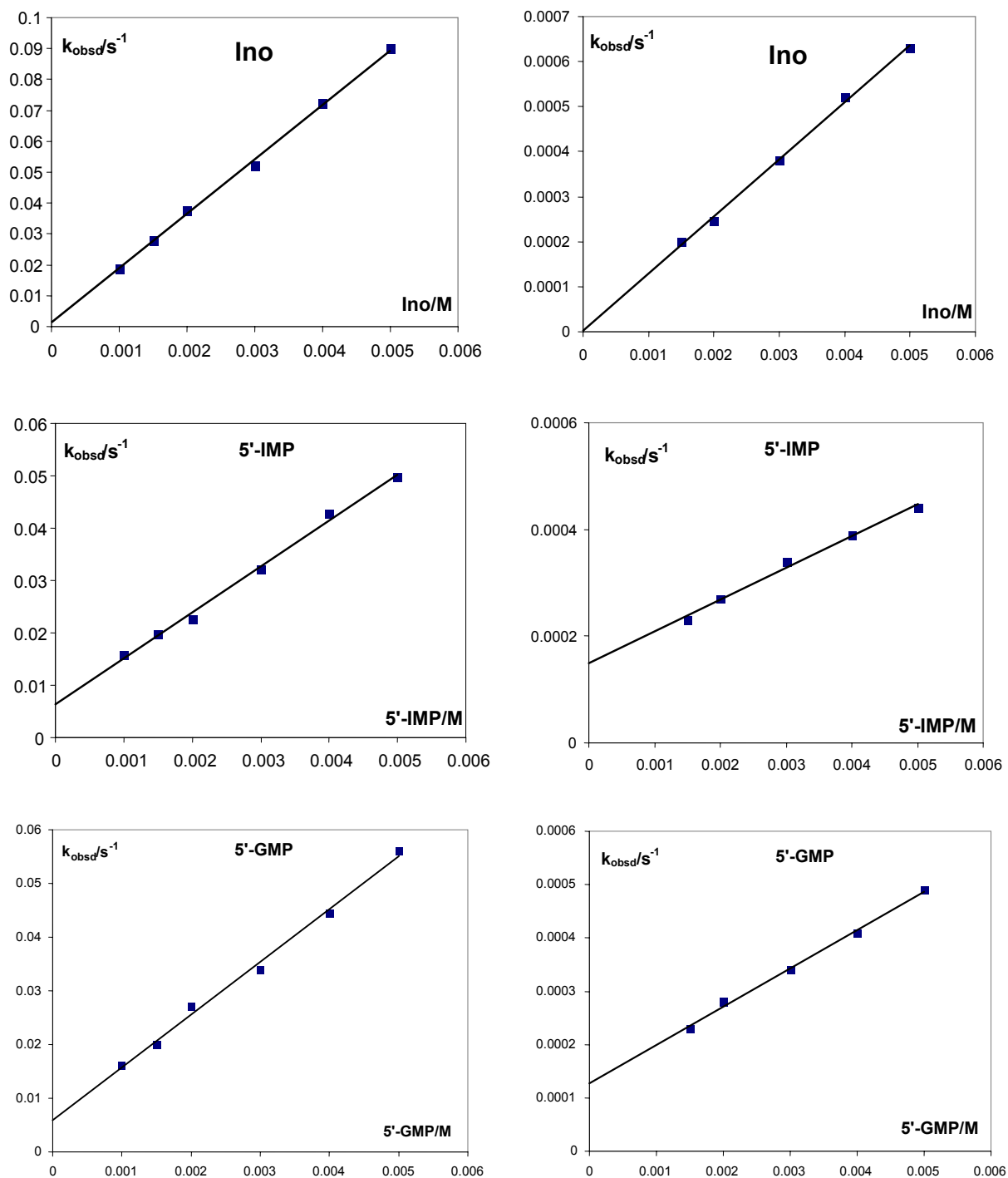


Fig. S4 Pseudo-first order rate constants as a function of nucleophile concentration for the first and second steps of the substitution reactions of $[\text{Pd}(\text{dach})(N,S\text{-met})]^+$ at $\text{pH} = 7.2$, 25 mM Heps, $T = 298 \text{ K}$