

Kinetic and mechanistic study of the reactions of Pd(II) complexes with azols and diazines. Crystal structure of [Pd(bpma)(H₂O)](ClO₄)₂·2H₂O

Živadin D. Bugarčić,^{a,b} Sharanappa T. Nandibewoor,^{a,c} Mohamed S. M. Hamza,^{a,d}
Frank Heinemann^a and Rudi van Eldik^{a,*}

Table S1. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of [Pd(dien)H₂O]²⁺ with triazole and pyrazole; 0.10 M NaClO₄, pH = 2.8.^a

T/°C	C _{triazole} /M	k _{obsd} /s ⁻¹	C _{pyrazole} /M	k _{obsd} /s ⁻¹
15	0.0075	45.4(5)	0.0075	27.5(5)
15	0.01	64.3(7)	0.01	41.1(7)
15	0.02	138(8)	0.015	60.2(5)
15	0.03	215(4)	0.02	87.1(6)
15	0.04	270(9)	0.04	170(4)
15	0.05	329(5)	0.05	200(8)

^aNumber of kinetic runs in parenthesis.

Table S2. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ with pyrimidine, pyrazine and pyridazine; 0.10 M NaClO_4 , pH = 2.8.^a

T/°C	C _{pyrimidine} /M	k _{obsd} /s ⁻¹	C _{pyrazine} /M	k _{obsd} /s ⁻¹	C _{pyridazine} /M	k _{obsd} /s ⁻¹
15	0.0075	22.3(5)	0.0075	18.7(5)	0.0075	36.1(5)
15	0.01	28.6(7)	0.01	24.9(5)	0.01	50(4)
15	0.02	57.9(4)	0.015	54.2(5)	0.02	105(7)
15	0.03	87.4(4)	0.02	74.2(7)	0.03	170(4)
15	0.04	115(8)	0.04	100(4)	0.04	215(4)
15	0.05	140(5)	0.05	128(6)	0.05	253(8)

^aNumber of kinetic runs in parenthesis.

Table S3. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{bpma})\text{H}_2\text{O}]^{2+}$ with triazole and pyrazole; 0.10 M NaClO_4 , pH = 2.8.^a

T/°C	C _{triazole} /M	k _{obsd} /s ⁻¹	C _{pyrazole} /M	k _{obsd} /s ⁻¹
15	0.0015	50.6(5)	0.02	256.7(5)
15	0.003	100.1(4)	0.03	323.1(5)
15	0.0045	142.2(7)	0.04	463.2(5)
15	0.006	179.9(4)	0.05	610(6)
15	0.0075	208.6(8)	0.06	700(4)
15	0.01	267.8(5)		

^aNumber of kinetic runs in parenthesis.

Table S4. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{bpma})\text{H}_2\text{O}]^{2+}$ with pyrimidine, pyrazine and pyridazine; 0.10 M NaClO_4 , pH = 2.8.^a

T/°C	C _{pyrimidine} /M	k _{obsd} /s ⁻¹	C _{pyrazine} /M	k _{obsd} /s ⁻¹	C _{pyridazine} /M	k _{obsd} /s ⁻¹
15	0.00075	11.3(5)	0.00075	13.2(5)		
15	0.001	12.7(7)	0.001	17.8(8)		
15	0.0015	18.1(4)	0.0015	22.6(5)	very fast	
15	0.00225	27.5(6)	0.0225	35.1(7)		
15	0.003	36.4(4)	0.003	44.9(4)		
15	0.00375	49(5)				

^a Number of kinetic runs in parenthesis.

Table S5. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with triazole and pyrazole; 0.10 M NaClO_4 , 0.010M NaCl , pH = 2.8.^a

T/°C	C _{triazole} /M	k _{obsd} /s ⁻¹	C _{pyrazole} /M	k _{obsd} /s ⁻¹
25	0.006	3.87(5)	0.006	3.63(8)
25	0.0075	5.26(4)	0.075	5.24(5)
25	0.01	6.90(7)	0.01	6.34(5)
25	0.015	10.9(4)	0.015	9.64(4)
25	0.02	14.6(6)	0.02	12.5(7)
25	0.03	20(5)	0.03	17.9(4)

^a Number of kinetic runs in parenthesis.

Table S6. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with pyrimidine, pyrazine and pyridazine; 0.10 M NaClO_4 , 0.010M NaCl , $\text{pH} = 2.8$.^a

$T/^\circ\text{C}$	$C_{\text{pyrimidine}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$	$C_{\text{pyrazine}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$	$C_{\text{pyridazine}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
25	0.006	3.27(5)	0.006	3.45(5)	0.006	5.92(5)
25	0.0075	4.27(4)	0.0075	4.28(5)	0.0075	7.87(6)
25	0.01	5.62(7)	0.01	5.55(7)	0.01	10.6(4)
25	0.015	8.42(4)	0.015	8.49(4)	0.015	14.4(8)
25	0.02	10.8(8)	0.02	10.3(6)	0.02	20.2(4)
25	0.03	16.4(5)	0.03	16.6(4)	0.03	28.4(7)
25					0.04	38.4(4)

^aNumber of kinetic runs in parenthesis.

Table S7. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{bpma})\text{Cl}]^+$ with triazole and pyrazole; 0.10 M NaClO_4 , 0.010M NaCl , $\text{pH} = 2.8$.^a

$T/^\circ\text{C}$	$C_{\text{triazole}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$	$C_{\text{pyrazole}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
25	0.0015	1.84(5)	0.0015	1.10(5)
25	0.003	3.38(4)	0.003	2.24(8)
25	0.0045	4.65(7)	0.0045	3.21(5)
25	0.006	6.03(4)	0.006	4.36(4)
25	0.0075	7.78(8)	0.0075	5.45(6)
25	0.01	10.8(4)	0.01	7.30(7)

^aNumber of kinetic runs in parenthesis.

Table S8. Observed pseudo-first-order rate constants as a function of nucleophile concentration for the reaction of $[\text{Pd}(\text{bpma})\text{Cl}]^+$ with pyrimidine, pyrazine and pyridazine; 0.10 M NaClO_4 , 0.010M NaCl , pH = 2.8.

T/°C	C _{pyrimidine} /M	k _{obsd} /s ⁻¹	C _{pyrazine} /M	k _{obsd} /s ⁻¹	C _{pyridazine} /M	k _{obsd} /s ⁻¹
25	0.00015	15(5)				
25	0.0003	30(8)				
25	0.00045	40.5(4)	very fast		very fast	
25	0.0006	60(7)				
25	0.00075	71(4)				

^aNumber of kinetic runs in parenthesis.

Table S9. Observed pseudo-first-order rate constants as a function of pressure for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with triazole (T = 16 °C); 0.10 M NaClO_4 , 0.010M NaCl , pH = 2.8.

Pressure, MPa	k _{obsd} /s ⁻¹
10	1.06
50	1.21
91(76) ^a	1.34
132	1.48

^aThe pressure for the second set of data.

Table S10. Observed pseudo-first-order rate constants as a function of pressure for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with pyrazole ($T = 16\text{ }^\circ\text{C}$); 0.10 M NaClO_4 , 0.010M NaCl , $\text{pH} = 2.8$.

Pressure, MPa	$k_{\text{obsd}}/\text{s}^{-1}$
10	0.45
50	0.54
91	0.62
132	0.67

Table S11. Observed pseudo-first-order rate constants as a function of pressure for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with pyrazine ($T = 16\text{ }^\circ\text{C}$); 0.10 M NaClO_4 , 0.010M NaCl , $\text{pH} = 2.8$.

Pressure, MPa	$k_{\text{obsd}}/\text{s}^{-1}$
10	1.17
50	1.35
91	1.55
132	1.75

Table S12. Observed pseudo-first-order rate constants as a function of temperature for the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with different ligands: $[\text{Pd}(\text{dien})\text{Cl}]^+ = 5.6 \times 10^{-4} \text{ M}$, $[\text{Ligand}] = 0.006 \text{ M}$, $[\text{Cl}^-] = 0.01 \text{ M}$, $I = 0.1 \text{ M}$ (NaClO_4), $\text{pH} = 2.8$

Ligand	Temp. (°C)	k_{obs} , s^{-1}	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)
Pyrazole	10	1.91	43 ± 1	-47 ± 4
	15	2.72		
	20	3.67		
	25	5.24		
	30	6.75		
Triazole	10	1.41	46 ± 1	-37 ± 2
	15	1.95		
	20	2.78		
	25	3.87		
	30	5.45		
Pyrimidine	10	1.26	44 ± 1	-45 ± 5
	15	1.82		
	20	2.47		
	25	3.26		
	30	4.79		
Pyrazine	10	1.23	47 ± 1	-34 ± 3
	15	1.72		
	20	2.54		
	25	3.44		
	30	4.92		
Pyridazine	10	2.16	45 ± 1	-38 ± 2
	15	3.10		
	20	4.42		
	25	5.92		
	30	8.16		

Tables S13. Observed pseudo-first-order rate constants as a function of temperature for the reaction of $[\text{Pd}(\text{bpma})\text{Cl}]^+$ with different ligands: $[\text{Pd}(\text{bpma})\text{Cl}]^+ = 1.2 \times 10^{-4} \text{ M}$, $[\text{Ligand}] = 0.0015 \text{ M}$ (0.00015 M for pyrimidine), $[\text{Cl}^-] = 0.01 \text{ M}$, $I = 0.1 \text{ M}$ (NaClO_4), $\text{pH} = 2.8$

Ligand	Temp. (°C)	k_{obs} , s^{-1}	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)
Pyrazole	10	0.72	45 ± 2	-34 ± 6
	15	1.1		
	20	1.5		
	25	2.0		
Triazole	10	1.59	39 ± 3	-48 ± 8
	15	1.83		
	20	3.22		
	25	4.0		
	30	4.65		
Pyrimidine	10	12.1	31 ± 1	-41 ± 4
	15	15.1		
	20	20.2		
	25	24.3		
Pyrazine	Very fast and hence not studied			
Pyridazine	Very fast and hence not studied			

Tables S14. Observed pseudo-first-order rate constants as a function of temperature for the reaction of $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ with different ligands: $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+} = 6.7 \times 10^{-4} \text{ M}$, $[\text{Ligand}] = 0.0075 \text{ M}$ (for pyrazole 0.01 M), $I = 0.1 \text{ M}$ (NaClO_4), $\text{pH} = 2.8$

Ligand	Temp. ($^{\circ}\text{C}$)	k_{obs} , s^{-1}	ΔH^{\ddagger} (kJ mol^{-1})	ΔS^{\ddagger} ($\text{J K}^{-1} \text{mol}^{-1}$)
Pyrazole	5	24.6	35 ± 1	-56 ± 3
	10	31.5		
	15	41.1		
	20	55.3		
	25	70.9		
	30	92.5		
Triazole	10	27.7	36 ± 1	-48 ± 4
	15	37.1		
	20	45.4		
	25	65.2		
	30	82.4		
		106.3		
Pyrimidine	10	12.2	36 ± 0.5	-53 ± 2
	15	16.2		
	20	22.3		
	25	28.7		
	30	37.5		
		47.9		
Pyrazine	10	9.14	37 ± 2	-52 ± 5
	15	12.0		
	20	18.7		
	25	22.2		
	30	28.9		
		37.4		
Pyridazine	10	36.1	37 ± 1	-42 ± 3
	15	50.5		
	20	66.2		
	25	92.0		
	30	112.3		
		146.6		

Tables S15. Observed pseudo-first-order rate constants as a function of temperature for the reaction of $[\text{Pd}(\text{bpma})\text{H}_2\text{O}]^{2+}$ with different ligands: $[\text{Pd}(\text{bpma})\text{H}_2\text{O}]^{2+} = 5.2 \times 10^{-5} / 2.1 \times 10^{-4} / 1.1 \times 10^{-4} \text{ M}$, $[\text{L}] = 5.8 \times 10^{-4} / 3 \times 10^{-4} / 2.1 \times 10^{-3} \text{ M}$, $I = 0.1 \text{ M}$ (NaClO_4), $\text{pH} = 2.8$

Ligand	Temp. (°C)	k_{obs} , s^{-1}	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)
Pyrazole	5	164.5	24 ± 2	-82 ± 5
	10	206.2		
	15	256		
	20	312.7		
	25	337.5		
	30	450.		
Triazole	5	32.8	29 ± 2	-58 ± 6
	10	43.5		
	15	50.6		
	20	72.4		
	25	80.9		
	30	99.8		
Pyrimidine	5	6.6	40 ± 1	-26 ± 4
	10	8.5		
	15	11.3		
	20	16.1		
	25	22.1		
	30	28.8		
Pyrazine	Very fast and hence not studied			
Pyridazine	Very fast and hence not studied			