Supporting Information

Mechanistic behaviour of alkylcobaloximes and imino-oxime complexes related to vitamin B_{12}

Basam M. Alzoubi, Fanny Vidali, Ralph Puchta, Carlos Dücker-Benfer, Alessandro Felluga, Lucio Randaccio, Giovanni Tauzher and Rudi van Eldik*

Table S1. Kinetic data for the reaction of *trans*-$[(CH_3)Co((DO)(DOH)pn)H_2O]^+$ with imidazole, 1-methylimidazole, pyrazole and 1,2,4-triazole as a function of temperature and pressure.[a]

	k, M^{-1} s^{-1}			
T, °C	imidazole	1-methylimidazole	pyrazole	1,2,4-triazole
5	11.8 ± 0.1	8.4 ± 0.1	12.3 ± 0.1	9.7 ± 0.1
10	22.2 ± 0.1	14.5 ± 0.1	23.3 ± 0.1	18.1 ± 0.1
15	35.8 ± 0.1	26.4 ± 0.2	39.4 ± 0.2	29.8 ± 0.1
20	59.4 ± 0.4	43.2 ± 0.8	66.2 ± 0.6	48.4 ± 0.2
25	94.6 ± 1.4	68.0 ± 0.4	105.6 ± 1.8	74.0 ± 0.6
$\Delta H^{\ddagger}$, kJ mol^{-1}	69 ± 2	70 ± 2	71 ± 2	67 ± 2
$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	+23 ± 6	+27 ± 5	+33 ± 6	+17 ± 7
Pressure, MPa	[b] k_{obs}, s^{-1}			
10	4.20 ± 0.09	3.70 ± 0.05	5.29 ± 0.08	3.85 ± 0.04
50	4.04 ± 0.19	3.56 ± 0.07	4.97 ± 0.04	3.66 ± 0.05
90	3.86 ± 0.08	3.39 ± 0.04	4.72 ± 0.10	3.45 ± 0.04
130	3.69 ± 0.02	3.22 ± 0.05	4.41 ± 0.10	3.28 ± 0.05
$\Delta V^{\ddagger}$, cm^3 mol^{-1}	+2.7 ± 0.1	+2.9 ± 0.1	+3.7 ± 0.1	+3.4 ± 0.1

[a] $[Co^{III}] = 1 \times 10^{-4}$ M, pH 9, I = 0.1 M. [b] [nucleophile] = 0.05 M, T = 25 °C.

Table S2. Kinetic data for the reaction of *trans*-$[(CH_3)Co((DO)(DOH)pn)MeOH]^+$ with imidazole, 1-methylimidazole, pyrazole, and 1,2,4-triazole as a function of temperature and pressure.[a]

	k, M^{-1} s^{-1}			
T, ^oC	imidazole	1-methylimidazole	pyrazole	1,2,4-triazole
5	3.3 ± 0.1	3.3 ± 0.1	2.4 ± 0.1	2.4 ± 0.1
10	5.5 ± 0.1	5.1 ± 0.1	4.1 ± 0.1	4.1 ± 0.1
15	9.8 ± 0.1	8.4 ± 0.1	7.0 ± 0.1	6.9 ± 0.1
20	16.5 ± 0.1	14.8 ± 0.1	11.7 ± 0.1	11.3 ± 0.1
25	26.0 ± 0.2	24.3 ± 0.2	21.0 ± 0.1	20.2 ± 0.1
$\Delta H^‡$, kJ mol^{-1}	70 ± 1	67 ± 2	72 ± 2	70 ± 2
$\Delta S^‡$, J mol^{-1} K^{-1}	+16 ± 4	+7 ± 8	+21 ± 5	+16 ± 5
Pressure, MPa	[b] k_{obs}, s^{-1}			
10	1.12 ± 0.02	0.90 ± 0.04	0.90 ± 0.01	0.85 ± 0.01
50	1.06 ± 0.01	0.84 ± 0.01	0.85 ± 0.01	0.80 ± 0.01
90	1.00 ± 0.01	0.79 ± 0.01	0.79 ± 0.01	0.74 ± 0.02
130	0.95 ± 0.01	0.73 ± 0.01	0.74 ± 0.01	0.69 ± 0.01
$\Delta V^‡$, cm^3 mol^{-1}	+3.4 ± 0.1	+4.3 ± 0.1	+4.1 ± 0.1	+4.4 ± 0.1

[a] $[Co^{III}]$= 1 x 10^{-4} M. [b] [Nucleophile] = 0.05 M, T = 25 ^oC.

Table S3. Kinetic data for the reaction of *trans*-[(R)Co(Hdmg)$_2$H$_2$O] with pyridine where R = CH_2Cl and CH_2Br as a function of temperature and pressure.[a]

T, ^oC	*trans*-[(CH_2Cl)Co(Hdmg)$_2$H$_2$O]			*trans*-[(CH_2Br)Co(Hdmg)$_2$H$_2$O]		
	k, s^{-1}	K, M^{-1}	k K, $M^{-1}s^{-1}$	k, s^{-1}	K, M^{-1}	k K, $M^{-1}s^{-1}$
20	4.1 ± 0.2	2.01 ± 0.08	8.2 ± 0.7	2.4 ± 0.2	1.51 ± 0.08	3.6 ± 0.5
25	8.0 ± 0.3	1.71 ± 0.08	13.7 ± 1.2	4.2 ± 0.3	1.44 ± 0.08	6.0 ± 0.8
30	15.4 ± 0.4	1.43 ± 0.08	22.0 ± 1.8	8.0 ± 0.4	1.30 ± 0.08	10.4 ± 1.2
35	28 ± 0.4	1.22 ± 0.08	34.2 ± 2.7	12.0 ± 0.3	1.33 ± 0.07	16.0 ± 1.2
40	47.0 ± 0.5	1.19 ± 0.08	55.9 ± 4.4	21.0 ± 0.3	1.34 ± 0.08	28.1 ± 2.1
$\Delta H^{\ddagger}$, kJ mol^{-1}			71 ± 1			76 ± 5
$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}			+14 ± 3			+25 ± 5
Pressure, MPa			[b] k, s^{-1}			
10	5.13 ± 0.20			5.24 ± 0.10		
50	4.76 ± 0.10			4.69 ± 0.20		
80	4.48 ± 0.30			4.42 ± 0.10		
120	4.07 +0.20			3.99 ± 0.30		
$\Delta V^{\ddagger}$, cm^3 mol^{-1}	+5.2 ± 0.2			+6.0 ± 0.2		

[a] [Co^{III}]= 1 x 10^{-3} M, pH = 8, I = 0.1 M. [b] T = 25 ^oC, [Py] = 0.64 M

Table S4. Kinetic data for the reaction of *trans*-[(R)Co(Hdmg)$_2$H$_2$O] with pyridine and thiourea where R = CH_2Cl, CH_2Br, and CH_2I as function of temperature and pressure.[a]

trans-[(R)Co(Hdmg)$_2$H$_2$O]						
	Thiourea			Pyridine		
	R= CH_2Cl	R= CH_2Br	R= CH_2I		R= CH_2I	
T, ^oC		k, M^{-1} s^{-1}		k, s^{-1}	K, M^{-1}	k K, M^{-1} s^{-1}
20	10.4 ± 0.2	4.2 ± 0.2	4.1 ± 0.1	2.6 ± 0.1	1.04 ± 0.09	2.7 ± 0.3
25	17.8 ± 0.3	7.3 ± 0.2	6.6 ± 0.1	5.7 ± 0.2	0.86 ± 0.08	4.9 ± 0.6
30	27.9 ± 0.5	11.7 ± 0.5	11.3 ± 0.1	15.0 ± 0.2	0.54 ± 0.08	8.1 ± 1.3
35	46 ± 1	19.6 ± 0.5	20.0 ± 0.2	62.0 ± 0.2	0.21 ±0.07	13.0 ± 4.4
40	74 ± 1	32.7 ± 0.4	28.7 ± 0.4	74.0 ± 0.9	0.31 ± 0.08	22.9 ± 6.2
$\Delta H^{\ddagger}$, kJ mol^{-1}	72 ± 1	75 ± 1	73 ± 3			78 ± 2
$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	+19 ± 3	+23 ± 4	+16 ± 10			+31 ± 6
Pressure, MPa			[b] k, s^{-1}			
10	11.0 ± 0.4	6.3 ± 0.3	4.9 ± 0.2	1.78 ± 0.04		
50	10.2 ± 0.3	5.3 ± 0.3	4.4 ± 0.1	1.67 ± 0.03		
80	9.4 ± 0.4	4.6 ± .2	4.0 ± 0.3	1.55 ± 0.05		
120	8.4 ± 0.3	4.0 ± 0.3	3.7 ± 0.2	1.44 ± 0.04		
$\Delta V^{\ddagger}$, cm^3 mol^{-1}	+6.1 ± 0.4	+10.4 ± 0.5	+6.4 ± 0.2	+4.9 ± 0.3		

[a] $[Co^{III}]$= 1 x 10^{-3} M, pH = 8, I = 0.1 M. [b] T = 25 ^oC, [TU] = 0.8 M, [Py] = 0.64M

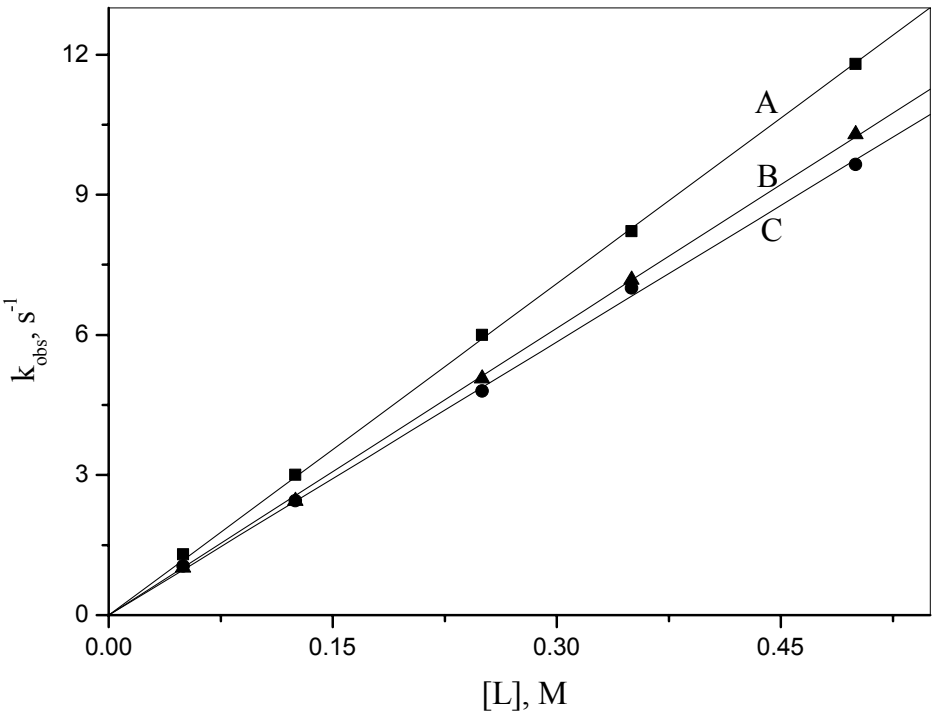

Figure S1. Plots of k_{obs} versus [imidazole] (A), [1,2,4-triazole] (B), and [pyrazole] (C) for the reaction with 1 x 10^{-4} M *trans*-[(CH_3) Co((DO)(DOH)pn)MeOH]$^+$ at 25.0 °C.

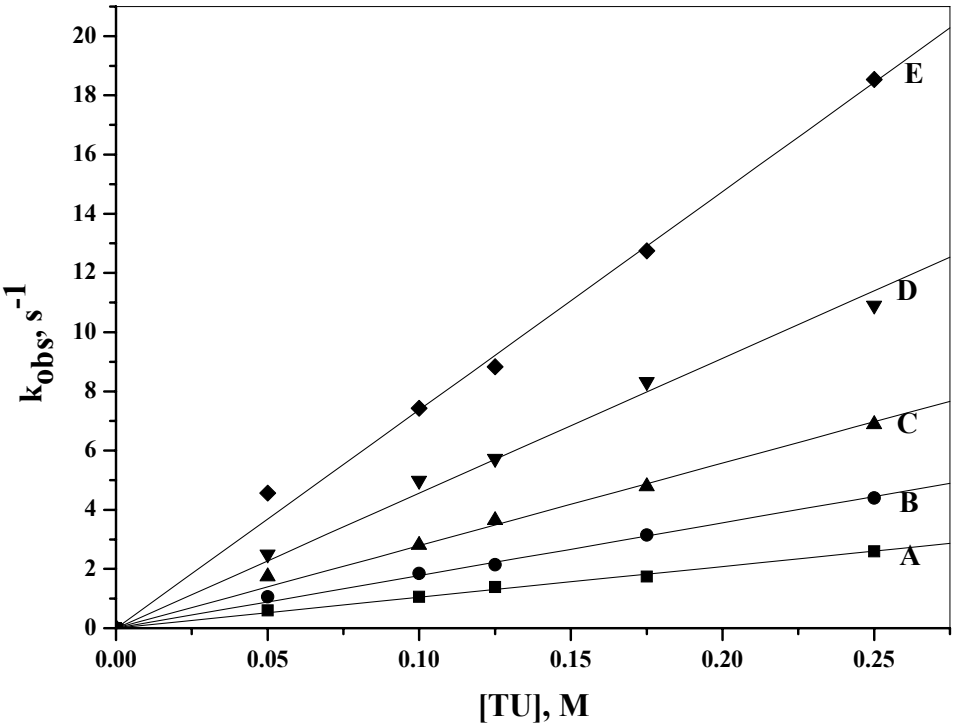

Figure S2. Plots of k_{obs} versus [Thiourea] for the reaction with 1 x 10^{-3} M *trans*-[$(CH_2Cl)Co(Hdmg)_2H_2O$] as a function of temperature. Experimental conditions: pH = 8, I = 0.1 M, and temperature 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

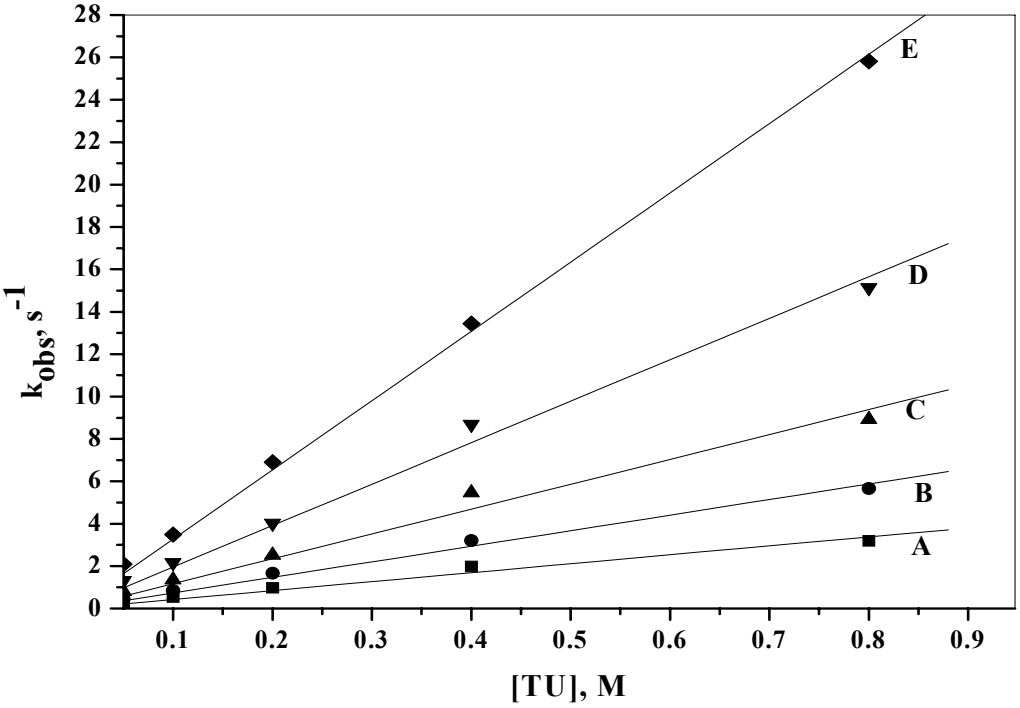

Figure S3. Plots of k_{obs} versus [Thiourea] for the reaction with 1 x 10^{-3} M *trans*-$[(CH_2Br)Co(Hdmg)_2H_2O]$ as a function of temperature. Experimental conditions: pH = 8, I = 0.1 M, and temperature: 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

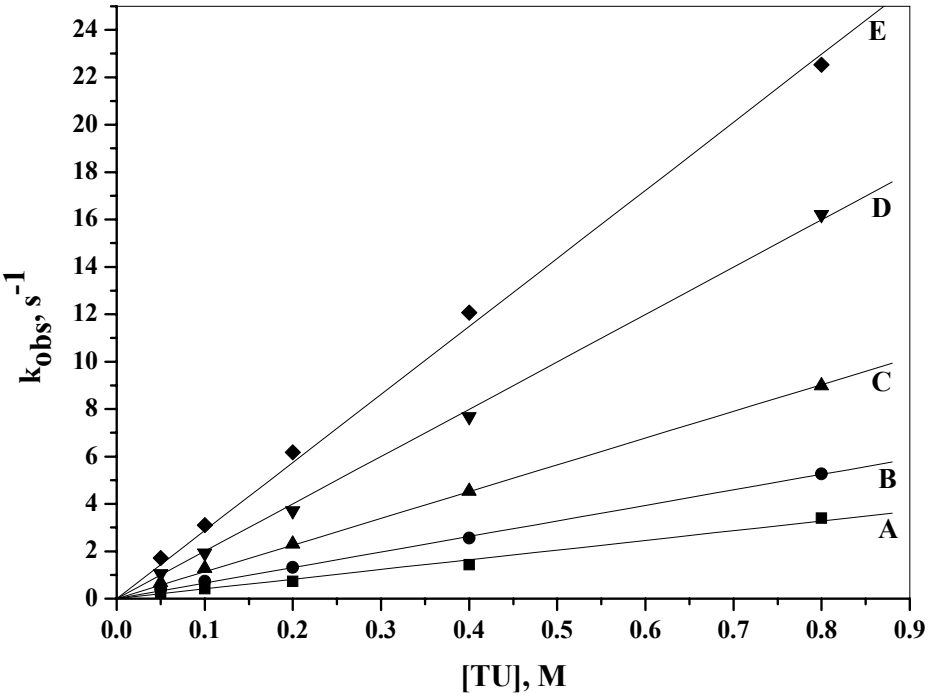

Figure S4. Plots of k_{obs} versus [Thiourea] for the reaction with 1 x 10^{-3} M *trans*-[$(CH_2I)Co(Hdmg)_2H_2O$] as a function of temperature. Experimental conditions: pH = 8, I = 0.1 M, and temperature: 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

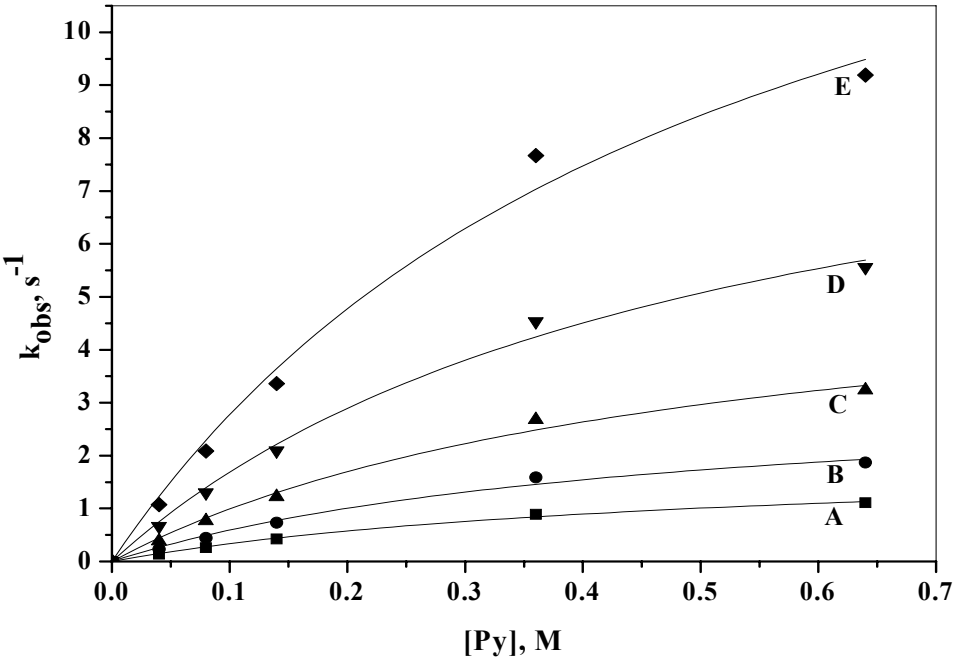

Figure S5. Plots of k_{obs} versus [Pyridine] for the reaction with 1 x 10^{-3} M *trans*-[$(CH_2Br)Co(Hdmg)_2H_2O$] as a function of temperature. Experimental conditions: pH = 8, I = 0.1 M, and temperature: 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

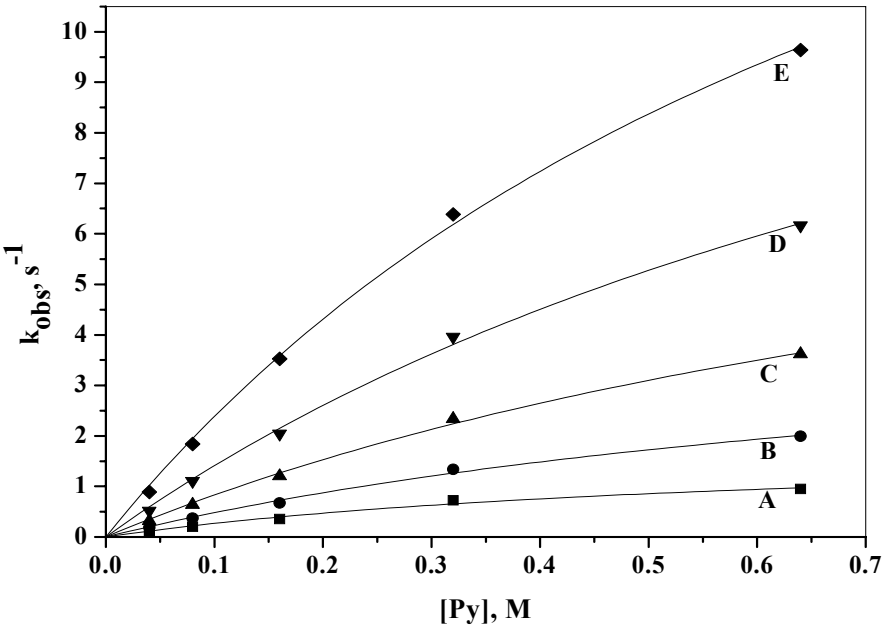

Figure S6. Plots of k_{obs} versus [Pyridine] for the reaction with 1 x 10^{-3} M *trans*-$[(CH_2I)Co(Hdmg)_2H_2O]$ as a function of temperature. Experimental conditions: pH = 8, I = 0.1 M, and temperature: 20 (A), 25 (B), 30 (C), 35 (D) and 40 (E) °C.

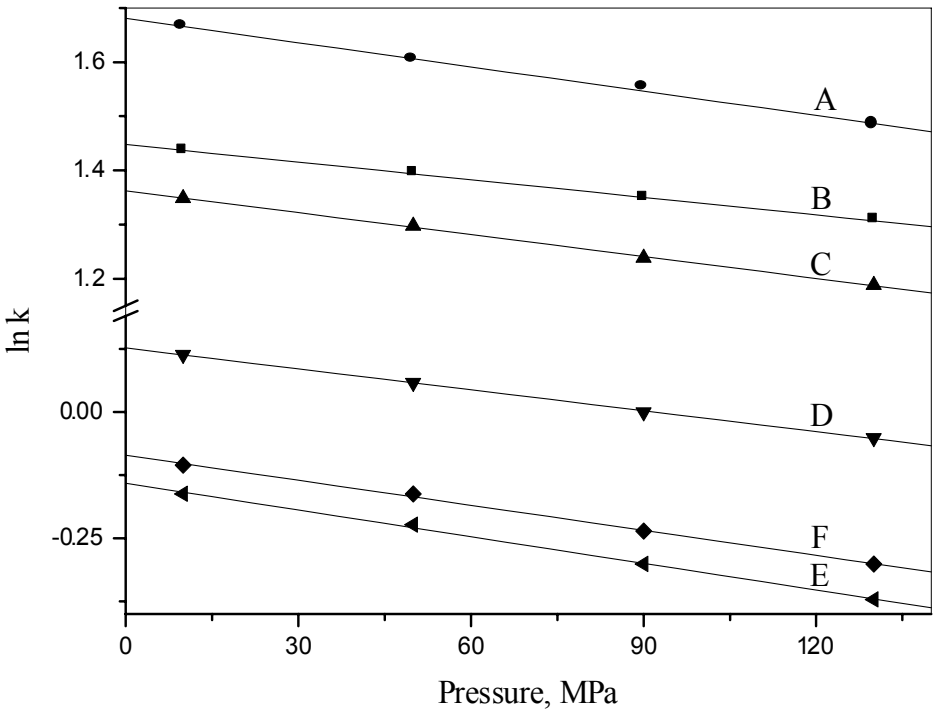

Figure S7. Plots of ln*k* versus pressure for the reaction of *trans*-$[(CH_3)Co((DO)(DOH)pn)S]^+$ with pyrazole (A), imidazole (B) and 1,2,4-triazole (C) for S = H_2O; imidazole (D), pyrazole (E) and 1,2,4-triazole (F) for S = MeOH. Experimental conditions: $[Co^{III}]$ = (0.9-1.5) x 10^{-4} M, [imidazole] = [1,2,4-triazole] = [pyrazole] = 0.05 M, Temp. = 25.0 °C, pH 9 and I = 0.1 M $NaClO_4$ in the case of S = H_2O.

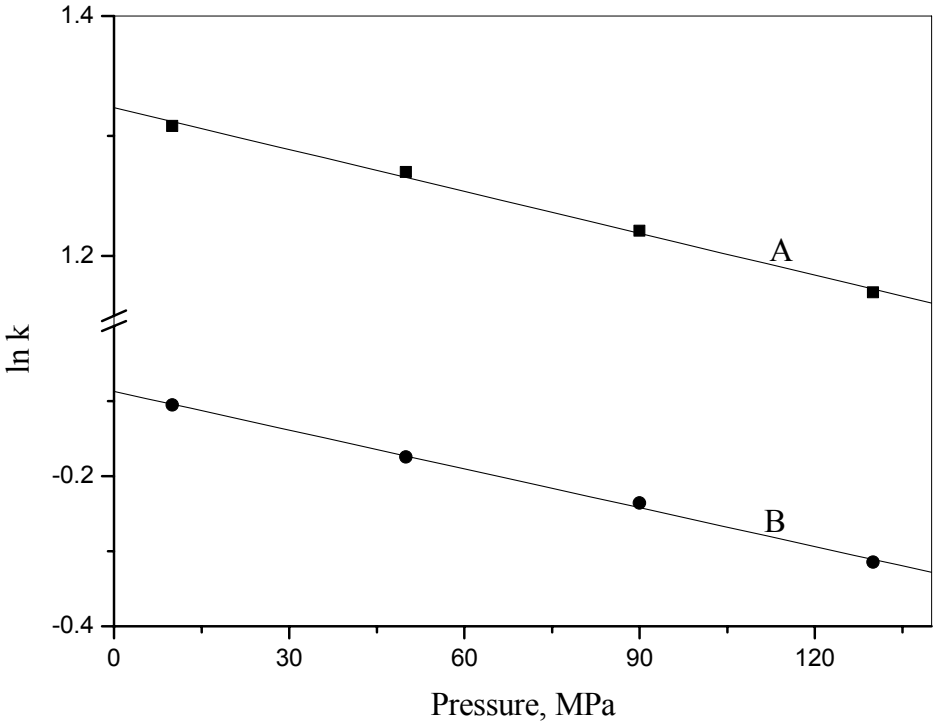

Figure S8. Plots of ln*k* versus pressure for the reaction of *trans*-$[(CH_3)Co((DO)(DOH)pn)S]^+$ with 1-methylimidazole for S = H_2O (A) and for S = MeOH (B). Experimental conditions: $[Co^{III}]$ = (0.9-1.5) x 10^{-4} M, [1-methylimidazole] = 0.05 M, Temp. = 25.0 ^oC, pH 9 and I = 0.1 M $NaClO_4$ in the case of S = H_2O.

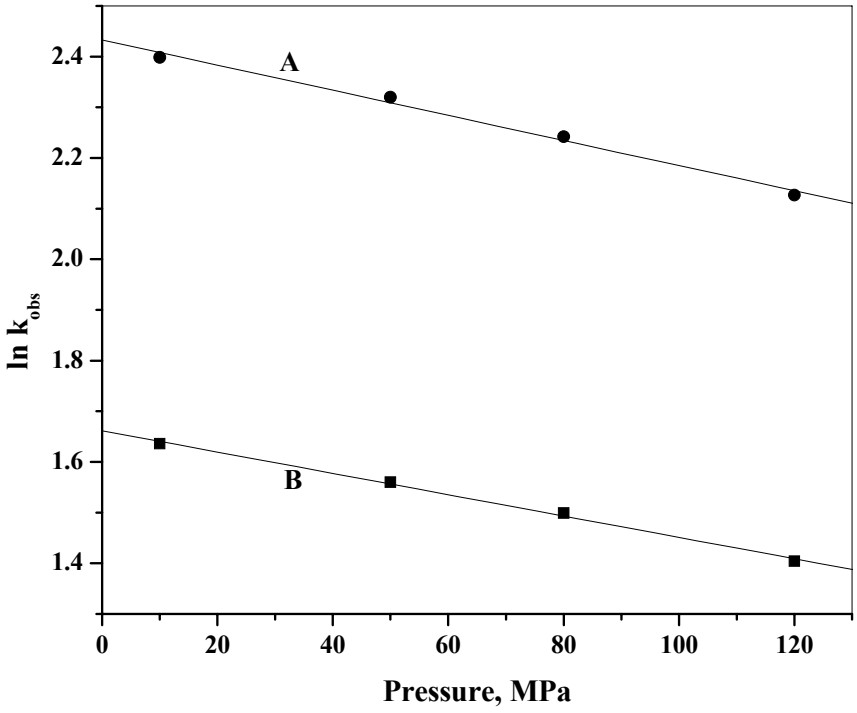

Figure S9. Plots of ln*k* versus pressure for the reaction of *trans*-[$(CH_2Cl)Co(Hdmg)_2H_2O$] with thiourea (A) and pyridine (B). Experimental conditions: [Co^{III}] = 1 x 10^{-3} M, [Py] = 0.64 and [TU] = 0.8 M, Temp. = 25.0 ^{o}C, pH 8 and I = 0.1 M.

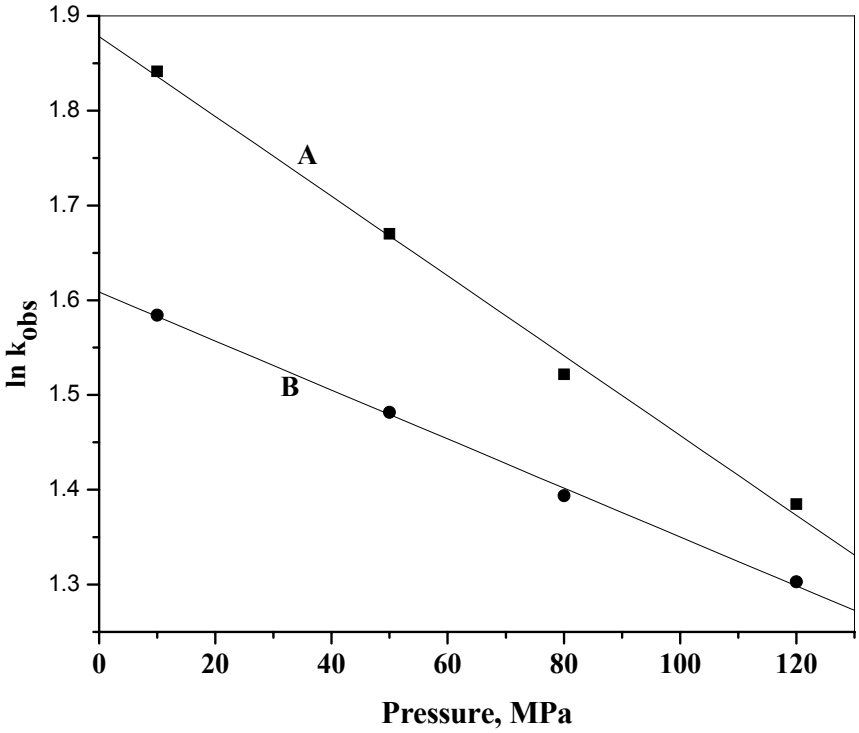

Figure S10. Plots of ln*k* versus pressure for the reaction of *trans*-[(R)Co(Hdmg)$_2$H$_2$O] with pyridine where R = CH_2Br (A) and CH_2I (B). Experimental conditions: [Co^{III}] = 1 x 10^{-3} M, [Py] = 0.64 M, Temp. = 25.0 ^{o}C, pH 8 and I = 0.1 M.

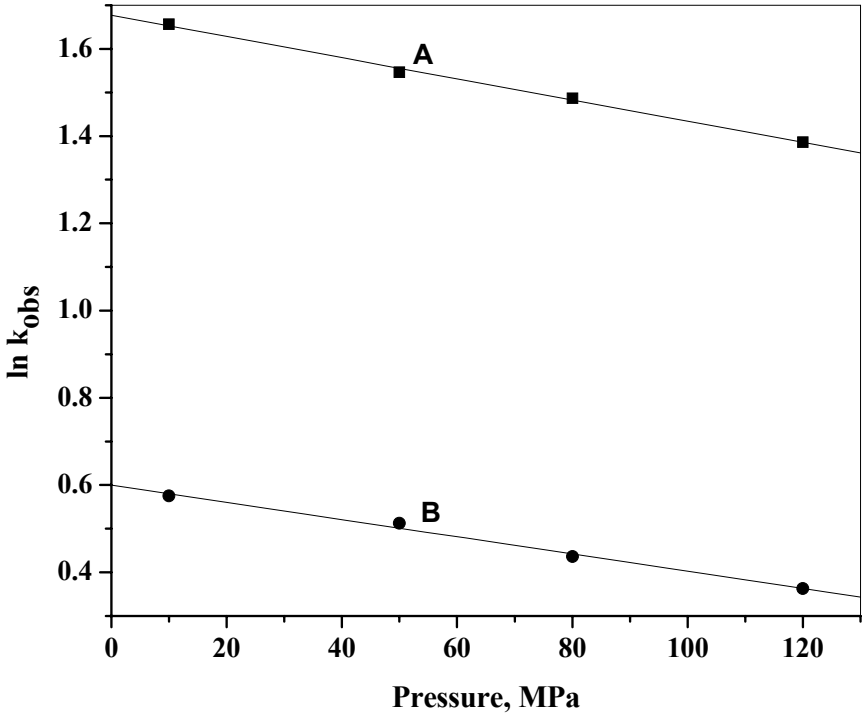

Figure S11. Plots of ln*k* versus pressure for the reaction of *trans*-[(R)Co(Hdmg)$_2$H$_2$O] with thiourea where R = CH_2Br (A) and CH_2I (B). Experimental conditions: [Co^{III}] = 1 x 10^{-3} M, [TU] = 0.8 M, Temp. = 25.0 ^oC, pH 8 and I = 0.1 M.

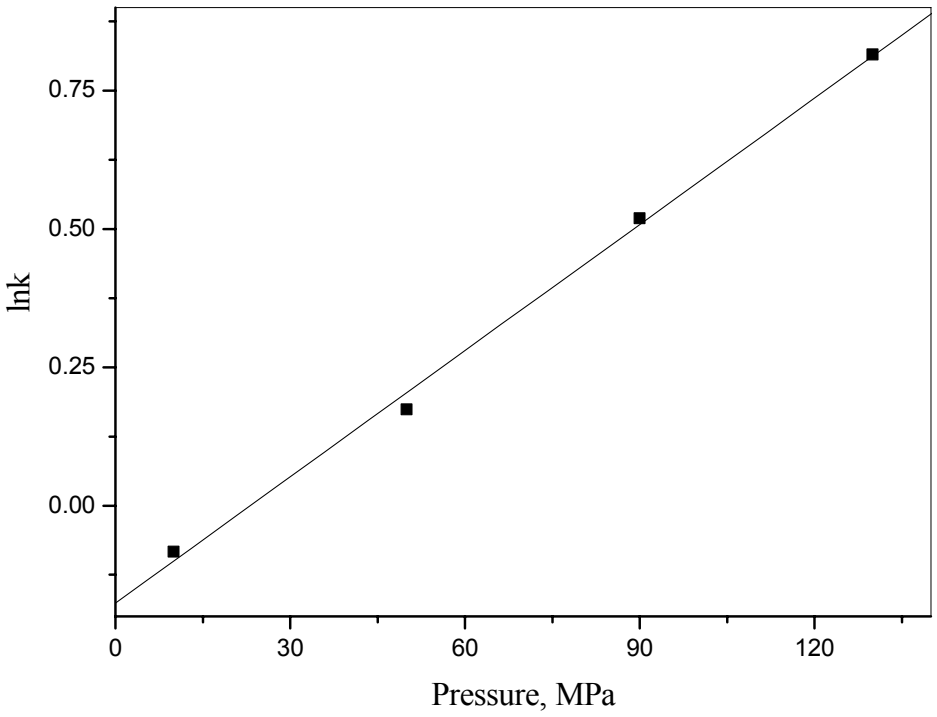

Figure S12. Plot of ln*k* versus pressure for the reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with acid. Experimental conditions: [Co^{III}] = 3 x 10^{-5} M, [H^+] = 1.25 x 10^{-2} M, Temp. = 25.0 ^oC, I = 0.2 M $NaClO_4$ in H_2O and MeOH (1:1) as solvent.

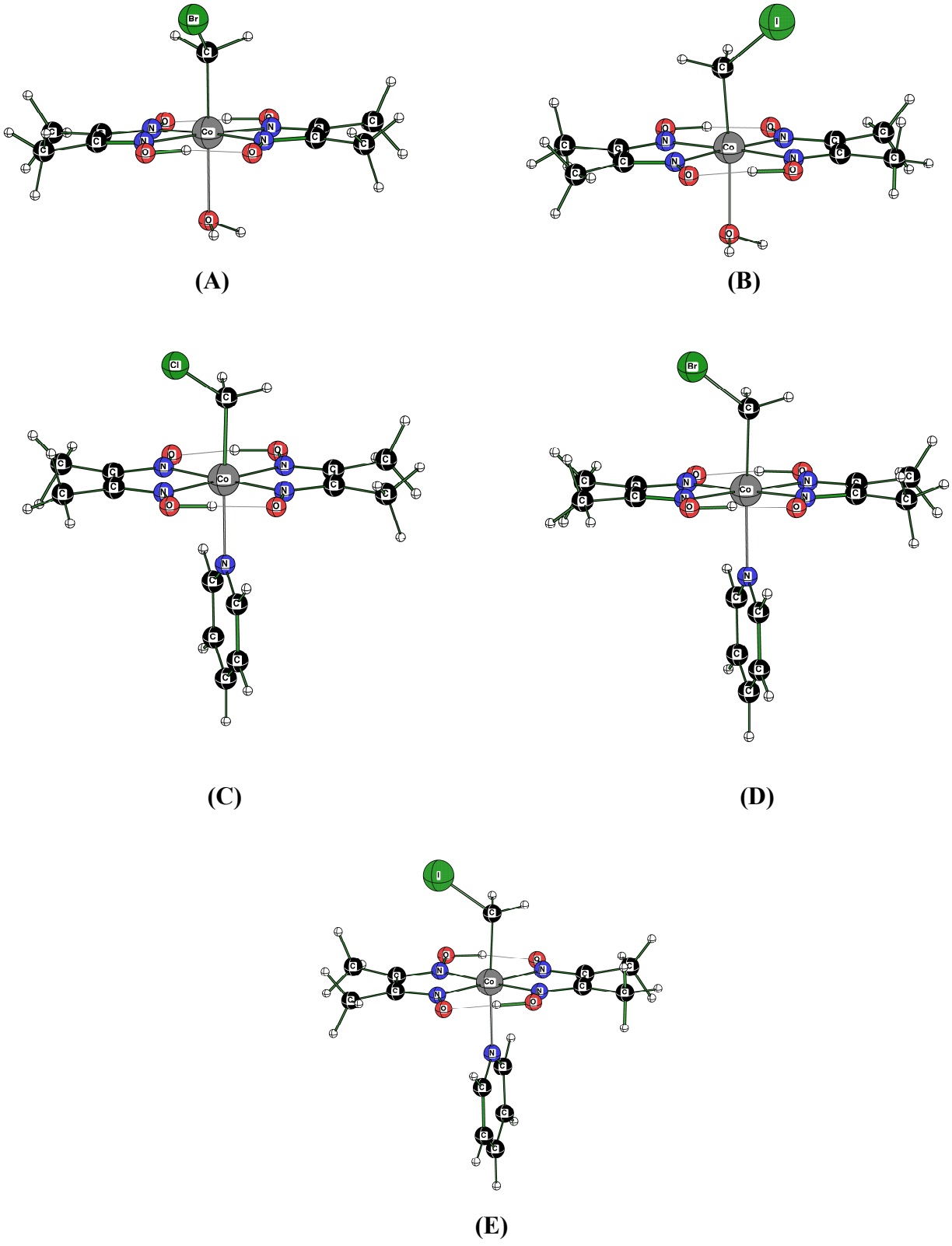

Figure S13. DFT calculated (B3LYP/LANL2DZp) structures of *trans*-[$(CH_2Br)Co(Hdmg)_2OH_2$] (A), *trans*-[$(CH_2I)Co(Hdmg)_2OH_2$](B), *trans*-[$(CH_2Cl)Co(Hdmg)_2Py$] (C), *trans*-[$(CH_2Br)Co(Hdmg)_2Py$] (D) and *trans*-[$(CH_2I)Co(Hdmg)_2Py$] (E).

Synopsis

Mechanistic behaviour of alkylcobaloximes and imino-oxime complexes related to vitamin B_{12}

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Ligand substitution reactions of complexes of the type *trans*-[(R)Co(Chel)S]$^{+/0}$ were studied as a function of temperature and pressure. The activation parameters support the operation of a dissociative interchange (I_d) mechanism. The reaction of *trans*-[$(CH_3)_2$Co((DO)(DOH)pn)] with acid was studied in H_2O/methanol (1:1) as solvent. The mechanism involves protonation of the methyl group followed by release of methane.