Ambient and High Pressure Kinetic Investigation of the Methanol Substitution in *fac*-[Re(Trop)(CO)$_3$(MeOH)] by Different Monodentate Nucleophiles

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Supplementary Data

The methanol substitution reactions between *fac*-[Re(Trop)$(CO)_3$(MeOH)] and bromide ions (Br^-), iodide ions (I^-), pyridine (Py), imidazole (Im), thiocyanate ions (NCS^-), thiourea (TU) and 1-methyl-2-thiourea as entering ligands were followed. Each reaction was performed at four temperatures (approximately 15, 25, 35 and 45 °C) and the Rhenium concentration was kept constant at 1 x 10^{-4} M throughout.

Table S1: Temperature and [Br^-] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)$(CO)_3$(MeOH)] and bromide ions. [Re] = 1 x 10^{-4} M, λ = 430 nm, MeOH.

	k_{obs} (s^{-1})			
[Br^-] (M)	**15.7 °C**	**25.1 °C**	**34.9 °C**	**44.9 °C**
0.2	0.204(6)	0.578(3)	1.6810(7)	3.9610(7)
0.3	0.223(8)	0.628(2)	1.826(3)	4.335(2)
0.4	0.241(3)	0.6799(6)	1.968(3)	4.700(2)
0.5	0.2601(2)	0.729(1)	2.1084(8)	5.085(3)

Figure S1: Plot of k_{obs} *vs* [Br^-] for the reaction between *fac*-[Re(Trop)$(CO)_3$(MeOH)] and bromide ions at different temperatures. [Re] = 1.0 x 10^{-4} M, [Br^-] = 2.0 x 10^{-1} M – 5.0 x 10^{-1} M, 430 nm, MeOH.

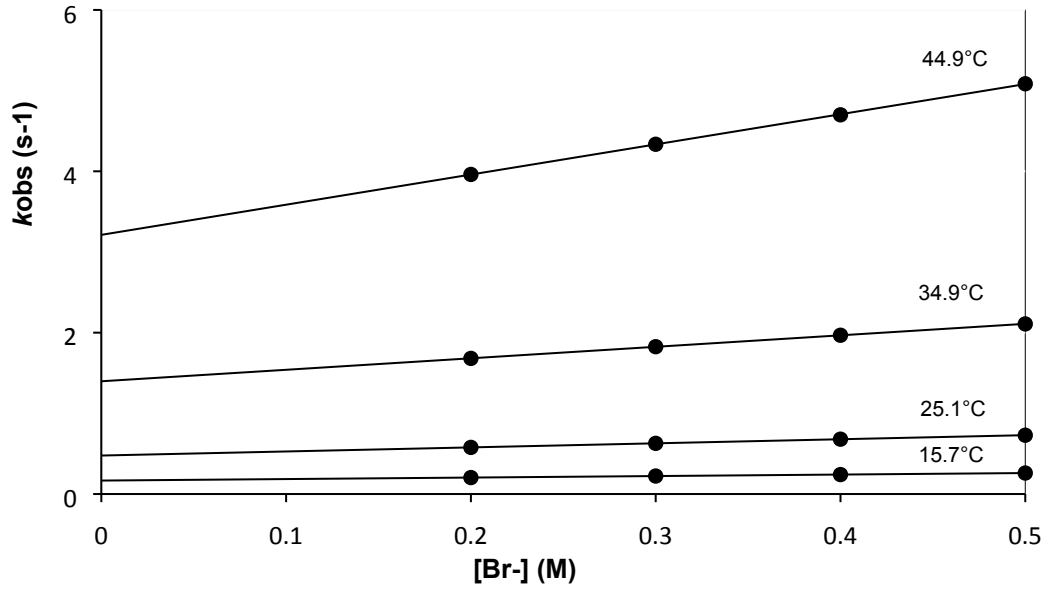


Table S2: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and bromide ions at different temperatures.

	15.7 °C	25.1 °C	34.9 °C	44.9 °C
k_L ($M^{-1}s^{-1}$)	0.186(1)	0.505(4)	1.424(7)	3.74(3)
k_{-L} (s^{-1})	0.1668(5)	0.477(1)	1.397(3)	3.21(1)
K_L (M^{-1})	1.115(7)	1.059(9)	1.019(5)	1.16(1)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		76.1(6)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		5(2)		

Figure S2: Eyring plot of ln(k_L/T) *vs* 1/T for the reactions between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and bromide ions for a temperature range of 15.7 °C to 44.9 °C.

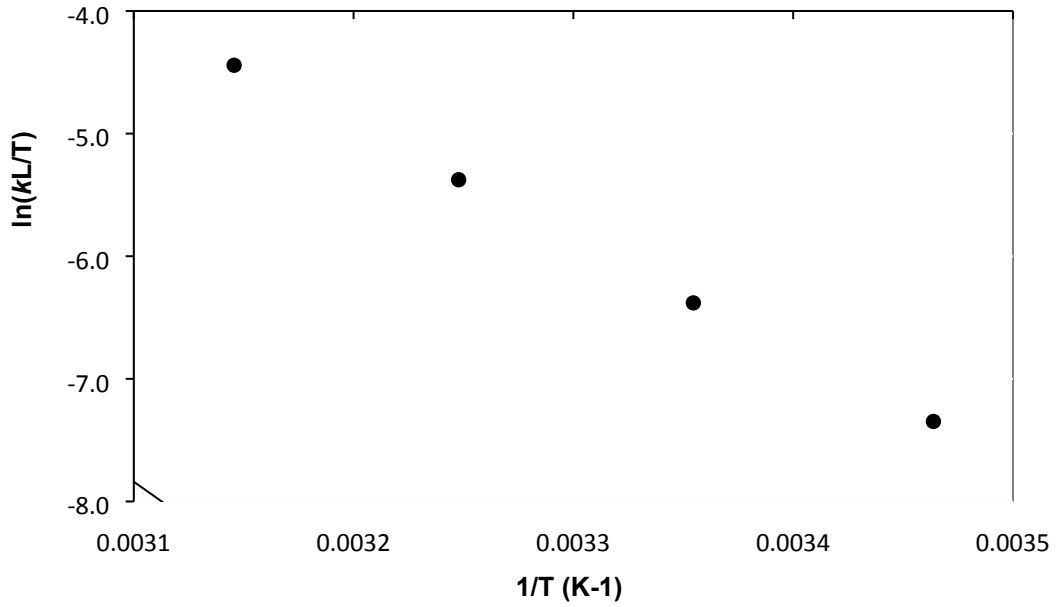


Table S3: Temperature and [I^-] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and iodide ions. [Re] = 1 x 10^{-4} M, λ = 430 nm, MeOH.

	k_{obs} (s^{-1})			
[I^-] (M)	15.8 °C	24.3 °C	34.4 °C	44.2 °C
0.2	0.306(3)	0.827(4)	2.51(1)	6.146(4)
0.3	0.338(4)	0.902(3)	2.748(7)	6.733(2)
0.4	0.370(2)	0.980(4)	2.969(6)	7.313(3)
0.5	0.402(1)	1.057(4)	3.191(4)	7.879(2)
0.6	0.433(2)	1.133(6)	3.411(5)	8.45(3)
0.7	0.4648(8)	1.2085(8)	3.624(5)	9.00(4)

Figure S3: Plot of k_{obs} *vs* [I^-] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and iodide ions at different temperatures. [Re] = 1.0 x 10^{-4} M, [I^-] = 2.0 x 10^{-1} M – 7.0 x 10^{-1} M, 430 nm, MeOH.

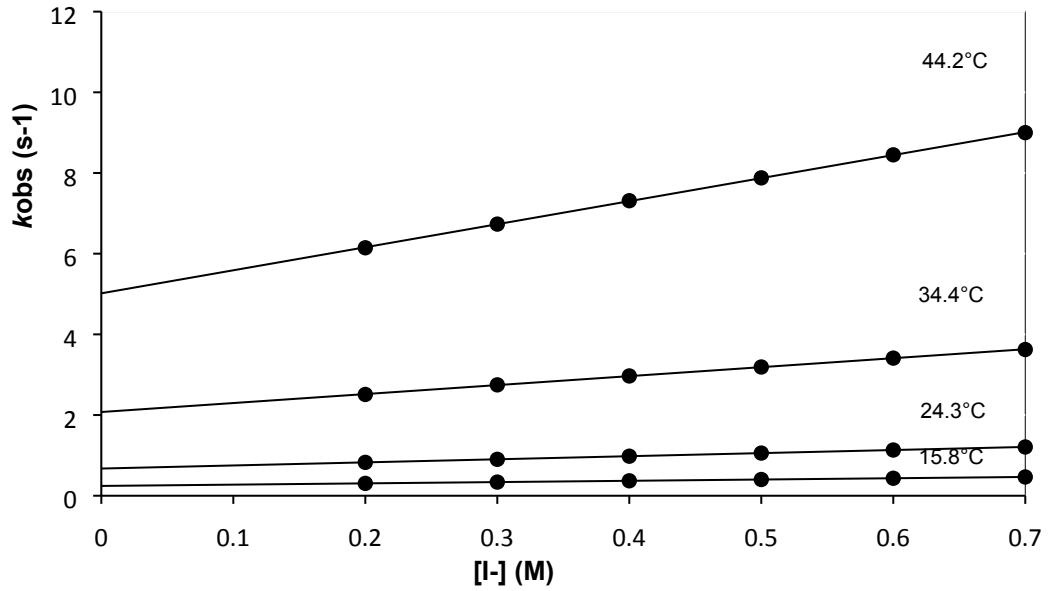


Table S4: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and iodide ions at different temperatures.

	15.8 °C	24.3 °C	34.4 °C	44.2 °C
k_L ($M^{-1}s^{-1}$)	0.3174(8)	0.765(2)	2.22(2)	5.71(3)
k_{-L} (s^{-1})	0.2428(4)	0.674(1)	2.075(9)	5.02(1)
K_L (M^{-1})	1.307(4)	1.136(3)	1.07(1)	1.137(6)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		75.3(9)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		6(3)		

Figure S4: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and iodide ions for a temperature range of 15.8 °C to 44.2 °C.

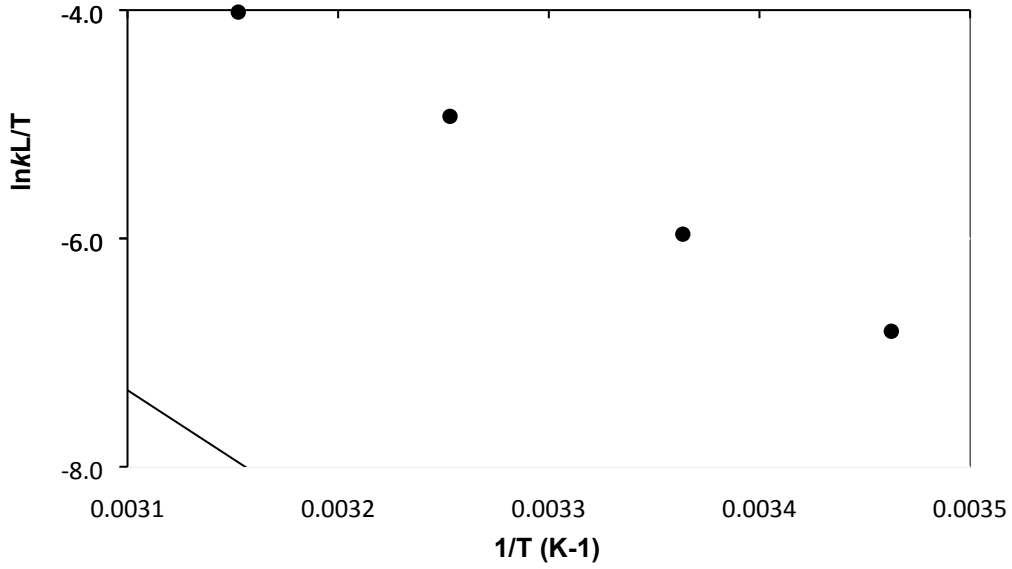


Table S5: Temperature and [Py] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine. [Re] = 1 x 10^{-4} M, λ = 312 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[Py] (M)	15.0 °C	25.0 °C	35.0 °C	45.0 °C
0.02	2.31(2)	5.34(2)	13.38(9)	36.1(2)
0.03	3.4(1)	7.97(1)	19.8(2)	52.7(4)
0.04	4.51(3)	10.6(3)	26.2(4)	67.4(1)
0.05	5.57(2)	13.2(6)	32.9(2)	82.5(4)
0.1	11.0(8)	26.4(8)	65.6(1)	157(8)
0.2	21.7(6)	52.7(3)	131.1(7)	308.5(9)

Figure S5a: Plot of k_{obs} *vs* [Py] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine at different temperatures. [Re] = 1.0 x 10^{-4} M, [Py] = 2.0 x 10^{-2} M – 2.0 x 10^{-1} M, 312 nm, MeOH.

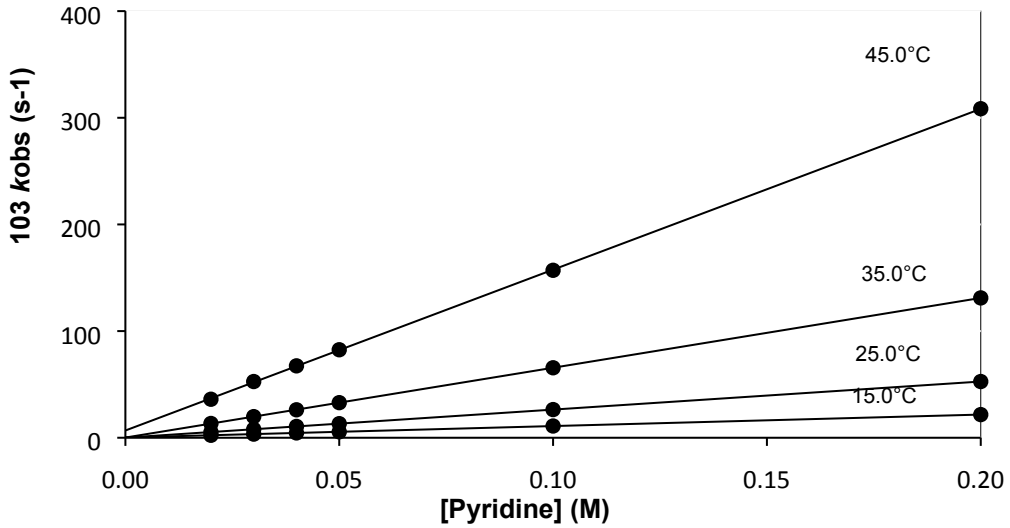


Figure S5b: Global fit of the Eyring Eq for k_{obs} *vs* [Py] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine at different temperatures. [Re] = 1.0 x 10^{-4} M, [Py] = 2.0 x 10^{-2} M – 2.0 x 10^{-1} M, 312 nm, MeOH.

Results from Global fit:

$\Delta H^{\neq}$ =(67± 1) kJ mol^{-1}; $\Delta S^{\neq}$ = (-30±3) JK^{-1}mol^{-1}.

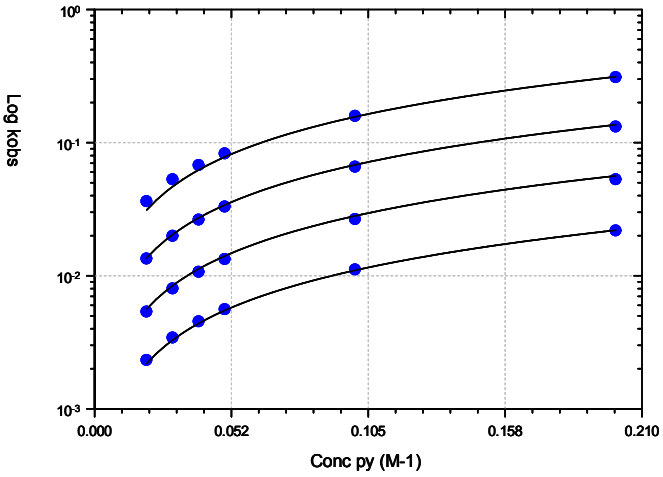


Table S6: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.1077(2)	0.2632(1)	0.6546(6)	1.508(4)
$10^3 k_{-L}$ (s^{-1})	0.18(2)	0.07(1)	0.16(6)	6.8(4)
K_L (M^{-1})	598(66)	3760(537)	4091(1534)	222(13)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		64.7(9)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-39(3)		

Figure S6: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine for a temperature range of 15.0 °C to 45.0 °C.

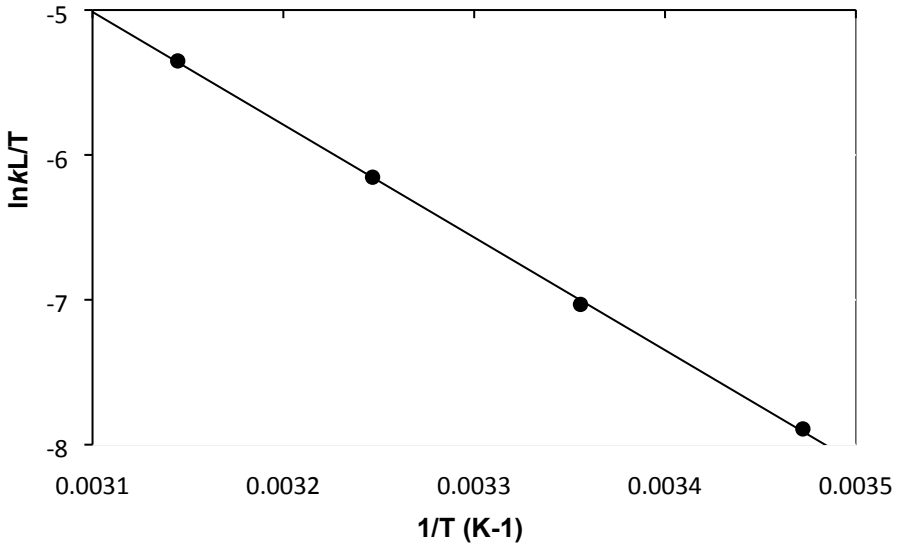


Table S7: Temperature and [Im] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and imidazole. [Re] = 1 x 10^{-4} M, λ = 255 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[Im] (M)	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.005	0.87(2)	1.826(9)	4.63(2)	10.65(4)
0.01	1.47(1)	3.45(4)	8.05(2)	18.6(3)
0.02	2.69(4)	6.22(3)	14.8(2)	32.8(6)
0.03	3.9(1)	8.91(2)	21.4(7)	49.0(8)
0.04	5.10(6)	12.0(4)	28.3(4)	63.9(2)
0.05	6.31(2)	14.80(9)	35.1(2)	79(1)

Figure S7: Plot of k_{obs} *vs* [Im] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and imidazole at different temperatures. [Re] = 1.0 x 10^{-4} M, [Im] = 5.0 x 10^{-3} – 5.0 x 10^{-2} M, 255 nm, MeOH.

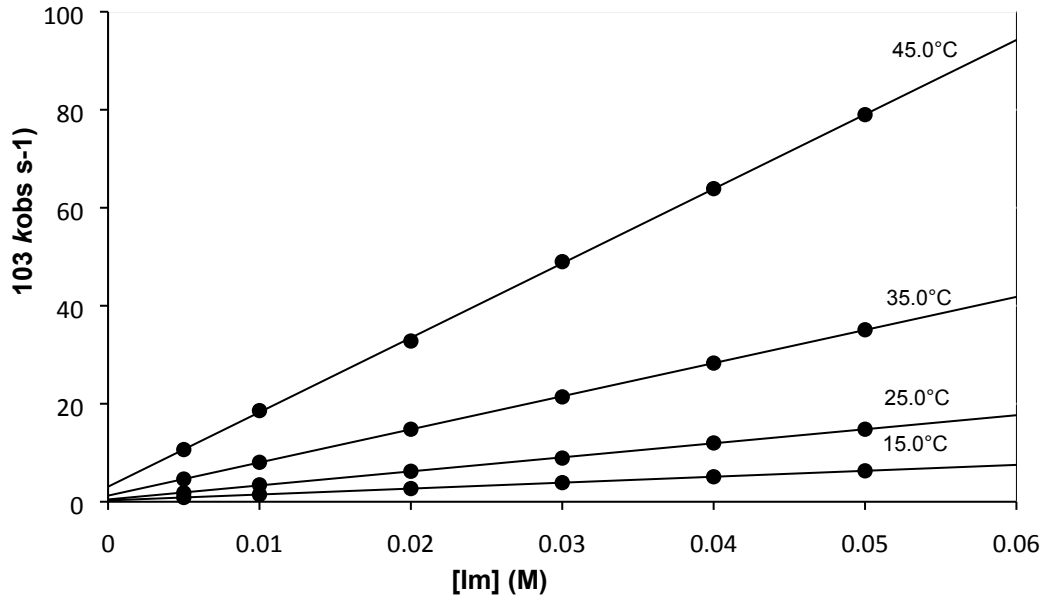


Table S8: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and imidazole at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.1209(1)	0.287(3)	0.676(2)	1.52(1)
$10^3 k_{-L}$ (s^{-1})	0.266(4)	0.46(9)	1.25(6)	3.1(3)
K_L (M^{-1})	455(7)	624(122)	541(26)	490(48)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		61.8(7)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-48(2)		

Figure S8: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and imidazole for a temperature range of 15.0 °C to 45.0 °C.

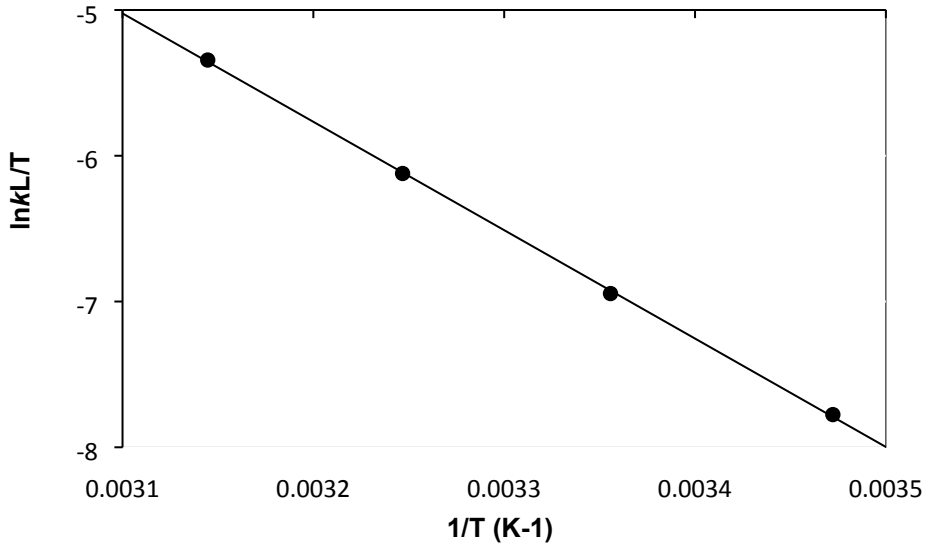


Table S9: Temperature and [NCS^-] dependence of the *pseudo* first-order reaction between *fac*-[$Re(Trop)(CO)_3(MeOH)$] and thiocyanate ions. [Re] = 1 x 10^{-4} M, λ = 265 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[NCS^-] (M)	15.0 °C	25.0 °C	35.0 °C	45.0 °C
0.02	3.80(2)	9.2(1)	24.2(7)	48.6(9)
0.03	4.93(1)	12.5(3)	29.6(4)	59.9(3)
0.04	6.13(4)	15.2(3)	35.1(9)	72.0(7)
0.05	7.193(6)	18.12(9)	41(2)	83.33(8)
0.1	12.2(4)	31.51(6)	72.1(3)	149(3)
0.2	22.16(6)	57.87(9)	136(2)	279(1)

Figure S9: Plot of k_{obs} *vs* [NCS^-] for the reaction between *fac*-[$Re(Trop)(CO)_3(MeOH)$] and NCS^- ions at different temperatures. [Re] = 1.0 x 10^{-4} M, [NCS^-] = 2.0 x 10^{-2} – 2.0 x 10^{-1} M, 265 nm, MeOH.

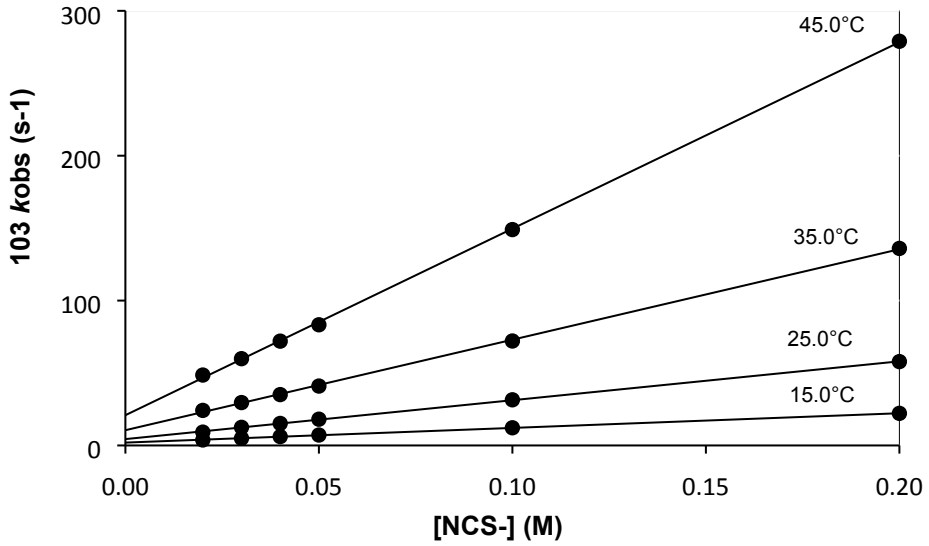


Table S10: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and NCS$^-$ ions at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.101(1)	0.268(2)	0.625(6)	1.29(1)
$10^3 k_{-L}$ (s^{-1})	2.0(1)	4.4(2)	10.5(6)	20.9(9)
K_L (M^{-1})	51(3)	61(3)	60(3)	62(3)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		62(2)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-48(6)		

Figure S10: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and NCS$^-$ ions for a temperature range of 15.0 °C to 45.0 °C.

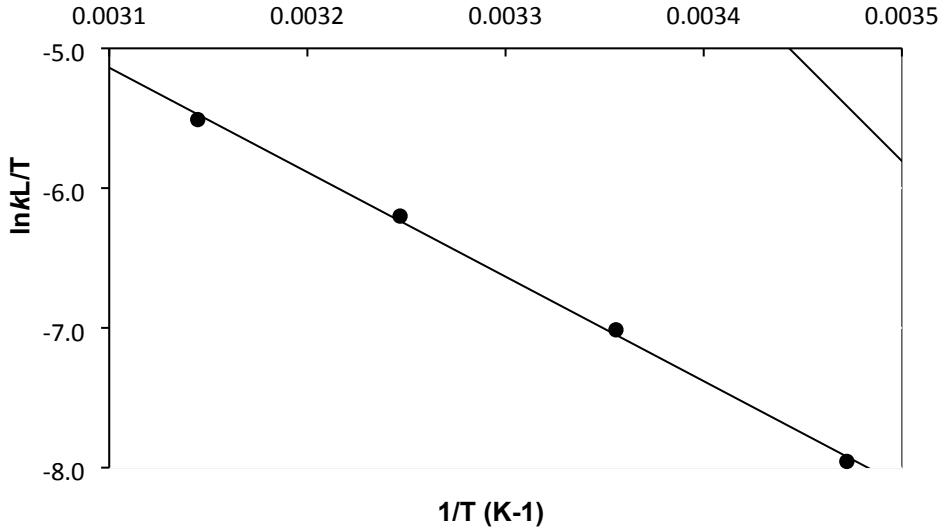


Table S11: Temperature and [DMAP] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and 4-dimethylaminopyridine. [Re] = 1 x 10^{-4} M, λ = 318 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[DMAP] (M)	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.005	1.37(4)	3.31(4)	6.75(3)	13.1(3)
0.01	2.14(3)	5.17(6)	11.09(8)	22.9(6)
0.02	3.7(1)	8.56(9)	18.9(6)	41.1(8)
0.03	5.27(8)	11.8(3)	26.9(4)	59.9(7)
0.04	6.83(2)	15.4(3)	35.7(7)	79.9(6)
0.05	8.4(1)	18.7(2)	44(1)	99(8)

Figure S11: Plot of k_{obs} *vs* [DMAP] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and DMAP at different temperatures. [Re] = 1.0 x 10^{-4} M, [DMAP] = 5.0 x 10^{-3} – 5.0 x 10^{-2} M, 318 nm, MeOH.

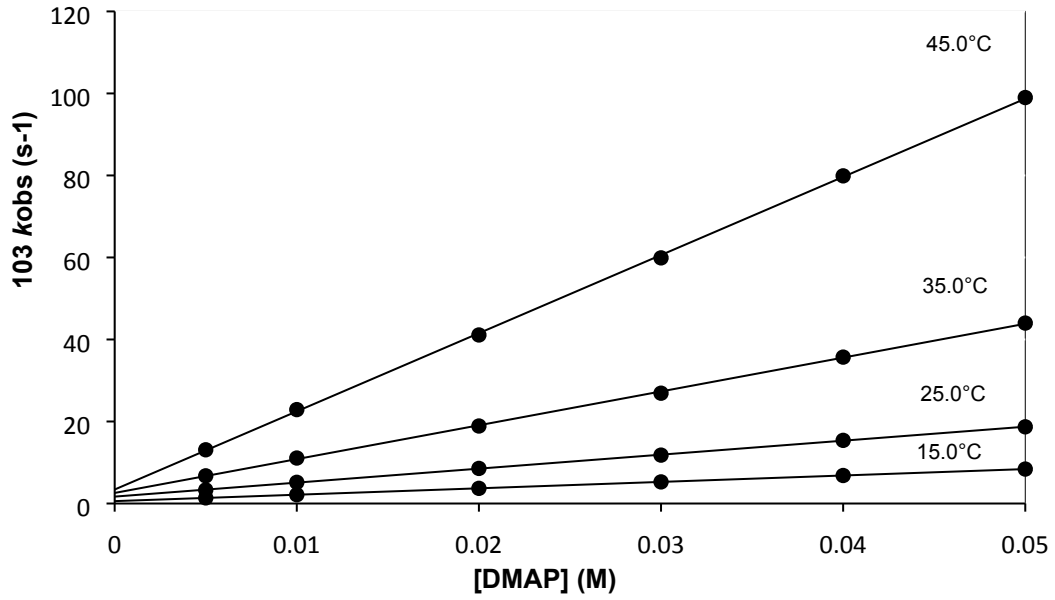


Table S12: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and DMAP at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.1563(2)	0.341(2)	0.825(7)	1.91(1)
$10^3 k_L$ (s^{-1})	0.581(5)	1.68(7)	2.6(2)	3.4(4)
K_L (M^{-1})	269(2)	203(9)	317(25)	562(66)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		61(2)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-47(7)		

Figure S12: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and DMAP for a temperature range of 15.0 °C to 45.0 °C.

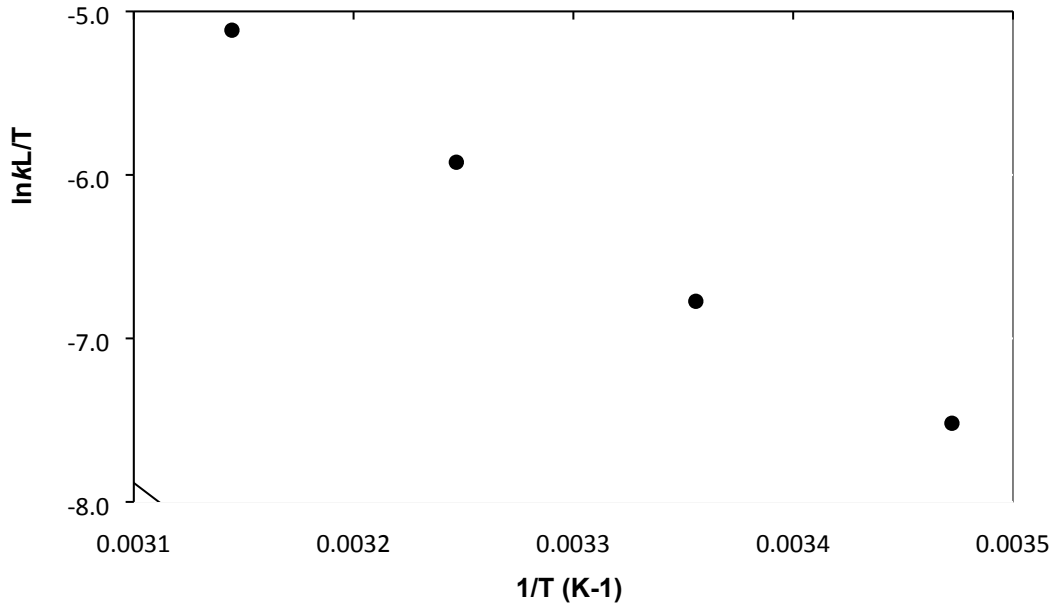


Table S13: Temperature and [TU] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and thiourea. [Re] = 1 x 10^{-4} M, λ = 440 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[TU] (M)	15.0 °C	25.0 °C	35.0 °C	45.0 °C
0.005	1.61(4)	3.710(8)	10.0(8)	27.31(9)
0.01	2.74(2)	6.62(4)	15.7(2)	40.8(4)
0.02	5.28(4)	12.1(8)	27.6(2)	66.7(2)
0.03	7.79(9)	17.5(2)	41.1(4)	95(1)
0.04	10.2(2)	23.14(8)	53.10(8)	120.9(6)
0.05	12.7(1)	28.91(9)	66(1)	147(2)

Figure S13a: Plot of k_{obs} *vs* [TU] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and thiourea at different temperatures. [Re] = 1.0 x 10^{-4} M, [TU] = 5.0 x 10^{-3} – 5.0 x 10^{-2} M, 440 nm, MeOH.

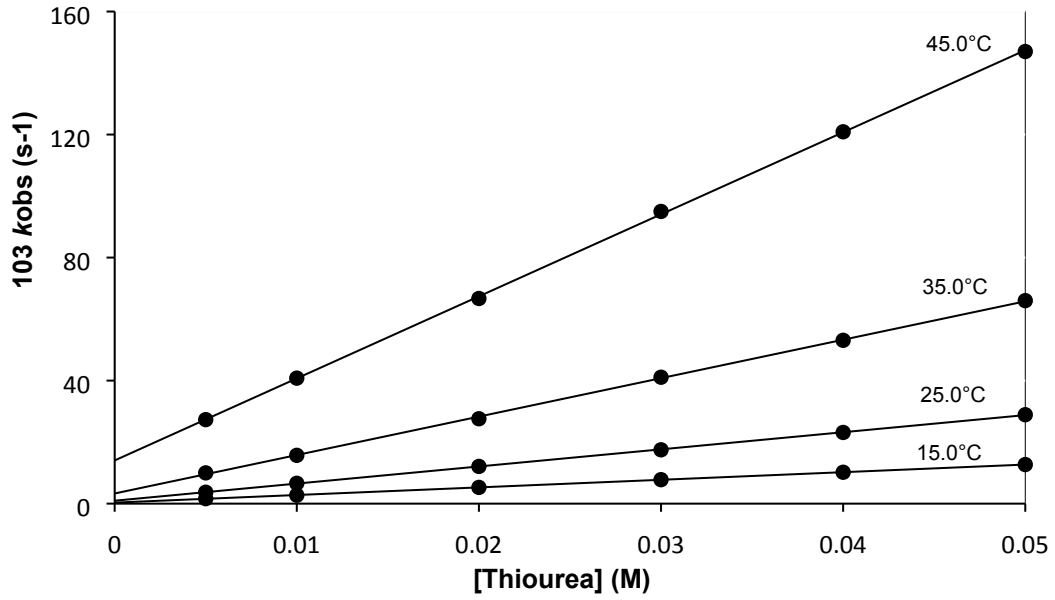


Figure S13b: Plot of A_{obs} *vs* [TU] for the reaction of *fac*-[Re(Trop)(CO)$_3$(MeOH)] with thiourea. [Re] = 1.0 x 10^{-4} M, 25.0 °C, 440 nm.

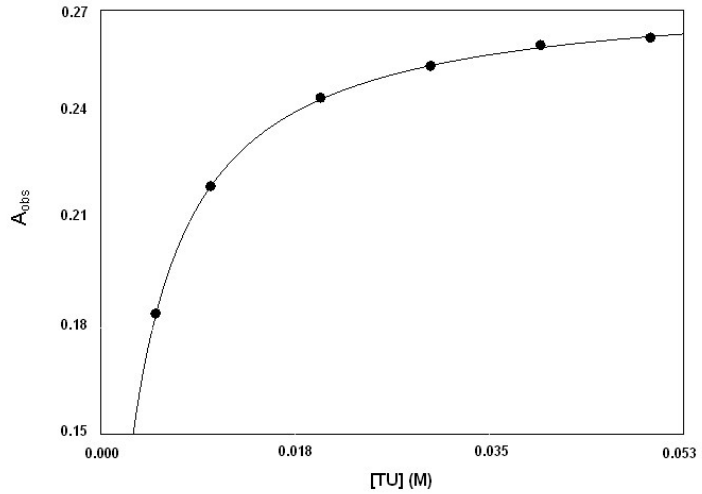


Table S14: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and thiourea at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.247(1)	0.556(3)	1.25(1)	2.67(2)
$10^3 k_{-L}$ (s^{-1})	0.33(3)	0.95(10)	3.3(4)	14.0(5)
K_L (M^{-1})	748(68)	585(62)	379(46)	191(7)
K_L (M^{-1})[a]	808(74)	373(35)	355(48)	344(33)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		58.0(7)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-55(2)		

[a] Thermodynamically determined.

Figure S14: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and thiourea for a temperature range of 15.0 °C to 45.0 °C.

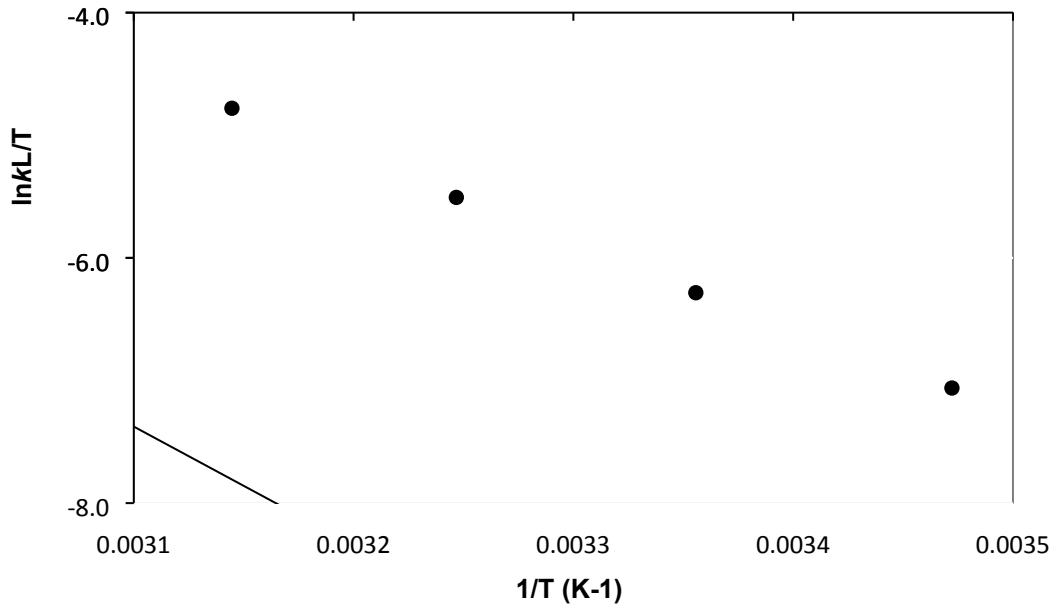


Table S15: Temperature and [MeTU] dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and 1-methyl-2-thiourea. [Re] = 1 x 10^{-4} M, λ = 435 nm, MeOH.

	10^3 k_{obs} (s^{-1})			
[MeTU] (M)	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.005	2.1(1)	5.00(3)	12.7(6)	33.6(3)
0.01	3.31(4)	8.12(4)	19.6(2)	49.1(2)
0.02	6.05(2)	14.3(2)	33.4(7)	79.2(4)
0.03	8.68(7)	20.6(3)	47.1(8)	109(3)
0.04	11.3(2)	26.8(4)	61.0(9)	139(7)
0.05	14.0(6)	33.2(3)	74.6(2)	169(8)

Figure S15: Plot of k_{obs} *vs* [MeTU] for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and MeTU at different temperatures. [Re] = 1.0 x 10^{-4} M, [MeTU] = 5.0 x 10^{-3} – 5.0 x 10^{-2} M, 435 nm, MeOH.

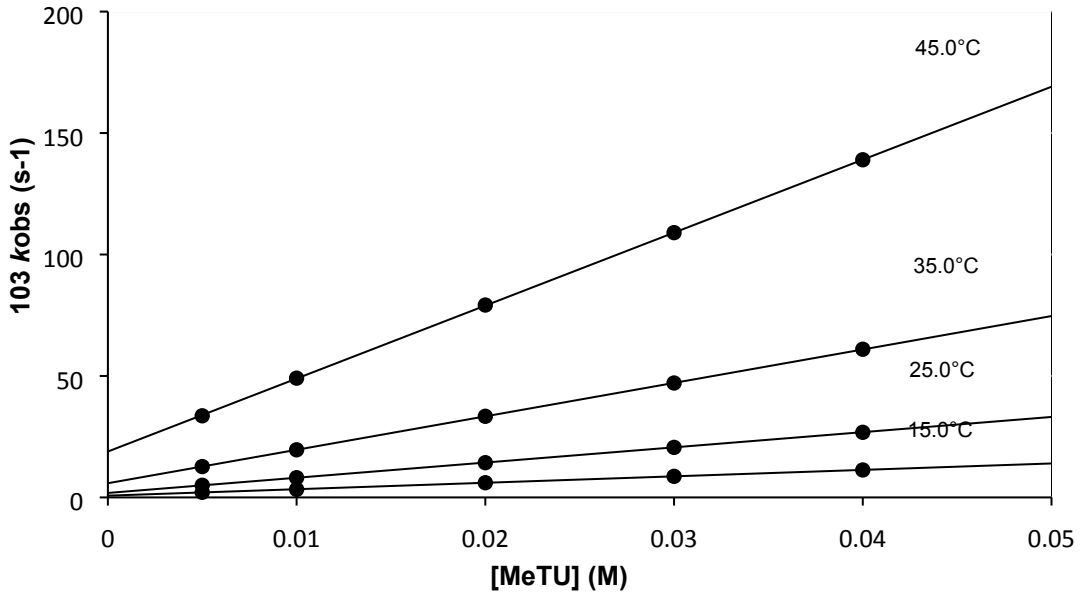


Table S16: Summary of the rate constants and activation parameters of the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and MeTU at different temperatures.

	15.0 °C	25.0 °C	35.0 °C	45.0 °C
k_L ($M^{-1}s^{-1}$)	0.265(1)	0.626(2)	1.377(2)	3.004(6)
$10^3 k_{-L}$ (s^{-1})	0.73(4)	1.84(5)	5.84(5)	18.9(2)
K_L (M^{-1})	363(20)	340(9)	236(2)	159(2)
$\Delta H^{\ddagger}_{(kL)}$ (kJ mol^{-1})		59.0(4)		
$\Delta S^{\ddagger}_{(kL)}$ (J K^{-1} mol^{-1})		-51(1)		

Figure S16: Eyring plot of ln(k_L/T) *vs* 1/T for the reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and MeTU for a temperature range of 15.0 °C to 45.0 °C.

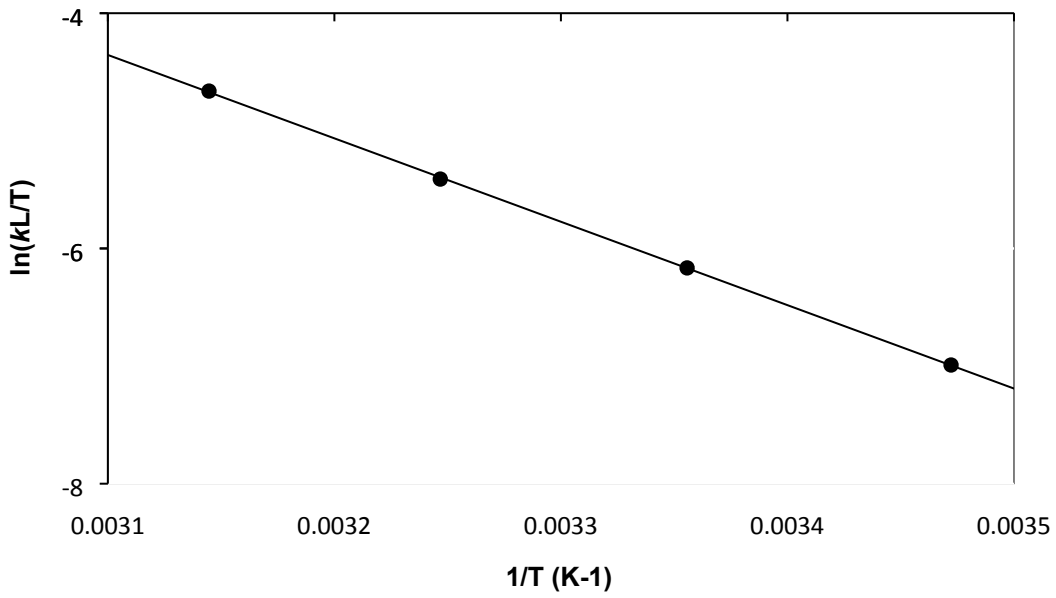
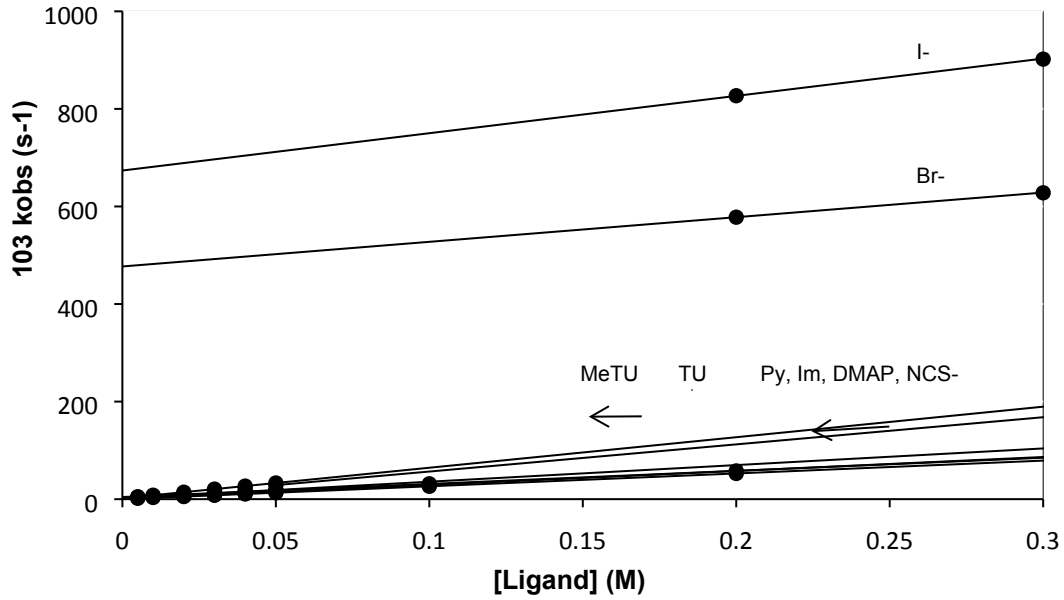


Figure S17: Plot of k_{obs} *vs* [ligand] of the reactions between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and various entering ligands at ~25 °C.



The methanol substitution reactions between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine (Py), imidazole (Im), thiourea (TU) and 1-methyl-2-thiourea as entering ligands were followed. Each reaction was performed at six pressures (0.6, 5, 10, 50, 80 and 100 MPa) and the Rhenium concentration was kept constant at 1 x 10^{-4} M throughout.

Table S17a: Pressure dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and pyridine. [Re] = 1 x 10^{-4} M, [Py] = 5 x 10^{-2} M, λ = 312 nm, 25.9 °C, MeOH.

Pressure (MPa)	k_{obs}
0.6	0.0113(7)
5	0.0111(7)
10	0.0107(3)
50	0.00929(9)
80	0.0081(2)
100	0.00755(7)

Table S17b: Pressure dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and imidazole. [Re] = 1 x 10^{-4} M, [Im] = 5 x 10^{-2} M, λ = 450 nm, 25.8 °C, MeOH.

Pressure (MPa)	k_{obs}
0.6	0.0177(2)
5	0.0172(4)
10	0.0169(8)
50	0.0145(9)
80	0.0131(7)
100	0.0123(3)

Table S17c: Pressure dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and thiourea. [Re] = 1 x 10^{-4} M, [TU] = 5 x 10^{-2} M, λ = 440 nm, 25.6 °C, MeOH.

Pressure (MPa)	k_{obs}
0.6	0.0342(3)
5	0.033(2)
10	0.032(1)
50	0.028(1)
80	0.0246(7)
100	0.0225(6)

Table S17d: Pressure dependence of the *pseudo* first-order reaction between *fac*-[Re(Trop)(CO)$_3$(MeOH)] and 1-methyl-2-thiourea. [Re] = 1 x 10^{-4} M, [MeTU] = 5 x 10^{-2} M, λ = 435 nm, 25.9 °C, MeOH.

Pressure (MPa)	k_{obs}
0.6	0.042(1)
5	0.0409(7)
10	0.0389(6)
50	0.0316(6)
80	0.0262(9)
100	0.0234(3)