

**Quantitation of Ligand Effect in oxo-transfer reactions from dioxo-Mo(VI) trispyrazolyl borate
complexes**

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Supporting Information.

Table S1. Phosphine parameters used in this investigation.

Phosphine	χ_d	Θ	E_{ar}	π_p
PMe ₃	8.55	118	0	0
PEt ₃	6.3	132	0	0
P ⁿ Bu ₃	5.25	136	0	0
PPh ₃	13.25	145	2.7	0
P(OMe) ₃	17.7	107	1	2.8
PMePh ₂	12.6	136	2.2	0
PEtPh ₂	11.1	140	2.3	0
PMe ₂ Ph	10.5	122	1	0
PEt ₂ Ph	8.6	136	1.1	0
P(OEt) ₂ Ph	15	121	1.7	1.9
P(OMe) ₂ Ph	16.4	120	1.7	1.9

Table S2. Phosphine oxide parameters used in this investigation.

Phosphine oxide	pK _a	Θ	E_{ar}	π_p
OPMe ₃	0.72	115.2	0	0
OPMe ₂ Ph	-0.49	111.7	1	0
OPEt ₃	0.72	113.5	0	0
PEt ₂ Ph	-7.98	111.7 ^a	1.1	0
OPBu ⁿ ₃	0.77	113.5 ^a	0	0
PMe Ph ₂	-1.28	123	2.2	0
PEtPh ₂	-7.98	123 ^a	2.3	0

Table S3: Variable Temperature rate constants of the reaction of Tp^{Me2}MoO₂(SPh) with PEtPh₂ in acetonitrile ([Tp^{Me2}MoO₂(SPh)] ~ 3.16 μM).

temp (°C)	k (M*sec) ⁻¹	k x10 ⁵ sec ⁻¹	lnk	ln(kh/k _b T)
14.5	0.0545	17.2	-8.67	-38.09
20	0.0752	23.8	-8.34	-37.78
26.5	0.126	39.9	-7.83	-37.29
31	0.210	66.3	-7.32	-36.80

lnA, 15.8 (±2.4); E_a, 58.7 (±6.7) kJ/mol (R² = 98.9); ΔH[‡], 59.0 (±5.1) kJ/mol; ΔS[‡], -112.4 (±17.1) J* mol⁻¹*K⁻¹ (R² = 99); ΔG[‡]₂₉₈, 92.5 kJ/mol.

Table S4: Variable Temperature rate constants of the reaction of Tp^{Me2}MoO₂(SPh) with PMe₃ in acetonitrile ([Tp^{Me2}MoO₂(SPh)] ~ 3.16 μM) (determined at 726 nm)

temp (°C)	k (M*sec) ⁻¹	k x10 ⁵ sec ⁻¹	lnk	ln(kh/k _b T)
10.5	0.0744	23.5	-8.36	-37.76

20	0.3855	122	-6.71	-36.15
40	0.4828	152	-6.49	-35.99

$\ln A, 9.8 (\pm 11.5)$; $E_a, 41.7 (\pm 28.2)$ kJ/mol ($R^2 = 83$); $\Delta H^\ddagger, 39.2 (\pm 28.1)$ kJ/mol; $\Delta S^\ddagger, -172.1 (\pm 94.9)$ J* mol^{-1} * K^{-1} ($R^2 = 81$); $\Delta G^\ddagger_{298}, 92.53$ kJ/mol.

Table S5: Variable Temperature rate constants of the reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}_2(\text{OPh})$ with PMe_3 in acetonitrile.

temp ($^\circ\text{C}$)	k ($\text{M}^*\text{sec}^{-1}$)	$k \times 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
4	0.0039	1.3	-11.26	-40.64
10	0.0151	5.1	-9.88	-39.29
18	0.0342	12.4	-9.00	-38.43
22.5	0.0418	15.1	-8.80	-38.25
27.5	0.0386	17.8	-8.63	-38.10

$\ln A, 22.03 (\pm 5.8)$; $E_a, 75.8 (\pm 13.9)$ kJ/mol ($R^2 = 95.3$); $\Delta H^\ddagger, 73.3 (\pm 13.9)$ kJ/mol; $\Delta S^\ddagger, -70.25 (\pm 48.9)$ J* mol^{-1} * K^{-1} ($R^2 = 95.0$); $\Delta G^\ddagger_{298}, 94.27$ kJ/mol.

Table S6: Variable Temperature rate constants of the reaction of $\text{TpMe}_2\text{MoO}_2(\text{OPh})$ with PMe_2Ph in acetonitrile.

temp ($^\circ\text{C}$)	k ($\text{M}^*\text{sec}^{-1}$)	$k \times 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
6	0.01448	4.8	-9.94	-39.33
11.5	0.02120	7.1	-9.56	-38.97
17.9	0.03969	13.3	-8.93	-38.36
22	0.06524	20.5	-8.49	-37.94

$\ln A, 16.75 (\pm 1.9)$; $E_a, 62.08 (\pm 4.6)$ kJ/mol ($R^2 = 99.5$); $\Delta H^\ddagger, 59.9 (\pm 4.5)$ kJ/mol; $\Delta S^\ddagger, -113.61 (\pm 15.6)$ J* mol^{-1} * K^{-1} ($R^2 = 99.5$); $\Delta G^\ddagger_{298}, 93.57$ kJ/mol.

Table S7: Variable Temperature rate constants of the reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}_2(\text{OPh})$ with PEt_3 in acetonitrile.

temp ($^\circ\text{C}$)	k ($\text{M}^*\text{sec}^{-1}$)	$k \times 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
7.5	0.00747	2.5	-10.58	-39.98
12	0.00793	2.7	-10.52	-39.93
17	0.01588	5.4	-9.83	-39.26
19	0.02879	9.8	-9.23	-38.67
23	0.02746	9.3	-9.28	-38.73

$\ln A, 18.9 (\pm 6.4)$; $E_a, 69.16 (\pm 15.3)$ kJ/mol ($R^2 = 93.4$); $\Delta H^\ddagger, 66.8 (\pm 15.1)$ kJ/mol; $\Delta S^\ddagger, -95.3 (\pm 52.3)$ J* mol^{-1} * K^{-1} ($R^2 = 93.1$); $\Delta G^\ddagger_{298}, 95.28$ kJ/mol.

Table S8: Variable Temperature rate constants of the reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}_2(\text{OPh})$ with PEt_2Ph in acetonitrile.

temp (°C)	$k \text{ M}^{-1}\text{sec}^{-1}$	$k \times 10^5 \text{ sec}^{-1}$	$\ln k$	$\ln(kh/k_bT)$
12.5	0.00583	1.9	-10.85	-28.96
17.5	0.00863	2.9	-10.46	-28.55
23.5	0.01517	4.8	-9.95	-28.02
31	0.030501	7.9	-9.44	-27.48

$\ln A, 12.5 (\pm 0.5)$; $E_a, 55.50 (\pm 1.3) \text{ kJ/mol}$ ($R^2 = 99.9$); $\Delta H^\ddagger, 58.2 (\pm 1.2) \text{ kJ/mol}$; $\Delta S^\ddagger, -36.9 (\pm 4.2) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ($R^2 = 99.9$); $\Delta G^\ddagger_{298}, 69.23 \text{ kJ/mol}$.

Table S9: Variable Temperature rate constants of the reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}_2(\text{OPh})$ with PMePh_2 in acetonitrile.

temp (°C)	$k \text{ (M}^{-1}\text{sec)}^{-1}$	$k \times 10^5 \text{ (sec)}^{-1}$	$\ln k$	$\ln(kh/k_bT)$
10	0.0039	1.29	-11.26	-29.37
16	0.0055	1.82	-10.91	-29.01
22	0.0101	3.17	-10.36	-28.43
27	0.0143	4.75	-9.96	-28.01
31	0.0147	4.86	-9.93	-27.97

$\ln A, 9.71 (\pm 1.9)$; $E_a, 49.4 (\pm 4.7) \text{ kJ/mol}$ ($R^2 = 98.7$); $\Delta H^\ddagger, 51.9 (\pm 4.8) \text{ kJ/mol}$; $\Delta S^\ddagger, -60.8 (\pm 16.4) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ($R^2 = 98.7$); $\Delta G^\ddagger_{298}, 70.09 \text{ kJ/mol}$.

Table S10. Variable Temperature rate constants of the reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}_2(\text{OPh})$ with PEtPh_2 in acetonitrile.

temp (°C)	$k \text{ (M}^{-1}\text{sec)}^{-1}$	$k \times 10^5 \text{ (sec)}^{-1}$	$\ln k$	$\ln(kh/k_bT)$
10	0.0013	0.43	-12.35	-30.47
16	0.00193	0.65	-11.94	-30.04
26	0.00364	1.24	-11.30	-29.36
31	0.0064	2.12	-10.76	-28.80

$\ln A, 9.9 (\pm 1.8)$; $E_a, 52.4 (\pm 4.4) \text{ kJ/mol}$ ($R^2 = 99.3$); $\Delta H^\ddagger, 55.2 (\pm 4.5) \text{ kJ/mol}$; $\Delta S^\ddagger, -58.6 (\pm 15.2) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ($R^2 = 99.3$); $\Delta G^\ddagger_{298}, 72.69 \text{ kJ/mol}$.

Table S11. Variable Temperature rate constants for the solvation reaction of $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPMe}_3)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$

T (°C)	$k \cdot 10^5 \text{ (sec)}^{-1}$	$\ln k$	$\ln(kh/k_bT)$
20	4.12	-10.10	-39.54
26	8.33	-9.39	-38.85
32	17.00	-8.68	-38.16
37	31.30	-8.069	-37.57

$\ln A$, 26.9 (± 0.54); E_a , 90.1 (± 1.3) kJ/mol ($R^2=99.9$); ΔH^\ddagger , 87.4 (± 1.2) kJ/mol; ΔS^\ddagger , -30.6 (± 4.0) J* mol^{-1} * K^{-1} ($R^2=99.9$); ΔG^\ddagger_{298} , 96.6 kJ/mol.

Table S12. Variable Temperature rate constants for the solvation reaction of $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPMe}_2\text{Ph})$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$.

T (°C)	$k \cdot 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
9	3.30	-10.32	-39.72
16	8.04	-9.43	-38.86
21	18.0	-8.62	-38.08
32	54.9	-7.51	-36.99

$\ln A$, 27.4 (± 2.0); E_a , 88.4 (± 4.8) kJ/mol ($R^2 = 99.7$); ΔH^\ddagger , 88.9 (± 4.5) kJ/mol; ΔS^\ddagger , -25.6 (± 15.6) J* mol^{-1} * K^{-1} ($R^2 = 99.7$); ΔG^\ddagger_{298} , 96.5 kJ/mol.

Table S13. Variable Temperature rate constants for the solvation reaction of $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPEt}_3)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$.

T (°C)	$k \cdot 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
9	2.24	-10.71	-40.11
16	6.52	-9.638	-39.06
21	12.1	-9.021	-38.46
32	33.6	-7.99	-37.48

$\ln A$, 25.0 (± 2.6); E_a , 84.0 (± 6.3) kJ/mol ($R^2 = 99.4$); ΔH^\ddagger , 81.13 (± 6.6) kJ/mol; ΔS^\ddagger , -44.7 (± 22.5) J* mol^{-1} * K^{-1} ($R^2 = 99.3$); ΔG^\ddagger_{298} , 94.5 kJ/mol.

Table S14. Variable Temperature rate constants for the solvation reaction of $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPEt}_2\text{Ph})$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$.

T (°C)	T (1/K)	$k \cdot 10^5$ (sec^{-1})	$\ln k$	$\ln(kh/k_bT)$
9	0.003544	10.2	-9.19	-38.60
16	0.003458	26.00	-8.25	-37.68
21	0.0034	56.6	-7.48	-36.92
32	0.003277	190.3	-6.26	-35.75

$\ln A$, 29.9 (± 1.4); E_a , 91.77 (± 3.4) kJ/mol ($R^2 = 99.8$); ΔH^\ddagger , 89.3 (± 3.7) kJ/mol; ΔS^\ddagger , -4.0 (± 12.7) J* mol^{-1} * K^{-1} ($R^2 = 99.8$); ΔG^\ddagger_{298} , 91.8 kJ/mol.

Table S15. Variable Temperature rate constants for the solvation reaction $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPBu}^n_3)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$

T (°C)	T (1/K)	$k \cdot 10^5$ (sec ⁻¹)	lnk	ln(kh/k _b T)
16	0.003458	6.60	-9.63	-39.05
21	0.0034	12.60	-8.98	-38.42
26	0.003343	18.50	-8.60	-38.06
32	0.003277	44.60	-7.72	-37.20

lnA, 25.7 (±3.0); E_a, 84.9 (±7.3) kJ/mol (R² =99.3); ΔH[‡], 82.9 (±7.3) kJ/mol; ΔS[‡], -40.5 (±24.8) J* mol^{-1} *K⁻¹ (R² =99.2); ΔG[‡]₂₉₈, 94.23 kJ/mol.

Table S16. Variable Temperature rate constants for the solvation reaction $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPMePh}_2)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$.

T (°C)	$k \cdot 10^5$ (sec ⁻¹)	lnk	ln(kh/k _b T)	
16	57.50	-7.46	-36.89	
21	107.5	-6.84	-36.28	
27	190.9	-6.26	-35.73	
32	303.0	-5.80	-35.28	lnA,

24.

0 (±1.2); E_a, 75.6 (±3.1) kJ/mol (R² =99.8); ΔH[‡], 73.1 (±3.3) kJ/mol; ΔS[‡], -53.3 (±11.0) J* mol^{-1} *K⁻¹ (R² =99.8); ΔG[‡]₂₉₈, 98.06 kJ/mol.

Table S17: Variable Temperature rate constants for the solvation reaction $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPEtPh}_2)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$.

T (°C)	$k \cdot 10^5$ (sec ⁻¹)	lnk	ln(kh/k _b T)
16	117.3	-6.75	-36.18
21	237.6	-6.04	-35.49
27	416.1	-5.48	-34.95
32	693.4	-4.97	-34.45

lnA, 26.7 (±1.9); E_a, 80.13 (±4.8) kJ/mol (R² = 99.6); ΔH[‡], 80.1 (±4.8) kJ/mol; ΔS[‡], -31.1 (±15.8) J* mol^{-1} *K⁻¹ (R² = 99.6); ΔG[‡]₂₉₈, 89.4 kJ/mol.

Table S18. Variable Temperature rate constants for the solvation reaction of $\text{Tp}^{\text{Me}_2}\text{MoO}(\text{SPh})(\text{OPEtPh}_2)$ to $\text{Tp}^{\text{Me}_2}\text{MoO}(\text{SPh})(\text{NCMe})$.

T (°C)	$k \cdot 10^5$ (sec ⁻¹)	lnk	ln(kh/k _b T)
14.5	151.4	-6.49	-35.91
20	332.1	-5.71	-35.15
26.5	754.2	-4.89	-34.35
31	1498.2	-4.20	-33.68

lnA, 35.3 (±1.2); E_a, 99.6 (±2.9) kJ/mol (R² =99.9); ΔH[‡], 97.0 (±2.8) kJ/mol; ΔS[‡], 38.6 (±9.5) J*mol⁻¹*K⁻¹ (R² =99.9); ΔG[‡]₂₉₈, 85.49 kJ/mol.

Table S19. Acetonitrile Dependence on the Solvation of $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPMe}_3)$ to $\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{NCMe})$

[$\text{Tp}^{\text{Me}_2}\text{MoOCl}(\text{OPMe}_3)$] (M)	[MeCN] (M)	$k \cdot 10^5$ (M·sec) ⁻¹
0.003059	0.2	5.82
0.00516	3.8	13.67
0.005736	7.6	14.02
0.004015	11.42	21.67
0.004971	15.2	19.06
0.00325	17.1	23.04
0.00516	19.0	31.45