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^nBu_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_2Ph	10.5	122	1	0
PEt_2Ph	8.6	136	1.1	0
$P(OEt)_2Ph$	15	121	1.7	1.9
$P(OMe)_2Ph$	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
$OPMe_2Ph$	-0.49	111.7	1	0
$OPEt_3$	0.72	113.5	0	0
PEt_2Ph	-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 $Tp^{Me2}MoO_2(SPh)$ with $PEtPh_2$ in acetonitrile ([$Tp^{Me2}MoO_2(SPh)$] ~ 3.16 μM).

temp (°C)	k $(M*sec)^{-1}$	k x10^5 sec^{-1}	lnk	ln(kh/k_bT)
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 (R^2 = 98.9); $\Delta H^{\ddagger}$, 59.0 (±5.1) kJ/mol; $\Delta S^{\ddagger}$, -112.4 (±17.1) $J*mol^{-1}*K^{-1}$ (R^2 = 99); $\Delta G^{\ddagger}_{298}$, 92.5 kJ/mol.

Table S4: Variable Temperature rate constants of the reaction of $Tp^{Me2}MoO_2(SPh)$ with PMe_3 in acetonitrile ([$Tp^{Me2}MoO_2(SPh)$] ~ 3.16 μM) (determined at 726 nm)

temp (°C)	k $(M*sec)^{-1}$	k x10^5 sec^{-1}	lnk	ln(kh/k_bT)
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

lnA,9.8 (±11.5); E_a, 41.7 (±28.2) kJ/mol (R^2 = 83); $\Delta H^{\ddagger}$, 39.2 (±28.1) kJ/mol; $\Delta S^{\ddagger}$, -172.1 (±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 $Tp^{Me2}MoO_2(OPh)$ with PMe_3 in acetonitrile.

temp (°C)	k (M*sec)$^{-1}$	k x 10^5(sec)$^{-1}$	lnk	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

lnA,22.03 (±5.8); E_a, 75.8 (±13.9) kJ/mol (R^2= 95.3); $\Delta H^{\ddagger}$, 73.3 (±13.9) kJ/mol; $\Delta S^{\ddagger}$, -70.25 (±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 TpMe2MoO2(OPh) with PMe_2Ph in acetonitrile.

temp (°C)	k (M*sec)$^{-1}$	k x 10^5(sec)$^{-1}$	lnk	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

lnA,16.75 (±1.9); E_a, 62.08 (±4.6) kJ/mol (R^2 = 99.5); $\Delta H^{\ddagger}$, 59.9 (±4.5) kJ/mol; $\Delta S^{\ddagger}$, -113.61 (±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 $Tp^{Me2}MoO_2(OPh)$ with PEt_3 in acetonitrile.

temp (°C)	k (M*sec)$^{-1}$	k x 10^{5}sec^{-1}	lnk	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

lnA,18.9 (±6.4); E_a, 69.16 (±15.3) kJ/mol(R^2 =93.4); $\Delta H^{\ddagger}$, 66.8 (±15.1) kJ/mol; $\Delta S^{\ddagger}$, -95.3 (±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 $Tp^{Me2}MoO_2(OPh)$ with PEt_2Ph in acetonitrile.

temp (°C)	k $M*sec^{-1}$	k x $10^5 sec^{-1}$	lnk	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

lnA,12.5 (±0.5); E_a, 55.50 (±1.3) kJ/mol (R^2 = 99.9); $\Delta H^{‡}$, 58.2 (±1.2) kJ/mol; $\Delta S^{‡}$, -36.9 (±4.2) $J*mol^{-1}*K^{-1}$(R^2 = 99.9); $\Delta G^{‡}_{298}$, 69.23 kJ/mol.

Table S9: Variable Temperature rate constants of the reaction of $Tp^{Me2}MoO_2(OPh)$ with $PMePh_2$ in acetonitrile.

temp (ºC)	k $(M*sec)^{-1}$	k x $10^5(sec)^{-1}$	lnk	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

lnA, 9.71 (±1.9); E_a, 49.4 (±4.7) kJ/mol (R^2 =98.7); $\Delta H^{‡}$, 51.9 (±4.8) kJ/mol; $\Delta S^{‡}$, -60.8 (±16.4) $J*mol^{-1}*K^{-1}$(R^2 =98.7); $\Delta G^{‡}_{298}$, 70.09 kJ/mol.

Table S10. Variable Temperature rate constants of the reaction of $Tp^{Me2}MoO_2(OPh)$ with $PEtPh_2$ in acetonitrile.

temp (°C)	k $(M*sec)^{-1}$	k x $10^5(sec)^{-1}$	lnk	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

lnA,9.9 (±1.8); E_a, 52.4 (±4.4) kJ/mol (R^2 =99.3); $\Delta H^{‡}$, 55.2 (±4.5) kJ/mol; $\Delta S^{‡}$, -58.6 (±15.2) $J*mol^{-1}*K^{-1}$ (R^2 =99.3); $\Delta G^{‡}_{298}$, 72.69 kJ/mol.

Table S11. Variable Temperature rate constants for the solvation reaction of $Tp^{Me2}MoOCl(OPMe_3)$ to $Tp^{Me2}MoOCl(NCMe)$

T (°C)	k·10^5 (sec^{-1})	lnk	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

lnA, 26.9 (±0.54); E_a, 90.1 (±1.3) kJ/mol (R^2=99.9); $\Delta H^{‡}$, 87.4 (±1.2) kJ/mol; $\Delta S^{‡}$, -30.6 (±4.0) J*mol^{-1}*K^{-1} (R^2=99.9); $\Delta G^{‡}_{298}$, 96.6 kJ/mol.

Table S12. Variable Temperature rate constants for the solvation reaction o $Tp^{Me2}MoOCl(OPMe_2Ph)$ to $Tp^{Me2}MoOCl(NCMe)$.

T (°C)	k·10^5 (sec^{-1})	lnk	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

lnA, 27.4 (±2.0); E_a, 88.4 (±4.8) kJ/mol (R^2 =99.7); $\Delta H^{‡}$, 88.9 (±4.5) kJ/mol; $\Delta S^{‡}$, -25.6 (± 15.6) J*mol^{-1}*K^{-1} (R^2 =99.7); $\Delta G^{‡}_{298}$, 96.5 kJ/mol.

Table S13. Variable Temperature rate constants for the solvation reaction of $Tp^{Me2}MoOCl(OPEt_3)$ to $Tp^{Me2}MoOCl(NCMe)$.

T (°C)	k·10^5 (sec^{-1})	lnk	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

lnA, 25.0 (±2.6); E_a, 84.0 (±6.3) kJ/mol (R^2 =99.4); $\Delta H^{‡}$, 81.13 (±6.6) kJ/mol; $\Delta S^{‡}$, -44.7 (±22.5) J*mol^{-1}*K^{-1} (R^2 =99.3); $\Delta G^{‡}_{298}$, 94.5 kJ/mol.

Table S14. Variable Temperature rate constants for the solvation reaction of $Tp^{Me2}MoOCl(OPEt_2Ph)$ to $Tp^{Me2}MoOCl(NCMe)$.

T (°C)	T (1/K)	k·10^5 (sec^{-1})	lnk	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

lnA, 29.9 (±1.4); E_a, 91.77 (±3.4) kJ/mol (R^2 =99.8); $\Delta H^{‡}$, 89.3 (±3.7) kJ/mol; $\Delta S^{‡}$, -4.0 (±12.7) J*mol^{-1}*K^{-1} (R^2 =99.8); $\Delta G^{‡}_{298}$, 91.8 kJ/mol.

Table S15. Variable Temperature rate constants for the solvation reaction $Tp^{Me2}MoOCl(OPBu^n_3)$ to $Tp^{Me2}MoOCl(NCMe)$

T (°C)	T (1/K)	$k \cdot 10^5$ (sec^{-1})	lnk	$ln(kh/k_bT)$
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 (R^2 =99.3); $\Delta H^{\ddagger}$, 82.9 (±7.3) kJ/mol; $\Delta S^{\ddagger}$, -40.5 (±24.8) $J*mol^{-1}*K^{-1}$ (R^2 =99.2); $\Delta G^{\ddagger}_{298}$, 94.23 kJ/mol.

Table S16. Variable Temperature rate constants for the solvation reaction $Tp^{Me2}MoOCl(OPMePh_2)$ to $Tp^{Me2}MoOCl(NCMe)$.

T (ºC)	$k \cdot 10^5$ (sec^{-1})	lnk	$ln(kh/k_bT)$
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 (R^2 =99.8); $\Delta H^{\ddagger}$, 73.1 (±3.3) kJ/mol; $\Delta S^{\ddagger}$, -53.3 (±11.0) $J*mol^{-1}*K^{-1}$ (R^2 =99.8); $\Delta G^{\ddagger}_{298}$, 98.06 kJ/mol.

Table S17: Variable Temperature rate constants for the solvation reaction $Tp^{Me2}MoOCl(OPEtPh_2)$ to $Tp^{Me2}MoOCl(NCMe)$.

T (ºC)	$k \cdot 10^5$ (sec^{-1})	lnk	$ln(kh/k_bT)$
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 (R^2 = 99.6); $\Delta H^{\ddagger}$, 80.1 (±4.8) kJ/mol; $\Delta S^{\ddagger}$, -31.1 (±15.8) $J*mol^{-1}*K^{-1}$ (R^2 = 99.6); $\Delta G^{\ddagger}_{298}$, 89.4 kJ/mol.

Table S18. Variable Temperature rate constants for the solvation reaction of $Tp^{Me2}MoO(SPh)(OPEtPh_2)$ to $Tp^{Me2}MoO(SPh)(NCMe)$.

T (°C)	$k \cdot 10^5$ (sec^{-1})	lnk	$ln(kh/k_bT)$
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 (R^2 =99.9); $\Delta H^{\ddagger}$, 97.0 (±2.8) kJ/mol; $\Delta S^{\ddagger}$, 38.6 (±9.5) J*mol^{-1}*K^{-1} (R^2 =99.9); $\Delta G^{\ddagger}_{298}$, 85.49 kJ/mol.

Table S19. Acetonitrile Dependence on the Solvation of $Tp^{Me2}MoOCl(OPMe_3)$ to $Tp^{Me2}MoOCl(NCMe)$

$[Tp^{Me2}MoOCl(OPMe_3)]$ (M)	[MeCN] (M)	$k \cdot 10^5$ $(M \cdot sec)^{-1}$
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