The Influence of the Oxygen Atom Acceptor on the Reaction Coordinate and Mechanism of Oxygen Atom Transfer From the Dioxo-Mo(VI) Complex, $Tp^{iPr}MoO_2(OPh)$, to Tertiary Phosphines

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Supporting Information.

Contents:

Table S1. ^{31}P chemical shifts (ppm) for complexes (**2a**-**2g**), the free phosphine and free phosphine oxide.					
complexes	OPR_3^F	PR_3^F	$Mo(OPR_3)^C$	$\Delta(PR_3^F - Mo(OPR_3)^C)$	$\Delta(OPR_3^F - Mo(OPR_3)^C)$
$OPMe_3$ **(2a)**	35.6	-62.0	64.0	-126	-28.4
$OPMe_2Ph$ **(2b)**	28.9	-46.9	58.4	-105.3	-29.5
$OPEt_3$ **(2c)**	48.3	-20.4	74.9	-95.3	-26.6
$OPEt_2Ph$ **(2d)**	42.1	-15.1	64.8	-79.9	-22.7
$OPBu^n_3$ **(2e)**	45.5	-32.2	74.4	-106.6	-28.9
$OPMePh_2$ **(2f)**	32.4	-10.8	72.8	-83.6	-40.4
$OPEtPh_2$ **(2g)**	31.9	-12.0	43.2	-55.2	-11.3
F and C indicate free phosphine (or free phosphine oxide) and coordinated phosphine oxide.					

Table S2. Selected ^{1}H NMR data (for the *i*-Pr and 5-methine protons of Tp^{iPr}) for **2a**-**2g**.						
Complex	CH (*i*-Pr^1)	CH (*i*-Pr^2)	CH (*i*-Pr^3)	CH^1	CH^2	CH^3
2a	2.73	4.09	4.41	5.84	5.99	6.30
2b	3.46	4.02	4.79	6.44	6.70	6.70
2c	3.11	3.69	4.29	6.06	6.27	6.43
2d	2.72	4.17	4.34	5.87	5.98	6.02
2e	2.61	4.23	4.45	5.87	5.96	6.01
2f	3.46	4.02	4.60	5.89	6.21	6.23
2g	3.46	4.02	4.60	6.46	6.70	6.78

Table S3a. Rate constants for the reaction of $Tp^{iPr}MoO_2(OPh)$ with PMe_3 in MeCN.

Temp (°C)	Temp, T (K)	1/T (K^{-1})	k ($M^{-1}sec^{-1}$)	$k\cdot10^5$ (sec^{-1})
5	278.15	0.003595	0.0165	6.02
11	284.15	0.003519	0.0609	22.2
16.5	289.65	0.003452	0.141	51.4
22.5	295.65	0.003382	0.252	92.0
38	311.15	0.003214	0.651	237.1

Table S3b. Rate constants for the reaction of $Tp^{iPr}MoO_2(OPh)$ with PMe_2Ph in MeCN.

Temp (°C)	Temp, T (K)	1/T (K^{-1})	k ($M^{-1}sec^{-1}$)	$k\cdot10^5$ (sec^{-1})
5.9	279.05	0.003584	0.0896	32.2
12.5	285.65	0.003501	0.135	48.4
18	291.15	0.003435	0.218	78.5
22.5	295.65	0.003382	0.258	92.6

Table S3c. Rate constants for the reaction of $Tp^{iPr}MoO_2(OPh)$ with PEt_2Ph in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	k ($M^{-1}sec^{-1}$)	$k\cdot10^5$ (sec^{-1})
10	283.15	0.003532	0.0183	6.59
17.5	290.65	0.003441	0.0367	13.2
23.5	296.65	0.003371	0.0793	28.5
28	301.15	0.003321	0.0983	35.3

Table S3d. Rate constants for the reaction of $Tp^{iPr}MoO_2(OPh)$ with PBu^n_3 substrate measured in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	k ($M^{-1}sec^{-1}$)	$k\cdot10^5$ (sec^{-1})
13	286.15	0.003495	0.0148	5.27
16	289.15	0.003458	0.0166	5.94
21	294.15	0.0034	0.0397	14.2
26	299.15	0.003343	0.0850	30.4
32	305.15	0.003277	0.1114	39.8

Table S3e. Rate constants for the reaction of $Tp^{iPr}MoO_2(OPh)$ with $PEtPh_2$ in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	k ($M^{-1}sec^{-1}$)	$k{\cdot}10^5$ (sec^{-1})
15.5	288.65	0.003464	0.0048	1.73
22.5	295.65	0.003382	0.0102	3.65
28.5	301.65	0.003315	0.0219	8.18
35	308.15	0.003245	0.0420	15.66

Table S4a. Rate constants (uncorrected) for the solvolysis reaction of $Tp^{iPr}MoO(OPh)(OPMe_3)$ in MeCN.

Temp (°C)	Temp, T (K)	1/T (K^{-1})	$k{\cdot}10^5$ ($M^{-1}sec^{-1}$)
26	299.15	0.003343	23.4
32	305.15	0.003277	44.6
38	311.15	0.003214	49.0
43	316.15	0.003163	89.1

Table S4b. Rate constants(uncorrected) for the solvolysis reaction of $Tp^{iPr}MoO(OPh)(OPMe_2Ph)$ in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	$k{\cdot}10^5$ ($M^{-1}sec^{-1}$)
5.9	279.05	0.003584	8.43
11.5	284.65	0.003513	25.19
18	291.15	0.003435	62.54
22.5	295.65	0.003382	124.50

Table S4c. Rate constants (uncorrected) for the solvolysis reaction of $Tp^{iPr}MoO(OPh)(OPEt_2Ph)$ in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	$k{\cdot}10^5$ ($M^{-1}sec^{-1}$)
0	273.15	0.003661	8.63
4	277.15	0.003608	32.08
10	283.15	0.003532	73.81
17.5	290.65	0.003441	105.82
23.5	296.65	0.003371	222.52
26	299.15	0.003343	676.67
28	301.15	0.003321	599.52

Table S4d. Rate constants (uncorrected) for the solvolysis reaction of $Tp^{iPr}MoO(OPh)(OPEtPh_2)$ in MeCN.

Temp (ºC)	Temp, T (K)	1/T (K^{-1})	$k{\cdot}10^5$ ($M^{-1}sec^{-1}$)
10	283.15	0.003532	85.30
16	289.15	0.003458	157.38
20	293.15	0.003411	383.14
31.5	304.65	0.003282	610.50