Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information PCCP

Table S1 - Key geometry parameters obtained by optimizations at different level of theory for the Mo-oxo species. All distances in Å, all angles in °.

[(PY5Me2)MoO]$^{+}$	BP86-D3(BJ)/def2-TZVP	B3LYP/SDD:6-31G(d)	M06-2X/def2-TZVP
Mo-O	1.72	1.73	1.69
Mo-N1	2.14	2.19	2.19
Mo-N2	2.14	2.19	2.19
Mo-N3	2.14	2.19	2.19
Mo-N4	2.14	2.19	2.19
Mo-N5	2.26	2.25	2.22
O-Mo-N1	96.6	96.4	96.8
O-Mo-N2	96.6	96.4	96.8
O-Mo-N3	96.6	96.4	96.8
O-Mo-N4	96.6	96.4	96.8
O-Mo-N5	180.0	180.0	180.0
N5-Mo-N1	83.4	83.6	83.2
N5-Mo-N2	83.4	83.6	83.2
N5-Mo-N3	83.4	83.6	83.2
N5-Mo-N4	83.4	83.6	83.2

[(PY5Me2)MoOH]$^{+2}$	BP86-D3(BJ)/def2-TZVP	B3LYP/SDD:6-31G(d)	M06-2X/def2-TZVP
Mo-O	1.89	1.91	1.89
O-H	0.98	0.97	0.96
Mo-N1	2.13	2.18	2.18
Mo-N2	2.15	2.20	2.19
Mo-N3	2.14	2.19	2.18
Mo-N4	2.15	2.20	2.19

Mo-N5	2.21	2.23	2.23
Mo-O-H	127.6	124.4	127.7
O-Mo-N1	106.2	104.9	103.8
O-Mo-N2	90.2	89.5	89.4
O-Mo-N3	95.4	95.5	96.4
O-Mo-N4	93.5	95.4	96.0
O-Mo-N5	173.7	173.8	174.4
N5-Mo-N1	79.6	80.2	80.2
N5-Mo-N2	88.1	87.6	87.4
N5-Mo-N3	78.7	79.4	79.6
N5-Mo-N4	88.1	87.5	87.1

[(QY5Me2)MoO]$^{+}$	BP86-D3(BJ)/def2-TZVP	B3LYP/SDD:6-31G(d)	M06-2X/def2-TZVP
Mo-O	1.72	1.73	1.74
Mo-N1	2.14	2.18	2.19
Mo-N2	2.14	2.18	2.19
Mo-N3	2.14	2.18	2.19
Mo-N4	2.14	2.18	2.19
Mo-N5	2.27	2.27	2.32
O-Mo-N1	97.4	96.4	96.2
O-Mo-N2	96.3	96.4	96.2
O-Mo-N3	97.3	96.4	96.2
O-Mo-N4	96.3	96.5	96.2
O-Mo-N5	179.9	179.9	180.0
N5-Mo-N1	82.7	83.6	83.8
N5-Mo-N2	83.7	83.6	83.8
N5-Mo-N3	82.6	83.6	83.8
N5-Mo-N4	83.7	83.6	83.8

[(QY5Me2)MoOH]$^{+2}$	BP86-D3(BJ)/def2-TZVP	B3LYP/SDD:6-31G(d)	M06-2X/def2-TZVP
Mo-O	1.90	1.92	1.90
O-H	0.98	0.97	0.96
Mo-N1	2.14	2.18	2.18
Mo-N2	2.14	2.20	2.19
Mo-N3	2.11	2.17	2.17
Mo-N4	2.15	2.20	2.20
Mo-N5	2.22	2.24	2.23
Mo-O-H	125.2	122.4	125.7
O-Mo-N1	95.6	95.5	96.1
O-Mo-N2	92.7	94.3	95.1
O-Mo-N3	108.4	107.2	106.4
O-Mo-N4	89.6	88.9	88.7
O-Mo-N5	172.9	172.9	173.3
N5-Mo-N1	77.6	78.2	78.4
N5-Mo-N2	88.8	88.2	87.9
N5-Mo-N3	78.4	79.0	79.1
N5-Mo-N4	88.9	79.0	88.3

Table S2 - Protonation energies (kcal/mol) computed at different levels of theory as single-point calculation on geometries optimized at the BP86-D3(BJ)/def2-TZVP level of theory for the reaction:

$$[(PY5Me2)Mo{=}O]^{+} + H_3O^{+} \rightarrow [(PY5Me2)Mo\text{-}OH]^{2+} + H_2O$$

DFT	basis set	vacuum	water	$\Delta\Delta E_{water/vacuum}$
DFT functional effect				
BP86	def2-TZVP	-15.72	-29.47	-13.75
BLYP		-18.39	-32.76	-14.37
B3LYP*		-24.82	-38.48	-13.66
B3LYP		-28.67	-41.80	-13.13
TPSS		-18.93	-32.48	-13.55
TPSSH		-23.93	-36.95	-13.02
M06L		-20.48	-34.39	-13.91
Basis set effect				
BP86	def2-SVP	-8.84	-22.05	-13.21
	def2-TZVP	-15.72	-29.47	-13.75
	def2-TZVPD	-18.11	-31.31	-13.20
	def2-QZVP	-17.22	-30.55	-13.33
Dispersion corrections effect				
BP86	def2-TZVP	-15.72	-29.47	-13.75
BP86-D3		-16.16	-30.00	-13.84
BP86-D3(BJ)		-16.26	-30.20	-13.94

Table S3 - NBO charges computed in vacuum for the Mo-oxo species at the BP86-D3(BJ)/def2-TZVP level.

Atom or group	[(PY5Me2)MoO]$^{+}$	[(QY5Me2)MoO]$^{+}$	Δ_{charge}	[(PY5Me2)MoOH]$^{+2}$	[(QY5Me2)MoOH]$^{+2}$	Δ_{charge}
Mo	1.11	1.14	0.03	1.14	1.14	0.00
O	-0.51	-0.51	0.00	-0.77	-0.79	-0.02
H(OH)				0.49	0.48	-0.01
N1	-0.41	-0.42	-0.01	-0.40	-0.40	0.00
N2	-0.41	-0.42	-0.01	-0.43	-0.43	0.00
N3	-0.41	-0.42	-0.01	-0.42	-0.41	0.01
N4	-0.41	-0.42	-0.01	-0.41	-0.43	-0.02
N5	-0.49	-0.48	0.01	-0.43	-0.43	0.00
N1-ring	0.13	0.12	-0.01	0.28	0.30	0.02
N2-ring	0.13	0.11	-0.02	0.19	0.19	0.00
N3-ring	0.13	0.12	-0.01	0.28	0.30	-0.02
N4-ring	0.13	0.11	-0.02	0.21	0.21	0.00
N5-ring	-0.01	0.02	0.03	0.26	0.24	-0.02
C1-CH3	-0.06	-0.05	0.01	-0.04	-0.04	0.00
C2-CH3	-0.06	-0.05	0.01	-0.04	-0.04	0.00

Table S4 - NBO charges computed in vacuum for the Mo-sulphide species at the BP86-D3(BJ)/def2-TZVP level.

Atom or group	[(PY5Me2)MoS_2]$^{+}$	[(QY5Me2)MoS_2]$^{+}$	Δ_{charge}	[(PY5Me2)MoSSH]$^{+2}$	[(QY5Me2)MoSSH]$^{+2}$	Δ_{charge}
Mo	0.43	0.44	0.01	0.47	0.48	0.01
S1	-0.07	-0.06	0.01	0.22	0.21	-0.01
S2	-0.02	-0.05	-0.03	0.00	-0.03	-0.03
H(SH)				0.13	0.12	-0.01
N1	-0.38	-0.39	-0.01	-0.39	-0.40	-0.01
N2	-0.40	-0.40	0.00	-0.41	-0.42	-0.01
N3	-0.38	-0.39	-0.01	-0.39	-0.39	0.00
N4	-0.39	-0.40	-0.01	-0.40	-0.41	-0.01
N5	-0.40	-0.40	0.00	-0.39	-0.39	0.00
N1-ring	0.23	0.22	0.01	0.30	0.31	0.01
N2-ring	0.12	0.12	0.00	0.17	0.18	0.01
N3-ring	0.20	0.23	0.03	0.28	0.29	0.01
N4-ring	0.15	0.12	-0.03	0.24	0.26	0.02

N5-ring	0.07	0.08	0.01	0.27	0.25	-0.02
C1-CH3	-0.06	-0.09	-0.03	-0.04	-0.07	-0.03
C2-CH3	-0.06	-0.05	0.01	-0.04	-0.04	0.00

Table S5 - Solvation energy (kcal/mol) and total non-electrostatic contribution computed as single point calculations on the BP86-D3(BJ)/def2-TZVP optimized geometries.

	BP86-D3(BJ)/def2-TZVP **(SMD wat)**	B3LYP-D3(BJ)/def2-TZVP **(SMD wat)**	M06-2X-D3(BJ)/def2-TZVP **(SMD wat)**
$[(PY5Me2)MoO]^{+}$	-40.40	-42.51	-45.89
$[(PY5Me2)MoOH]^{+2}$	-135.01	-135.94	-135.77
$[(QY5Me2)MoO]^{+}$	-39.78	-41.83	-46.05
$[(QY5Me2)MoOH]^{+2}$	-122.94	-124.15	-124.97

Table S6 - Average Mo–X distances during MD simulations along with the standard deviation, compared to the QM-optimized distances in the implicit solvent (BP86-D3(BJ)/def2-TZVP; C-PCM, solvent=water).

	PyO			PyOH		
	QM	MM		QM	MM	
		mean value	stand. dev		mean value	stand. dev
Mo-O	1.73	1.73	0.03	1.89	1.89	0.04
Mo-N1	2.14	2.16	0.03	2.13	2.13	0.05
Mo-N2	2.14	2.16	0.03	2.14	2.16	0.05
Mo-N3	2.14	2.16	0.03	2.13	2.13	0.05
Mo-N4	2.14	2.16	0.03	2.14	2.15	0.05
Mo-N5	2.25	2.23	0.03	2.21	2.14	0.04

	QyO			QyOH		
	QM	MM		QM	MM	
		mean value	stand. dev		mean value	stand. dev
Mo-O	1.73	1.73	0.03	1.90	1.89	0.04
Mo-N1	2.14	2.07	0.05	2.14	2.16	0.04

Mo-N2	2.14	2.08	0.05	2.11	2.14	0.04
Mo-N3	2.14	2.05	0.05	2.15	2.16	0.05
Mo-N4	2.14	2.05	0.05	2.13	2.14	0.05
Mo-N5	2.28	1.92	0.05	2.22	2.11	0.05

Figure S1 - Graphic reporting the radial distribution function of the water hydrogen atoms around the oxo α-ligand of Mo derived from MD simulations.