

Supporting Information

Hydrogen activation by high-valent oxo-molybdenum(VI) and – rhenium(VII) and (V) compounds

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- **Coordinates of the DFT optimized compounds**

H₂

H	0.000000000	0.000000000	-0.071396000
H	0.000000000	0.000000000	0.671396000

Complex 6

Mo	0.000040000	-1.339826000	-0.000038000
S	2.128925000	-0.644944000	1.079568000
S	-2.128820000	-0.644824000	-1.079697000
O	-0.373828000	-2.346785000	1.310632000
O	0.373870000	-2.346571000	-1.310882000
S	1.211580000	0.783067000	-1.317840000
S	-1.211810000	0.782743000	1.318116000
C	2.428056000	0.586360000	-0.137308000
C	-2.428104000	0.586253000	0.137362000
N	3.547333000	1.322732000	-0.113761000
N	-3.547356000	1.322654000	0.113809000
C	4.637788000	1.112919000	0.838651000
C	-4.637646000	1.113109000	-0.838845000
C	3.764913000	2.362786000	-1.123169000
C	-3.765016000	2.362489000	1.123431000
H	4.768238000	2.003849000	1.462390000
H	4.422343000	0.260114000	1.479333000
H	5.569037000	0.921370000	0.295094000
H	-5.568974000	0.921278000	-0.295520000
H	-4.768068000	2.004260000	-1.462273000
H	-4.422029000	0.260563000	-1.479815000
H	4.593214000	2.993617000	-0.796822000
H	4.006755000	1.919598000	-2.095132000
H	2.866105000	2.972415000	-1.236452000
H	-4.006786000	1.919099000	2.095320000
H	-2.866261000	2.972183000	1.236815000
H	-4.593387000	2.993299000	0.797236000

TS_{6-II}

Mo	-0.131527000	-1.022878000	0.547133000
S	2.521326000	-1.125092000	0.716987000
S	-2.026945000	-0.295564000	-0.884177000
O	-0.638076000	-2.151648000	1.867444000
O	0.166569000	-2.031549000	-0.788508000
S	1.023603000	1.195110000	-0.196480000
S	-1.835687000	0.884331000	1.773197000
C	2.568154000	0.504172000	0.164283000
C	-2.716412000	0.779733000	0.318208000
N	3.720708000	1.176362000	0.022483000
N	-3.853130000	1.449563000	0.092857000
C	5.006681000	0.557670000	0.345301000
C	-4.649318000	1.300201000	-1.126120000
C	3.790830000	2.519193000	-0.550424000
C	-4.426892000	2.296727000	1.143150000

H	5.716424000	1.346036000	0.606098000
H	4.897215000	-0.117909000	1.194683000
H	5.397467000	-0.008347000	-0.508515000
H	-4.101791000	0.718836000	-1.865586000
H	-5.593539000	0.791108000	-0.901472000
H	-4.869460000	2.288303000	-1.541666000
H	4.163715000	3.228464000	0.196750000
H	4.472743000	2.517135000	-1.407772000
H	2.804917000	2.838601000	-0.882912000
H	-3.659114000	2.952175000	1.559649000
H	-5.222990000	2.900756000	0.705561000
H	-4.838539000	1.686891000	1.954392000
H	-0.117895000	-1.260540000	2.474578000
H	0.470836000	-0.353366000	2.277206000

I1

Mo	-0.053318000	1.415498000	-0.011534000
S	-2.119457000	0.571976000	1.144497000
S	1.970675000	0.309922000	-1.244844000
O	1.458473000	2.533393000	0.506842000
O	-0.858606000	2.477768000	-1.034403000
S	-1.105234000	-0.666245000	-1.232333000
S	1.165483000	-0.639468000	1.436068000
C	-2.392440000	-0.613858000	-0.097571000
C	2.283302000	-0.706254000	0.132141000
N	-3.474774000	-1.398360000	-0.135423000
N	3.374218000	-1.497324000	0.128043000
C	-4.506396000	-1.373235000	0.899893000
C	4.308245000	-1.491200000	-0.998656000
C	-3.658689000	-2.411203000	-1.173459000
C	3.763986000	-2.306857000	1.279976000
H	-4.509427000	-2.321280000	1.449800000
H	-4.325393000	-0.558218000	1.598798000
H	-5.487063000	-1.231541000	0.434454000
H	3.767111000	-1.565966000	-1.944752000
H	4.907014000	-0.573459000	-1.013707000
H	4.973451000	-2.351008000	-0.901461000
H	-3.455633000	-3.411093000	-0.772568000
H	-4.692895000	-2.374371000	-1.528241000
H	-2.987230000	-2.217571000	-2.008923000
H	2.996990000	-2.243947000	2.049115000
H	3.886551000	-3.351580000	0.974670000
H	4.713910000	-1.944887000	1.690938000
H	1.381816000	3.002367000	1.345295000
H	-0.396395000	2.068784000	1.474994000

TS_{I1-I2}

Mo	-0.072471000	1.184857000	-0.320501000
S	-2.164535000	0.729264000	0.944643000
S	2.166869000	0.409670000	-1.245198000
O	1.275978000	2.280370000	0.911145000
O	-0.441221000	2.290946000	-1.517566000
S	-1.316481000	-0.753472000	-1.402591000
S	1.058296000	-0.927214000	1.151011000
C	-2.507449000	-0.575577000	-0.171300000
C	2.367652000	-0.733817000	0.051965000
N	-3.576895000	-1.367957000	-0.060508000
N	3.522131000	-1.420378000	0.146241000
C	-4.628178000	-1.152886000	0.934106000
C	4.606233000	-1.218666000	-0.817361000
C	-3.813100000	-2.465986000	-1.000470000
C	3.744778000	-2.457150000	1.151259000
H	-4.689647000	-2.017738000	1.603104000
H	-4.416762000	-0.261219000	1.520933000
H	-5.590737000	-1.027765000	0.426852000
H	4.363974000	-1.667565000	-1.787390000
H	4.790726000	-0.152617000	-0.966009000
H	5.510116000	-1.687000000	-0.424116000
H	-2.863363000	-2.865763000	-1.356080000
H	-4.364589000	-3.254282000	-0.483004000
H	-4.399764000	-2.122852000	-1.860319000
H	2.869813000	-2.540323000	1.792446000

H	3.926503000	-3.420508000	0.660830000
H	4.617545000	-2.202467000	1.762621000
H	1.165152000	2.249860000	1.871588000
H	-0.212299000	2.279019000	0.931319000

I2

Mo	-0.110292000	1.119756000	-0.241582000
S	-2.104474000	0.636890000	1.161521000
S	2.088564000	0.318973000	-1.279530000
O	1.139979000	2.494508000	1.253652000
O	-0.440786000	2.554683000	-1.021009000
S	-1.443890000	-0.582204000	-1.384548000
S	1.380480000	-0.545942000	1.458071000
C	-2.581880000	-0.511016000	-0.062012000
C	2.503182000	-0.592910000	0.124085000
N	-3.664564000	-1.289175000	0.031859000
N	3.621588000	-1.339172000	0.143217000
C	-4.587072000	-1.224499000	1.164543000
C	4.513675000	-1.365839000	-1.018781000
C	-4.046509000	-2.240232000	-1.011606000
C	4.011475000	-2.171012000	1.279672000
H	-4.755851000	-2.235309000	1.550003000
H	-4.168657000	-0.602802000	1.953540000
H	-5.547277000	-0.804907000	0.843327000
H	3.991180000	-1.752375000	-1.899319000
H	4.876273000	-0.360328000	-1.251739000
H	5.363016000	-2.010775000	-0.789753000
H	-3.317210000	-2.226580000	-1.818748000
H	-4.099831000	-3.248794000	-0.587399000
H	-5.031815000	-1.973349000	-1.409624000
H	3.272535000	-2.077974000	2.072730000
H	4.076591000	-3.220128000	0.969782000
H	4.989961000	-1.853615000	1.657197000
H	1.555136000	1.783472000	1.778462000
H	0.527365000	2.948199000	1.847696000

TS_{I2-7}

Mo	-0.056815000	0.757066000	-0.060131000
S	-1.977819000	0.128083000	1.404198000
S	1.959891000	-0.042538000	-1.342130000
O	1.477939000	2.490862000	1.458551000
O	-0.331383000	2.356506000	-0.483473000
S	-1.611346000	-0.560204000	-1.382718000
S	1.538117000	-0.628945000	1.485585000
C	-2.657280000	-0.674968000	0.016912000
C	2.598541000	-0.735059000	0.117000000
N	-3.810991000	-1.347029000	0.028644000
N	3.791872000	-1.348009000	0.157207000
C	-4.648047000	-1.455247000	1.223281000
C	4.653667000	-1.456500000	-1.018679000
C	-4.352109000	-2.011194000	-1.157129000
C	4.292807000	-2.031025000	1.347711000
H	-4.871401000	-2.510210000	1.413632000
H	-4.130003000	-1.034973000	2.082964000
H	-5.590295000	-0.917729000	1.068626000
H	4.560935000	-2.449172000	-1.475923000
H	4.384298000	-0.699877000	-1.753532000
H	5.692413000	-1.305980000	-0.710326000
H	-3.687312000	-1.867315000	-2.006193000
H	-4.462573000	-3.083155000	-0.960273000
H	-5.336776000	-1.593394000	-1.393448000
H	3.581017000	-1.929762000	2.164167000
H	4.443155000	-3.094688000	1.128690000
H	5.252344000	-1.595467000	1.647039000
H	1.067971000	2.383985000	2.326459000
H	0.933311000	3.146417000	0.996965000

Complex 7

Mo	-0.167279000	-0.099345000	1.064553000
S	-2.015623000	-1.468777000	0.125699000
S	1.631823000	1.455256000	0.346529000
O	-0.121143000	-0.281586000	2.715039000
S	-2.035219000	1.414936000	0.443532000
S	1.656123000	-1.428038000	0.023896000
C	-2.936127000	0.003977000	-0.051828000
C	2.531828000	0.064628000	-0.204847000
N	-4.170044000	0.051836000	-0.560877000
N	3.731294000	0.139734000	-0.787651000
C	-4.896085000	-1.143599000	-0.989793000
C	4.442047000	1.404502000	-0.975610000
C	-4.910412000	1.302699000	-0.725974000
C	4.453569000	-1.039111000	-1.266097000
H	-5.158032000	-1.053144000	-2.049652000
H	-4.281736000	-2.029499000	-0.844004000
H	-5.818092000	-1.241499000	-0.406505000
H	4.623027000	1.569524000	-2.043391000
H	3.854946000	2.229161000	-0.577166000
H	5.406403000	1.362470000	-0.457786000
H	-4.309802000	2.143493000	-0.385650000
H	-5.164721000	1.441669000	-1.782494000
H	-5.837369000	1.259712000	-0.143934000
H	3.833765000	-1.927370000	-1.163638000
H	4.717958000	-0.899800000	-2.319699000
H	5.374099000	-1.170362000	-0.686535000

H₂O

O	-1.444997000	0.000023000	-2.473453000
H	-2.027736000	-0.488113000	-1.879176000
H	-0.862341000	0.488090000	-1.879040000

MoO₂Cl₂ (1)

Mo	0.026984000	0.175769000	0.360832000
Cl	1.458373000	1.866725000	0.841532000
Cl	0.978421000	-1.851493000	0.715584000
O	-0.464265000	0.291642000	-1.237984000
O	-1.349849000	0.322608000	1.306635000

TS₁₋₁₃

Mo	0.515339000	-0.117468000	-0.144121000
Cl	1.651096000	1.579837000	0.874538000
Cl	2.419797000	-1.455957000	-0.030607000
O	0.230792000	0.374396000	-1.713165000
O	-1.042389000	-0.310991000	0.720260000
H	-0.117702000	-1.824647000	-0.487044000
H	-0.879179000	-1.374734000	0.143585000

I3

Mo	0.612053000	-0.197093000	-0.307112000
Cl	1.433595000	1.323706000	1.226353000
Cl	2.651364000	-1.280240000	-0.494304000
O	0.381369000	0.286787000	-1.881470000
O	-1.133224000	-0.282660000	0.354852000
H	0.303173000	-1.826276000	-0.236005000
H	-1.559789000	-0.990034000	0.857783000

TS₁₃₋₁₄

Mo	0.912260000	-0.177554000	-0.388524000
Cl	1.201332000	1.455092000	1.193713000
Cl	2.760404000	-1.485102000	-0.605397000
O	0.205058000	0.248830000	-1.829505000
O	-0.796537000	-0.590782000	0.773639000

H	-0.015426000	-1.512945000	0.084683000
H	-1.578550000	-0.903350000	0.291488000

I4

Mo	0.184474000	-0.243212000	0.175998000
Cl	1.127722000	1.553768000	1.414118000
Cl	1.121601000	-2.308485000	0.550590000
O	-0.239615000	0.306868000	-1.328816000
O	-1.388576000	0.328994000	1.485815000
H	-1.214534000	1.204737000	1.889432000
H	-2.328854000	0.184905000	1.318055000

MoOCl₂

Mo	0.998694000	0.682869000	-2.021489000
Cl	-0.000778000	2.699227000	-1.928000000
Cl	0.824404000	-0.806230000	-3.702339000
O	1.918030000	0.242015000	-0.721221000