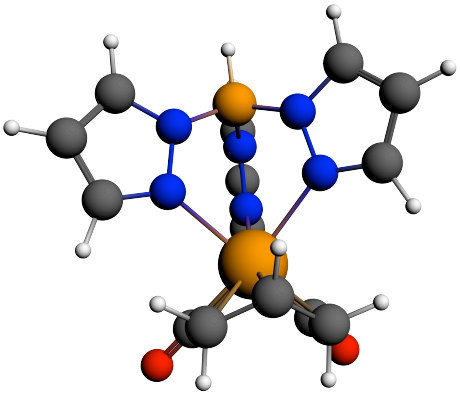
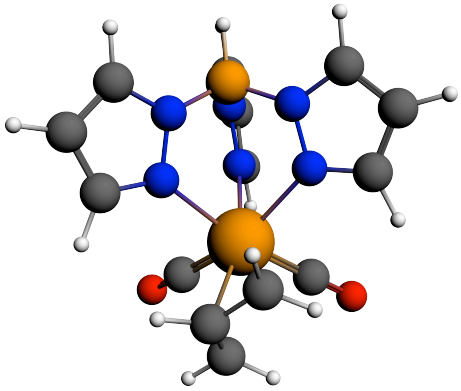
SUPPLEMENTAL INFORMATION



1a: *exo*-TpMo(CO)$_2$(η^3-C$_3$H$_5$)



1b: TpMo(CO)$_2$(η^3-C$_3$H$_5$)
exo ↔ *gauche* transition state

TZP/BP

Coordinates (XYZ):

B	0.01990767	2.38179913	0.17699617
H	0.05423169	3.57607670	0.30711176
H	3.78090294	2.09622227	-2.70203911
H	0.84232066	-0.99877203	3.18308559
H	-3.54232998	-0.33914890	-0.85428258
N	-1.38639535	1.94757465	-0.26567166
N	-1.71429823	0.62691172	-0.39935717
C	-2.47472738	2.72719070	-0.48182247
C	-3.55437608	1.90125318	-0.76738588
C	-3.02761000	0.60143640	-0.70297202
C	2.38973372	0.54854700	-1.87739778
C	2.90266658	1.83130101	-2.12362995
N	1.07415641	1.94131150	-0.85652254
H	-2.39978905	3.80641021	-0.41109865
H	1.19016486	1.30083943	4.66499512
H	-4.57442634	2.19581492	-0.98831773
N	0.34987464	1.69365168	1.51871445
N	0.39934868	0.33102722	1.60481851
C	0.65890925	2.23995526	2.71797968
C	0.91657731	1.21058281	3.61965761
C	0.74254147	0.03568745	2.87533642
H	2.04498789	3.76559646	-1.33915477
C	2.03999345	2.68681632	-1.44748189
H	2.77733300	-0.41163335	-2.19525770
H	0.67575977	3.31715552	2.84180481
N	1.27742308	0.61602482	-1.11853428
Mo	-0.04935494	-0.98961820	-0.13203144
H	-2.69958421	-2.09876511	-0.97360624
O	2.44503058	-2.78820632	0.50046764
O	-1.28464919	-2.93057062	2.01012153
C	-0.87850241	-2.19116139	1.19288409
C	1.50825103	-2.12337711	0.25505437
C	-0.85131485	-1.76219124	-2.08458224
H	-1.20925665	-0.91407471	-2.66689528
C	0.50111781	-2.17190792	-2.11751070
H	1.19265794	-1.65537394	-2.78028020
H	0.74853009	-3.21132073	-1.89810110
H	-1.46945267	-3.44955683	-0.87851450
C	-1.66180854	-2.39918616	-1.10225008

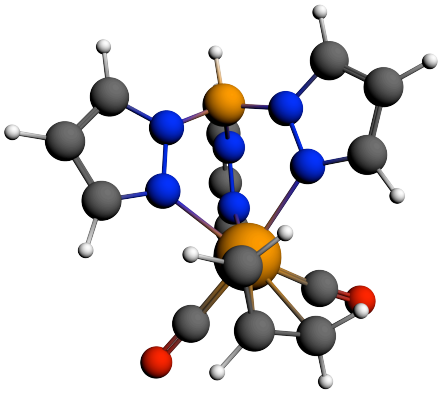
ΔH = 0.0 kcal mol^{-1}
ΔG = 0.0 kcal mol^{-1}

TZP/BP

Coodinates (XYZ):

B	-0.14874672	2.41274802	0.00000000
H	-0.28554703	3.60693013	0.00000000
H	1.82286028	2.15396523	4.30233352
H	-3.22740632	-0.99407956	0.00000000
H	1.61260097	-0.35644469	-3.21038209
N	0.60458302	1.97100787	-1.26416435
N	0.83961572	0.64789571	-1.51803021
C	0.96128749	2.72609571	-2.33288049
C	1.44899361	1.88025118	-3.32181085
C	1.34809152	0.59538710	-2.76666851
C	1.34809152	0.59538710	2.76666851
C	1.44899361	1.88025118	3.32181085
N	0.60458302	1.97100787	1.26416435
H	0.83991320	3.80324153	-2.30926206
H	-4.77951565	1.28344242	0.00000000
H	1.82286028	2.15396523	-4.30233352
N	-1.52887360	1.72149704	0.00000000
N	-1.60496922	0.35721966	0.00000000
C	-2.77317798	2.25041880	0.00000000
C	-3.69795500	1.20824276	0.00000000
C	-2.91845549	0.04438828	0.00000000
H	0.83991320	3.80324153	2.30926206
C	0.96128749	2.72609571	2.33288049
H	1.61260097	-0.35644469	3.21038209
H	-2.91253325	3.32605600	0.00000000
N	0.83961572	0.64789571	1.51803021
Mo	0.16171708	-0.99267770	0.00000000
H	1.71350005	-2.51494839	-2.15173870
O	-1.49804743	-2.82186748	1.94863735
O	-1.49804743	-2.82186748	-1.94863735
C	-0.83724827	-2.14202063	-1.25712979
C	-0.83724827	-2.14202063	1.25712979
C	1.74245243	-2.74835278	0.00000000
H	1.29036590	-3.73994139	0.00000000
C	1.92379989	-2.03390136	1.19736216
H	1.71350005	-2.51494839	2.15173870
H	2.65369332	-1.22368199	1.21334439
H	2.65369332	-1.22368199	-1.21334439
C	1.92379989	-2.03390136	-1.19736216

ΔH = 8.6 kcal mol^{-1}
ΔG = 9.7 kcal mol^{-1}



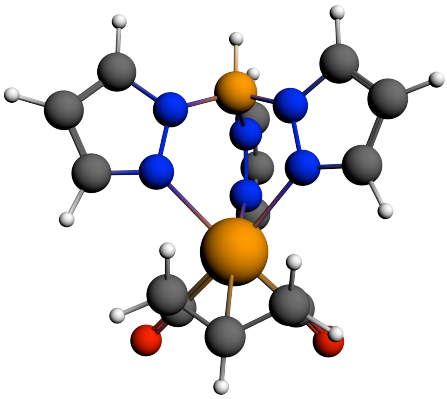
1c: *gauche*-TpMo(CO)$_2$(η^3-C_3H_5)

TZP/BP

Coordinates (XYZ):

B	-0.12981784	-2.35058469	-0.12086837
H	-0.18853504	-3.54734289	-0.21511746
H	3.80142902	-2.21564234	2.55699359
H	0.88995684	0.85009596	-3.26298198
H	-3.30061841	0.67190208	1.26662597
N	-1.45805120	-1.80754526	0.43667004
N	-1.64354425	-0.46700306	0.61581830
C	-2.59065179	-2.48444077	0.75732151
C	-3.54817156	-1.56322423	1.16545341
C	-2.90766212	-0.31677346	1.05478550
C	2.50810868	-0.60842260	1.68555059
C	2.92373378	-1.91312029	1.99660402
N	1.03971170	-1.95061076	0.80666713
H	-2.62909508	-3.56460254	0.67297011
H	0.90908994	-1.51157406	-4.68955024
H	-4.56340479	-1.76410036	1.48956174
N	0.14472391	-1.72289304	-1.50562120
N	0.35252495	-0.37900689	-1.63521576
C	0.34901684	-2.33415306	-2.69957189
C	0.68650783	-1.36528933	-3.63843554
C	0.67813027	-0.15725330	-2.92291066
H	1.88011045	-3.81515843	1.37201803
C	1.96583188	-2.73518573	1.41140805
H	2.97322153	0.33987400	1.93102871
H	0.24831034	-3.40990472	-2.78808238
N	1.36783683	-0.63599500	0.97042745
Mo	0.05843745	0.99612785	0.10622477
H	0.71955944	1.08391746	3.03334432
O	2.60041333	2.64719851	-0.68498375
O	-1.91316051	2.26872536	-2.01296289
C	-1.16433788	1.86421155	-1.21011970
C	1.62950002	2.03620348	-0.41063309
C	0.02820378	2.65907702	1.71322207
H	0.91825197	3.28386786	1.77260592
C	-1.04912346	2.97379912	0.82302269
H	-0.97522057	3.88501942	0.22990132
H	-2.06403594	2.71832981	1.13771108
H	-1.08750282	1.06137368	2.65800520
C	-0.09887867	1.45248787	2.41618945

ΔH = 6.6 kcal mol^{-1}
ΔG = 6.5 kcal mol^{-1}



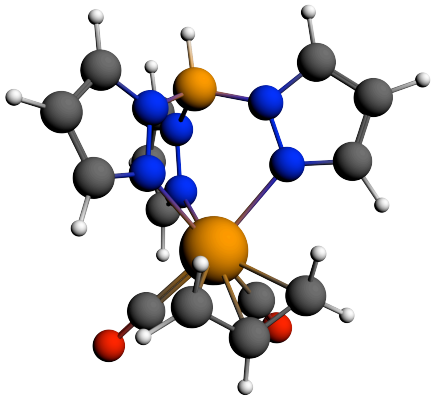
1d: TpMo(CO)$_2$(η^3-C_3H_5)
gauche ↔ *endo* transition state

TZP/BP

Coordinates (XYZ):

B	-0.12949400	2.40436000	0.22717600
H	-0.16731000	3.59480000	0.38984100
H	3.37433000	2.45372000	-2.97402000
H	1.03878000	-1.00235000	3.07919000
H	-3.54022000	-0.54907100	-0.63310500
N	-1.52208000	1.88490000	-0.16035800
N	-1.75384000	0.54841700	-0.34100600
C	-2.68775000	2.57736000	-0.20321800
C	-3.72309000	1.67634000	-0.41697700
C	-3.08976000	0.42533600	-0.49066200
C	2.19306000	0.78929400	-2.05406000
C	2.58523000	2.11121000	-2.31360000
N	0.89923100	2.05691000	-0.86029600
H	-2.69221000	3.65402000	-0.07533140
H	1.32280000	1.26718000	4.61875000
H	-4.78218000	1.89220000	-0.50600200
N	0.30316700	1.70394000	1.53218000
N	0.43516600	0.34387800	1.56953000
C	0.64072900	2.23104000	2.73104000
C	1.00137000	1.19215000	3.58603000
C	0.85801000	0.03233460	2.81321000
H	1.66856000	3.95998000	-1.39832000
C	1.73699000	2.88598000	-1.53023000
H	2.60133000	-0.13092600	-2.45300000
H	0.60538000	3.30362000	2.88810000
N	1.16820000	0.75586300	-1.17826000
Mo	0.01731170	-0.98837700	-0.15913200
H	1.52443000	-2.14352000	-2.55684000
O	2.60256000	-2.66525000	0.45237000
O	-1.07301000	-3.01413000	1.99645000
C	-0.71365600	-2.25327000	1.18022000
C	1.63768000	-2.03802000	0.21626600
C	-0.37979800	-2.72396000	-1.72077000
H	-0.04113570	-3.70195000	-1.37886000
C	-1.63774000	-2.21732000	-1.34232000
H	-2.34329000	-2.85020000	-0.80545200
H	-2.06911000	-1.42893000	-1.95890000
H	0.10601700	-1.01403000	-2.94164000
C	0.50768600	-1.82451000	-2.33179000

ΔH = 8.0 kcal mol^{-1}
ΔG = 7.8 kcal mol^{-1}



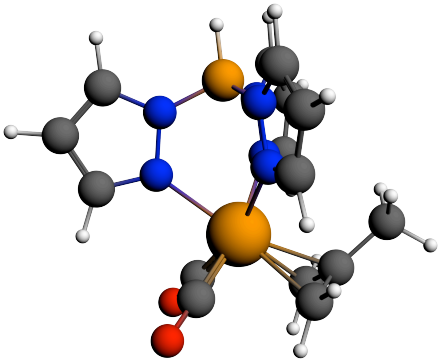
1e: *endo*-TpMo(CO)$_2$(η^3-C$_3$H$_5$)

TZP/BP

Coodinates (XYZ):

B	-0.14874672	2.41274802	0.00000000
H	-0.28554703	3.60693013	0.00000000
H	1.82286028	2.15396523	4.30233352
H	-3.22740632	-0.99407956	0.00000000
H	1.61260097	-0.35644469	-3.21038209
N	0.60458302	1.97100787	-1.26416435
N	0.83961572	0.64789571	-1.51803021
C	0.96128749	2.72609571	-2.33288049
C	1.44899361	1.88025118	-3.32181085
C	1.34809152	0.59538710	-2.76666851
C	1.34809152	0.59538710	2.76666851
C	1.44899361	1.88025118	3.32181085
N	0.60458302	1.97100787	1.26416435
H	0.83991320	3.80324153	-2.30926206
H	-4.77951565	1.28344242	0.00000000
H	1.82286028	2.15396523	-4.30233352
N	-1.52887360	1.72149704	0.00000000
N	-1.60496922	0.35721966	0.00000000
C	-2.77317798	2.25041880	0.00000000
C	-3.69795500	1.20824276	0.00000000
C	-2.91845549	0.04438828	0.00000000
H	0.83991320	3.80324153	2.30926206
C	0.96128749	2.72609571	2.33288049
H	1.61260097	-0.35644469	3.21038209
H	-2.91253325	3.32605600	0.00000000
N	0.83961572	0.64789571	1.51803021
Mo	0.16171708	-0.99267770	0.00000000
H	1.71350005	-2.51494839	-2.15173870
O	-1.49804743	-2.82186748	1.94863735
O	-1.49804743	-2.82186748	-1.94863735
C	-0.83724827	-2.14202063	-1.25712979
C	-0.83724827	-2.14202063	1.25712979
C	1.74245243	-2.74835278	0.00000000
H	1.29036590	-3.73994139	0.00000000
C	1.92379989	-2.03390136	1.19736216
H	1.71350005	-2.51494839	2.15173870
H	2.65369332	-1.22368199	1.21334439
H	2.65369332	-1.22368199	-1.21334439
C	1.92379989	-2.03390136	-1.19736216

ΔH = 7.8 kcal mol^{-1}
ΔG = 7.8 kcal mol^{-1}



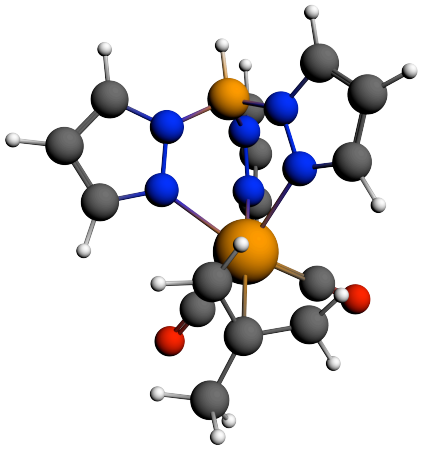
2a: *exo*-TpMo(CO)$_2$(η^3-C$_3$H$_4$Me)

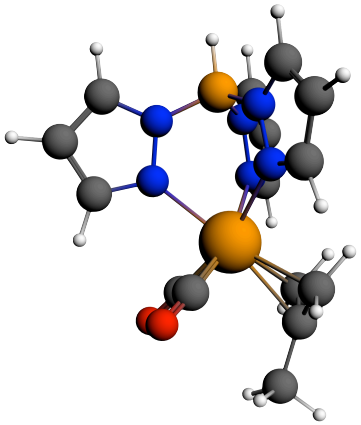
TZP/BP

Coodinates (XYZ):

B	0.02017141	2.38857517	0.16807226
H	0.05162232	3.58404119	0.29343065
H	3.62135741	2.18250994	-2.90894990
H	0.90870484	-0.99000657	3.15650501
H	-3.58153736	-0.37854093	-0.48586787
N	-1.40442912	1.94635005	-0.20905062
N	-1.72814704	0.62096180	-0.29323937
C	-2.52301126	2.70881783	-0.29356760
C	-3.61796033	1.86515817	-0.43521207
C	-3.06876536	0.57284070	-0.42257359
C	2.34239287	0.59707716	-1.97793289
C	2.78886083	1.89429264	-2.27661381
N	1.03714948	1.95496874	-0.90349432
H	-2.45747542	3.78932411	-0.23329289
H	1.30231395	1.30958277	4.62842067
H	-4.66212032	2.14355109	-0.52587993
N	0.40086701	1.70404354	1.49899612
N	0.44438451	0.34081672	1.58651943
C	0.73260783	2.24946343	2.69261141
C	1.00620622	1.21970638	3.58932114
C	0.80839810	0.04489515	2.85035356
H	1.90079555	3.80757513	-1.47505301
C	1.93335651	2.72773647	-1.56604779
H	2.74935720	-0.35015900	-2.30840349
H	0.75292577	3.32651566	2.81680196
N	1.27705554	0.63246343	-1.15316641
Mo	-0.04531131	-0.98080164	-0.13702514
H	-2.64551160	-1.92451880	-1.32333191
O	2.26948699	-2.90559126	0.76076981
O	-1.52643990	-2.85705966	1.90348722
C	-1.01047496	-2.14867594	1.12150628
C	1.43482485	-2.16565754	0.39150526
C	-0.66230895	-1.74709310	-2.18965371
H	-0.15874232	-0.07995634	-3.48445095
C	0.64700015	-2.26912469	-1.98965197
H	1.46883481	-1.86726993	-2.58154419
H	0.76078098	-3.31676648	-1.70766392
H	-1.53275695	-3.34530220	-1.00194498
C	-1.62225816	-2.29744996	-1.29213640
C	-1.00546109	-0.74049104	-3.25987722
H	-1.26982665	-1.27521742	-4.18678734
H	-1.86364623	-0.12020172	-2.97446731

ΔH = 0.0 kcal mol^{-1}
ΔG = 0.0 kcal mol^{-1}





2b: *gauche*-TpMo(CO)$_2$(η^3-C$_3$H$_4$Me)

TZP/BP

Coodinates (XYZ):

B	-0.16550738	-2.36738021	-0.11488105
H	-0.24034505	-3.56385314	-0.20665877
H	3.83545825	-2.29246091	2.45575897
H	0.88934807	0.81690765	-3.25314219
H	-3.31923546	0.65292984	1.33549916
N	-1.47549039	-1.81279916	0.46959846
N	-1.66014441	-0.47006059	0.64917628
C	-2.59602146	-2.49464910	0.81890615
C	-3.54925563	-1.57789555	1.24396074
C	-2.91646382	-0.32950147	1.11691524
C	2.53204113	-0.66522056	1.63909900
C	2.94566788	-1.97611627	1.92265252
N	1.02828193	-1.98411613	0.78698505
H	-2.63080401	-3.57517175	0.73696976
H	0.84018900	-1.53644741	-4.69022691
H	-4.55660396	-1.78196805	1.58996940
N	0.08790541	-1.74437066	-1.50337430
N	0.32520850	-0.40401257	-1.62732221
C	0.27270653	-2.35453765	-2.70038660
C	0.62447007	-1.38904410	-3.63782891
C	0.65106064	-0.18549664	-2.91622505
H	1.86591376	-3.86199429	1.30997749
C	1.96362728	-2.78319889	1.35624277
H	3.01204298	0.27602668	1.88121891
H	0.15214157	-3.42819195	-2.79210115
N	1.37166667	-0.67390377	0.95629722
Mo	0.07732280	0.98158400	0.10881990
H	1.00656452	1.29509994	2.99447650
O	2.61932406	2.59114016	-0.73719466
O	-1.49691160	2.52310191	-2.16806830
C	-0.94114385	1.98523840	-1.29134039
C	1.65439196	1.99565408	-0.40350554
C	-0.07719365	2.68977182	1.74871060
H	0.93379630	4.42222304	0.92475902
C	-1.25324356	2.75339329	0.93165018
H	-1.42806486	3.67396483	0.37267557
H	-2.16335566	2.27448754	1.29394744
H	-0.77276575	0.87607386	2.72155023
C	0.08960351	1.47730882	2.43301328
C	0.88833394	3.84069641	1.85362483
H	0.55222649	4.51420015	2.65949002
H	1.90202201	3.50106646	2.10096085

ΔH = 5.7 kcal mol^{-1}
ΔG = 5.2 kcal mol^{-1}

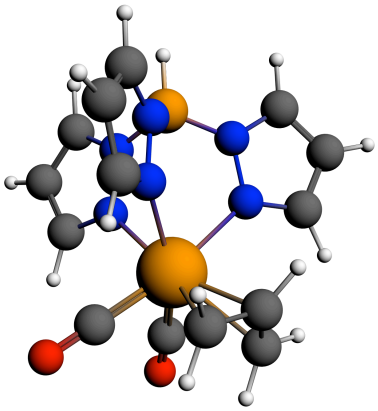
2c: *endo*-TpMo(CO)$_2$(η^3-C$_3$H$_4$Me)

TZP/BP

Coodinates (XYZ):

B	-0.14290723	2.41796285	-0.00004806
H	-0.27084239	3.61308728	-0.00013267
H	1.83139955	2.14526351	4.30105061
H	-3.24508717	-0.96666498	-0.00159822
H	1.60066712	-0.36533189	-3.20780062
N	0.60627397	1.97080311	-1.26514508
N	0.83221488	0.64612885	-1.51845036
C	0.96965925	2.72285201	-2.33385290
C	1.45266184	1.87302189	-3.32183193
C	1.34184619	0.58907873	-2.76615286
C	1.34389545	0.59018865	2.76556960
C	1.45433396	1.87431418	3.32092933
N	0.60777490	1.97125923	1.26429839
H	0.85618279	3.80084307	-2.31083310
H	-4.78136475	1.32189057	-0.00146566
H	1.82970008	2.14363464	-4.30205499
N	-1.52760987	1.73690148	0.00067920
N	-1.61330963	0.37327954	-0.00001470
C	-2.76827858	2.27476241	0.00033351
C	-3.70029066	1.23920276	-0.00076985
C	-2.92881106	0.06971656	-0.00077466
H	0.85707936	3.80172413	2.30958185
C	0.97090717	2.72373613	2.33285239
H	1.60280271	-0.36396551	3.20778872
H	-2.89996407	3.35136607	0.00054033
N	0.83441925	0.64666818	1.51770946
Mo	0.14586291	-0.99093530	0.00037850
H	1.71658905	-2.50718645	-2.14664685
O	-1.53154022	-2.80449529	1.94542092
O	-1.52668667	-2.80573582	-1.94708571
C	-0.85948608	-2.13005455	-1.25586666
C	-0.86307401	-2.12916196	1.25534069
C	1.73248222	-2.78517562	0.00114115
H	2.18594906	-4.86907252	-0.00488179
C	1.89861216	-2.04085602	1.18910127
H	1.70294291	-2.51797625	2.15032302
H	2.61994702	-1.22312606	1.19698192
H	2.62736737	-1.21668865	-1.18119606
C	1.90690754	-2.03523997	-1.18181945
C	1.29076033	-4.22596414	-0.00386674
H	0.70022622	-4.47545711	0.88621230
H	0.70229765	-4.47005443	-0.89682995

ΔH = 6.1 kcal mol^{-1}
ΔG = 6.0 kcal mol^{-1}



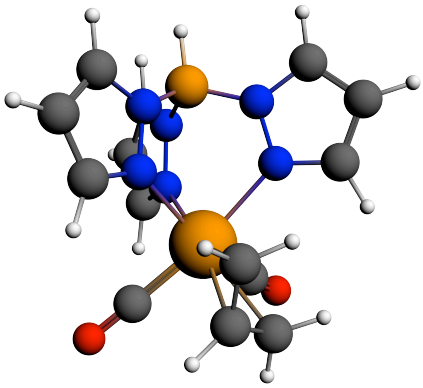
3a: *exo*-TpW(CO)$_2$(η^3-C$_3$H$_5$)

TZP/BP

Coordinates (XYZ):

B	0.01796255	2.39896739	0.17239798
H	0.04878119	3.59385487	0.29827745
H	3.80496827	2.05694967	-2.66710336
H	0.83633300	-1.00859471	3.14378094
H	-3.50482213	-0.37445945	-0.83910264
N	-1.38593593	1.95057337	-0.26504457
N	-1.69271316	0.62363542	-0.39897230
C	-2.48962307	2.70976020	-0.46935811
C	-3.55621074	1.86458847	-0.74893498
C	-3.00781812	0.57492348	-0.69066892
C	2.38709643	0.53244526	-1.85078178
C	2.91555920	1.80693767	-2.09959548
N	1.06930849	1.94964170	-0.86139599
H	-2.43414073	3.78981228	-0.39574869
H	1.20221477	1.27011403	4.64939766
H	-4.58312833	2.14069218	-0.96036906
N	0.35206290	1.70780856	1.51164386
N	0.39513246	0.34223099	1.58210763
C	0.66789308	2.23679140	2.71603701
C	0.92383347	1.19464637	3.60429816
C	0.74117273	0.02982633	2.84839958
H	2.06810518	3.75741940	-1.34486713
C	2.05148175	2.67798912	-1.44474461
H	2.76791760	-0.43486360	-2.15309453
H	0.69068151	3.31216356	2.85401980
N	1.26492873	0.61845154	-1.10816552
W	-0.04770509	-0.97693877	-0.13990330
H	-2.69426083	-2.12222246	-0.96742702
O	2.42751901	-2.79251143	0.50458553
O	-1.28593765	-2.91614117	2.00019927
C	-0.87378106	-2.17320748	1.18469062
C	1.49927241	-2.11247420	0.25383644
C	-0.85196051	-1.75245132	-2.08053736
H	-1.22995684	-0.93558350	-2.69507537
C	0.50722830	-2.15802470	-2.10854933
H	1.18702144	-1.64436534	-2.78620118
H	0.75410932	-3.20191601	-1.90970151
H	-1.45042614	-3.45448368	-0.88005430
C	-1.64966842	-2.40226461	-1.09024746

ΔH = 0.0 kcal mol^{-1}
ΔG = 0.0 kcal mol^{-1}



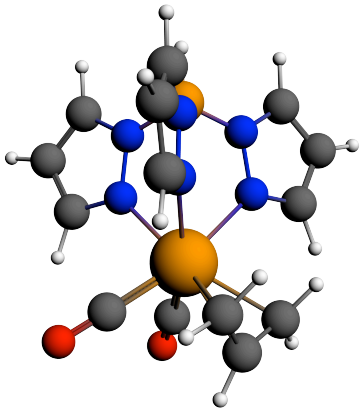
3b: *gauche*-TpW(CO)$_2$(η^3-C$_3$H$_5$)

TZP/BP

Coordinates (XYZ):

B	-0.12243242	-2.37028356	-0.12622430
H	-0.17876703	-3.56668523	-0.22342124
H	3.79974801	-2.17563443	2.56524530
H	0.86246991	0.87702325	-3.22785288
H	-3.25972089	0.68679923	1.24360003
N	-1.44893452	-1.82113681	0.42932922
N	-1.61963415	-0.47750050	0.60450073
C	-2.58944908	-2.48124988	0.75266491
C	-3.53591126	-1.54571636	1.15447374
C	-2.88137763	-0.30838489	1.03988056
C	2.48361068	-0.59276978	1.68797844
C	2.91876499	-1.88913354	2.00186258
N	1.04021543	-1.96190119	0.80585549
H	-2.64173741	-3.56103649	0.67280549
H	0.90118270	-1.46198067	-4.68844082
H	-4.55425529	-1.73156228	1.47716003
N	0.15447530	-1.73088992	-1.50494386
N	0.34747061	-0.38239739	-1.61635913
C	0.35856513	-2.32112229	-2.70877930
C	0.68162270	-1.33443066	-3.63433463
C	0.66433605	-0.13765934	-2.90235575
H	1.91262749	-3.80992197	1.37258737
C	1.97814942	-2.72857895	1.41283453
H	2.93137208	0.36352578	1.93256714
H	0.26739111	-3.39624603	-2.81364937
N	1.34586551	-0.64105478	0.96970540
W	0.05169589	0.98493653	0.11532029
H	0.65518887	1.05447358	3.01603274
O	2.59988552	2.62025543	-0.68514239
O	-1.93616202	2.26069447	-1.97976039
C	-1.17899493	1.85079474	-1.18216450
C	1.62391777	2.01433060	-0.40850217
C	0.06928345	2.66059240	1.67666151
H	0.96367139	3.27475118	1.77097732
C	-1.00860188	3.00276493	0.78988476
H	-0.90536625	3.90105151	0.18111740
H	-2.02873415	2.80896552	1.13482812
H	-1.14880507	1.16584153	2.66299911
C	-0.13383406	1.45241532	2.37799129

ΔH = 7.0 kcal mol^{-1}
ΔG = 7.0 kcal mol^{-1}



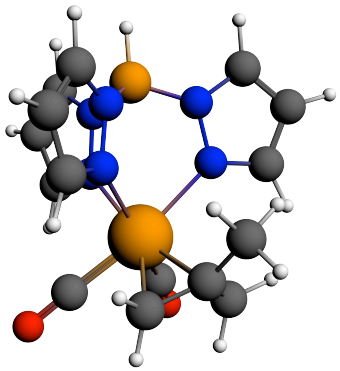
3c: *endo*-TpW(CO)$_2$(η^3-C$_3$H$_5$)

TZP/BP

Coordinates (XYZ):

B	-0.15080164	2.42924878	0.00000000
H	-0.28668612	3.62338111	0.00000000
H	1.81106235	2.10683169	4.30431331
H	-3.19596709	-1.00645483	0.00000000
H	1.60175983	-0.38309322	-3.17208821
N	0.60167387	1.97708309	-1.26036456
N	0.83340808	0.64801101	-1.49489571
C	0.95539583	2.71298805	-2.34198434
C	1.43928332	1.85022758	-3.31851005
C	1.33898961	0.57545777	-2.74436639
C	1.33898961	0.57545777	2.74436639
C	1.43928332	1.85022758	3.31851005
N	0.60167387	1.97708309	1.26036456
H	0.83546371	3.79047905	-2.33536147
H	-4.77226940	1.25050099	0.00000000
H	1.81106235	2.10683169	-4.30431331
N	-1.52777437	1.73115390	0.00000000
N	-1.58753915	0.36349590	0.00000000
C	-2.77750763	2.24311989	0.00000000
C	-3.68984054	1.18925104	0.00000000
C	-2.89836939	0.03551440	0.00000000
H	0.83546371	3.79047905	2.33536147
C	0.95539583	2.71298805	2.34198434
H	1.60175983	-0.38309322	3.17208821
H	-2.93099804	3.31684650	0.00000000
N	0.83340808	0.64801101	1.49489571
W	0.16525494	-0.98102729	0.00000000
H	1.70370993	-2.49704662	-2.14909508
O	-1.49713823	-2.80910191	1.94128881
O	-1.49713823	-2.80910191	-1.94128881
C	-0.83381155	-2.12918148	-1.24746382
C	-0.83381155	-2.12918148	1.24746382
C	1.72149938	-2.74614182	0.00000000
H	1.28077462	-3.74283170	0.00000000
C	1.91129982	-2.01797564	1.19271413
H	1.70370993	-2.49704662	2.14909508
H	2.68526730	-1.24728988	1.20139432
H	2.68526730	-1.24728988	-1.20139432
C	1.91129982	-2.01797564	-1.19271413

ΔH = 8.6 kcal mol^{-1}
ΔG = 8.7 kcal mol^{-1}



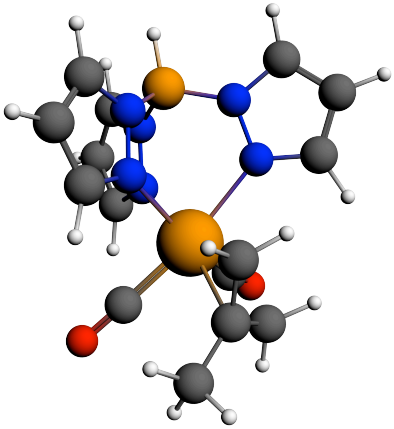
4a: *exo*-TpW(CO)$_2$(η^3-C$_3$H$_4$Me)

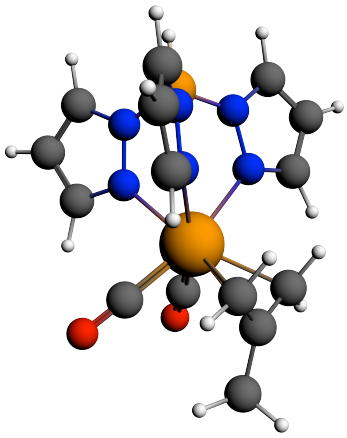
TZP/BP

Coodinates (XYZ):

B	0.01818582	2.40081082	0.16414958
H	0.04696527	3.59640539	0.28576784
H	3.63534895	2.13561239	-2.89019630
H	0.90526723	-1.00239567	3.12158565
H	-3.54205651	-0.42086913	-0.44979366
N	-1.40374503	1.94462589	-0.20845343
N	-1.70511478	0.61267886	-0.29408900
C	-2.53815310	2.68453028	-0.26144597
C	-3.61881515	1.82031749	-0.38912263
C	-3.04734115	0.53967613	-0.39374887
C	2.33372888	0.57419053	-1.95645703
C	2.79416284	1.86287020	-2.26262686
N	1.03131362	1.95658908	-0.90641577
H	-2.49260127	3.76554464	-0.19304547
H	1.31295020	1.27793720	4.61543620
H	-4.66978834	2.07826785	-0.45768889
N	0.40271638	1.71328523	1.49402923
N	0.43922308	0.34748852	1.56786504
C	0.74380527	2.24302829	2.69100128
C	1.01284374	1.20168638	3.57638822
C	0.80843152	0.03628847	2.82732788
H	1.92304257	3.79269314	-1.48228173
C	1.94304681	2.71203365	-1.56542889
H	2.73368326	-0.37992219	-2.27284622
H	0.77155284	3.31847829	2.82739646
N	1.25946395	0.62830049	-1.14402628
W	-0.04455396	-0.97160532	-0.14027996
H	-2.63833093	-1.92908532	-1.33440565
O	2.26835979	-2.89209990	0.76410140
O	-1.57365270	-2.82850259	1.87956730
C	-1.02672514	-2.12615363	1.10912601
C	1.42929239	-2.15123370	0.39789796
C	-0.64963821	-1.73592783	-2.18296885
H	-0.15043248	-0.11238261	-3.53882149
C	0.65859555	-2.26802714	-1.97118165
H	1.48012508	-1.87648207	-2.57084453
H	0.76369666	-3.32128460	-1.70496302
H	-1.52830859	-3.34760709	-1.01368717
C	-1.61258644	-2.29423156	-1.28718938
C	-0.99648764	-0.76689309	-3.28960181
H	-1.26077956	-1.33325989	-4.19839084
H	-1.85685879	-0.13733860	-3.02655898

ΔH = 0.0 kcal mol^{-1}
ΔG = 0.0 kcal mol^{-1}





4b: *gauche*-TpW(CO)$_2$(η^3-C$_3$H$_4$Me)

4c: *endo*-TpW(CO)$_2$(η^3-C$_3$H$_4$Me)

TZP/BP

Coodinates (XYZ):

B	-0.12652576	-2.37720267	-0.12392271
H	-0.18892006	-3.57382489	-0.21573388
H	3.79359196	-2.19991232	2.57158149
H	0.86685440	0.85989663	-3.23049904
H	-3.25462534	0.70148855	1.22090440
N	-1.45058791	-1.81897733	0.42911923
N	-1.61493375	-0.47374851	0.59954513
C	-2.59858022	-2.47123114	0.74221823
C	-3.54349161	-1.52922523	1.13170223
C	-2.87975069	-0.29620648	1.02333255
C	2.48821761	-0.61055340	1.69089824
C	2.91606234	-1.90876057	2.00515898
N	1.04001232	-1.97117695	0.80452315
H	-2.65741490	-3.55069013	0.66226394
H	0.89312275	-1.48004049	-4.68914058
H	-4.56635804	-1.70868391	1.44364191
N	0.14993270	-1.74370969	-1.50456723
N	0.34803498	-0.39565599	-1.61651345
C	0.35125189	-2.33541935	-2.70813595
C	0.67430177	-1.35026470	-3.63511891
C	0.66397967	-0.15333296	-2.90345054
H	1.89884339	-3.82401061	1.37729343
C	1.97146369	-2.74304996	1.41520325
H	2.94026197	0.34321693	1.93621626
H	0.25755013	-3.41049786	-2.81172573
N	1.35307772	-0.65190955	0.96825938
W	0.06660555	0.98218217	0.11593376
H	0.68432551	1.06472931	3.01891912
O	2.58828554	2.57547151	-0.83141199
O	-1.86557782	2.31912564	-1.99674069
C	-1.13798114	1.87296501	-1.19101890
C	1.62836390	1.99182595	-0.46306637
C	0.07902487	2.67738429	1.69851620
H	1.45480837	4.24943089	1.10149634
C	-1.01849158	2.96886010	0.80694594
H	-0.95166078	3.87955294	0.20860967
H	-2.03166454	2.74213678	1.15416004
H	-1.11720748	1.12749147	2.64601160
C	-0.10819882	1.44493219	2.37164184
C	1.19630548	3.64601243	1.98088905
H	0.88040954	4.33324101	2.78399790
H	2.10272245	3.12945610	2.32536405

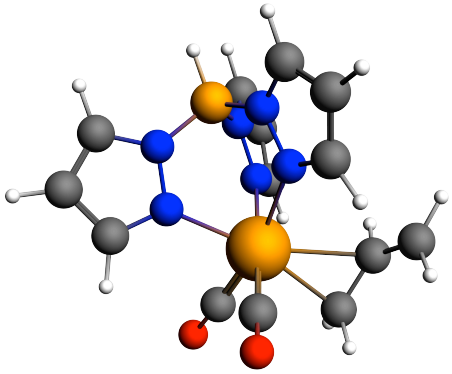
ΔH = 5.2 kcal mol^{-1}
ΔG = 6.6 kcal mol^{-1}

TZP/BP

Coodinates (XYZ):

B	-0.14198692	2.43260975	-0.00009788
H	-0.26938685	3.62761453	-0.00029554
H	1.81795509	2.09888957	4.30415734
H	-3.21252925	-0.97960281	-0.00070389
H	1.58656471	-0.39186864	-3.17331642
N	0.60677174	1.97496756	-1.26101012
N	0.82742455	0.64460486	-1.49646658
C	0.96766375	2.70934274	-2.34162271
C	1.44374250	1.84340301	-3.31888622
C	1.33232962	0.56897419	-2.74558046
C	1.33269608	0.56967136	2.74551417
C	1.44416829	1.84421164	3.31858059
N	0.60715274	1.97535779	1.26070556
H	0.85724900	3.78789637	-2.33386653
H	-4.77159631	1.28984592	0.00237209
H	1.81736377	2.09790742	-4.30456563
N	-1.52339768	1.74412882	0.00011233
N	-1.59354345	0.37704555	0.00025378
C	-2.76914329	2.26625197	-0.00101660
C	-3.68964794	1.21990825	0.00124465
C	-2.90701905	0.06007286	-0.00052056
H	0.85553086	3.78830033	2.33405668
C	0.96678355	2.70984005	2.34170218
H	1.58727096	-0.39101532	3.17341123
H	-2.91387282	3.34116456	-0.00174637
N	0.82854194	0.64508250	1.49607666
W	0.14672246	-0.98326205	0.00011660
H	1.70427439	-2.49867439	-2.14421011
O	-1.52666632	-2.80197073	1.93723584
O	-1.52371271	-2.80265902	-1.93866395
C	-0.85731209	-2.12322201	-1.24493909
C	-0.85935408	-2.12271321	1.24428905
C	1.71535969	-2.78567715	0.00102373
H	2.20311586	-4.86004241	0.00024547
C	1.88869869	-2.02762984	1.18368837
H	1.69705370	-2.50294869	2.14693733
H	2.65011159	-1.24466188	1.18452527
H	2.65397742	-1.24201568	-1.17632617
C	1.89286297	-2.02529335	-1.17943205
C	1.29619924	-4.23212989	-0.00119324
H	0.70961227	-4.49093111	0.88989431
H	0.71353322	-4.48931062	-0.89530920

ΔH = 6.1 kcal mol^{-1}
ΔG = 7.6 kcal mol^{-1}

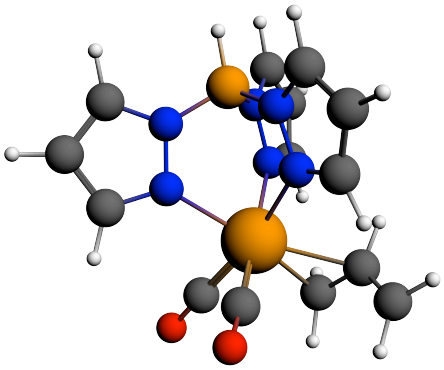


exo-TpMo(CO)$_2$(η^3-C$_3$H$_5$) 1A

ATZP/BP

Coodinates (XYZ):

B	0.06895593	2.36068685	0.18702505
H	0.08161868	3.56166280	0.27818037
H	3.65036044	1.92656492	-2.89592243
H	0.84164709	-0.90386478	3.33888947
H	-3.47932000	-0.47568730	-0.63374097
N	-1.35350494	1.88759714	-0.22082263
N	-1.67335866	0.55980473	-0.28993488
C	-2.46138997	2.62796734	-0.43781391
C	-3.53172419	1.77328479	-0.67353363
C	-2.99190477	0.48956374	-0.55153945
C	2.29862496	0.43396717	-1.92374419
C	2.81659093	1.69715241	-2.24420954
N	1.09251187	1.88488782	-0.85558222
H	-2.40986536	3.70991621	-0.40276902
H	1.29136972	1.44975358	4.69513537
H	-4.55764264	2.04249990	-0.88993716
N	0.43448373	1.71910618	1.54552679
N	0.44768895	0.36214263	1.70008572
C	0.73563679	2.31046344	2.72366434
C	1.00678725	1.31913359	3.65882180
C	0.78203464	0.11720084	2.98057059
H	2.05529499	3.67221893	-1.46949949
C	2.02486659	2.59098265	-1.53809706
H	2.61833938	-0.54473819	-2.26012793
H	0.73055951	3.39069657	2.81056755
N	1.25491203	0.55003807	-1.08508371
Mo	-0.08297891	-0.97376540	0.02056510
H	-1.79981852	-3.07715047	-1.05595478
O	2.38478991	-2.91349100	0.50053961
O	-1.83168255	-2.54640568	2.05527523
C	-1.17603880	-1.98483252	1.26817792
C	1.47689962	-2.22190180	0.32059636
C	-0.65950991	-1.78584436	-2.38355891
H	-1.51051844	-1.11516864	-2.54269984
C	0.36144823	-1.68490758	-3.31515639
H	0.35280866	-0.90550577	-4.07198700
H	1.18091099	-2.40260206	-3.33960448
H	-0.06945434	-3.56936835	-1.34328084
C	-0.79994074	-2.75870641	-1.34570452



exo-TpMo(CO)$_2$(η^3-C$_3$H$_5$) 2A

ATZP/BP

Coodinates (XYZ):

B	0.03316191	2.36711105	0.24988130
H	0.07673931	3.56400167	0.35085475
H	3.58635240	1.99186365	-2.89635183
H	0.97392588	-0.95221183	3.27650266
H	-3.47107243	-0.35316653	-1.01062487
N	-1.38136825	1.93660940	-0.19956944
N	-1.69445139	0.61632236	-0.38807074
C	-2.45159148	2.71325759	-0.49173520
C	-3.50428638	1.88785842	-0.87581829
C	-2.98095293	0.58976941	-0.80068050
C	2.21910999	0.47336089	-1.98365517
C	2.76018686	1.74251475	-2.23956317
N	1.07022020	1.89038905	-0.79157433
H	-2.38537418	3.79231215	-0.40969903
H	1.28546926	1.37136535	4.72902550
H	-4.50582632	2.18573151	-1.16587217
N	0.35401593	1.70745065	1.60155057
N	0.44666639	0.34540161	1.69650072
C	0.68271446	2.27771500	2.78966986
C	0.98614950	1.26438299	3.69229355
C	0.82682840	0.07486963	2.96298866
H	2.04864821	3.68917814	-1.34631936
C	1.99978375	2.61257289	-1.46470717
H	2.50327719	-0.49648259	-2.37562064
H	0.68669667	3.35638607	2.89928359
N	1.19557053	0.56446601	-1.11114973
Mo	-0.09527351	-0.94647065	-0.02087191
H	-2.44722644	-2.07011842	-1.23385294
O	2.46428918	-2.74253861	0.44044473
O	-1.39620416	-2.92117171	2.11445416
C	-0.98453418	-2.17130591	1.32165402
C	1.50274406	-2.09711051	0.24298158
C	-0.56370343	-1.76447098	-2.27255275
H	-0.92983815	-0.84257782	-2.73287737
C	0.54904615	-2.37167334	-2.86285989
H	1.07228100	-1.89826372	-3.69117957
H	0.91765079	-3.33569827	-2.51224866
H	-1.24997484	-3.42627185	-1.05810213
C	-1.39649042	-2.36301991	-1.26451439

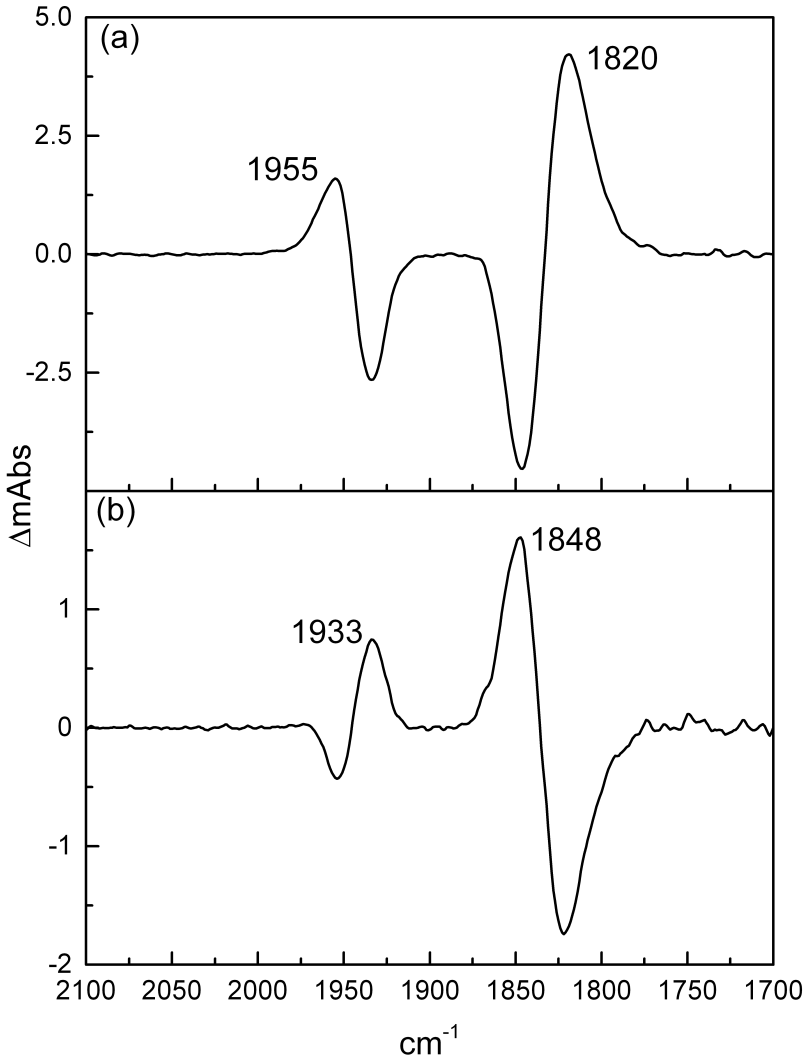


Figure S1: Photolysis of $TpMo(CO)_2(\eta^3\text{-}C_3H_4Me)$ in PVC at 85 K. (a) Difference spectrum obtained following λ_{irr} = 450 ± 50 nm photolysis of unphotolyzed sample. (b) Difference following λ_{irr} = 550 ± 50 nm back photolysis of λ_{irr} > 450 nm irradiated sample.

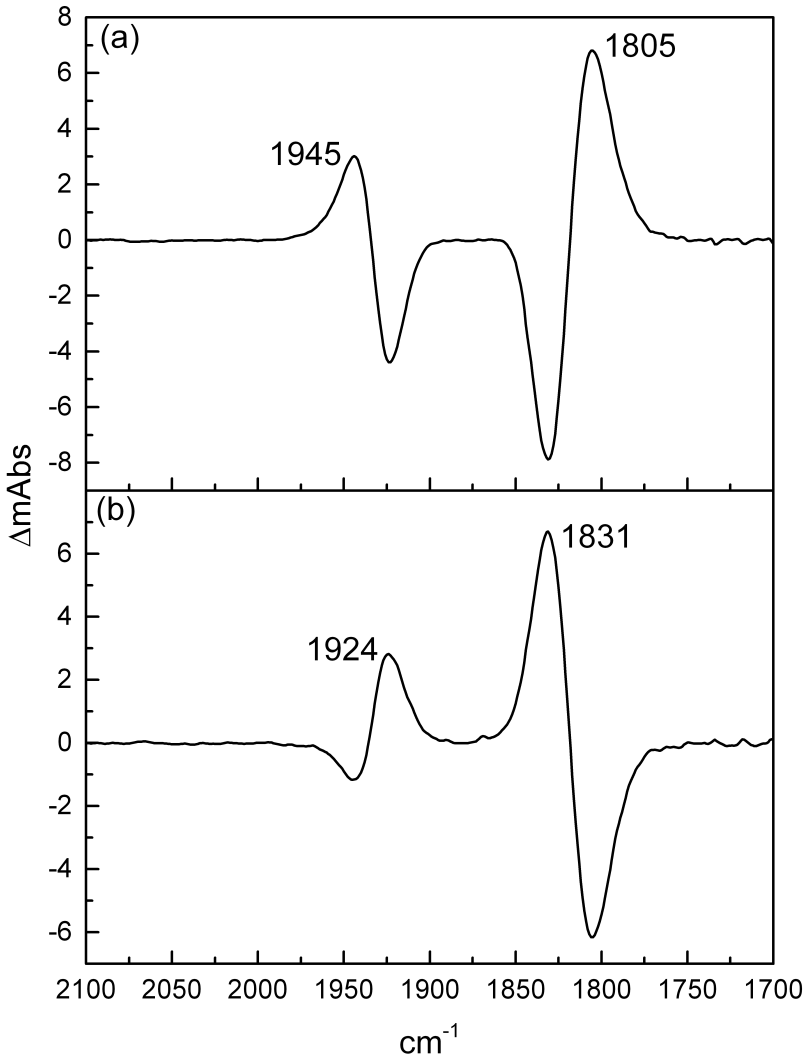


Figure S2: Photolysis of $TpW(CO)_2(\eta^3\text{-}C_3H_5)$ in PVC at 85 K. (a) Difference spectrum obtained following λ_{irr} = 400 ± 50 nm photolysis of unphotolyzed sample. (b) Difference following λ_{irr} = 550 ± 50 nm back photolysis of λ_{irr} > 400 nm irradiated sample.

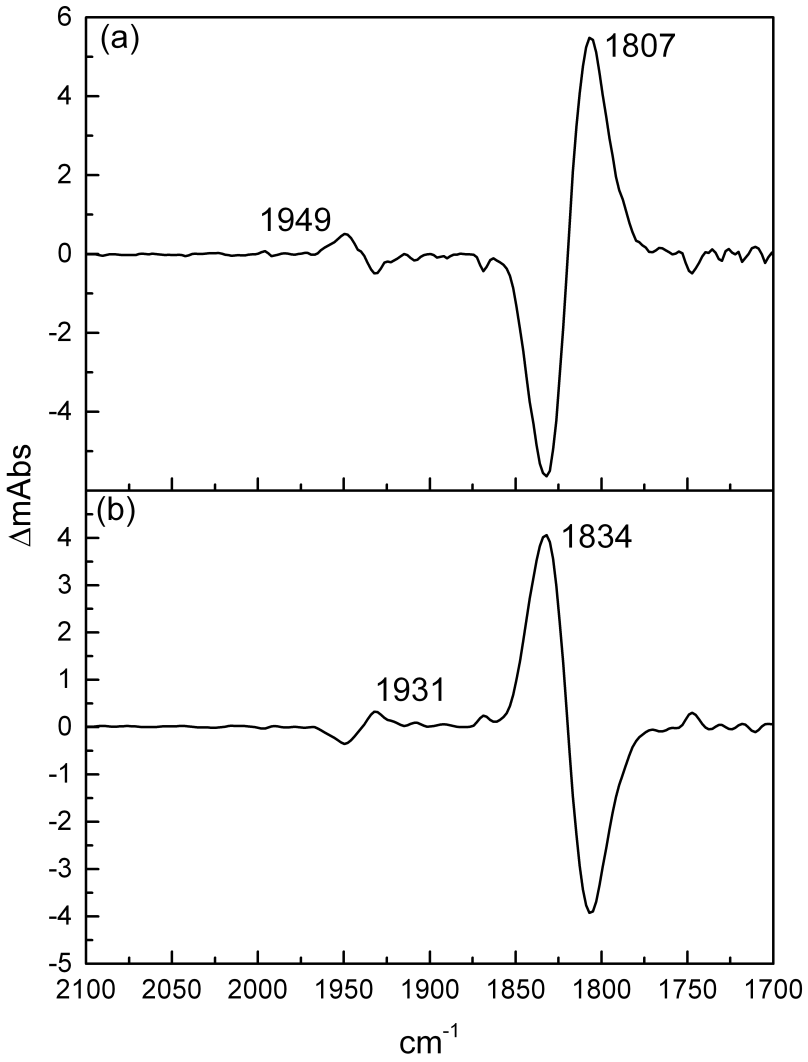


Figure S3: Photolysis of $TpW(CO)_2(\eta^3\text{-}C_3H_4Me)$ in PVC at 85 K. (a) Difference spectrum obtained following λ_{irr} = 400 ± 50 nm photolysis of unphotolyzed sample. (b) Difference following λ_{irr} = 550 ± 50 nm back photolysis of λ_{irr} > 400 nm irradiated sample.

exo-TpMo(CO)$_2$(η^3-C$_3$H$_5$) SAOP Excitation Energies

no.	E/a.u.	E/eV	f	Symmetry
1:	0.11980	3.25986	0.1170E-01	A
2:	0.12330	3.35504	0.3527E-01	A
3:	0.13624	3.70728	0.9321E-03	A
4:	0.14488	3.94232	0.1003	A
5:	0.15078	4.10306	0.8684E-02	A
6:	0.15249	4.14942	0.2723E-01	A
7:	0.15715	4.27614	0.2617E-02	A
8:	0.15939	4.33727	0.2420	A
9:	0.16272	4.42789	0.9107E-02	A
10:	0.16821	4.57735	0.1351E-01	A
11:	0.16858	4.58732	0.1117E-01	A
12:	0.16994	4.62429	0.6341E-01	A
13:	0.17133	4.66202	0.3427E-02	A
14:	0.17171	4.67240	0.2255E-01	A
15:	0.17192	4.67820	0.3666E-01	A
16:	0.17374	4.72770	0.1693E-01	A
17:	0.17754	4.83104	0.4153E-01	A
18:	0.17850	4.85730	0.1864E-01	A
19:	0.18013	4.90148	0.5203E-02	A
20:	0.18043	4.90980	0.3094E-02	A
21:	0.18137	4.93526	0.2679E-01	A
22:	0.18284	4.97540	0.5630E-02	A
23:	0.18532	5.04283	0.1635E-01	A
24:	0.18776	5.10922	0.1745E-01	A
25:	0.18910	5.14562	0.2486E-01	A
26:	0.19124	5.20378	0.3300E-01	A
27:	0.19289	5.24890	0.4284E-01	A
28:	0.19346	5.26438	0.4683E-01	A
29:	0.19472	5.29862	0.8900E-01	A
30:	0.19609	5.33576	0.4876E-01	A
31:	0.19737	5.37062	0.2752E-01	A
32:	0.19788	5.38459	0.1106E-01	A
33:	0.19898	5.41465	0.2646E-01	A
34:	0.19952	5.42919	0.3808E-01	A
35:	0.20056	5.45758	0.6709E-01	A
36:	0.20109	5.47196	0.3696E-02	A
37:	0.20155	5.48436	0.4010E-01	A
38:	0.20246	5.50929	0.9644E-03	A
39:	0.20412	5.55435	0.1570E-02	A
40:	0.20468	5.56955	0.1936E-01	A
41:	0.20491	5.57591	0.1112E-01	A
42:	0.20583	5.60090	0.5611E-02	A
43:	0.20675	5.62586	0.5939E-01	A
44:	0.20721	5.63849	0.5609E-02	A
45:	0.20774	5.65299	0.7729E-02	A
46:	0.20942	5.69856	0.5342E-01	A
47:	0.20998	5.71380	0.2229E-01	A
48:	0.21050	5.72794	0.6564E-03	A
49:	0.21063	5.73156	0.1755E-01	A
50:	0.21112	5.74495	0.1499E-01	A

gauche-TpMo(CO)$_2$(η^3-C$_3$H$_5$) SAOP Excitation Energies

no.	E/a.u.	E/eV	f	Symmetry
1:	0.11073	3.01299	0.1749E-01	A
2:	0.11870	3.22999	0.3096E-01	A
3:	0.12052	3.27952	0.7239E-01	A
4:	0.12925	3.51707	0.4605E-02	A
5:	0.12993	3.53568	0.2293E-01	A
6:	0.13551	3.68750	0.2362E-01	A
7:	0.14560	3.96192	0.1136	A
8:	0.15148	4.12186	0.3782E-01	A
9:	0.15632	4.25381	0.2643E-01	A
10:	0.15757	4.28757	0.9321E-04	A
11:	0.16137	4.39120	0.2525E-01	A
12:	0.16249	4.42160	0.5533E-01	A
13:	0.16607	4.51890	0.1258	A
14:	0.16909	4.60110	0.3746E-02	A
15:	0.16914	4.60265	0.7897E-02	A
16:	0.17159	4.66930	0.1194	A
17:	0.17274	4.70054	0.3448E-02	A
18:	0.17335	4.71722	0.2979E-01	A
19:	0.17372	4.72724	0.1474E-01	A
20:	0.17583	4.78452	0.3999E-01	A
21:	0.17731	4.82494	0.1736E-02	A
22:	0.17811	4.84656	0.9082E-02	A
23:	0.17986	4.89434	0.3627E-02	A
24:	0.18012	4.90129	0.2633E-01	A
25:	0.18140	4.93613	0.1051E-01	A
26:	0.18432	5.01548	0.5759E-01	A
27:	0.18526	5.04111	0.9064E-01	A
28:	0.18612	5.06455	0.2015E-01	A
29:	0.18710	5.09128	0.6145E-02	A
30:	0.18751	5.10244	0.5622E-01	A
31:	0.18819	5.12103	0.1454E-01	A
32:	0.18932	5.15172	0.1199E-01	A
33:	0.19106	5.19898	0.8078E-02	A
34:	0.19131	5.20590	0.1726E-01	A
35:	0.19322	5.25769	0.1920E-01	A
36:	0.19420	5.28449	0.2909E-01	A
37:	0.19448	5.29219	0.4674E-02	A
38:	0.19495	5.30482	0.2681E-01	A
39:	0.19590	5.33083	0.5776E-01	A
40:	0.19613	5.33706	0.1721E-02	A
41:	0.19758	5.37630	0.6259E-01	A
42:	0.19898	5.41450	0.8544E-02	A
43:	0.19958	5.43097	0.3442E-01	A
44:	0.19978	5.43619	0.4289E-01	A
45:	0.20122	5.47548	0.3601E-01	A
46:	0.20191	5.49425	0.2865E-01	A
47:	0.20247	5.50944	0.3341E-01	A
48:	0.20387	5.54764	0.5123E-01	A
49:	0.20401	5.55140	0.1896E-01	A
50:	0.20534	5.58766	0.8431E-02	A