Electronic Supplementary Material (ESI) for Chemical Communications

Alkene oxidation by Ti-containing polyoxometalates. Unambiguous characterization of the role of protonation state.

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Experimental Section

Materials. Cyclohexene, *cis*-cyclooctene, cyclooctene and cyclohexene oxides, biphenyl, trifluoromethanesulfonic acid (TFMS) were purchased from Aldrich. Acetonitrile (Fluka) was dried and stored over activated 4A molecular sieves. The concentration of hydrogen peroxide (*ca*. 30 wt. % in water) was determined by iodometric titration prior to use. $[Bu_4N]_4[PTi(OH)W_{11}O_{39}]$ (hereinafter referred to as TBA-**1**) was synthesized as described elsewhere[1] and characterized by ^{31}P NMR and FT-IR spectroscopic techniques .

Instrumentation. GC analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (30×0.25) filled with Supelco MDN-5S. GC-MS analyses were carried out using a gas chromatograph Agilent 6890 (quartz capillary column 30m×0.25mm/HP-5ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973.

Catalytic runs and kinetic measurements. Catalytic oxidations of cyclooctene and cyclohexene with H_2O_2 were carried out in temperature-controlled glass vessels equipped with a magnetic stirrer (500 rpm). The reaction was initiated by injection of the oxidant (0.1 M) to a MeCN solution (5 mL) containing alkene (0.1 M) and Ti-POM (0.002 M). To evaluate the effect of protons, 1 or 2 equiv (0.002 or 0.004 M) of TFMS was added to the reaction mixture before the addition of H_2O_2. Samples were taken during the reaction course by a syringe, and the reaction products were identified by GC-MS and GC using reference compounds. Substrate conversions and product yields were quantified by GC using biphenyl as internal standard. Study on the effect of protons on the activation energy of alkene epoxidation catalyzed by Ti-POM was carried out using cyclooctene as substrate because it is much less volatile compared to cyclohexene, which facilitates kinetic measurements. The activation energy values (Ea) were evaluated in the temperature range of 40–70 ^{o}C from the initial rates of cyclooctene consumption. The corresponding kinetic curves are shown in Figures S1-S3. Each experiment was reproduced at least three times. The error in determination of Ea was in the range of ± 1.0 kcal.mol^{-1}.

Computational Details. Calculations were performed with Gaussian09 package[2] and NBO program (version 3.0)[3] at the DFT level by means of the hybrid exchange-correlation B3LYP[4] functional. For Ti, W and As atoms, the LANL2DZ pseudopotential was used.[5] The 6-31G(d, p) basis set[6] was used for the C and H atoms,

as well as for the O atoms of hydrogen peroxide and directly bound to Ti. For the rest of atoms, we employed a 6-31G basis set.[6] Geometry optimization in gas phase of all reactants, intermediates and of the transition states were performed without any symmetry constrains. The transition states were characterized by a single imaginary frequency and the normal mode which corresponds to the expected reaction path. Solvent effects were included by means of SMD model[7] single point calculations as implemented in Gaussian09,[2] using the most common experimental reported acetonitrile dielectric constant, $\varepsilon = 36.64$. Natural Bond Orbital (NBO) method[3,8] was used to compute atomic charges and to analyze the resultant wave function in terms of optimally chosen localized orbitals, localized orbitals corresponding to a Lewis structure representation of chemical bonding.

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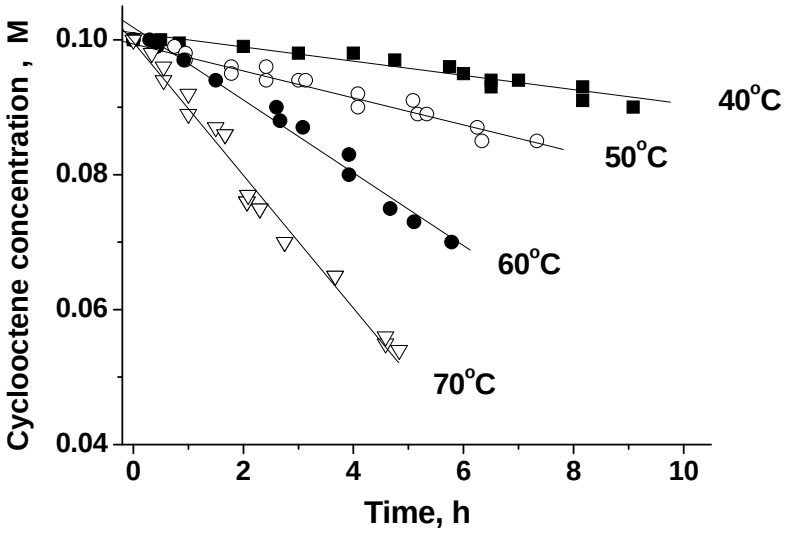

Figure S1. Kinetic curves (initial portions) for cyclooctene consumption at different temperatures. Reaction conditions: 0.1 M alkene, 0.1 M H_2O_2, 0.002 M TBA-**1**, CH_3CN 5 mL.

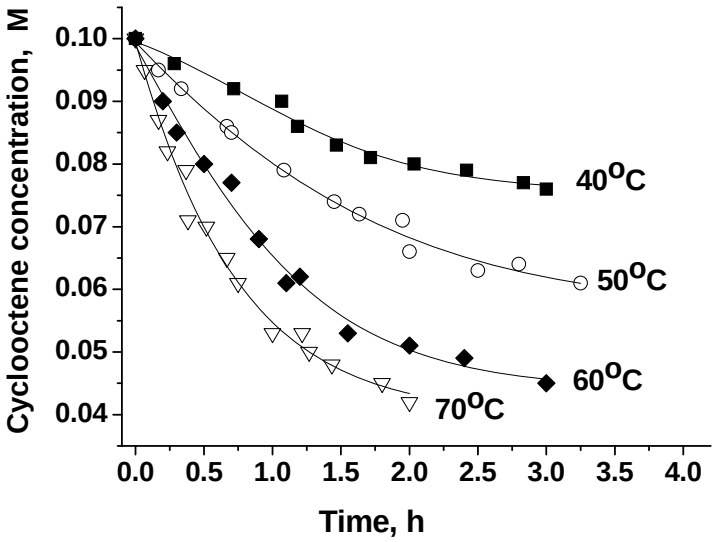

Figure S2. Kinetic curves for cyclooctene consumption at different temperatures in the presence of 1 eq (0.002 M) of TFMS. Other reaction conditions as in Figure S1.

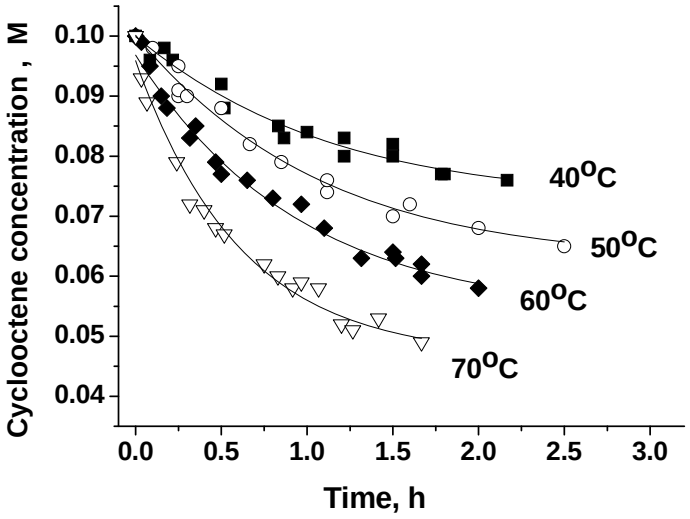

Figure S3. Kinetic curves for cyclooctene consumption at different temperatures in the presence of 2 eq of TFMS. Other reaction conditions as in Figure S1.

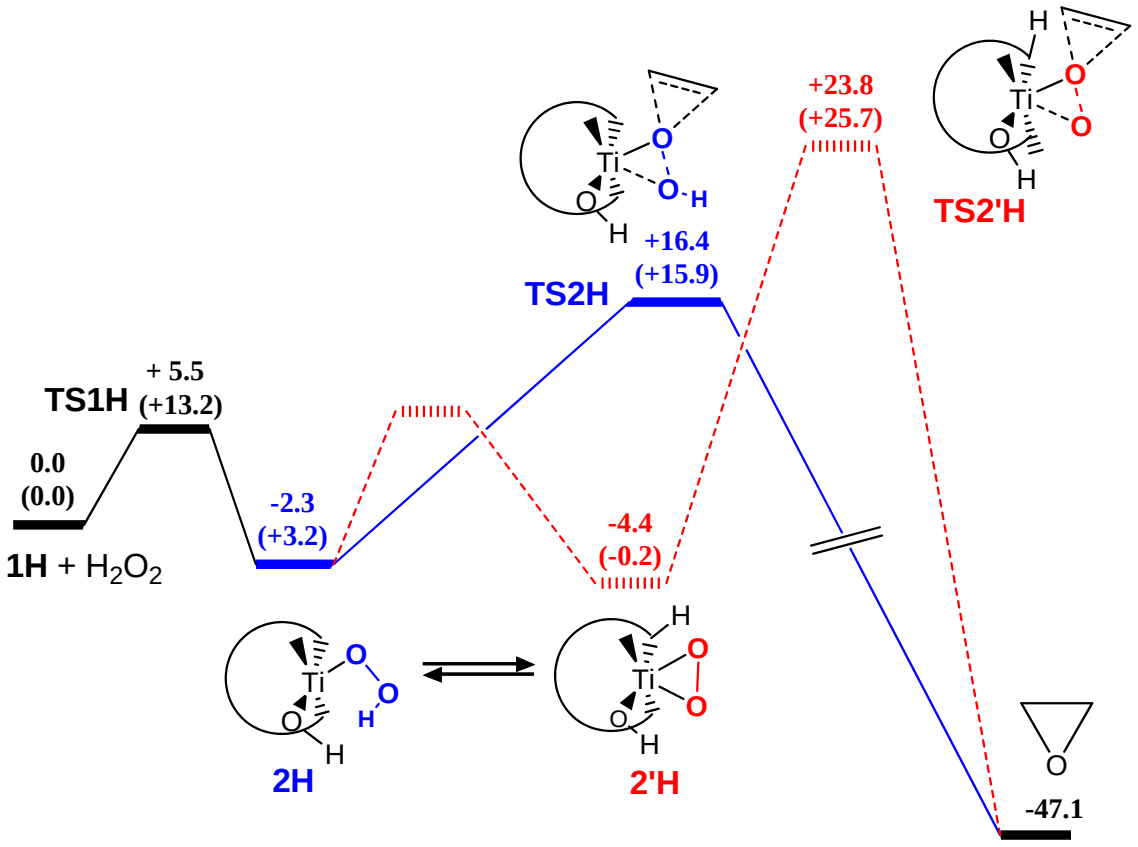

Figure S4. Calculated potential energy profile (kcal.mol^{-1}) for ethene epoxidation with H_2O_2 by $[HPTi(OH)W_{11}O_{39}]^{3-}$ (**1H**) anion in vacuum. Dashed red lines correspond to the less favorable peroxo path. Values in parenthesis correspond to solvent calculations in MeCN.

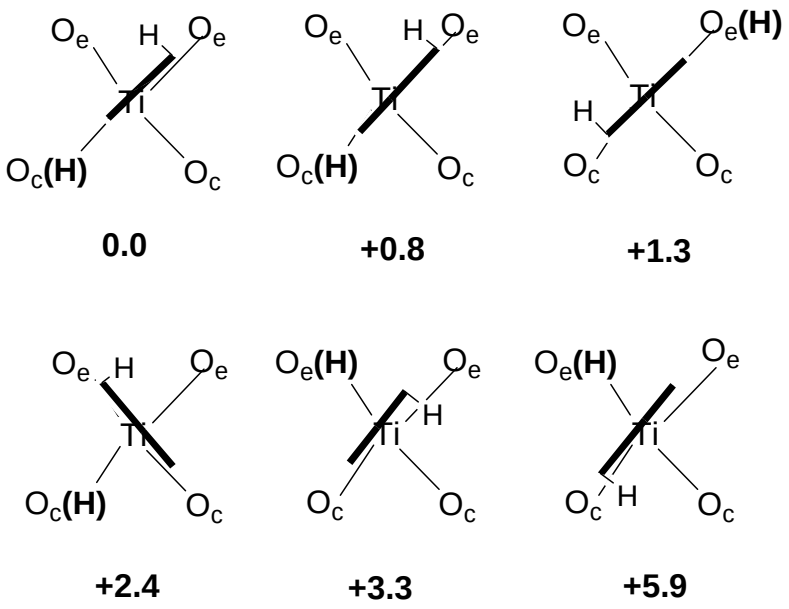

Figure S5. Schematic representation of the geometries and relative energies (kcal.mol^{-1}) of the possible isomers for the Ti-hydroperoxo $[HPTi(OOH)W_{11}O_{39}]^{3-}$ anion. The O_e and O_c labels denote edge- and corner-sharing oxygens.

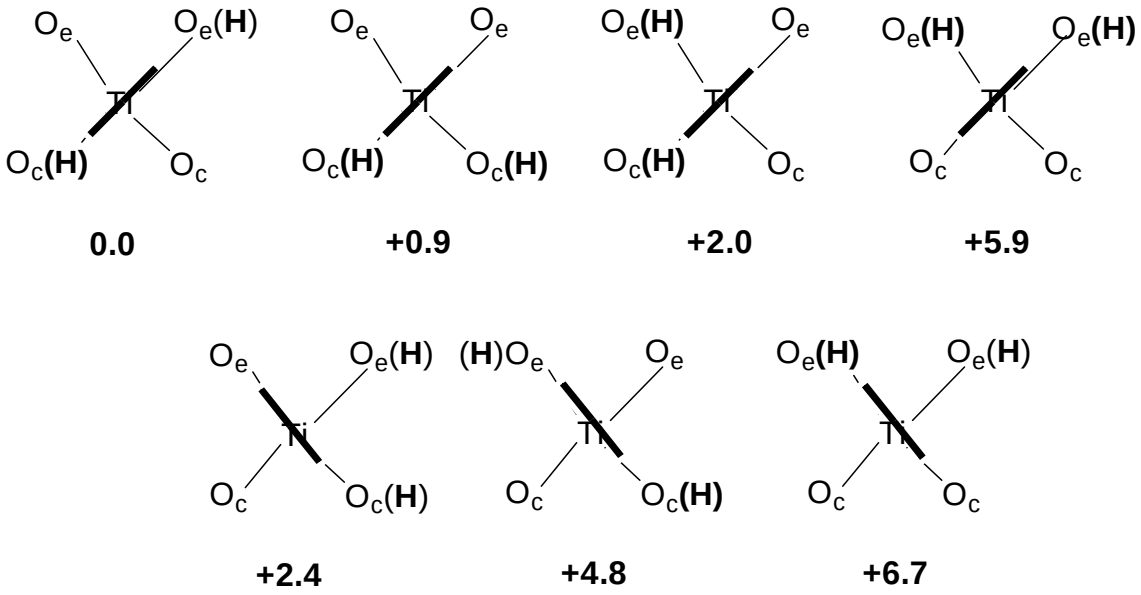

Figure S6. Schematic representation of the geometries and relative energies (kcal.mol^{-1}) of the possible isomers for the Ti-peroxo $[H_2PTi(O_2)W_{11}O_{39}]^{3-}$ anion. The O_e and O_c labels denote edge- and corner-sharing oxygens.

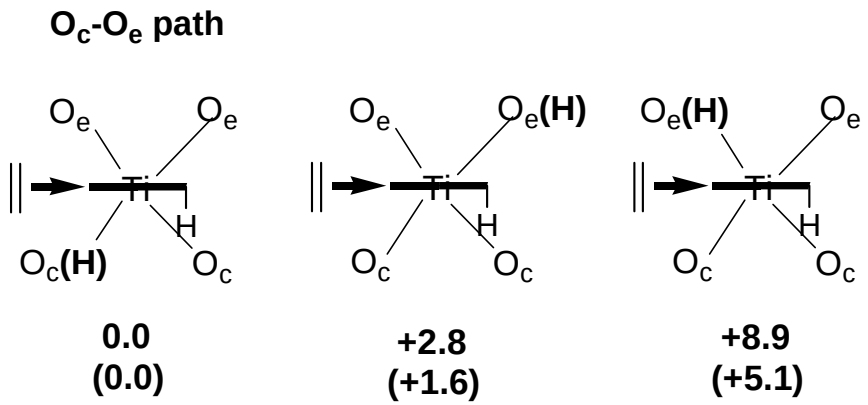

Figure S7. Schematic geometries and the relative energies (kcal.mol^{-1}) of the possible approaching paths of the alkene substrate to the oxygen α for the hydroperoxo species. Values in parenthesis correspond to single point calculation including solvent via SMD. The O_e and O_c labels denote edge- and corner-sharing oxygens.

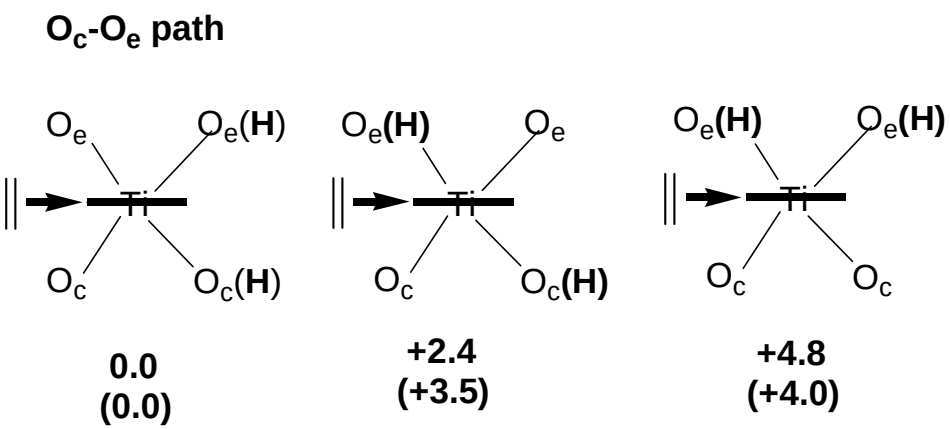

Figure S8. Schematic geometries and the relative energies (kcal.mol^{-1}) of the possible approaching paths of the alkene substrate to the oxygen α for the peroxo species. Values in parenthesis correspond to single point calculation including solvent via SMD. The O_e and O_c labels denote edge- and corner-sharing oxygens.

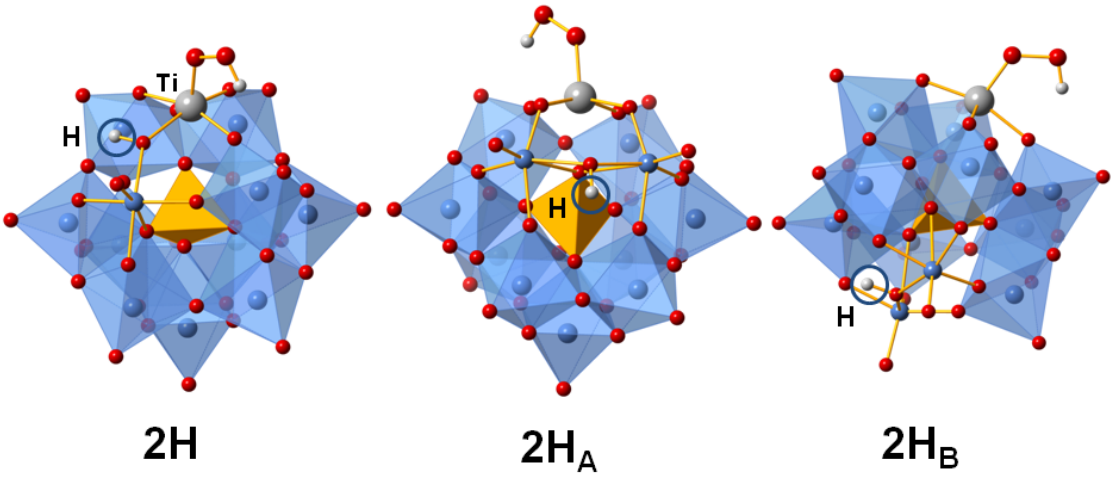

Figure S9. Structures for Keggin-type hydroperoxo **2H**, **2H$_A$**, **2H$_B$** species.

Cartesian coordinates in Å and the electronic energies for some of the most representative structures:

$[HPTi(OH)W_{11}O_{39}]^{3-}$ (**1H)**

E= -4157.746785 u.a.

O	-0.824552	-0.522509	-1.481070
W	-3.220055	-0.222045	-1.900967
O	-4.890362	-0.175456	-2.398083
O	-3.362807	-0.653720	0.015032
W	-3.005819	-0.361672	1.850851
O	-4.583861	-0.340619	2.589112
O	-0.655800	-0.653949	1.182409
W	-0.787691	-3.038958	1.619323
O	-1.004673	-4.665565	2.204685
O	-2.713616	1.460447	1.346366
W	-2.237034	2.847505	0.061642
O	-3.557737	3.974993	0.193442
O	-0.113670	1.631005	-0.092228
P	-0.007186	0.002105	-0.168822
O	1.579495	-0.412535	-0.250744
W	2.366252	-2.714964	-0.364671
O	3.212977	-4.233069	-0.488101
O	1.044970	-3.053390	0.974756
O	0.914626	-2.899321	-1.617154
W	-0.969207	-2.844181	-2.159864
O	-1.227344	-4.437229	-2.821952
O	3.402967	-1.753297	0.949534
W	3.247161	0.112861	1.490594
O	4.638749	0.335017	2.512793
O	3.284888	-1.644014	-1.704413
W	3.147781	0.289690	-1.974063
O	4.438806	0.599922	-3.101348
O	-2.894528	1.553670	-1.216093
O	-1.142154	3.647094	-1.264957
W	0.677427	3.109282	-1.849764
O	1.134630	4.399336	-2.927029
O	-0.994366	3.518459	1.400388
W	0.863782	3.013737	1.640622
O	1.435614	4.239300	2.737641
O	-1.230254	-3.143380	-0.214934
O	-2.741277	-2.095837	-2.175377
O	-0.507442	-1.850828	-3.652856
Ti	-0.424630	0.131511	-3.666404
O	-0.254082	0.575750	-5.442795
O	-0.128560	1.789101	-2.986935
O	1.616507	-0.337869	-3.208574
O	-2.322006	0.162295	-3.483014
O	-2.495844	-2.234378	2.021484
O	-1.831422	-0.076241	3.385438
W	0.083623	-0.204275	3.459172
O	0.394234	-0.079324	5.168635
O	1.872496	-0.394588	2.715271
O	0.231241	1.594459	2.832043
O	-0.139538	-2.106746	3.206600
O	2.395599	1.823851	1.491401
O	1.242541	3.758124	-0.055614

O	2.219623	1.918114	-1.909790
O	3.984016	0.517271	-0.267653
H	0.093860	1.475928	-5.513549
H	1.630869	-1.312034	-3.216480

$[HPTi(OH)(H_2O_2)W11O39]^{3-}$ (**TS1H)**

E: -4309.404355 u.a.

O	0.525939	0.702777	1.485124
W	2.847642	1.452093	1.878417
O	4.390164	2.034589	2.424144
O	3.326841	-0.130077	0.839014
W	3.315321	-1.264846	-0.679073
O	4.993859	-1.573541	-0.983658
O	0.875968	-1.255477	-0.318774
W	1.036784	-3.235783	1.059285
O	1.328472	-4.764344	1.824227
O	2.968224	0.367067	-1.664127
W	2.300204	2.155719	-1.772152
O	3.614690	3.041775	-2.473456
O	0.163092	1.180871	-1.094745
P	-0.008665	0.062039	0.081195
O	-1.585725	-0.379388	0.174869
W	-2.414336	-2.003152	1.773916
O	-3.287606	-3.086670	2.808770
O	-0.886615	-3.012941	1.259694
O	-1.233387	-1.066807	2.971278
W	0.526832	-0.452583	3.572835
O	0.621884	-1.076078	5.190790
O	-3.194921	-2.354408	0.018870
W	-2.895826	-1.426324	-1.636613
O	-4.059206	-2.131547	-2.710557
O	-3.561878	-0.428394	1.786944
W	-3.429642	1.118383	0.626567
O	-4.856305	2.010327	1.065966
O	2.659741	2.228226	0.100079
O	0.948136	3.562029	-1.521731
W	-0.879620	3.359944	-1.024372
O	-1.520895	4.952647	-1.268076
O	1.256990	1.656216	-3.327971
W	-0.492227	0.838589	-3.404542
O	-0.846386	0.910763	-5.099780
O	1.126447	-1.982431	2.473533
O	2.297423	0.278107	3.311220
O	-0.120992	1.275116	3.842812
Ti	-0.229065	2.707816	2.535074
O	-0.444546	3.341156	0.823501
O	-2.129953	1.691186	2.112204
O	1.677572	2.726182	2.561307
O	2.806029	-2.748417	0.450416
O	2.440335	-2.235087	-2.117127
W	0.574363	-2.614048	-2.341598
O	0.586236	-3.731784	-3.666375
O	-1.327689	-2.432379	-1.965839
O	0.331342	-0.892397	-3.179826
O	0.707917	-3.748707	-0.799014
O	-2.044000	-0.056960	-2.682815
O	-1.181663	2.524521	-2.752561
O	-2.461239	2.346316	-0.400696

O	-3.955493	0.033726	-0.818616
H	-0.749485	4.307618	3.952359
O	-1.669766	3.481086	3.954501
O	0.209824	4.555944	3.352637
O	-2.754616	4.139191	3.243404
H	-3.107262	3.370193	2.756536
H	1.094199	4.498914	3.737945
H	-2.164630	1.033377	2.829506

$[HPTi(OOH)W11O39]^{3-}$ (**2H)**

E= -4232.998679 u.a.

O	-0.780201	-0.232121	1.549461
W	-0.814756	-2.335134	2.727386
O	-0.982767	-3.726666	3.749925
O	-1.028850	-3.087813	0.931491
W	-0.563493	-3.393202	-0.888490
O	-0.670120	-5.114304	-1.067577
O	-0.607637	-0.974495	-1.014725
W	-2.953021	-1.010557	-1.735004
O	-4.517313	-1.260329	-2.438959
O	1.249464	-3.131379	-0.251770
W	2.526936	-2.406273	0.969117
O	3.461887	-3.786694	1.445677
O	1.602972	-0.267068	0.286728
P	-0.002392	0.015670	0.134678
O	-0.238071	1.566586	-0.314370
W	-2.421330	2.558098	-0.773278
O	-3.789337	3.551114	-1.155810
O	-2.779048	0.919649	-1.690657
O	-2.979586	1.610811	0.791260
W	-3.219577	0.015242	1.879040
O	-4.886816	0.083246	2.353295
O	-1.154074	3.041520	-2.160066
W	0.705501	2.548517	-2.325671
O	1.219247	3.527186	-3.660714
O	-1.360394	3.748036	0.371991
W	0.411308	3.477242	1.027584
O	0.792584	5.010101	1.749728
O	1.079672	-2.376229	2.234054
O	3.374210	-0.977538	1.982800
W	3.111812	0.937442	1.774423
O	4.352348	1.586592	2.798750
O	3.527145	-1.715288	-0.553722
W	3.251968	-0.081891	-1.530606
O	4.625350	-0.011465	-2.585478
O	-3.307686	-0.837750	0.118571
O	-2.627156	-1.686127	2.594274
O	-2.351598	0.850453	3.303683
Ti	-0.475131	0.885664	3.500102
O	-0.279105	1.746745	5.098233
O	1.596661	0.518083	3.102703
O	-0.223947	2.484829	2.500297
O	-0.444248	-0.965055	3.962960
O	-2.322841	-2.814656	-1.449349
O	0.028144	-2.818494	-2.650928
W	0.127183	-1.027321	-3.353037
O	0.443253	-1.276978	-5.038753
O	0.162589	0.888796	-3.148723

O	1.916693	-0.904492	-2.597329
O	-1.787265	-0.999100	-3.295510
O	2.297808	1.548824	-1.887627
O	3.948237	0.812814	0.085428
O	2.059527	2.420838	1.341904
O	1.033923	3.691534	-0.800743
O	-0.053773	3.156111	5.191814
H	-0.047337	3.406464	4.242315
H	1.709731	-0.404836	3.389342

$[HPTi(O\cdot)W11O39]^{3-}$

E= -4157.184671 u.a.

O	-0.789900	-0.576949	-1.481568
W	-3.215909	-0.374095	-1.885556
O	-4.881120	-0.393463	-2.371893
O	-3.325040	-0.767827	0.030380
W	-2.973359	-0.496874	1.873190
O	-4.542114	-0.541003	2.609775
O	-0.624613	-0.671284	1.183161
W	-0.628347	-3.054634	1.625225
O	-0.766511	-4.681029	2.210122
O	-2.764997	1.364191	1.362650
W	-2.376607	2.720464	0.075943
O	-3.723736	3.803992	0.200414
O	-0.206044	1.613099	-0.117649
P	-0.002643	-0.005199	-0.172416
O	1.597397	-0.346673	-0.245652
W	2.481997	-2.598738	-0.390286
O	3.393734	-4.068526	-0.517426
O	1.195859	-2.981980	0.966057
O	1.041078	-2.846902	-1.633065
W	-0.849999	-2.884161	-2.147228
O	-1.038049	-4.478256	-2.808343
O	3.499586	-1.576375	0.924000
W	3.248615	0.245506	1.477975
O	4.623409	0.546794	2.489705
O	3.356221	-1.468700	-1.715565
W	3.125871	0.440670	-1.975754
O	4.375509	0.804246	-3.123085
O	-2.951444	1.436939	-1.213433
O	-1.287901	3.577230	-1.321724
W	0.483303	3.143400	-1.869889
O	0.896335	4.454931	-2.927549
O	-1.098533	3.505461	1.308507
W	0.747968	3.030560	1.608414
O	1.277886	4.293977	2.670187
O	-1.080474	-3.181933	-0.211465
O	-2.657775	-2.205491	-2.167401
O	-0.457404	-1.854905	-3.655563
Ti	-0.454123	0.088251	-3.658318
O	-0.251564	0.385522	-5.450980
O	-0.175367	1.817877	-3.073363
O	1.599716	-0.253221	-3.167211
O	-2.332709	0.086050	-3.461858
O	-2.376359	-2.326003	2.032464
O	-1.808605	-0.127315	3.389496
W	0.105725	-0.183234	3.460786
O	0.416751	-0.027373	5.158901

O	1.899557	-0.269988	2.707479
O	0.176904	1.632670	2.804955
O	-0.025686	-2.084440	3.209118
O	2.320656	1.930966	1.425056
O	1.100670	3.776487	-0.149346
O	2.098450	2.004795	-1.916749
O	3.959059	0.717102	-0.303642
H	1.682612	-1.221076	-3.222687

$[HPTi(O\cdot)W11O39]^{3-}$ **(TS2H)**

E= -4311.560958 u.a.

P	0.007115	0.023824	0.081918
Ti	2.553420	1.258304	2.356761
W	-2.542143	-0.023157	2.616872
W	-2.326197	-1.495108	-2.282497
W	2.477945	0.211141	-2.561715
W	0.856116	-1.590136	3.154136
W	0.762420	-3.017639	-1.797033
W	-0.610905	1.775721	-3.010901
W	-1.057745	3.026024	1.826754
W	-3.280958	1.583132	-0.390985
W	1.698741	3.073591	-0.743776
W	3.227218	-1.583936	0.656118
W	-1.624591	-3.109498	0.730069
O	1.181607	-0.321986	1.161217
O	-1.239197	0.842226	0.764979
O	-0.579963	-1.359397	-0.569989
O	0.644685	0.935018	-1.115246
O	0.166680	3.404143	0.460736
O	-0.242864	-2.730619	1.959546
O	-2.015254	2.125931	-1.734984
O	2.041665	-2.683541	-0.434938
O	-2.543986	-1.642028	1.612635
O	3.245172	-0.474840	-0.950862
O	-3.211353	-0.110546	-1.244481
O	2.427884	2.250511	0.786865
O	-1.379456	0.009504	-3.042433
O	0.522743	2.067882	2.675378
O	1.544471	-1.452884	-2.637684
O	-0.818451	-0.580437	3.263367
O	2.395053	-2.320366	2.232491
O	-2.579371	3.064714	0.705680
O	-0.364637	-3.906881	-0.508864
O	0.436123	3.197341	-2.212199
O	3.697538	-0.094516	1.670916
O	-2.699614	-2.728697	-0.861525
O	2.815927	2.025823	-1.888073
O	-3.733964	0.759079	1.284383
O	-2.022217	1.813933	2.996242
O	1.070987	1.034622	-3.609989
O	1.848381	-0.081995	3.589511
O	-0.869407	-2.642749	-2.779436
O	2.792288	2.510398	3.886932
O	-3.613237	-0.365746	3.937879
O	-3.520235	-1.886425	-3.477274
O	3.751301	0.023583	-3.724696
O	0.858365	-2.488666	4.640846
O	1.441929	-4.339221	-2.691081

O	-1.211343	2.514851	-4.459968
O	-1.138257	4.517307	2.716584
O	-4.790077	2.242630	-0.932949
O	2.483504	4.624907	-0.774572
O	4.734283	-2.446929	0.570120
O	-2.413135	-4.507594	1.387526
O	4.242334	2.166582	2.900687
C	5.592442	2.154400	1.294398
H	5.025659	1.708047	0.486219
H	5.801101	3.217000	1.226885
C	6.052072	1.403486	2.333675
H	6.657845	1.841975	3.120526
H	5.863691	0.337661	2.368539
H	2.536616	3.388141	3.556727
H	0.198217	1.490441	3.387812