Electronic Supplementary Material (ESI) for Dalton Transactions

Kinetic, DFT and TD-DFT studies on the mechanism of stabilization of pyramidal H_3PO_3 at the $[Mo_3M´S_4(H_2O)_{10}]^{4+}$ clusters (M´ = Pd, Ni).

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Electronic Supplementary Information (ESI)

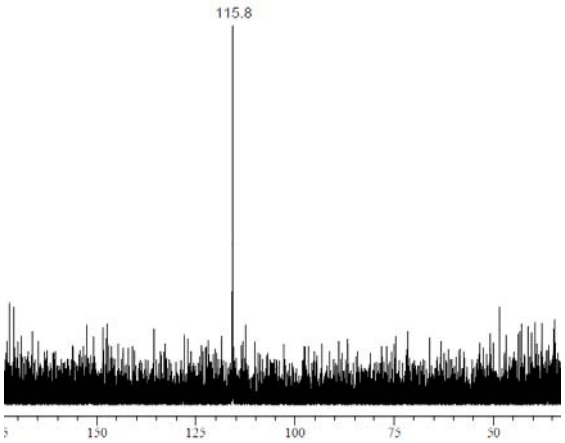

Figure S1. $^{31}P\{^1H\}$ NMR spectrum showing that the only observable reaction product in the reaction of $[1\text{-}OH_2]^{4+}$ with H_3PO_3 is $[Mo_3Pd(pyr\text{-}H_3PO_3)S_4(H_2O)_9]^{4+}$ ($[1\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$), characterized by a singlet at 115.8 ppm

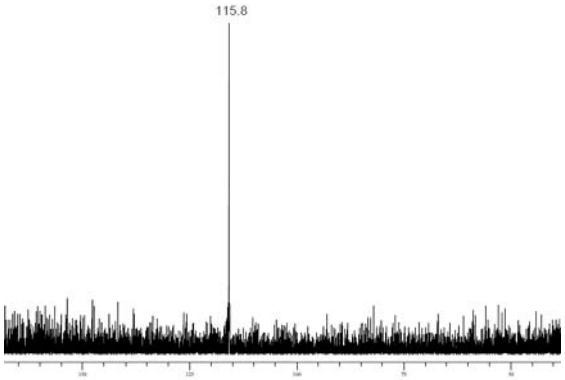

Figure S2. ^{31}P NMR spectrum for the same sample than Figure S1 showing that the singlet at 115.8 ppm for $[Mo_3Pd(pyr\text{-}H_3PO_3)S_4(H_2O)_9]^{4+}$ ($[1\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$)does not split when protons are not decoupled, which indicates that all the H atoms in coordinated H_3PO_3 are in OH groups.

Table S1. Frontier molecular orbital composition for $[1\text{-}OH_2]^{4+}$, $[1\text{-}O\text{-}tet\text{-}H_3PO_3]^{4+}$ and $[1\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$.

Complex	Orbital	*E* (eV)	Main Component (%)			
			H_2O-Pd	Pd	Mo_3S_4(Mo,S)	H_2O-Mo
$[1\text{-}OH_2]^{4+}$	L+4	-15.12	0	0	98 (74,24)	2
	L+3	-15.14	0	0	98 (71,27)	2
	L+2	-15.73	3	19	78 (43,35)	1
	L+1	-15.89	0	12	86 (67,19)	3
	LUMO	-15.91	0	11	85 (68,17)	4
	HOMO	-18.82	6	43	50 (22,28)	0
	H-1	-18.97	1	37	63 (36,27)	0
	H-2	-19.27	3	16	81 (64,17)	0
	H-3	-19.31	0	24	74 (54,20)	1
	H-4	-19.37	6	31	61 (52,9)	2
$[1\text{-}O\text{-}tet\text{-}H_3PO_3]^{4+}$	L+4	-14.64	0	0	99 (72,27)	1
	L+3	-14.65	0	0	98 (71,27)	2
	L+2	-15.15	4	23	73 (38,35)	0
	L+1	-15.37	0	12	85 (67,18)	3
	LUMO	-15.39	0	12	85 (67,18)	3
	HOMO	-18.21	21	39	39 (14,25)	0
	H-1	-18.28	13	42	44 (18,26)	0
	H-2	-18.66	19	26	55 (45,10)	1
	H-3	-18.71	11	12	78 (64,14)	0
	H-4	-18.80	3	16	81 (64,17)	0
$[1\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$	L+4	-14.59	0	0	99 (72,27)	1
	L+3	-14.6	0	0	99 (72,27)	1
	L+2	-14.94	12	26	62 (30,32)	0
	L+1	-15.50	0	9	87 (68,19)	4
	LUMO	-15.51	0	9	87 (68,19)	4
	HOMO	-18.21	45	12	43 (34,9)	1
	H-1	-18.52	4	31	67 (42,25)	0
	H-2	-18.54	3	31	68 (42,26)	0
	H-3	-18.95	2	23	74 (53,21)	1
	H-4	-18.96	2	24	73 (52,21)	1

Cartesian coordinates of the BS-I gas phase optimized species and BS-II/PCM absolute energies (Hartree).

H_2O (-76.47397018)

O	0.000000	0.112037	0.000000
H	0.800454	-0.448178	0.000000
H	-0.800454	-0.448118	0.000000

H_3PO_3-*tet* (-569.0746144)

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.517061
O	1.479343	0.000000	2.223813
O	-0.816891	1.233344	2.223664
H	-0.572385	-1.065831	2.235996
H	-1.000288	2.032494	1.691348
H	2.247114	0.288095	1.691676

H_3PO_3-*pyr* (-569.0561524)

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.667665
O	1.627547	0.000000	2.033822
O	-0.354209	-1.666929	1.746147
H	-0.103669	-0.862544	-0.454597
H	2.252236	-0.580003	1.547867
H	-0.628091	-2.039714	2.607292

$H_4PO_3^+$ (-569.4946072)

O	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.575114
O	1.480772	0.000000	2.108049
O	-0.877115	-1.247639	2.008909
H	-0.512829	1.198209	2.093846
H	2.274543	-0.491314	1.812462
H	-1.104440	-1.597914	2.894746
H	-0.627423	-0.408185	-0.630911

$[1\text{-}OH_2]^{4+}$ (-1134.31923271)

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.458032
S	2.330806	0.000000	3.116046
Pd	1.413246	2.367672	3.164796
O	2.171296	3.618827	4.796335
Mo	2.159600	0.831344	0.851235
O	4.349010	1.082960	1.078607
Mo	-0.241977	2.294917	0.838090
S	-1.078140	2.081356	3.111361
O	2.979718	-1.086311	0.101423
S	1.988385	3.248872	0.848637
O	-0.836304	4.421887	0.918716
O	-2.432153	2.246064	0.321557
O	-2.136180	-0.732642	2.431465
O	0.086075	-2.207121	2.282799
O	-0.422346	2.830126	-1.308354
O	2.831180	1.193212	-1.270151
O	-0.291910	-0.705999	4.539928
H	-2.384326	-1.599637	2.047336
H	-2.922649	-0.271454	2.788487

H	-1.182703	-0.908557	4.896304
H	0.356080	-0.609913	5.270589
H	0.110886	-2.796428	1.501666
H	0.207925	-2.709709	3.118093
H	-3.194955	2.144975	0.926512
H	-2.720666	2.234688	-0.615731
H	-0.344526	2.260840	-2.101442
H	-0.488812	3.780769	-1.546409
H	-0.264838	5.174217	1.182514
H	-1.783654	4.673547	0.960794
H	2.927021	2.060874	-1.714648
H	3.078364	0.456549	-1.868142
H	4.888433	1.495541	0.370383
H	4.841712	1.070693	1.926363
H	2.533534	-1.846668	-0.324438
H	3.914366	-1.293152	0.322007
H	3.115834	3.786092	4.988599
H	1.601109	4.079732	5.444477

$[1\text{-}OH_2]^{4+}\cdots H_3PO_3$ (-1703.399929)

S	-2.29864	-0.43739	1.55828
Mo	-1.76746	-0.97937	-0.78044
O	-1.9011	-1.95461	-2.76596
Mo	0.13484	-0.80032	1.27385
O	2.16936	-1.29572	1.70117
Mo	-1.27999	1.49332	0.43767
O	-3.29775	2.49437	0.27173
O	0.30426	-0.56471	3.45865
S	1.0645	1.41718	1.0166
Pd	0.7082	0.38095	-1.25029
S	0.38879	-2.08848	-0.75693
O	-1.65606	2.55026	2.35336
S	-1.60331	1.14435	-1.95158
O	-3.96291	-0.78478	-1.29129
O	2.43599	0.77815	-2.49816
O	4.03415	-0.26568	0.53595
P	5.35799	0.28301	0.00432
O	5.03791	0.73797	-1.54822
O	-2.71856	-2.92205	-0.30838
O	-0.16224	-2.87094	2.14663
O	-0.77723	3.59856	-0.04507
H	-3.76702	2.81144	1.07151
H	-3.84887	2.59971	-0.52956
H	-1.46399	4.20815	-0.38847
H	0.12161	3.93419	-0.2431
H	-2.03244	2.21944	3.19327
H	-1.26982	3.44679	2.45611
H	-4.39358	-0.09305	-1.83244
H	-4.62245	-1.39982	-0.90788
H	-3.02201	-3.26028	0.55811
H	-2.73596	-3.61428	-1.00374
H	-1.14005	-2.30255	-3.27616
H	-2.67768	-1.8157	-3.34783
H	-0.02866	-3.71919	1.67689
H	-0.33015	-3.00774	3.10216
H	2.3819	-2.21645	1.95642
H	3.01431	-0.82835	1.21865
H	-0.33314	-0.34946	4.16799
H	1.23737	-0.52929	3.76589
H	3.37065	0.74246	-2.1589
H	2.3875	1.00094	-3.44661

H	5.77101	1.02333	-2.14079
H	5.83842	1.41927	0.6744
O	6.6518	-0.62874	0.00761
H	6.84299	-1.55774	-0.22865

[1-O-*tet*-H_3PO_3]$^{4+}$ ···H_2O (-1703.4001306)

S	-2.7142	0.77971	0.30911
Mo	-0.45718	1.65144	-0.18446
O	-1.07844	3.40863	0.99497
Mo	-1.01388	-0.47815	1.56653
O	-2.74265	-1.51113	2.50495
Mo	-1.50413	-0.76589	-1.17603
S	0.22659	0.5568	-2.23807
Pd	1.17837	-0.65326	-0.23397
O	3.2345	-1.18248	-0.62679
P	4.75232	-1.01972	-0.56176
O	5.10329	0.50501	-0.05476
S	-0.5533	-2.46729	0.26243
S	0.92917	0.95222	1.68493
O	-1.56392	0.68039	3.43219
O	-1.12448	-2.28484	-2.75045
O	-3.38066	-1.96715	-1.23428
O	1.15336	3.01024	-0.47637
O	3.47704	2.72858	0.13928
O	-2.75144	-0.04101	-2.90209
O	-1.43127	3.08574	-1.64259
O	-0.07997	-1.68359	3.17841
H	-2.39873	0.50558	3.91436
H	-1.05816	1.41406	3.83697
H	0.0653	-1.30547	4.07101
H	0.48264	-2.47296	3.03539
H	-3.70218	-1.409	2.34495
H	-2.54953	-2.2911	3.06901
H	-0.38552	4.09701	1.09707
H	-1.88085	3.59349	1.52272
H	-2.06329	3.76701	-1.33255
H	-1.23503	3.18973	-2.59545
H	2.22863	2.86056	-0.17784
H	1.09247	3.62163	-1.23881
H	-2.52412	0.63411	-3.57157
H	-3.69299	-0.30543	-2.96327
H	-1.33103	-2.08252	-3.68744
H	-0.48515	-3.02485	-2.68385
H	-4.22046	-1.87393	-0.7417
H	-3.3176	-2.83928	-1.68096
H	3.99296	3.50166	0.43929
H	4.03156	1.91015	0.0205
H	5.35202	-1.19057	-1.82568
H	5.99713	0.67282	0.32495
O	5.55314	-1.88406	0.51288
H	5.90987	-2.79494	0.46144

[1-O-*tet*-H_3PO_3]$^{4+}$ (-1626.9130957)

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.466176
O	0.762316	0.000000	4.550880
Mo	-1.590025	-1.666427	0.875721
O	-2.682605	-3.573532	1.143115
Mo	-2.028408	1.124979	0.854537
O	-1.090762	3.022537	0.184003

O	-2.107032	-2.254169	-1.239121
S	-3.747558	-0.591666	0.802863
Pd	-2.744859	-0.347644	3.102180
S	-0.905929	-2.144775	3.152908
O	-2.742039	1.509790	-1.239331
S	-1.453331	1.799998	3.119448
O	1.528485	1.664429	2.416749
O	-4.466128	0.028074	4.371692
P	-5.418363	1.182828	4.689813
O	-5.255888	1.955879	6.072049
O	-5.115629	2.432851	3.633030
O	-0.110582	-3.197508	0.209863
O	1.999918	-0.958758	2.311088
O	-3.707448	2.478573	1.269076
H	-0.216624	3.161657	-0.234323
H	-1.512213	3.871836	0.438524
H	-4.273251	2.819374	0.546295
H	-4.197062	2.480186	2.151127
H	-2.267633	2.129009	-1.832628
H	-3.508961	1.103507	-1.691300
H	1.380296	2.610483	2.619911
H	2.460477	1.492002	2.167279
H	2.530706	-1.229637	1.535136
H	2.386398	-1.296139	3.148544
H	0.397980	-0.542631	5.282103
H	1.277213	0.756803	4.902773
H	0.770011	-3.100853	-0.205293
H	-0.275923	-4.124016	0.490970
H	-2.935828	-3.966456	2.005242
H	-3.222202	-3.948580	0.415164
H	-1.462653	-2.757437	-1.779647
H	-2.892675	-2.004628	-1.765852
H	-6.769568	0.820573	4.519437
H	-5.425026	3.326315	3.914986
H	-5.531054	1.705583	6.979550

$[1\text{-}O\text{-}TS_{pt}\text{-}H_3PO_3]^{4+}$ (-1626.8105287)

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.470602
S	2.355849	0.000000	3.095596
Pd	1.407312	-2.297664	3.188582
O	1.732204	-2.958618	5.245508
P	1.995142	-2.274845	6.704507
O	3.525812	-1.839343	6.962508
Mo	2.149417	-0.854299	0.854629
O	3.105174	1.128203	0.347428
Mo	-0.244881	-2.298202	0.855535
S	1.976557	-3.277333	0.866765
O	4.316427	-1.324754	0.954915
O	-0.846330	-4.427172	0.965351
O	-2.430105	-2.223575	0.309061
S	-1.099448	-2.076425	3.100554
O	0.152197	2.206599	2.332956
O	-2.101880	0.795142	2.485507
O	1.338942	-0.734914	6.525334
O	-0.428532	-2.907637	-1.275606
O	2.779113	-0.945709	-1.277558
O	-0.189040	0.480193	4.605384
H	0.210080	2.773471	1.536899

H	0.303236	2.718490	3.156796
H	-1.032410	0.803562	4.983236
H	0.380152	0.027906	5.305980
H	-2.309691	1.692344	2.150747
H	-2.907547	0.339747	2.802944
H	3.363188	1.841975	0.965550
H	3.293200	1.372101	-0.583003
H	2.296425	-0.737726	-2.102943
H	3.629245	-1.401407	-1.462570
H	4.694031	-2.182829	1.242014
H	4.987948	-0.612199	1.008070
H	-0.366178	-2.386033	-2.100912
H	-0.427450	-3.872660	-1.458024
H	-0.275774	-5.164545	1.269094
H	-1.793249	-4.679921	1.001010
H	-2.705784	-2.245743	-0.631168
H	-3.196590	-2.088132	0.901087
H	1.259395	-3.618234	6.412282
H	1.600786	-0.079952	7.217090
H	4.215034	-2.348787	7.444601

[1-O-*pyr*-H_2PO_3]$^{3+}$ (-1626.4424611)

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.458037
O	0.778097	0.000000	4.553299
Mo	-1.634178	-1.604613	0.927421
O	-2.819520	-3.473834	1.196714
Mo	-2.017558	1.161868	0.892475
O	-1.174421	3.068404	0.170292
O	-2.206056	-2.132710	-1.178983
S	-3.785908	-0.498359	0.923106
Pd	-2.701843	-0.260821	3.180013
S	-0.921761	-2.134406	3.193611
O	-2.663670	1.295318	-1.294856
S	-1.383663	1.845226	3.148265
O	1.576726	1.624216	2.401766
O	-4.350577	0.079658	4.428933
P	-4.881597	1.356324	5.154653
O	-3.488488	1.996669	5.798666
O	-4.880872	2.642044	3.512142
O	-3.499230	2.563732	1.244105
O	-0.250062	-3.223708	0.213780
O	2.001859	-0.997436	2.325003
H	-0.322694	3.388235	-0.182486
H	-1.801634	3.776691	0.444610
H	-4.227551	2.613605	0.587070
H	-4.287153	2.623976	2.676927
H	-2.095848	1.784275	-1.925172
H	-3.597935	1.292294	-1.586931
H	1.431315	2.582389	2.526149
H	2.494154	1.416011	2.133259
H	2.484731	-1.355471	1.555604
H	2.344064	-1.344805	3.175676
H	0.337670	-0.494597	5.275727
H	1.242259	0.790049	4.898896
H	0.640747	-3.165524	-0.182136
H	-0.452071	-4.124245	0.545186
H	-3.096790	-3.809154	2.074481
H	-3.458666	-3.729339	0.499478

H	-1.631678	-2.723337	-1.706725
H	-2.821660	-1.618274	-1.735756
H	-5.564555	3.341937	3.503761
H	-3.544658	2.702327	6.479344

$[1\text{-}O\text{-}pyr\text{-}H_3PO_3]^{4+}$ (-1626.8985295)

O	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.213740
S	2.415238	0.000000	2.163443
Pd	1.646457	0.034427	4.550634
S	1.437390	2.476878	5.177035
Mo	1.648352	2.211419	2.779297
O	1.747334	4.416100	2.643195
O	0.282224	-2.141909	1.715669
S	-0.688514	2.344276	1.957369
Mo	-0.671096	1.699298	4.328394
O	-1.524333	3.713935	4.664102
S	-0.781518	-0.734459	4.404086
O	-2.925171	1.481440	4.280572
O	2.388423	2.701162	0.712967
O	3.374944	-0.655827	5.811838
P	5.036722	-0.189058	5.605259
O	5.119617	-0.498759	3.987495
O	4.704138	1.482268	5.373738
O	3.731257	2.588515	3.254034
O	-2.062131	-0.658969	1.564378
O	-1.207139	1.683554	6.482762
H	0.289077	-0.815730	-0.463071
H	-0.141555	0.744444	-0.619553
H	-0.489349	-2.736866	1.604654
H	1.100588	-2.658926	1.869260
H	-2.397465	-0.465033	0.663905
H	-2.748440	-1.088868	2.113337
H	2.339004	3.615269	0.363221
H	2.839576	2.098951	0.087112
H	1.076927	5.088034	2.406182
H	2.542681	4.823293	3.052157
H	-3.509073	2.256370	4.141805
H	-3.444731	0.656720	4.365039
H	-1.714398	4.436408	4.032372
H	-1.632438	4.007481	5.594770
H	-2.086992	1.371507	6.782900
H	-0.570666	1.693666	7.228101
H	4.160352	2.167280	4.095670
H	4.392283	2.701954	2.540340
H	5.043491	2.073729	6.083076
H	3.223925	-1.311340	6.529769
H	5.836080	-1.071349	3.637076

$[1\text{-}O\text{-}TS_{isom}\text{-}H_3PO_3]^{4+}$ (-1626.8827322)

O	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.210302
O	2.161051	0.000000	1.729071
O	0.346429	-2.130349	1.545002
Pd	0.153210	1.627453	4.573531
S	0.316529	2.399415	2.168825
Mo	-1.980059	1.949854	2.775080
O	-4.148462	2.326830	2.620267

S	0.582192	-0.896845	4.389817
Mo	-1.803921	-0.428991	4.339049
O	-1.950510	-2.684392	4.335075
S	-2.419928	-0.351550	1.963334
S	-2.288218	1.777399	5.166210
O	-2.342886	2.718171	0.688720
O	-3.920283	-0.961443	4.694644
O	-2.124986	4.037742	3.209231
O	-0.888598	5.010288	5.098738
P	0.624445	4.319457	5.779055
O	0.985466	5.762875	6.571878
O	0.004196	3.372469	7.057204
O	-1.845209	-0.936147	6.493921
H	0.850708	0.151754	-0.466341
H	-0.759775	-0.006423	-0.617519
H	2.663698	-0.836615	1.631547
H	2.772441	0.756269	1.855042
H	0.101780	-2.422511	0.641740
H	0.704533	-2.873221	2.072000
H	-3.246633	2.771452	0.313250
H	-1.680914	3.121271	0.090317
H	-4.907967	1.765621	2.364180
H	-4.437561	3.174901	3.025203
H	-2.817855	-3.130347	4.235612
H	-1.219465	-3.334306	4.362403
H	-4.675239	-1.035545	4.076386
H	-4.213574	-1.001972	5.631296
H	-1.688397	-1.856138	6.795995
H	-1.700601	-0.300278	7.226696
H	-1.622312	4.490233	4.064350
H	-2.211368	4.675704	2.470681
H	-1.155834	5.879927	5.483723
H	-0.218628	3.741604	7.944829
H	1.865441	6.161341	6.743752

$[1\text{-P-}pyr\text{-}H_3PO_3]^{4+}$ (-1626.9242856)

S	0.000000	0.000000	0.000000
Mo	0.000000	0.000000	2.461345
O	0.815256	0.000000	4.527925
Mo	-1.984692	-1.145077	0.893445
O	-3.552746	-2.687056	1.148403
Mo	-1.616718	1.651523	0.873250
O	-0.184684	3.307212	0.389092
O	-2.651069	-1.525774	-1.228691
S	-3.752985	0.478443	0.884620
Pd	-2.797667	0.493877	3.172435
S	-1.514199	-1.752883	3.212833
O	-2.038114	2.190094	-1.227298
S	-0.916965	2.120463	3.156970
O	1.993109	0.901096	2.236154
P	-4.598106	1.616026	4.262104
O	-5.979630	0.812274	4.067130
O	-4.624057	2.363321	5.696603
O	-4.654854	3.005660	3.313721
O	-0.965094	-3.002404	0.233766
O	1.450721	-1.741395	2.411969
O	-2.969155	3.342410	1.210357
H	0.276227	3.879519	1.036377
H	0.005729	3.585744	-0.531029
H	-2.715645	4.273110	1.043032

H	-3.686206	3.269972	1.922109
H	-1.632193	1.845893	-2.049276
H	-2.811631	2.764589	-1.417375
H	2.472038	1.172199	3.049143
H	2.460115	1.182339	1.422941
H	2.382658	-1.646446	2.122899
H	1.250569	-2.658124	2.693363
H	0.512359	0.582493	5.256118
H	1.278949	-0.786525	4.886137
H	-0.070836	-3.116473	-0.147851
H	-1.392058	-3.863578	0.434672
H	-3.886320	-3.011289	2.011673
H	-4.190816	-2.887049	0.431044
H	-2.175928	-2.166029	-1.798876
H	-3.377202	-1.085191	-1.715735
H	-5.168747	3.778897	3.652814
H	-4.732268	1.986819	6.596087
H	-6.887324	1.038672	4.372714

$[1Ni\text{-}OH_2]^{4+}$ (-1176.9025793)

S	0.01809	0.01979	-2.16014
Mo	0.07959	1.6113	-0.29196
O	1.42025	2.77444	-1.58969
Mo	-1.43287	-0.75482	-0.33109
O	-3.10338	-1.77486	0.71461
Mo	1.37403	-0.872	-0.30107
O	3.24711	-0.25774	-1.39099
S	-0.10139	-2.21885	1.05834
Ni	-0.04105	-0.0149	1.87292
S	1.9393	0.98094	1.14095
S	-1.87167	1.16858	1.08733
O	-3.23578	-0.0563	-1.46913
O	-1.95141	-2.42243	-1.67732
O	-0.08784	-0.03173	3.83216
O	2.9429	-2.03024	0.76269
O	1.81593	-2.54446	-1.66181
O	0.29899	3.53586	0.79071
O	-1.28549	2.96697	-1.44429
H	-3.50067	-0.48079	-2.31252
H	-3.82493	0.69562	-1.25621
H	-4.03418	-1.5056	0.56219
H	-3.03039	-2.32842	1.52085
H	-1.64952	-2.63292	-2.58409
H	-2.5102	-3.14217	-1.31003
H	-2.18577	3.26101	-1.19624
H	-1.02452	3.33812	-2.31361
H	1.76703	2.55948	-2.47967
H	1.78643	3.61939	-1.24835
H	0.81448	3.67062	1.61432
H	-0.32136	4.28251	0.64951
H	3.86009	0.46418	-1.1402
H	3.55677	-0.72332	-2.19645
H	3.89248	-1.80315	0.66716
H	2.80482	-2.61618	1.53681
H	1.52826	-2.71531	-2.58165
H	2.31534	-3.30687	-1.2949
H	0.65085	-0.30705	4.41096
H	-0.85673	0.25614	4.36389

$[1Ni\text{-}OH_2]^{4+}\cdots H_3PO_2$ (-1670.6702965)

S	-2.12107	-0.20327	1.54239
Mo	-1.54208	-1.07632	-0.68016
O	-1.64109	-2.35005	-2.50267
Mo	0.32051	-0.58524	1.34208
O	2.36031	-0.99968	1.85512
Mo	-1.08463	1.54188	0.16102
O	-3.09427	2.47598	-0.22905
O	0.49924	-0.00259	3.45443
S	1.27893	1.51976	0.64463
S	0.67283	-2.05409	-0.53871
O	-1.47367	2.87321	1.88136
S	-1.21045	0.82378	-2.15859
O	-3.70922	-0.91958	-1.28389
O	2.29721	0.39438	-2.45508
O	4.17785	-0.14923	0.47931
P	5.47466	0.05105	-0.31457
O	5.0117	0.32433	-1.87826
O	-2.47823	-2.93988	0.03666
O	0.04876	-2.4972	2.49577
O	-0.57677	3.56769	-0.60791
H	-3.62112	2.86631	0.4993
H	-3.58883	2.49629	-1.07269
H	-1.25592	4.1235	-1.04456
H	0.32561	3.88333	-0.82191
H	-1.87511	2.68377	2.75285
H	-1.0962	3.77843	1.84362
H	-4.0937	-0.34307	-1.97424
H	-4.4072	-1.41957	-0.81156
H	-2.83443	-3.15151	0.92307
H	-2.48592	-3.71813	-0.56084
H	-0.87496	-2.78458	-2.93211
H	-2.4037	-2.30086	-3.11632
H	0.18109	-3.40458	2.15397
H	-0.15183	-2.49636	3.45456
H	2.57665	-1.86084	2.26651
H	3.18532	-0.62307	1.28841
H	-0.13638	0.31249	4.12721
H	1.4333	0.08773	3.74762
H	3.26224	0.35495	-2.21018
H	2.16334	0.53758	-3.41051
H	5.66182	0.45867	-2.60539
H	6.22321	1.18389	0.08448
Ni	0.81854	0.18113	-1.2101
H	6.3363	-1.07291	-0.34517

$[1Ni\text{-}O\text{-}\textit{tet}\text{-}H_3PO_2]^{4+}\cdots H_2O$ (-1670.673525)

S	-2.39784	0.97751	-0.46958
Mo	0.00433	1.31495	-0.93045
O	-0.43537	3.4646	-0.76821
Mo	-1.03677	0.38629	1.49439
O	-2.95573	0.07214	2.53791
Mo	-1.26523	-1.18091	-0.80494
S	0.82564	-0.72824	-1.94822
O	2.8769	-1.51803	0.767
P	4.38805	-1.79162	0.76582
O	5.16126	-0.56637	-0.02377
S	-0.58805	-1.98847	1.37086
S	1.13071	1.39831	1.21928
O	-1.54971	2.37657	2.4145
O	-0.9522	-3.31101	-1.3611

O	-3.26732	-2.09434	-0.57883
O	1.82593	2.23798	-1.57176
O	4.00772	1.93695	-0.54518
O	-2.12918	-1.3022	-2.87055
O	-0.60404	1.86317	-3.02996
O	-0.47002	0.08343	3.62536
H	-2.4436	2.57455	2.7634
H	-0.9564	3.15188	2.47962
H	-0.35545	0.84963	4.22594
H	-0.02278	-0.71194	3.98265
H	-3.8759	0.14674	2.21479
H	-2.9174	-0.3134	3.43998
H	0.3414	4.05391	-0.88217
H	-1.26715	3.95725	-0.62099
H	-1.2771	2.54967	-3.21786
H	-0.16391	1.56853	-3.85311
H	2.81466	2.10521	-1.09468
H	1.92717	2.48086	-2.51425
H	-1.68773	-1.06876	-3.71082
H	-3.08384	-1.47729	-3.00577
H	-1.01114	-3.5861	-2.30018
H	-0.47127	-3.97701	-0.82732
H	-4.13718	-1.68746	-0.39322
H	-3.30706	-3.07393	-0.52769
H	4.60154	2.69311	-0.37322
H	4.43326	1.0583	-0.37462
H	4.92513	-1.82887	2.07416
H	4.75112	-2.98166	0.08885
H	6.09997	-0.64691	-0.31284
Ni	1.14899	-0.7609	0.35191

$[1Ni\text{-}OH_2]^{4+}\cdots H_3PO_3$ (-1745.9766108)

S	-2.27842	-0.27228	1.52174
Mo	-1.66873	-1.07825	-0.71827
O	-1.73195	-2.3067	-2.57288
Mo	0.16937	-0.61306	1.33125
O	2.20968	-1.01333	1.85529
Mo	-1.25771	1.52368	0.19533
O	-3.27701	2.43981	-0.17966
O	0.32282	-0.08526	3.45964
S	1.10347	1.52272	0.69678
S	0.56151	-2.02344	-0.58577
O	-1.67736	2.80519	1.94799
S	-1.356	0.86528	-2.14321
O	-3.83406	-0.93692	-1.33132
O	2.16035	0.50798	-2.41645
O	4.0431	-0.18873	0.48431
P	5.2967	0.32826	-0.21712
O	4.81027	0.62035	-1.77134
O	-2.58011	-2.9745	-0.0558
O	-0.08566	-2.56072	2.42736
O	-0.77569	3.57462	-0.5201
H	-3.80788	2.80844	0.55701
H	-3.77645	2.46138	-1.02036
H	-1.46236	4.12985	-0.94563
H	0.12229	3.90747	-0.726
H	-2.08037	2.58693	2.81199
H	-1.31057	3.71552	1.9373
H	-4.21986	-0.36358	-2.02369
H	-4.5293	-1.45112	-0.87038

H	-2.93921	-3.21403	0.82226
H	-2.57638	-3.73595	-0.67456
H	-0.95351	-2.71675	-3.00423
H	-2.4883	-2.25621	-3.19412
H	0.06472	-3.45536	2.0604
H	-0.29878	-2.59157	3.38296
H	2.42753	-1.88072	2.25296
H	3.03676	-0.63249	1.29355
H	-0.32182	0.20019	4.13703
H	1.25366	0.01073	3.76121
H	3.12506	0.52043	-2.15276
H	2.0355	0.63343	-3.37544
H	5.47588	0.84448	-2.46181
H	5.80838	1.53851	0.2777
O	6.60702	-0.55484	-0.26808
H	6.80019	-1.509	-0.35478
Ni	0.67648	0.23121	-1.19597

$[1Ni\text{-}O\text{-}\textit{tet}\text{-}H_3PO_3]^{4+}\cdots H_2O$ (-1745.9809608)

S	-2.7142	0.77971	0.30911
Mo	-0.45718	1.65144	-0.18446
O	-1.07844	3.40863	0.99497
Mo	-1.01388	-0.47815	1.56653
O	-2.74265	-1.51113	2.50495
Mo	-1.50413	-0.76589	-1.17603
S	0.22659	0.5568	-2.23807
Pd	1.17837	-0.65326	-0.23397
O	3.2345	-1.18248	-0.62679
P	4.75232	-1.01972	-0.56176
O	5.10329	0.50501	-0.05476
S	-0.5533	-2.46729	0.26243
S	0.92917	0.95222	1.68493
O	-1.56392	0.68039	3.43219
O	-1.12448	-2.28484	-2.75045
O	-3.38066	-1.96715	-1.23428
O	1.15336	3.01024	-0.47637
O	3.47704	2.72858	0.13928
O	-2.75144	-0.04101	-2.90209
O	-1.43127	3.08574	-1.64259
O	-0.07997	-1.68359	3.17841
H	-2.39873	0.50558	3.91436
H	-1.05816	1.41406	3.83697
H	0.0653	-1.30547	4.07101
H	0.48264	-2.47296	3.03539
H	-3.70218	-1.409	2.34495
H	-2.54953	-2.2911	3.06901
H	-0.38552	4.09701	1.09707
H	-1.88085	3.59349	1.52272
H	-2.06329	3.76701	-1.33255
H	-1.23503	3.18973	-2.59545
H	2.22863	2.86056	-0.17784
H	1.09247	3.62163	-1.23881
H	-2.52412	0.63411	-3.57157
H	-3.69299	-0.30543	-2.96327
H	-1.33103	-2.08252	-3.68744
H	-0.48515	-3.02485	-2.68385
H	-4.22046	-1.87393	-0.7417
H	-3.3176	-2.83928	-1.68096
H	3.99296	3.50166	0.43929
H	4.03156	1.91015	0.0205

H	5.35202	-1.19057	-1.82568
H	5.99713	0.67282	0.32495
O	5.55314	-1.88406	0.51288
H	5.90987	-2.79494	0.46144

$[1Ni\text{-}O\text{-}tet\text{-}H_3PO_3]^{4+}$ (-1669.4984003)

S	2.32692	-0.03167	1.20401
Mo	1.08532	1.49249	-0.27945
O	3.06968	2.14336	-1.00976
Mo	-0.10462	-0.23746	1.58322
O	-2.14235	-0.5558	2.38411
Mo	1.26436	-1.25734	-0.65757
O	3.30137	-1.48043	-1.47842
S	-0.85424	-2.04572	0.1493
Ni	-1.10817	0.03494	-0.85548
S	-1.11411	1.77779	0.66717
O	0.39987	-1.74599	3.11823
O	0.07674	0.9685	3.45863
O	-2.89773	-0.07296	-1.57702
P	-4.34329	-0.25244	-1.09537
O	-4.3164	-0.54646	0.53002
S	0.66673	0.34521	-2.37324
O	2.03943	-3.18737	0.20192
O	1.00737	-2.67348	-2.34927
O	0.64409	3.26925	-1.53568
O	1.67036	3.20736	1.04388
H	-4.97007	-1.34909	-1.72043
H	1.28408	-1.99907	3.45345
H	-0.30717	-2.29546	3.5193
H	-2.4314	-0.32272	3.28926
H	-2.91458	-0.64986	1.75745
H	0.66803	0.72798	4.20203
H	-0.46826	1.75019	3.6824
H	1.51688	-3.8639	0.67874
H	2.98856	-3.42899	0.16625
H	4.16807	-1.18571	-1.13362
H	3.38064	-1.85569	-2.38253
H	0.55172	-2.46892	-3.19302
H	1.0623	-3.64225	-2.20829
H	3.9729	1.88009	-0.74227
H	3.08216	2.7383	-1.79084
H	0.18422	3.25791	-2.40147
H	0.6171	4.16416	-1.13563
H	2.59819	3.51921	1.09327
H	1.11152	3.65963	1.70704
O	-5.30384	1.01044	-1.16725
H	-5.18403	-0.54494	1.00021
H	-5.81904	1.39311	-1.90887

$[1Ni\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$ (-1669.5029207)

S	2.35928	-0.14807	1.0594
Mo	1.16333	-1.16511	-0.8369
O	3.03889	-1.01555	-2.07026
Mo	0.99812	1.50619	-0.14836
O	2.91706	2.23965	-0.94877
Mo	-0.03674	-0.45182	1.59781
O	-2.00619	-0.73321	2.53198
O	1.66238	3.05032	1.34382
S	-1.11773	1.64033	0.97896
Ni	-1.25914	0.08748	-0.70862

S	0.34768	0.58468	-2.31982
O	0.45826	3.41185	-1.1507
O	0.3874	0.40292	3.58283
S	-0.90937	-2.06902	0.01186
O	0.45336	-2.24357	2.83511
O	2.30313	-2.96682	-0.29967
O	0.75801	-2.57957	-2.50379
P	-3.48725	0.14897	-0.9086
O	-3.9859	1.64731	-1.22313
O	-4.415	-0.89672	-1.71756
O	-3.9566	-0.2805	0.63925
H	0.13944	-3.15509	2.66304
H	0.95661	-2.19535	3.6745
H	-2.20235	-1.36524	3.25315
H	-2.81885	-0.52188	1.9783
H	1.24681	0.64952	3.98173
H	-0.36524	0.65515	4.16057
H	2.14197	-3.79198	-0.80644
H	2.902	-3.11444	0.46055
H	3.83484	-1.55632	-1.88284
H	3.17381	-0.43318	-2.84594
H	-0.08032	-3.06785	-2.64431
H	1.28289	-2.54839	-3.33156
H	3.82533	1.90714	-0.79836
H	2.89767	2.98589	-1.58657
H	-0.05795	3.48526	-1.98111
H	0.43562	4.25628	-0.65251
H	2.59261	3.35419	1.39854
H	1.11289	3.46423	2.04049
H	-4.88972	-0.56656	0.79446
H	-4.69845	-0.89312	-2.65648
H	-4.89886	2.00309	-1.31525

Cartesian coordinates of the BS-I/PCM optimized species and BS-II/PCM absolute energies (Hartree).

H_2O (-76.4750189)

O	0.007008	0.000000	-0.019989
H	0.001205	0.000000	0.965820
H	0.942138	0.000000	-0.331831

H_3O^+ (-76.870949)

O	0.106700	-0.161203	0.060992
H	-0.035380	0.085755	1.013543
H	0.963226	0.074239	-0.386013
H	-0.532028	-0.774463	-0.391188

$H_2PO_2^-$ (-493.3078061)

O	-1.354429	-0.457231	0.000047
P	-0.000083	0.322063	-0.000010
O	1.354557	-0.457176	-0.000079
H	-0.000511	1.242411	-1.106233
H	0.000726	1.241898	1.106638

H_3PO_2 (-493.7615787)

O	1.342496	-0.531179	-0.000003
P	0.108856	0.380364	-0.000022
O	-1.277442	-0.489877	-0.000078
H	0.007779	1.244546	1.128812
H	0.007612	1.245319	-1.128259
H	-2.168671	-0.026881	0.000426

$H_4PO_2^+$ (-494.1866103)

O	-1.352612	-0.411002	-0.130472
P	0.000000	0.416446	0.045847
O	1.352613	-0.411000	-0.130470
H	0.000001	1.302676	-1.050996
H	-0.000002	1.088570	1.298137
H	-1.733279	-1.030954	0.576348
H	1.733271	-1.030966	0.576343

$[1\text{-}OH_2]^{4+}$ (-1134.3200585)

S	0.048285	0.073513	-2.267073
Mo	-1.272642	-0.959083	-0.484162
S	0.267751	-2.320689	0.800265
Pd	-0.070061	-0.067280	1.921983
O	-0.105375	-0.132187	4.109447
Mo	1.496239	-0.622951	-0.410338
O	3.180650	-1.503550	0.632646
Mo	-0.173868	1.601931	-0.375119
S	-2.137606	0.873707	0.861677
O	2.161042	-2.133745	-1.787877
S	1.826975	1.332881	0.977977
O	-0.303242	3.465975	0.711124
O	-1.664341	2.726000	-1.529359
O	-3.064353	-0.519919	-1.666343
O	-1.470177	-2.588450	-1.871968
O	0.938887	2.941356	-1.641775
O	3.193395	0.243610	-1.493108
O	-2.745712	-2.225464	0.482741

H	-3.200869	-0.928326	-2.559790
H	-3.807454	0.087826	-1.417158
H	-3.714082	-2.100105	0.304979
H	-2.592310	-2.754002	1.307934
H	-1.098127	-2.696040	-2.785682
H	-1.929409	-3.409532	-1.552810
H	-2.649789	2.713181	-1.420550
H	-1.386210	3.229234	-2.337766
H	1.335077	2.767206	-2.534716
H	1.205511	3.826745	-1.277895
H	0.160747	3.678241	1.561651
H	-1.068149	4.077490	0.551791
H	3.667112	1.087654	-1.278667
H	3.559801	-0.197322	-2.302537
H	4.086864	-1.108441	0.540279
H	3.117871	-2.097071	1.425155
H	1.856337	-2.319348	-2.714069
H	2.784038	-2.830604	-1.450893
H	0.605669	-0.525987	4.670201
H	-0.851068	0.218761	4.653533

[1-O-*tet*-H_3PO_2]$^{4+}$ (-1551.6055377)

S	-0.024677	-0.000291	0.046164
Mo	-0.048719	-0.023481	2.497896
S	2.288409	0.089273	3.173729
Pd	1.446777	-2.280884	3.209512
O	1.924965	-2.974266	5.288243
P	1.899567	-2.209197	6.624454
O	1.130509	-0.752679	6.488901
Mo	2.142750	-0.754299	0.919067
O	2.889886	1.258482	0.445600
Mo	-0.167259	-2.298872	0.880624
S	2.098310	-3.188477	0.913844
O	4.285683	-1.056433	1.015263
O	-0.709389	-4.393792	0.934388
O	-2.285256	-2.233215	0.324060
S	-1.068092	-2.144945	3.121097
O	0.032024	2.119517	2.293740
O	-2.135542	0.624133	2.411036
H	3.186141	-1.888990	7.144135
O	2.694530	-0.824135	-1.160300
O	-0.232774	-2.799163	-1.219661
O	-0.341964	0.502372	4.573220
H	0.068621	2.654007	1.458803
H	0.146123	2.685703	3.102210
H	-1.245169	0.793606	4.884537
H	0.169151	0.030677	5.289690
H	-2.375310	1.518286	2.055817
H	-2.938041	0.095537	2.652958
H	3.082688	1.988317	1.087423
H	2.992677	1.559269	-0.493040
H	2.149364	-0.629096	-1.965729
H	3.591239	-1.180261	-1.397622
H	4.733346	-1.880709	1.336761
H	4.887689	-0.269304	1.072829
H	-0.186463	-2.200403	-2.009331
H	-0.215797	-3.756336	-1.482704
H	-0.143591	-5.130600	1.280674
H	-1.671271	-4.639407	0.935689
H	-2.545219	-2.199768	-0.632678

H	-3.064339	-2.101664	0.922115
H	1.200526	-2.933789	7.626710
H	1.245268	-0.078038	7.239507

[1-O-*pyr*-H_2PO_2]$^{3+}$ (-1551.1514109)

S	-2.072722	-0.222213	1.448102
Mo	-1.213127	-1.235798	-0.608678
S	0.996954	-2.094029	-0.097574
Pd	1.194447	0.173921	-1.143052
S	-1.052652	0.519041	-2.305199
Mo	-1.094416	1.458967	-0.048531
O	-0.908528	3.334080	-1.133814
Mo	0.381056	-0.340618	1.488167
O	0.118408	-2.060857	2.820196
S	1.163082	1.843913	0.720720
O	0.179898	0.562611	3.437954
O	3.131408	0.283265	-2.042726
P	4.475663	0.455170	-1.150182
O	4.228190	-0.507995	0.304900
O	-1.576691	2.928034	1.513683
O	-1.169982	-2.532211	-2.354165
O	-1.853674	-3.162738	0.239961
O	2.434962	-0.500571	2.120546
O	-3.308828	-1.405956	-1.117517
O	-3.166070	1.987386	-0.399078
H	4.201531	1.670472	-0.399979
H	-0.652975	0.784221	3.926957
H	0.989945	0.869078	3.922784
H	2.661965	-1.131773	2.860422
H	3.184906	-0.450710	1.404360
H	-0.378447	-2.001480	3.675129
H	0.641421	-2.900085	2.756699
H	-0.940178	3.335528	2.152883
H	-2.517957	3.144681	1.736848
H	-3.989019	1.592408	-0.014694
H	-3.370066	2.677484	-1.082289
H	-0.513102	3.421483	-2.038056
H	-0.841087	4.180551	-0.620337
H	-4.105809	-1.116325	-0.604927
H	-3.548969	-1.741049	-2.019947
H	-0.779904	-2.288003	-3.231478
H	-1.177034	-3.514403	-2.217446
H	-2.817101	-3.357608	0.366897
H	-1.283703	-3.800531	0.736833
H	4.641158	-1.416795	0.245859

[1-O-*pyr*-H_4PO_2]$^{5+}$ (-1552.0055225)

S	-2.182568	-0.056024	1.482263
Mo	-2.672861	-0.728059	-0.819114
S	-0.892405	0.213354	-2.188462
Pd	-2.918321	1.688617	-2.240834
S	-4.821919	0.264076	-1.362257
Mo	-3.813086	1.476320	0.477382
O	-5.573882	2.714203	0.302807
Mo	-1.075007	1.446722	-0.093847
O	0.741374	0.325913	0.370903
S	-2.543042	3.361545	-0.343245
O	-0.355650	2.379624	1.704732
O	-3.493634	3.362678	-3.904348

P	-2.485587	4.411100	-4.597192
O	-1.189427	4.297219	-3.675996
O	-3.719601	2.621195	2.344848
O	-3.124799	-2.020464	-2.494491
O	-1.204601	-2.327846	-0.547675
O	-3.741107	-2.334695	0.126001
O	-5.177558	0.493091	1.812265
O	0.411078	2.795216	-0.904378
H	-2.227574	4.022207	-5.942115
H	-0.476599	2.084850	2.644569
H	0.196123	3.203533	1.642421
H	1.395044	2.597481	-0.866299
H	0.210576	3.444432	-1.606350
H	1.070497	0.201136	1.298313
H	1.367301	-0.057602	-0.296401
H	-3.249995	3.481490	2.491951
H	-4.081759	2.250381	3.190203
H	-5.008729	-0.249490	2.449136
H	-6.136400	0.755976	1.795701
H	-6.211420	2.730879	-0.456466
H	-5.670230	3.517077	0.878679
H	-3.867917	-2.524268	1.092023
H	-4.254341	-2.964117	-0.447444
H	-3.763295	-1.815196	-3.225073
H	-2.468373	-2.711408	-2.772140
H	-1.410984	-3.095821	0.045835
H	-0.257936	-2.333069	-0.839139
H	-3.033666	5.721955	-4.541561
H	-4.307121	3.013155	-4.422064
H	-0.361464	4.878716	-3.830779

$[1\text{-P-}pyr\text{-}H_3PO_2]^{4+}$ (-1551.6244673)

S	-2.248826	-0.384302	1.206532
Mo	0.150696	-0.907067	1.349487
S	0.675614	-2.135082	-0.695139
Pd	1.381743	0.234398	-0.917116
S	1.280703	1.249497	1.365771
Mo	-0.906996	1.507234	0.407253
S	-0.668931	1.327947	-2.017142
Mo	-1.321420	-0.813112	-1.017683
O	-1.267051	-1.446966	-3.066078
O	-2.318149	-2.752429	-0.930648
O	-0.263272	3.570487	0.173837
O	-1.616569	2.435344	2.194758
O	-0.067906	-0.656193	3.467261
O	-0.380834	-2.891542	2.059620
P	3.712077	0.161411	-1.139922
O	4.115616	-0.656278	0.273370
O	4.517554	1.594695	-1.102595
O	-2.778284	2.484722	-0.177471
O	-3.372417	-0.428166	-1.682356
O	2.137231	-1.550066	1.936319
H	0.748300	-0.602554	4.033348
H	-0.891073	-0.461025	3.985047
H	2.277592	-2.412641	2.424145
H	2.926216	-1.299732	1.369039
H	-0.894592	-3.030761	2.896211
H	-0.110025	-3.750037	1.642788
H	-1.264512	3.334994	2.430222
H	-2.203991	2.062535	2.902816

H	-3.412502	2.838420	0.499587
H	-3.086487	2.659719	-1.102382
H	0.673659	3.894494	0.191979
H	-0.856320	4.214372	-0.295164
H	-4.152135	-0.120292	-1.150712
H	-3.569222	-0.450101	-2.655793
H	-0.804181	-0.975981	-3.805473
H	-1.447025	-2.397232	-3.289146
H	-3.309298	-2.802807	-0.942521
H	-1.903488	-3.633610	-0.747499
H	4.471904	-0.585732	-2.114206
H	5.078309	-0.923883	0.416583
H	5.487502	1.624240	-1.371598

$H_2PO_3^-$ (-568.6211043)

O	0.201469	1.514994	-0.233564
P	-0.119879	0.071079	0.241517
O	-1.393934	-0.661194	-0.251673
H	-0.076836	0.024583	1.670289
O	1.170846	-0.931588	-0.145725
H	2.047980	-0.468461	-0.245353

H_3PO_3 (-569.0743912)

O	0.398350	1.489914	-0.254848
P	0.014214	0.109868	0.281620
O	1.051845	-1.085696	-0.125936
H	-0.090005	-0.054339	1.688428
O	-1.467906	-0.443134	-0.124037
H	1.775653	-0.876817	-0.788609
H	-1.757163	-0.405535	-1.085548

$H_4PO_3^+$ (-569.4997573)

O	0.067846	1.478887	-0.228378
P	-0.003827	-0.021396	0.310106
O	-1.329655	-0.777957	-0.143216
O	1.354125	-0.712636	-0.131582
H	-0.024389	-0.128932	1.728573
H	1.696493	-0.723608	-1.085283
H	-1.634478	-0.847359	-1.108038
H	-0.718752	2.114494	-0.161437

$[1\text{-}O\text{-}\textit{tet}\text{-}H_3PO_3]^{4+}$ (-1626.9187127)

S	-2.339676	-0.026279	1.300539
Mo	-1.019999	1.577798	-0.011692
O	-0.475945	3.447096	-0.955653
Mo	-1.493644	-1.054196	-0.757886
O	-1.486006	-2.233683	-2.576682
Mo	0.055991	-0.512059	1.501783
O	-0.164711	0.297986	3.485045
O	-2.472997	-2.904075	-0.103626
S	0.505356	-2.262866	-0.134013
Pd	1.11741	0.014353	-1.037174
S	-0.978714	0.756339	-2.302779
O	-0.462966	-2.217377	2.767275
S	1.194769	1.566495	0.939847
O	-1.364966	3.025804	1.601269

O	3.257097	-0.183909	-1.663804
P	4.543712	-0.274403	-0.82983
O	5.456685	1.055419	-0.774796
O	4.21337	-0.485898	0.759018
O	-3.546026	-0.888234	-1.410042
O	-2.93563	2.459822	-0.428142
O	2.015493	-0.995762	2.256212
H	-0.977361	0.682616	3.905272
H	0.646676	0.446418	4.040201
H	2.133706	-1.7947	2.84849
H	2.83547	-0.789745	1.726142
H	-0.87076	-2.078306	3.660501
H	-0.387837	-3.178812	2.539241
H	-0.711957	3.320213	2.286699
H	-2.262851	3.417917	1.754756
H	-3.841456	2.160796	-0.154609
H	-2.972574	3.212066	-1.076805
H	-0.054464	3.534693	-1.849066
H	-0.310565	4.246805	-0.390925
H	-4.321785	-0.479709	-0.94508
H	-3.759525	-1.114354	-2.353787
H	-1.020034	-1.990513	-3.417392
H	-1.663765	-3.20881	-2.524466
H	-3.461529	-2.975836	-0.088314
H	-2.044044	-3.685763	0.329246
H	5.371033	-1.36357	-1.238794
H	4.955158	-0.280078	1.421626
H	6.00842	1.333108	-1.574228

[1-O-*pyr*-H_2PO_3]$^{3+}$ (-1626.4496041)

S	-2.700658	-0.014035	0.491835
Mo	-0.564539	-0.543046	1.564463
S	0.778678	1.494901	1.52848
Pd	1.393286	0.030883	-0.421211
O	3.457877	-0.030926	-0.946753
P	4.59745	0.077571	0.196313
O	5.481904	-1.363362	-0.000479
Mo	-0.956655	1.579622	-0.174795
O	-1.849688	2.984342	1.260883
Mo	-1.142893	-1.029679	-1.102331
S	-0.0813	0.801272	-2.313669
O	-0.076533	3.459197	-0.811985
O	-0.461921	-2.198207	-2.808377
O	-2.296954	-2.877989	-0.86997
S	0.506049	-2.256829	0.202248
O	-1.561307	0.24993	3.306943
O	-1.63203	-2.277088	2.373355
O	5.62775	1.17288	-0.627567
O	0.826535	-1.113969	3.130181
O	-2.799905	-0.844453	-2.477752
O	-2.573889	2.502156	-1.262973
H	-2.467787	0.646075	3.367783
H	-1.096099	0.244553	4.183692
H	0.88157	-2.037731	3.476661
H	-2.456649	-2.174061	2.913522
H	-1.288945	-3.206866	2.397879
H	-1.472439	3.244494	2.13831
H	-2.758316	3.356589	1.126408
H	-3.523522	2.224881	-1.320207
H	-2.375574	3.274555	-1.853929

H	0.651074	3.542812	-1.48073
H	-0.092443	4.237803	-0.196536
H	-3.697179	-0.453382	-2.321288
H	-2.650572	-1.055805	-3.436059
H	0.267839	-1.94727	-3.390186
H	-0.620125	-3.191409	-2.835793
H	-3.21155	-2.942285	-1.249556
H	-2.098214	-3.629402	-0.256315
H	5.680094	-1.647385	-0.940981
H	6.394708	1.497987	-0.077006
H	1.593876	-0.563017	3.450838

$[1\text{-}O\text{-}pyr\text{-}H_4PO_3]^{5+}$ (-1627.333687)

S	-2.026025	-0.151958	1.708884
Mo	-1.847045	-1.006283	-0.565371
S	0.271451	-2.215631	-0.683621
Pd	0.546668	0.150371	-1.560581
O	4.666137	1.389252	-0.555432
P	5.369108	-0.003632	-0.798256
O	6.937134	0.094688	-0.588562
Mo	0.308462	-0.654569	1.173324
O	-0.000881	-2.491824	2.350307
Mo	-1.109452	1.574882	0.245771
S	1.300957	1.448837	0.510749
O	2.330789	-1.289116	1.602367
O	-0.684703	3.553649	-0.513640
O	-3.094455	2.508040	0.289699
S	-1.815278	0.957952	-1.997404
O	-2.685878	-2.774212	0.330330
O	-4.010225	-0.695478	-0.693360
O	4.753454	-1.018677	0.291606
O	-1.144916	2.762819	2.044012
O	0.603628	-0.053371	3.224048
O	-2.323705	-2.186048	-2.310515
H	-2.971732	-2.910907	1.270207
H	-2.819610	-3.588753	-0.222130
H	-3.249826	-2.214342	-2.666802
H	-1.667515	-2.472416	-2.996845
H	-4.640861	-1.103883	-0.046132
H	-4.486007	-0.186003	-1.398814
H	-0.057026	-3.412389	1.988223
H	-0.208341	-2.465400	3.320148
H	-0.072964	0.246582	3.884999
H	1.528651	0.059753	3.568459
H	3.203945	-1.142362	1.159872
H	2.393968	-2.057486	2.241515
H	-1.400313	2.501393	2.965938
H	-0.772552	3.682867	2.009839
H	0.183315	3.858782	-0.883083
H	-1.434885	4.126149	-0.822758
H	-3.434256	2.926344	1.122201
H	-3.802496	2.443945	-0.400227
H	5.000325	-0.394896	-2.123834
H	4.876260	2.015493	0.217861
H	7.622959	-0.327257	-1.210717
H	5.274298	-1.862010	0.541621

$[1\text{-}P\text{-}pyr\text{-}H_3PO_3]^{4+}$ (-1626.9316)

S	2.448817	-0.110490	1.073257
Mo	1.149854	1.462133	-0.275477

O	1.920743	3.012548	1.063479
Mo	0.064059	-0.284232	1.621906
O	0.605550	0.682468	3.459985
Mo	1.227102	-1.256129	-0.717644
O	2.309837	-2.951500	0.029343
S	-0.908210	1.838866	0.907102
Pd	-1.364368	0.074169	-0.795081
P	-3.707465	0.096331	-0.700141
O	-4.706711	-1.100972	-1.234591
S	-0.804286	-2.111167	0.261915
O	0.576880	-1.920208	2.967165
S	0.608133	0.392215	-2.409001
O	0.819198	-2.748540	-2.229063
O	0.722976	3.263855	-1.394862
O	-3.960223	-0.112969	0.935140
O	3.074216	1.960556	-1.085947
O	3.100003	-1.245858	-1.861217
O	-1.840095	-0.430503	2.649118
H	0.337106	-2.875586	2.855477
H	1.116192	-1.763189	3.784782
H	-1.966357	-1.114729	3.369252
H	-2.682808	-0.285299	2.126229
H	1.506373	0.962775	3.768269
H	-0.111160	0.972024	4.085154
H	2.159535	-3.846619	-0.375156
H	2.929315	-2.992861	0.803529
H	3.899306	-1.748078	-1.558167
H	3.282611	-0.726447	-2.685745
H	-0.054216	-3.192309	-2.385409
H	1.400485	-2.791057	-3.033323
H	3.960470	1.561528	-0.888739
H	3.122515	2.649905	-1.800505
H	0.199819	3.312553	-2.235722
H	0.766491	4.144185	-0.937141
H	2.887037	3.235932	1.091825
H	1.416111	3.478369	1.778742
O	-4.458827	1.493142	-1.106296
H	-4.900796	-0.255843	1.275450
H	-4.777417	-1.249637	-2.228212
H	-5.459956	1.586333	-1.014101

Cartesian coordinates of the BS-II optimized species for the TD-DFT calculations.

$[1\text{-}OH_2]^{4+}$

S	0.057915	0.058234	-2.236936
Mo	-1.383907	-0.783417	-0.474834
S	-0.040673	-2.301561	0.797651
Pd	-0.079617	-0.054228	1.901054
O	-0.126177	-0.109743	4.111064
Mo	1.396009	-0.812233	-0.398752
O	3.002720	-1.948437	0.673154
Mo	0.038795	1.606194	-0.370003
S	-1.975573	1.132131	0.852126
O	1.920442	-2.466872	-1.817756
S	1.953625	1.067184	0.970009
O	0.169194	3.537508	0.749147
O	-1.317986	3.002999	-1.560504
O	-3.206036	-0.126121	-1.695004
O	-1.844316	-2.453368	-1.901517
O	1.354233	2.864330	-1.682812
O	3.291891	-0.157987	-1.516509
O	-3.060132	-1.887450	0.524166
H	-3.449422	-0.503147	-2.552304
H	-3.890815	0.510159	-1.450060
H	-3.989036	-1.638106	0.411866
H	-2.996835	-2.378093	1.356759
H	-1.546204	-2.648405	-2.799655
H	-2.389812	-3.195784	-1.599675
H	-2.264260	3.167874	-1.457042
H	-1.023720	3.472491	-2.353810
H	1.708513	2.696054	-2.566454
H	1.747588	3.684357	-1.347406
H	0.621235	3.682545	1.593204
H	-0.513710	4.219624	0.669021
H	3.901092	0.556039	-1.284360
H	3.640037	-0.604272	-2.301329
H	3.929559	-1.668039	0.656331
H	2.885206	-2.495919	1.462881
H	1.647725	-2.648728	-2.726751
H	2.407540	-3.239250	-1.491966
H	0.489193	-0.568493	4.695886
H	-0.784506	0.316029	4.674083

$[1\text{-}O\text{-}tet\text{-}H_3PO_3]^{4+}$

S	2.694826	0.320960	0.279783
Mo	0.788405	-0.498845	1.537712
S	-0.127704	-2.327315	0.278627
Pd	-1.368221	-0.228094	-0.225305
O	-3.394395	-0.628759	-0.683260
P	-4.833588	-0.289944	-0.460053
O	-4.935928	1.230059	-0.082166
Mo	1.186706	-0.936969	-1.160010
O	2.628370	-2.725750	-1.001665
Mo	0.711090	1.631087	-0.222967
S	-0.191731	0.696348	-2.231873
O	0.493262	-2.221849	-2.866174
O	-0.559933	3.378830	-0.830426
O	1.504207	3.311718	1.118608
S	-0.800121	1.305442	1.622963
O	2.280124	-1.923941	2.436685

O	1.646809	0.513735	3.401186
O	-5.522723	-1.062652	0.713152
O	2.084091	2.900592	-1.477602
O	2.747489	-0.651062	-2.747011
O	-0.347311	-1.474581	3.206020
H	3.211745	-2.070920	2.227108
H	1.988702	-2.617238	3.046992
H	-0.427204	-1.060712	4.077535
H	-1.131615	-2.028256	3.082645
H	2.474417	0.245902	3.824205
H	1.290334	1.262277	3.896008
H	2.438458	-3.586186	-0.604740
H	3.462247	-2.798199	-1.486454
H	3.608476	-0.213503	-2.735069
H	2.551245	-0.907391	-3.660691
H	-0.326175	-2.063470	-3.357347
H	0.644258	-3.178032	-2.878854
H	3.027615	2.832930	-1.672412
H	1.703392	3.570982	-2.064554
H	-1.368673	3.296971	-1.355986
H	-0.674969	4.146943	-0.252774
H	2.276001	3.852498	0.900855
H	1.133918	3.643207	1.946336
H	-5.567725	-0.535009	-1.617732
H	-5.791387	1.570446	0.220698
H	-6.098380	-1.820921	0.539451

$[1\text{-P-}pyr\text{-}H_3PO_3]^{4+}$

S	-2.692583	-0.056794	-0.104618
Mo	-0.783887	-1.266446	-0.990611
S	0.502383	-2.047646	0.883502
Pd	1.548996	0.046198	0.095056
P	3.882259	0.043454	0.068978
O	4.332450	-1.198945	-0.789485
Mo	-0.929000	-0.227882	1.550443
O	-2.324048	-1.664627	2.562364
Mo	-0.866602	1.455958	-0.620464
S	0.389615	1.779910	1.414794
O	0.021627	-0.618347	3.549686
O	0.151580	3.368954	-1.209777
O	-2.005346	2.038428	-2.522685
S	0.594215	0.328118	-2.156571
O	-1.955420	-3.208053	-0.678719
O	-2.054967	-1.511430	-2.819626
O	4.365644	1.399821	-0.579633
O	4.664248	-0.171803	1.428688
O	-2.298984	3.068248	-0.006861
O	-2.229298	1.052677	2.940358
O	0.365399	-2.721814	-2.257566
H	-1.748001	-3.925863	-0.065628
H	-2.707480	-3.485789	-1.219853
H	0.313292	-3.676205	-2.103207
H	1.252830	-2.541692	-2.599884
H	-2.946872	-1.195492	-3.015203
H	-1.691486	-1.923076	-3.617638
H	-2.051680	-2.136385	3.363292
H	-3.196013	-1.986337	2.298223
H	-3.024670	0.732543	3.388230
H	-2.011495	1.920796	3.305019
H	0.858634	-1.090380	3.664670
H	-0.053676	0.004717	4.286628

H	-3.192775	3.013913	0.356296
H	-2.003870	3.989681	0.039539
H	0.987837	3.671877	-0.827813
H	0.129058	3.688275	-2.123416
H	-2.804979	2.582671	-2.527971
H	-1.733420	1.897486	-3.439236
H	5.229924	-1.555598	-0.677196
H	4.984321	0.588378	1.935211
H	5.300194	1.538796	-0.808444