Electronic Supporting Information for

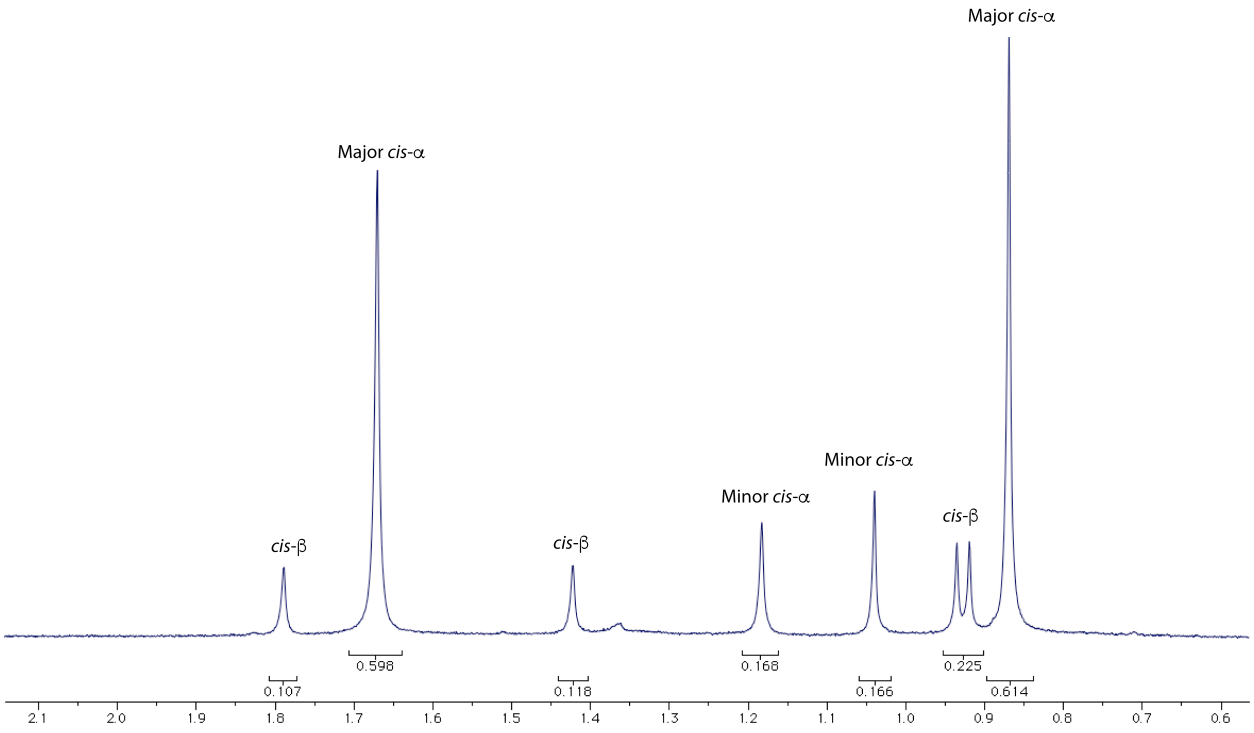
High-valent osmium iminoxolene complexes

Jacqueline Gianino, Alexander N. Erickson, Sean J. Markovitz and Seth N. Brown*

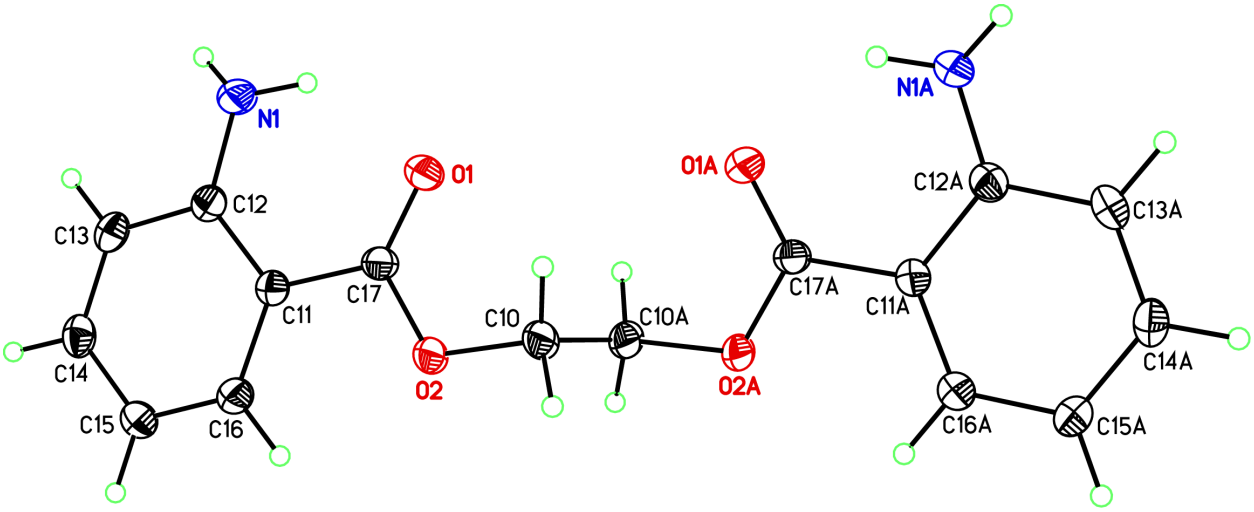
251 Nieuwland Science Hall
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556-5670 USA
E-mail: Seth.N.Brown.114@nd.edu

Contents:

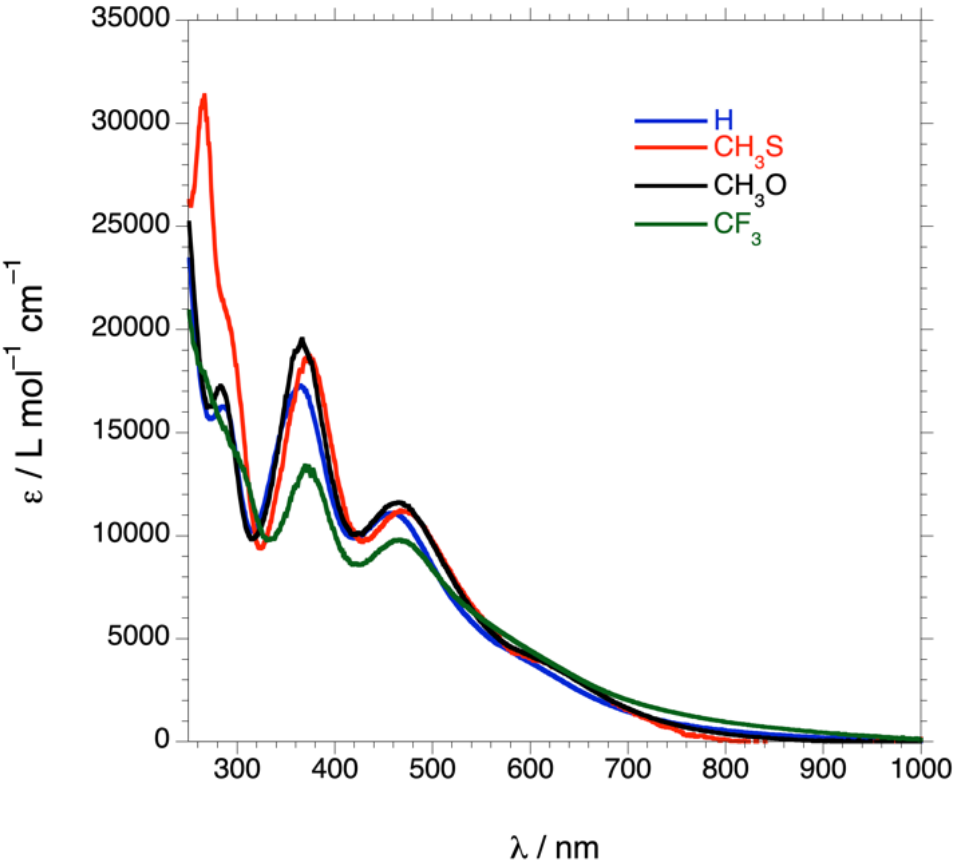
I. Figure S1. ^{1}H NMR spectrum (*tert*-butyl region) of $(^{H}ap)_2OsCl_2$ (C_6D_6, 400 MHz, 22 °C).



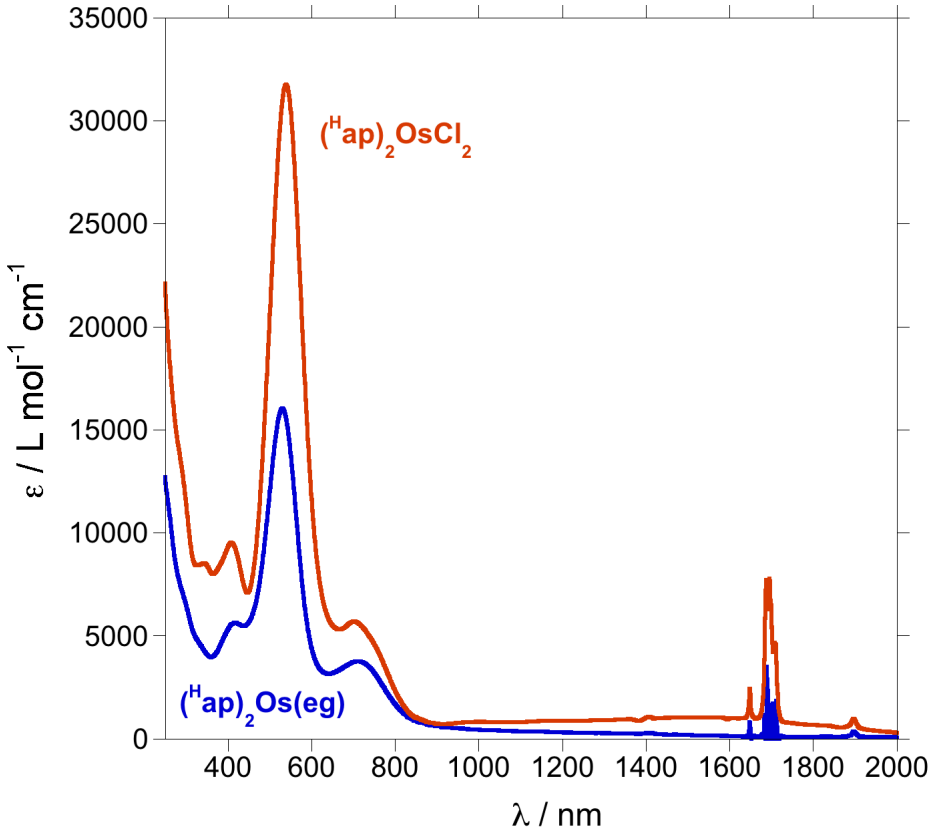
II. Figure S2. Thermal ellipsoid plot of $C_2H_4(O_2CC_6H_4\text{-}2\text{-}NH_2)_2$



III. Optical Spectroscopy

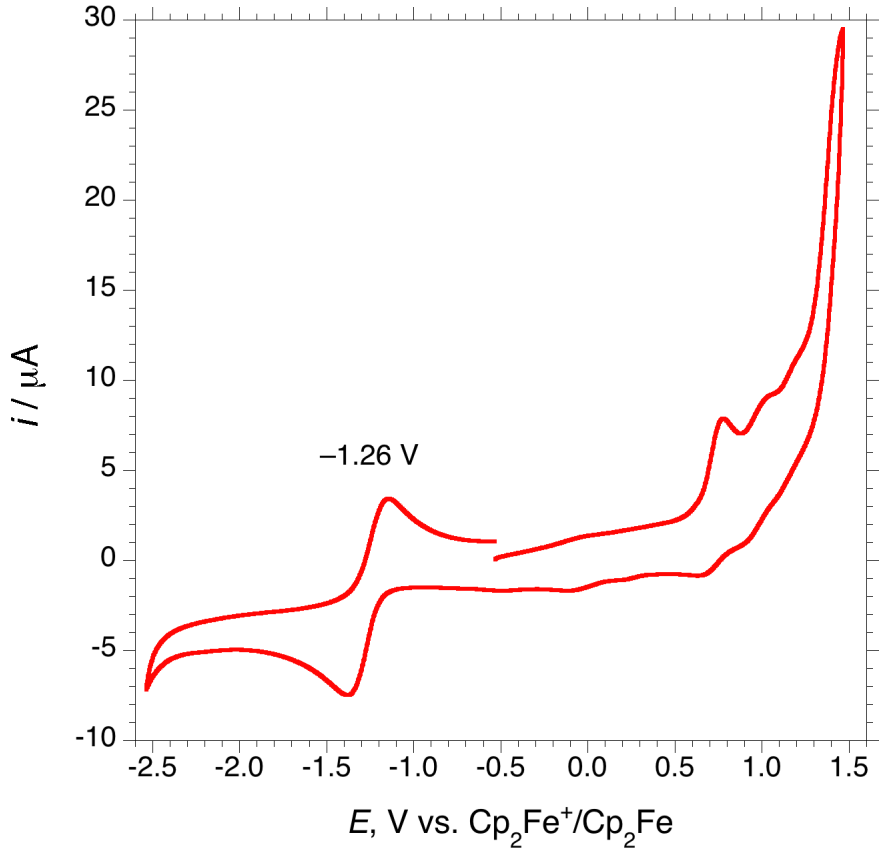


A. Figure S3. UV-visible spectra of (^{R}ap)$_2$OsO in CH_2Cl_2. R = H (blue trace), CH_3S (red trace), CH_3O (black trace) and CF_3 (green trace).

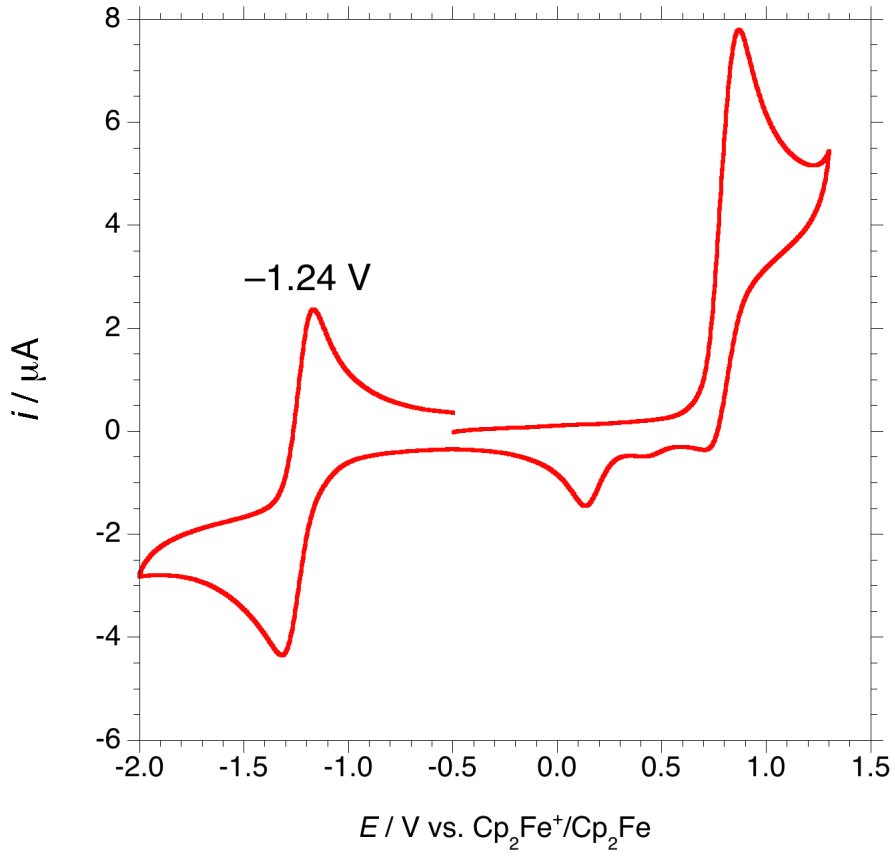


B. Figure S4. UV-visible-NIR spectra of $(^{H}ap)_2Os(OCH_2CH_2O)$ (blue trace) and $(^{H}ap)_2OsCl_2$ (red trace) in CH_2Cl_2.

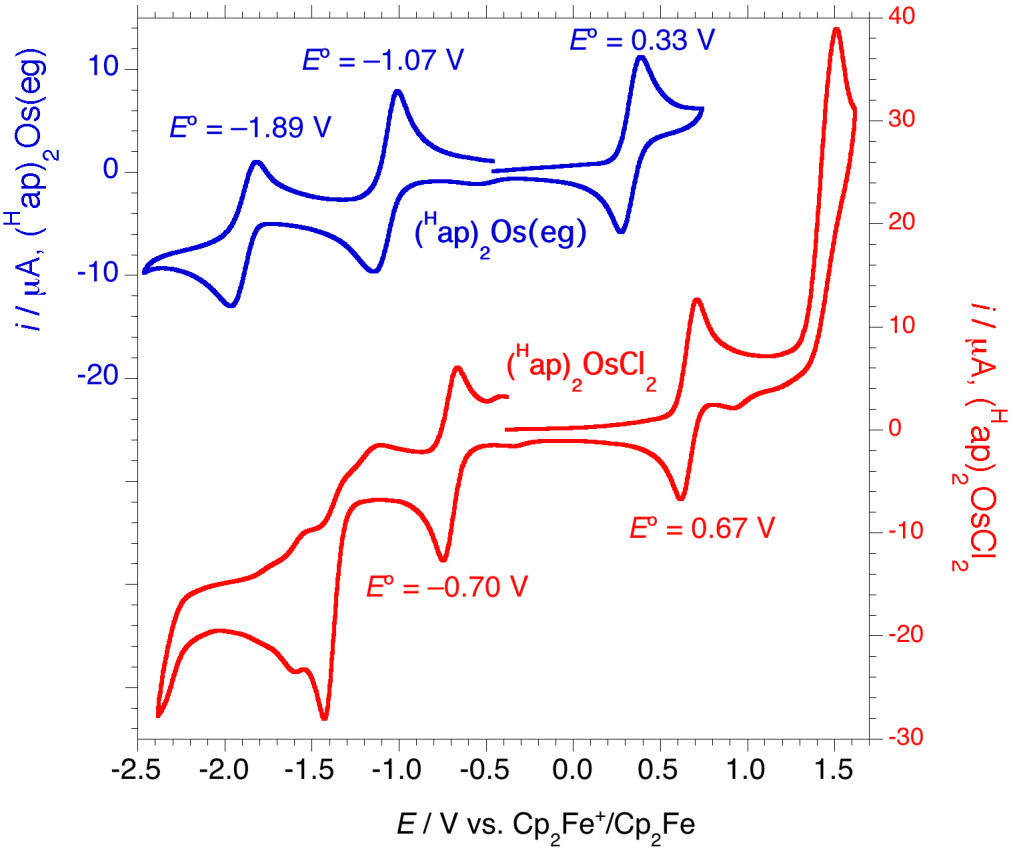
IV. Electrochemistry



A. Figure S5. Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6 supporting electrolyte, 100 mV s^{-1}) of (Egan)OsO.



B. **Figure S6.** Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6 supporting electrolyte, 60 mV s^{-1}) of (^{H}ap)OsO(pin).



C. **Figure S7.** Cyclic voltammogram (CH_2Cl_2, 0.1 M Bu_4NPF_6 supporting electrolyte, 60 mV s^{-1}) of $(^{H}ap)_2Os(OCH_2CH_2O)$ (blue trace, left *y*-axis) and $(^{H}ap)_2OsCl_2$ (red trace, right *y*-axis).

V. Energies and Cartesian coordinates of calculated structures

A. $(^{H}ap)_2OsO$

Energy of optimized structure = –1351.33865947 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	76	-0.000000	0.000006	0.671356
2	8	-0.000091	0.000098	2.392331
3	8	-0.326220	-1.784233	-0.067532
4	7	1.848492	-0.473242	0.122049
5	6	0.791767	-2.501955	-0.372667
6	6	2.009814	-1.804074	-0.302634
7	6	3.203647	-2.471981	-0.606974
8	1	4.153113	-1.952520	-0.539311
9	6	3.151922	-3.816356	-0.979647
10	1	4.076508	-4.338868	-1.207599
11	6	1.930570	-4.495522	-1.057248
12	1	1.908030	-5.540231	-1.353385
13	6	0.735389	-3.839212	-0.753712
14	1	-0.225774	-4.340838	-0.803740
15	6	2.901580	0.469476	-0.035830
16	6	3.266473	1.266264	1.057971
17	1	2.746648	1.135783	2.002253
18	6	4.286385	2.207901	0.926538
19	1	4.565092	2.819225	1.780387
20	6	4.947125	2.363861	-0.293819
21	1	5.741329	3.098357	-0.394590
22	6	4.579959	1.574282	-1.387523
23	1	5.082944	1.698383	-2.342723
24	6	3.560866	0.631962	-1.264538
25	1	3.263648	0.026354	-2.115179
26	8	0.326206	1.784173	-0.067610
27	7	-1.848483	0.473235	0.122194
28	6	-0.791775	2.501903	-0.372727
29	6	-2.009817	1.804075	-0.302550
30	6	-3.203658	2.471992	-0.606807
31	1	-4.153097	1.952585	-0.539027
32	6	-3.151926	3.816348	-0.979565
33	1	-4.076520	4.338874	-1.207445
34	6	-1.930568	4.495462	-1.057329
35	1	-1.908012	5.540153	-1.353531
36	6	-0.735380	3.839116	-0.753868
37	1	0.225796	4.340705	-0.804007
38	6	-2.901550	-0.469485	-0.035779
39	6	-3.560855	-0.631826	-1.264500
40	1	-3.263674	-0.026148	-2.115024
41	6	-4.579952	-1.574134	-1.387572
42	1	-5.082947	-1.698131	-2.342783
43	6	-4.947112	-2.363826	-0.293946
44	1	-5.741313	-3.098306	-0.394789
45	6	-4.286359	-2.207997	0.926421

46	1	-4.565062	-2.819408	1.780210
47	6	-3.266434	-1.266387	1.057944
48	1	-2.746608	-1.136018	2.002207

B. (^{H}ap)$_2$Os(OCH$_2$CH$_2$O) (*cis*-α, N trans)

Energy of optimized structure = –1505.17064076 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	76	-0.000010	-0.000039	0.461794
2	8	0.315155	1.616529	-0.708657
3	7	-1.873295	0.536194	0.009334
4	8	-0.315041	-1.616558	-0.708753
5	7	1.873329	-0.536186	0.009399
6	8	-0.543624	-1.144944	1.981429
7	8	0.543437	1.144658	1.981637
8	6	0.004229	-0.765007	3.225339
9	1	1.039787	-1.130687	3.328531
10	1	-0.606192	-1.194786	4.030884
11	6	-0.004680	0.764622	3.225406
12	1	-1.040257	1.130299	3.328417
13	1	0.605581	1.194336	4.031108
14	6	-0.759551	2.318662	-1.014524
15	6	-2.010352	1.735208	-0.670579
16	6	-3.210143	2.386108	-1.025152
17	1	-4.165100	1.945827	-0.760093
18	6	-3.144961	3.605897	-1.681784
19	1	-4.063929	4.126413	-1.935068
20	6	-1.901588	4.184861	-2.013055
21	1	-1.877650	5.140845	-2.528778
22	6	-0.710951	3.553389	-1.686536
23	1	0.255918	3.979200	-1.934706
24	6	0.759701	-2.318641	-1.014596
25	6	2.010464	-1.735152	-0.670579
26	6	3.210295	-2.385984	-1.025139
27	1	4.165225	-1.945676	-0.760021
28	6	3.145188	-3.605749	-1.681823
29	1	4.064187	-4.126214	-1.935100
30	6	1.901851	-4.184756	-2.013152
31	1	1.877972	-5.140724	-2.528909
32	6	0.711175	-3.553350	-1.686648
33	1	-0.255666	-3.979198	-1.934860
34	6	-2.983286	-0.363901	0.020263
35	6	-3.558732	-0.786120	-1.188156
36	1	-3.147077	-0.429509	-2.126834
37	6	-4.636121	-1.670090	-1.174812
38	1	-5.071412	-1.999718	-2.114251
39	6	-5.151001	-2.131759	0.038964
40	1	-5.992680	-2.818849	0.047976
41	6	-4.577156	-1.710387	1.240965

42	1	-4.973306	-2.066329	2.188002
43	6	-3.491480	-0.836234	1.236380
44	1	-3.027671	-0.518261	2.161257
45	6	2.983270	0.363966	0.020387
46	6	3.491379	0.836323	1.236531
47	1	3.027537	0.518332	2.161370
48	6	4.577010	1.710532	1.241166
49	1	4.973096	2.066495	2.188221
50	6	5.150889	2.131936	0.039192
51	1	5.992537	2.819064	0.048247
52	6	4.636086	1.670250	-1.174611
53	1	5.071398	1.999913	-2.114028
54	6	3.558743	0.786225	-1.188006
55	1	3.147140	0.429605	-2.126704

C. $(^{H}ap)_2OsCl_2$ (*cis*-α, O trans)

Energy of optimized structure = –2196.55203488 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	76	0.000000	0.000000	1.046030
2	8	-1.015893	1.759913	0.995828
3	7	1.081372	1.049539	-0.276616
4	17	1.403916	0.901809	2.757555
5	6	-0.340082	2.741173	0.481236
6	6	0.847873	2.390433	-0.259100
7	6	1.610843	3.410487	-0.889330
8	1	2.523845	3.155393	-1.414856
9	6	1.188801	4.716619	-0.788874
10	1	1.776809	5.507314	-1.244982
11	6	0.000000	5.055080	-0.082003
12	1	-0.299057	6.097823	-0.023613
13	6	-0.762828	4.092343	0.539855
14	1	-1.663025	4.332343	1.095541
15	6	2.052009	0.507220	-1.169807
16	6	3.096051	-0.274421	-0.656094
17	1	3.159460	-0.434527	0.413869
18	6	4.039513	-0.814614	-1.528713
19	1	4.857046	-1.407409	-1.128467
20	6	3.938420	-0.599527	-2.905891
21	1	4.673072	-1.030845	-3.579968
22	6	2.888928	0.169617	-3.414695
23	1	2.799944	0.334009	-4.484959
24	6	1.947883	0.730418	-2.551931
25	1	1.124107	1.322794	-2.938340
26	8	1.015893	-1.759913	0.995828
27	7	-1.081372	-1.049539	-0.276616
28	17	-1.403916	-0.901809	2.757555
29	6	0.340082	-2.741173	0.481236
30	6	-0.847873	-2.390433	-0.259100

31	6	-1.610843	-3.410487	-0.889330
32	1	-2.523845	-3.155393	-1.414856
33	6	-1.188801	-4.716619	-0.788874
34	1	-1.776809	-5.507314	-1.244982
35	6	-0.000000	-5.055080	-0.082003
36	1	0.299057	-6.097823	-0.023613
37	6	0.762828	-4.092343	0.539855
38	1	1.663025	-4.332343	1.095541
39	6	-2.052009	-0.507220	-1.169807
40	6	-3.096051	0.274421	-0.656094
41	1	-3.159460	0.434527	0.413869
42	6	-4.039513	0.814614	-1.528713
43	1	-4.857046	1.407409	-1.128467
44	6	-3.938420	0.599527	-2.905891
45	1	-4.673072	1.030845	-3.579968
46	6	-2.888928	-0.169617	-3.414695
47	1	-2.799944	-0.334009	-4.484959
48	6	-1.947883	-0.730418	-2.551931
49	1	-1.124107	-1.322794	-2.938340

D. (^{H}ap)OsO(OCH$_2$CH$_2$O)

Energy of optimized structure = –987.712877450 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	76	-1.106113	-0.221203	0.302731
2	8	-1.457796	-0.159790	1.971398
3	8	-0.581930	-2.037847	-0.180918
4	7	0.842801	0.045675	0.180388
5	6	0.759865	-2.269852	-0.176537
6	6	1.579812	-1.141876	0.001153
7	6	2.971815	-1.296185	0.018697
8	1	3.615982	-0.438230	0.175748
9	6	3.512955	-2.571641	-0.153516
10	1	4.591664	-2.696478	-0.132598
11	6	2.686152	-3.684095	-0.347545
12	1	3.123992	-4.668624	-0.483531
13	6	1.297022	-3.540199	-0.363413
14	1	0.631863	-4.385340	-0.508276
15	6	1.477185	1.315164	0.077916
16	6	1.273485	2.261114	1.091040
17	1	0.642576	2.002945	1.936180
18	6	1.880145	3.513505	1.007748
19	1	1.720823	4.240370	1.799319
20	6	2.688110	3.832716	-0.085864
21	1	3.158955	4.809707	-0.149569

22	6	2.885159	2.892614	-1.101274
23	1	3.504048	3.138643	-1.959811
24	6	2.282251	1.638481	-1.025087
25	1	2.424099	0.909059	-1.816655
26	8	-1.300273	1.484705	-0.580442
27	8	-2.705517	-0.618782	-0.731022
28	6	-2.456227	1.638882	-1.420914
29	6	-3.457130	0.556399	-1.051319
30	1	-2.127414	1.543015	-2.464177
31	1	-2.850544	2.649957	-1.267082
32	1	-4.056386	0.852330	-0.178662
33	1	-4.134124	0.317927	-1.879777

E. (Egan)OsO

Energy of optimized structure = –1805.87873909 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	76	0.000000	0.000000	1.304199
2	8	0.000000	0.000000	3.021914
3	8	-0.664480	-1.738176	0.685562
4	7	1.693931	-0.789039	0.674578
5	6	0.293673	-2.629141	0.312230
6	8	0.664480	1.738176	0.685562
7	7	-1.693931	0.789039	0.674578
8	6	-0.293673	2.629141	0.312230
9	6	1.608755	-2.135416	0.274812
10	6	-1.608755	2.135416	0.274812
11	8	-1.386708	0.097179	-2.042195
12	8	1.386708	-0.097179	-2.042195
13	6	2.655265	-2.976729	-0.119567
14	1	3.675674	-2.609734	-0.147010
15	6	-2.655265	2.976729	-0.119567
16	1	-3.675674	2.609734	-0.147010
17	6	2.364255	-4.298230	-0.467774
18	1	3.173308	-4.956789	-0.769778
19	6	-2.364255	4.298230	-0.467774
20	1	-3.173308	4.956789	-0.769778
21	6	1.050753	-4.778604	-0.431524
22	1	0.841796	-5.808067	-0.707418
23	6	-1.050753	4.778604	-0.431524
24	1	-0.841796	5.808067	-0.707418
25	6	-0.000000	-3.942071	-0.044835
26	1	-1.028157	-4.288459	-0.011560

27	6	0.000000	3.942071	-0.044835
28	1	1.028157	4.288459	-0.011560
29	6	-2.895730	0.057335	0.446042
30	6	2.895730	-0.057335	0.446042
31	6	-3.412767	-0.201113	-0.843785
32	6	3.412767	0.201113	-0.843785
33	6	-4.651010	-0.846957	-0.963071
34	1	-5.043655	-1.014279	-1.960590
35	6	4.651010	0.846957	-0.963071
36	1	5.043655	1.014279	-1.960590
37	6	-5.351160	-1.277132	0.161515
38	1	-6.302361	-1.788196	0.045347
39	6	5.351160	1.277132	0.161515
40	1	6.302361	1.788196	0.045347
41	6	-4.820604	-1.050609	1.432384
42	1	-5.354343	-1.383482	2.318076
43	6	4.820604	1.050609	1.432384
44	1	5.354343	1.383482	2.318076
45	6	-3.606144	-0.380269	1.569789
46	1	-3.192990	-0.173215	2.552235
47	6	3.606144	0.380269	1.569789
48	1	3.192990	0.173215	2.552235
49	6	0.632359	-0.413965	-3.226692
50	1	0.401216	-1.484067	-3.206589
51	1	1.232670	-0.194937	-4.113454
52	6	-0.632359	0.413965	-3.226692
53	1	-0.401216	1.484067	-3.206589
54	1	-1.232670	0.194937	-4.113454
55	6	-2.734756	0.143153	-2.133099
56	6	2.734756	-0.143153	-2.133099
57	8	-3.332755	0.375484	-3.164336
58	8	3.332755	-0.375484	-3.164336