Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information to Paper

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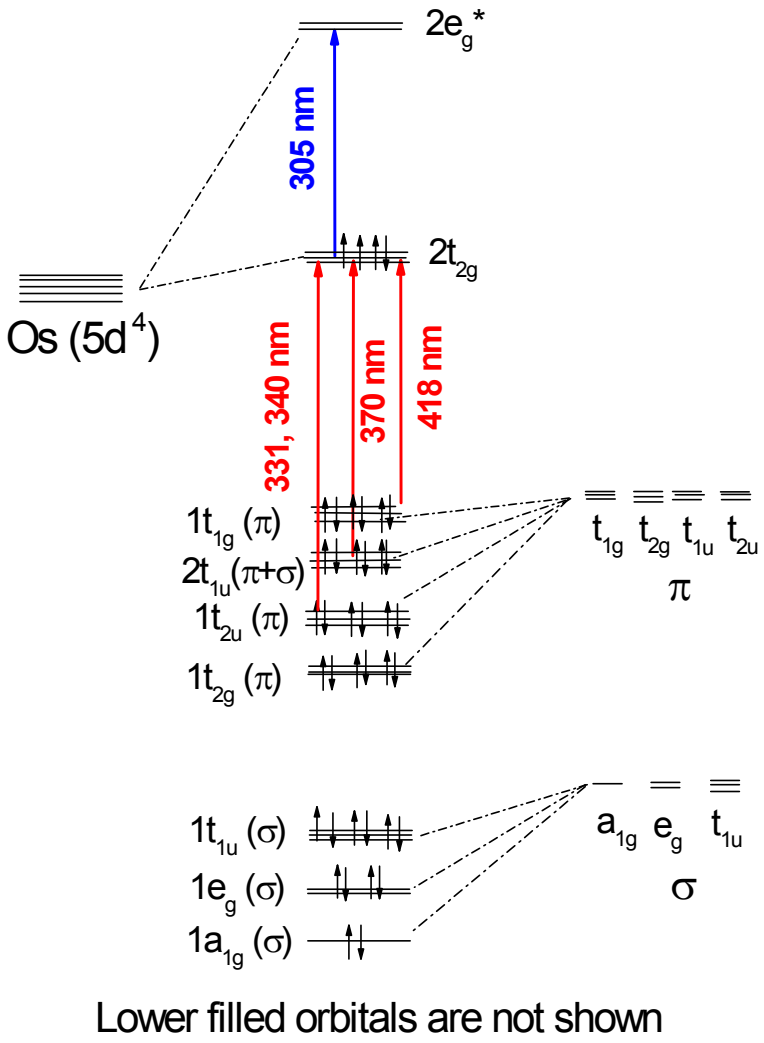
Photochemistry of Hexachloroosmate(IV) in Ethanol

Figure S1. The approximate structure of molecular orbitals of the $Os^{IV}Cl_6^{2-}$ complex according to [39] (non-relativistic approximation). Arrows correspond to the LMCT (red) and d-d (blue) transitions.



[39] C.K. Jørgensen, *Mol. Phys*., 1959, **2**, 309.

Figure S2. Example of raw data used for calculation of the $Os^{IV}Cl_5(C_2H_5OH)^-$ electronic absorption spectra from the experiment on the stationary photolysis (313 nm) of $Os^{IV}Cl_6^{2-}$ in ethanol.

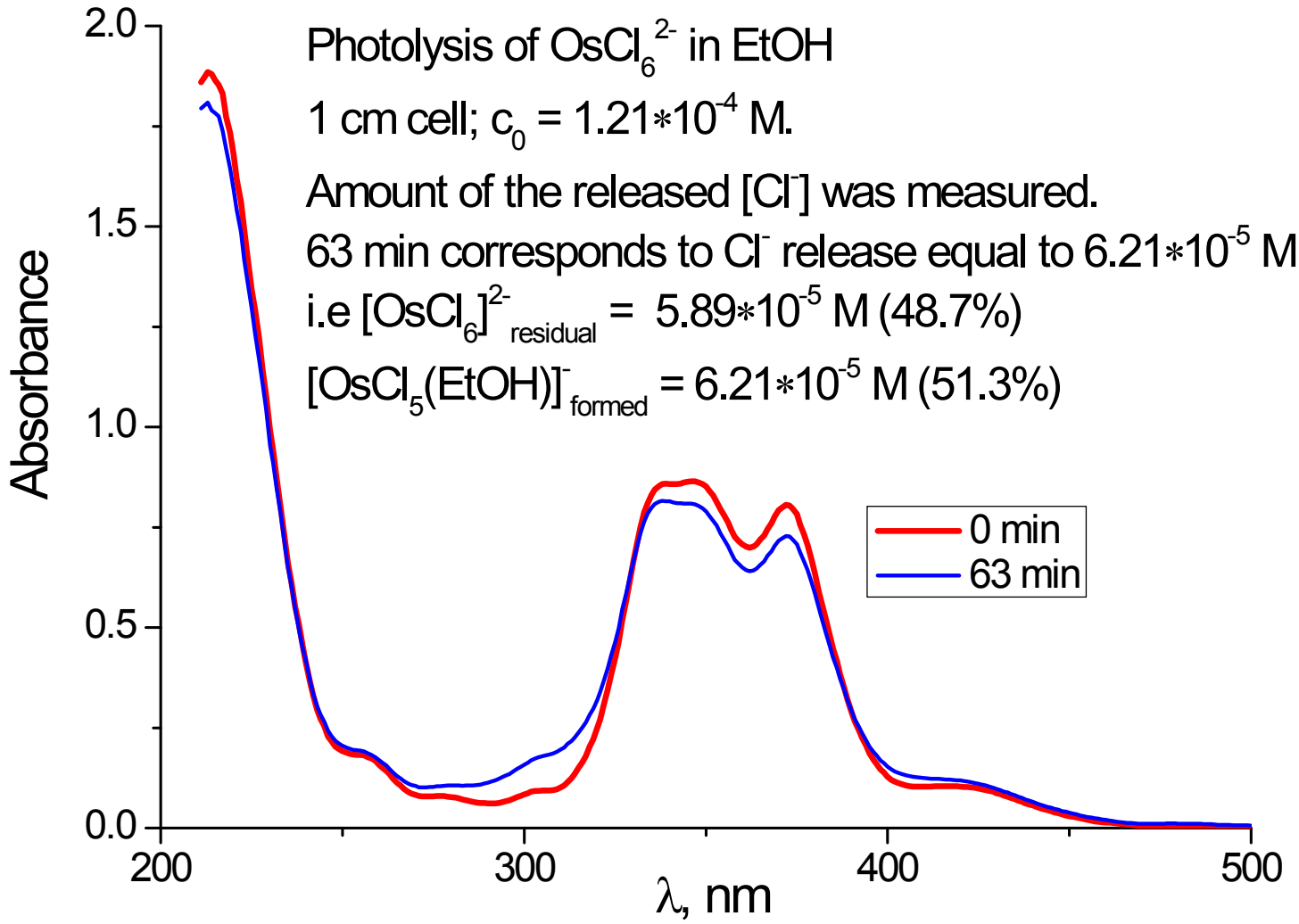


Figure S3. Laser flash photolysis (355 nm) of $Os^{IV}Cl_6^{2-}$ in ethanol (1.27×10^{-4} M, 1 cm cell). Dependence of intermediate absorption amplitude vs. laser pulse energy.

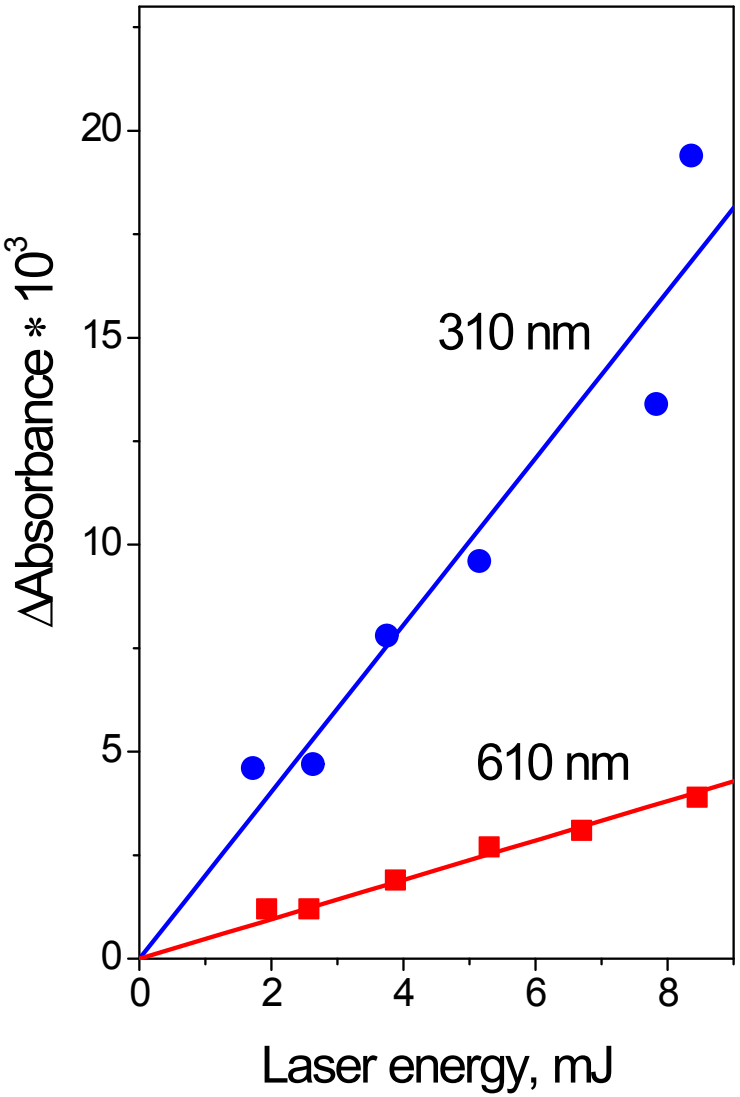


Table S1. Electronic and geometric structure of $Os^{IV}Cl_6^{2-}$ (Figure S4). Multiplicity, M; bond lengths, $R_{OsCl(i)}$; bond angles, $\angle Cl(6)OsCl(i)$, $\angle Cl(1)OsCl(3)$, $\angle Cl(3)OsCl(4)$, $\angle Cl(4)OsCl(5)$, $\angle Cl(5)OsCl(1)$; atom charges, q_{Os}, $q_{Cl(6)}$, $q_{Cl(7)}$, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$OsCl_6^{-2}$ conf.	M	$R_{OsCl(6)}$, $R_{OsCl(7)}$	$R_{OsCl(i)}$, i=1,3,4,5	$\angle Cl(6)OsCl(i)$ i=1,3,4,5	$\angle Cl(1)OsCl(3)$ $\angle Cl(3)OsCl(4)$ $\angle Cl(4)OsCl(5)$ $\angle Cl(5)OsCl(1)$	q_{Os}	$q_{Cl(6)}$, $q_{Cl(7)}$,	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas											
1	4GBP	1	2.406 2.406	2.406 2.406 2.406 2.406	90.33 90.33 89.67 89.67	90.33 89.67 90.33 89.67	0.311	-0.385 -0.385	-0.385 -0.385 -0.385 -0.385	-2850.880288 -77576.39	-2850.913736 -77577.35
2	4GBP	3	2.409 2.409	2.409 2.409 2.409 2.409	90.03 90.03 89.97 89.97	89.97 90.03 89.97 90.03	0.364	-0.394 -0.394	-0.394 -0.394 -0.394 -0.394	-2850.914871 -77577.34	-2850.949416 -77578.32
3	4GBP	5	2.382 2.382	2.722 2.382 2.722 2.382	90.00 90.00 90.00 90.00	90.00 90.00 90.00 90.00	0.475	-0.351 -0.351	-0.536 -0.351 -0.536 -0.351	-2850.872433 -77576.18	-2850.907954 -77577.20
Ethanol											
4	4GBP	1	2.388 2.388	2.392 2.389 2.392 2.389	90.37 90.27 89.63 89.73	90.32 89.68 90.32 89.68	0.221	-0.369 -0.369	-0.372 -0.369 -0.372 -0.369	-2851.155399 -77583,93	-2851.188756 -77584.84
5	4GBP	3	2.386 2.386	2.407 2.385 2.407 2.385	90.05 89.91 89.95 90.09	90.01 89.99 90.01 89.99	0.274	-0.369 -0.369	-0.400 -0.368 -0.400 -0.368	-2851.190042 -77584.82	-2851.224271 -77585.80
6	4GBP	5	2.368 2.368	2.685 2.368 2.685 2.368	89.98 90.00 90.02 90.00	90.00 90.00 90.00 90.00	0.394	-0.326 -0.326	-0.545 -0.326 -0.545 -0.326	-2851.144475 -77583.58	-2851.180215 -77584.61

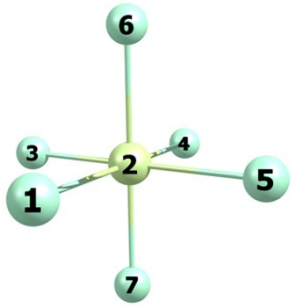


Figure S4. Optimal geometry of $Os^{IV}Cl_6^{2-}$ complex (tetragonal bipyramidal – 4GBP).

Table S2. Electronic and geometric structure of $Os^{IV}Cl_5^-$ (Figure S5(a,b)). Multiplicity, M; bond lengths, $R_{OsCl(6)}$, $R_{OsCl(i)}$; bond angles, $\angle Cl(6)OsCl(i)$, $\angle Cl(1)OsCl(3)$, $\angle Cl(3)OsCl(4)$, $\angle Cl(4)OsCl(5)$, $\angle Cl(5)OsCl(1)$; atom charges, q_{Os}, $q_{Cl(6)}$, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$OsCl_5^{-1}$ conf.	M	$R_{OsCl(6)}$	$R_{OsCl(i)}$, i=1,3,4,5	$\angle Cl(6)OsCl(i)$ i=1,3,4,5	$\angle Cl(1)OsCl(3)$ $\angle Cl(3)OsCl(4)$ $\angle Cl(4)OsCl(5)$ $\angle Cl(5)OsCl(1)$	q_{Os}	$q_{Cl(6)}$	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas											
1	4GP	1	2.338	2.344 2.344 2.344 2.344	93.21 93.21 93.21 93.21	89.82 89.82 89.82 89.82	0.336	-0.259	-0.269 -0.269 -0.269 -0.269	-2390.878933 -65059.12	-2390.908663 -65059.97
2	3GBP	1	2.262	2.400 2.262 2.400 2.262	93.35 119.55 86.62 119.73	93.44 86.63 86.60 93.36	0.361	-0.191	-0.378 -0.191 -0.411 -0.191	-2390.892706 -65059.50	-2390.924571 -65060.41
3	4GP	3	2.286	2.385 2.326 2.385 2.326	92.26 101.72 92.26 101.72	89.54 89.54 89.54 89.54	0.401	-0.200	-0.335 -0.265 -0.335 -0.265	-2390.910591 -65059.98	-2390.942791 -65060.90
4	4GP	5	2.471	2.347 2.347 2.347 2.347	98.51 98.51 98.51 98.51	88.75 88.75 88.75 88.75	0.481	-0.348	-0.283 -0.283 -0.283 -0.283	-2390.912141 -65060.03	-2390.944665 -65060.95
Ethanol											
5	4GP	1	2.336	2.341 2.341 2.341 2.341	92.78 92.80 92.73 92.81	89.85 89.87 89.88 89.85	0.342	-0.277	-0.266 -0.266 -0.266 -0.266	-2390.952225 -65061.12	-2390.983240 -65062.00
6	3GBP	1	2.250	2.423 2.250 2.442 2.250	90.98 119.83 88.99 120.03	91.03 89.06 88.99 90.95	0.338	-0.159	-0.423 -0.159 -0.438 -0.159	-2390.968678 -65061.56	-2391.000797 -65062.48
7	4GP	3	2.284	2.386 2.320 2.386 2.320	91.93 100.85 91.90 100.86	89.63 89.65 89.65 89.63	0.397	-0.191	-0.351 -0.253 -0.351 -0.253	-2390.983761 -65061.98	-2391.016657 -65062.91
8	4GP	5	2.484	2.341 2.341 2.341 2.341	97.91 97.93 97.85 97.93	88.91 88.92 88.92 88.91	0.461	-0.372	-0.272 -0.272 -0.272 -0.272	-2390.983174 -65061.96	-2391.017112 -65062.92

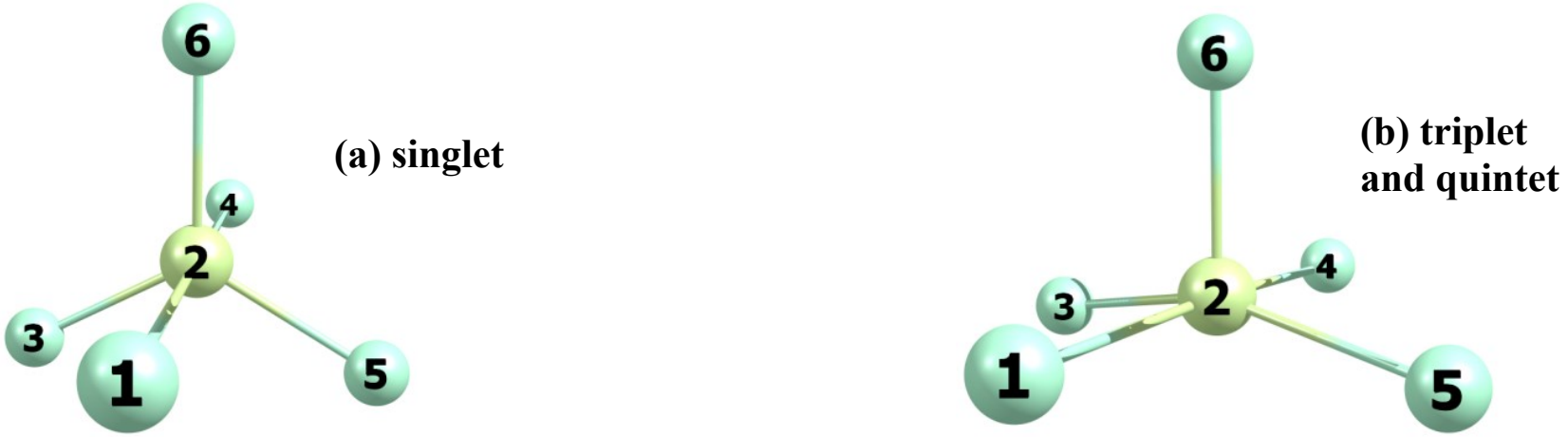


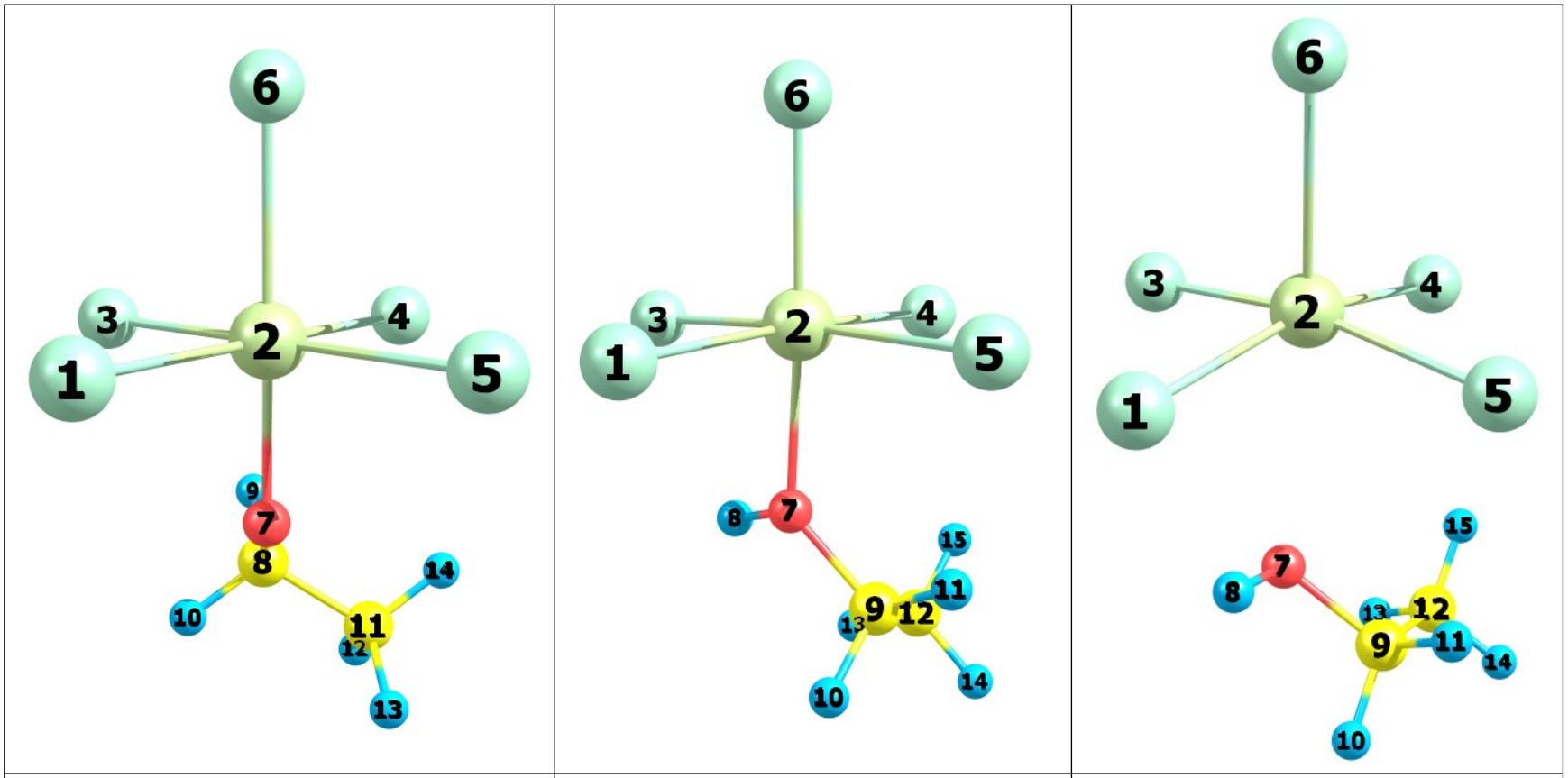
Figure S5. Optimal geometry of $Os^{IV}Cl_5^-$ intermediate in (**a**) singlet (trigonal bipyramidal – 3GBP), (**b**) triplet and quintet states (square pyramidal – 4GP).

Table S3. Electronic and geometric structure of $Os^{IV}Cl_5(C_2H_5O)^{2-}$ (Figure S6a). Multiplicity, M; bond lengths, $R_{OsCl(i)}$; bond angles, $\angle Cl(6)OsCl(i)$, $\angle Cl(1)OsCl(3)$, $\angle Cl(3)OsCl(4)$, $\angle Cl(4)OsCl(5)$, $\angle Cl(5)OsCl(1)$; atom charges, q_{Os}, $q_{Cl(6)}$, $q_{Cl(7)}$, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$Os^{IV}Cl_5(C_2H_5O)^{2-}$ conf.	M	$R_{OsCl(6)}$, $R_{OsO(7)}$	$R_{OsCl(i)}$, i=1,3,4,5	$\angle Cl(6)OsCl(i)$ i=1,3,4,5	$\angle Cl(1)OsCl(3)$ $\angle Cl(3)OsCl(4)$ $\angle Cl(4)OsCl(5)$ $\angle Cl(5)OsCl(1)$	q_{Os}	$q_{Cl(6)}$, $q_{O(7)}$	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas											
1	4GP	1	2.399 1.920	2.431 2.448 2.465 2.431	90.41 90.71 90.36 89.91	91.67 88.06 91.54 88.72	0.411	-0.376 -0.440	-0.419 -0.435 -0.439 -0.419	-2545.099720 -69255.68	-2545.066804 -69254.83
2	4GP	3	2.399 1.954	2.424 2.446 2.455 2.427	91.17 90.56 90.31 91.05	90.35 89.31 90.16 90.13	0.482	-0.386 -0.483	-0.415 -0.431 -0.429 -0.420	-2545.123428 -69256.33	-2545.091926 -69255.51
3	4GP	5	2.381 1.941	2.686 2.412 2.878 2.398	93.03 90.04 92.31 90.42	91.73 87.17 89.14 91.91	0.589	-0.363 -0.486	-0.523 -0.387 -0.558 -0.375	-2545.083907 -69255.25	-2545.054976 -69254.51
Ethanol											
4	4GP	1	2.411 1.900	2.420 2.420 2.426 2.426	90.28 90.33 89.36 89.28	89.90 91.34 88.38 91.37	0.297	-0.404 -0.448	-0.413 -0.413 -0.434 -0.434	-2545.382415 -69263.37	-2545.349389 -69262.52
5	4GP	3	2.406 1.924	2.420 2.424 2.422 2.420	90.30 89.88 89.93 90.39	90.31 89.63 90.11 89.94	0.391	-0.400 -0.500	-0.427 -0.428 -0.422 -0.429	-2545.400103 -69263.85	-2545.368270 -69263.03
6	4GP	5	2.383 1.919	2.688 2.403 2.741 2.401	91.31 89.82 90.48 90.13	91.00 88.48 89.99 90.53	0.511	-0.367 -0.501	-0.555 -0.380 -0.557 -0.380	-2545.356673 -69262.67	-2545.327601 -69261.93

Table S4. Electronic and geometric structure of $Os^{IV}Cl_5(C_2H_5OH)^-$ (Figure S6(b-c)). Multiplicity, M; bond lengths, $R_{OsCl(i)}$; bond angles, $\angle Cl(6)OsCl(i)$, $\angle Cl(1)OsCl(3)$, $\angle Cl(3)OsCl(4)$, $\angle Cl(4)OsCl(5)$, $\angle Cl(5)OsCl(1)$; atom charges, q_{Os}, $q_{Cl(6)}$, $q_{Cl(7)}$, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$OsCl_5^{-1}$ conf.	M	$R_{OsCl(6)}$, $R_{OsO(7)}$, $R_{Cl(1)H(8)}$, $R_{Cl(3)H(8)}$	$R_{OsCl(i)}$, i=1,3,4,5	$\angle Cl(6)OsCl(i)$ i=1,3,4,5	$\angle Cl(1)OsCl(3)$ $\angle Cl(3)OsCl(4)$ $\angle Cl(4)OsCl(5)$ $\angle Cl(5)OsCl(1)$	q_{Os}	$q_{Cl(6)}$, $q_{O(7)}$, $q_{H(8)}$	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas											
1	3GBP	1	2.263 4.784 3.880 2.259	2.258 2.482 2.261 2.377	119.76 85.87 120.00 93.82	86.12 86.26 93.86 94.06	0.379	-0.183 -0.353 0.152	-0.380 -0.175 -0.345 -0.172	-2545.742537 -69273.18	-2545.700406 -69272.07
2	4GP	3	2.320 2.216 2.255 3.404	2.431 2.337 2.387 2.367	95.88 94.43 90.39 93.31	89.87 90.73 90.00 88.56	0.386	-0.252 -0.305 0.189	-0.356 -0.266 -0.316 -0.295	-2545.776641 -69274.10	-2545.731486 -69272.92
3	4GP	5	2.461 4.169 2.317 3.850	2.379 2.348 2.334 2.336	98.08 98.21 99.32 98.53	88.16 89.14 89.38 88.27	0.484	-0.329 -0.340 0.162	-0.297 -0.264 -0.260 -0.261	-2545.754489 -69273.50	-2545.714944 -69272.46
Ethanol											
4	4GP	1	2.320 2.161 2.491 3.206	2.395 2.346 2.434 2.330	93.55 95.71 87.98 97.33	92.90 86.19 86.65 93.90	0.311	-0.265 -0.316 0.243	-0.363 -0.268 -0.386 -0.256	-2545.829803 -69275.55	-2545.784540 -69274.36
5	4GP	3	2.344 2.125 3.466 2.652	2.351 2.399 2.358 2.399	92.23 93.45 91.97 90.58	90.00 90.03 90.00 89.91	0.362	-0.304 -0.339 0.250	-0.290 -0.363 -0.293 -0.354	-2545.862640 -69276.44	-2545.818314 -69275.28
6	4GP	5	2.511 2.973 2.632 3.770	2.362 2.340 2.344 2.348	96.92 95.97 97.71 95.14	89.24 89.52 89.34 89.07	0.436	-0.389 -0.327 0.197	-0.295 -0.269 -0.269 -0.274	-2545.825964 -69275.44	-2545.786001 -69274.40



(**a**) $Os^{IV}Cl_5(C_2H_5O)^{2-}$ - S, T, Q	(b) $Os^{IV}Cl_5(C_2H_5OH)^{-}$ - S, T, Q	(**c**) $Os^{IV}Cl_5(C_2H_5OH)^{-}$ - S, Q

Figure S6. Optimal geometries of $Os^{IV}Cl_5(C_2H_5O)^{2-}$ complex in (**a**) singlet, triplet, quintet states and $Os^{IV}Cl_5(C_2H_5OH)^{-}$ complex in (**b**) singlet, triplet, quintet states (ethanol) and (**c**) singlet, quintet states (gas phase).

Table S5. Electronic and geometric structure of $Os^{III}Cl_4^-$ (Figure S7). Multiplicity, M; bond lengths, $R_{OsCl(i)}$; bond angles, ∠Cl(1)OsCl(3), ∠Cl(3)OsCl(4), ∠Cl(4)OsCl(5), ∠Cl(5)OsCl(1); atom charges, q_{Os}, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$OsCl_4^{-1}$ conf.	M	$R_{OsCl(i)}$, i=1,3,4,5	∠Cl(1)OsCl(3) ∠Cl(3)OsCl(4) ∠Cl(4)OsCl(5) ∠Cl(5)OsCl(1)	q_{Os}	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas								
1	4PL	2	2.336, 2.323, 2.336, 2.323	89.95, 90.04, 89.95, 90.04	0.239	-0.319, -0.300, -0.319, -0.300	-1930.874523 -52541.80	-1930.906285 -52542.66
2	4PL	4	2.334, 2.334, 2.334, 2.334	90.00, 90.00, 90.00, 90.00	0.271	-0.318, -0.318, -0.318, -0.318	-1930.896836 -52542.41	-1930.928419 -52543.26
Ethanol								
3	4PL	2	2.317, 2.333, 2.317, 2.333	90.00, 90.00, 90.00, 90.00	0.214	-0.290, -0.317, -0.290, -0.317	-1930.947619 -52543.79	-1930.979470 -52544.65
4	4PL	4	2.329, 2.329, 2.329, 2.329	90.00, 90.00, 90.00, 90.00	0.248	-0.312, -0.312, -0.312, -0.312	-1930.969823 -52544.39	-1931.002168 -52545.27

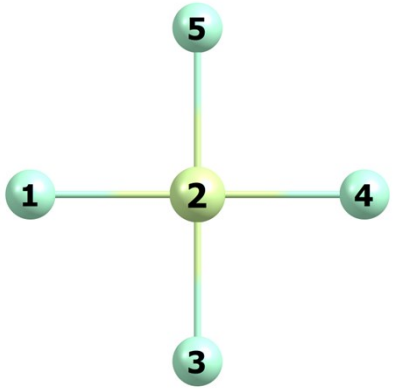


Figure S7. Optimal geometry of $Os^{III}Cl_4^-$ complex in doublet and quartet states (square planar – 4PL).

Table S6. Electronic and geometric structure of $Os^{III}Cl_5^{2-}$ (Figure S5(b)). Multiplicity, M; bond lengths, $R_{OsCl(6)}$, $R_{OsCl(i)}$; bond angles, $\angle Cl(6)OsCl(i)$, $\angle Cl(1)OsCl(3)$, $\angle Cl(3)OsCl(4)$, $\angle Cl(4)OsCl(5)$, $\angle Cl(5)OsCl(1)$; atom charges, q_{Os}, $q_{Cl(6)}$, $q_{Cl(i)}$, i=1,3,4,5; total energy, E_0; Gibbs free energy, E_G.

№	$OsCl_5^{-2}$ conf.	M	$R_{OsCl(6)}$	$R_{OsCl(i)}$, i=1,3,4,5	$\angle Cl(6)OsCl(i)$ i=1,3,4,5	$\angle Cl(1)OsCl(3)$ $\angle Cl(3)OsCl(4)$ $\angle Cl(4)OsCl(5)$ $\angle Cl(5)OsCl(1)$	q_{Os}	$q_{Cl(6)}$	$q_{Cl(i)}$, i=1,3,4,5	E_0, Hartree, eV	E_G, Hartree, eV
Gas											
1	4GP	2	2.381	2.435 2.435 2.435 2.435	94.61 94.61 94.61 94.61	89.63 89.63 89.63 89.63	0.237	-0.392	-0.461 -0.461 -0.461 -0.461	-2390.843242 -65058.19	-2390.877411 -65059.12
2	4GP	4	2.609	2.436 2.410 2.436 2.410	92.33 103.55 92.33 103.55	89.45 89.45 89.45 89.45	0.319	-0.535	-0.457 -0.435 -0.457 -0.435	-2390.845585 -65058,25	-2390.880952 -65059.22
Ethanol											
3	4GP	2	2.362	2.414 2.412 2.413 2.412	93.63 93.68 93.17 93.68	89.78 89.78 89.78 89.78	0.180	-0.383	-0.449 -0.449 -0.449 -0.449	-2391.126611 -65065.90	-2391.160510 -65066.82
4	4GP	4	2.602	2.419 2.372 2.419 2.372	92.09 100.05 92.11 100.02	89.64 89.63 89.63 89.64	0.222	-0.548	-0.447 -0.390 -0.447 -0.390	-2391.126865 -65065.91	-2391.161618 -65066.85