

Figure S1. The UV-VIS spectra of $[\text{OsO}_4]$ in both CCl_4 and water, obtained from this study. The literature reported spectrum of gaseous OsO_4 is included for comparison [29a,b].

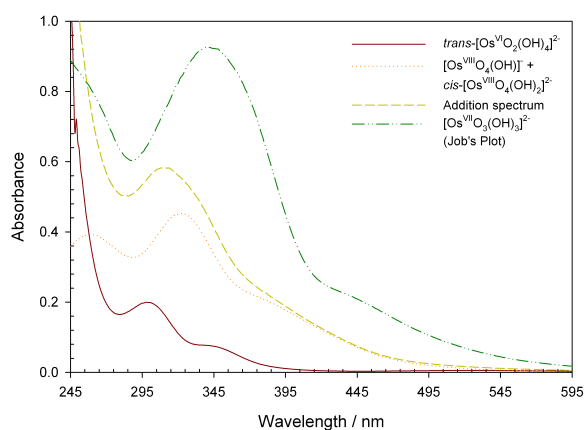
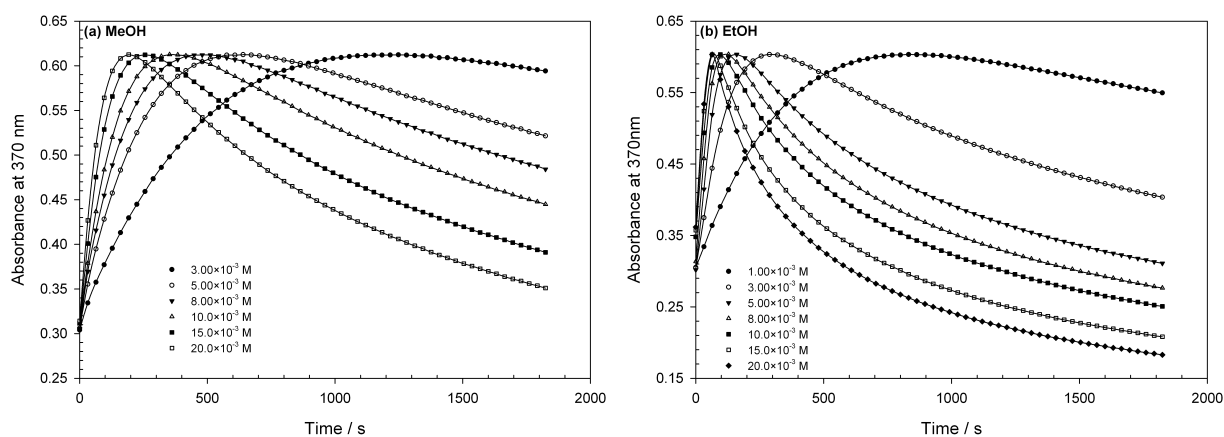


Figure S2. UV-VIS spectra of $\text{trans-}[\text{Os}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-}$ and $([\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})]^- \text{ \& } \text{cis-}[\text{Os}^{\text{VIII}}\text{O}_4(\text{OH})_2]^{2-})$ species, and the theoretically calculated addition spectrum of these complex anions. Included is the experimentally obtained spectrum when a mixture of OsVI and OsVIII is present. $[\text{Os}^{\text{VI}}] = 1.686 \times 10^{-4} \text{ M}$, $[\text{Os}^{\text{VIII}}] = 1.799 \times 10^{-4} \text{ M}$, $[\text{NaOH}] = 2.0 \text{ M}$, conducted at 298.1 K.



Figures S3 (a) and (b). Kinetic traces depicting the rate of change in absorbance as a function of time for the reaction between varying (a) methanol and (b) ethanol concentrations in a 2.0 M hydroxide medium at 298.1 K. $[\text{Os}] = 2.631 \times 10^{-4}$. Symbols = expt data; Lines = model fits of each individual trace using equations 9-11.

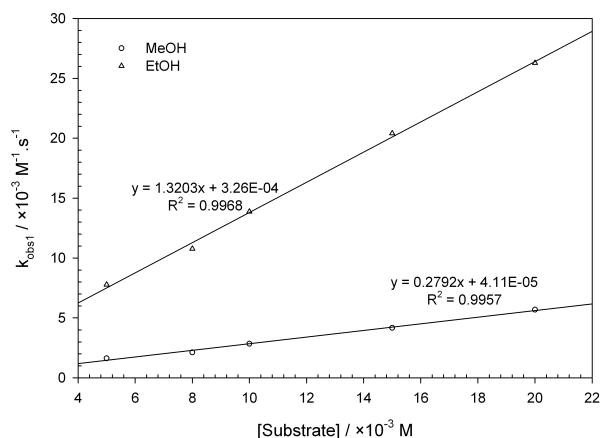


Figure S4. Plot of k_{obs1} versus [substrate] for the reaction between Os^{VIII} and MeOH/EtOH; implying first-order kinetics with respect to the substrate concentration. 2.0 M NaOH, $T = 298.1$ K

Experimental outline for ^{189}Os NMR investigations

^{189}Os NMR was attempted on solutions (a) 0.8 M $[\text{OsO}_4]$ in $\text{CCl}_4 + 20\% \text{ V/V CCl}_3\text{D}$ (b) 0.2 M $\text{Os}^{\text{VI}} + 2.0$ M NaOH + 20% V/V D_2O . No resonance signals were observed. The relative quadrupole moment of this nucleus (0.8 units) is probably responsible for fast relaxation (the T_1 relaxation time is estimated at $2.0 - 3.0 \times 10^{-4}$ s at a magnetic field of 2.35 T [1]). This could be even worse at our magnetic field strength of 14.1 T. Unfortunately our probes cannot tune for the spin $\frac{1}{2}$ ^{187}Os nucleus as it is out of range. Please view our comments above regarding ESR experiments.

46.588 MHz ^{189}Os NMR spectra were attempted at constant temperature ($292 \text{ K} \pm 0.1\text{K}$) using a Varian INOVA spectrometer with a 10mm low-gamma broad-band probe. Attempts to record ^{189}Os NMR spectra were conducted under conditions of optimal resolution using a 15.4 μs excitation pulse (corresponding to a $\sim 60^\circ$ pulse) at maximum practical power, an acquisition time of 0.2 s with a 0.31 s relaxation delay, in an attempt to ensure homogeneous and complete excitation over the entire spectral width.

[1] C. Brevard and P. Granger. *Handbook of High-Resolution Multinuclear NMR*, John Wiley & Sons, 1981 (pp 196-197)

Experimental outline for Osmium EPR/ESR investigations

EPR experiments were performed at Stellenbosch University (Bruker EMX Spectrometer) at room temperature (298 K) with several solutions (a) 0.4 mM $\text{Os}^{\text{VIII}} + 2.0$ M NaOH, (b) 0.4 mM $\text{Os}^{\text{VI}} + 2.0$ M NaOH and a mixture containing (c) 0.2 mM $\text{Os}^{\text{VI}} + 0.2$ mM $\text{Os}^{\text{VIII}} + 2.0$ M NaOH – solution (c) yielded a dark brown colour characteristic of the Os^{VII} species. Unfortunately, no resonance signals were observed and could be that the electron spin relaxation time is strongly temperature dependent. If the relaxation time becomes too short, then the signal becomes so broad that the signal is essentially undetectable explaining why J. S. Mayell, *I & EC Product Research and Development*, 1968, 7 (2) 129 performed their EPR experiments at 77 K. Regrettably we can currently only measure EPR spectra at room temperature. This is an aspect that will be attempted again when low temperature work becomes possible.