Figure S1. (A) $^{51}$V NMR spectra of: (1) The solution resulting when 2 millimoles/liter of CF$_3$SO$_3$H were added to a 2 mM solution of V$^{IV}$O(salen) in CH$_3$CN; (2) After O$_2$ was bubbled for 30 min. through a solution containing 2 mM V$^{III}$(salen)$^+$. (B) (1) EPR spectrum of 2 mM V$^{IV}$O(salen) in CH$_3$CN; (2) After addition of 2 millimoles/liter of CF$_3$SO$_3$H to the solution in (1).
Figure S2. UV-vis spectra of (1) $V^{IV}(\text{salen})^+$ and (2) $V^{III}(\text{salen})^+$ in $\text{CH}_3\text{CN}$.

Concentration of complex: 0.4 mM. Optical path length: 1 cm.
Figure S3. Pseudo-first-order kinetic plots for the reaction between $\text{V}^{\text{III}}(\text{salen})^+$ and excess $\text{O}_2$ as monitored spectrophotometrically at 570 nm. $A_0 =$ initial absorbance; $A_t =$ absorbance at time $t$; $A_\infty =$ absorbance after the completion of the reaction.