

## Electronic Supplementary Information

### **Catalytic reactions of chlorite with a polypyridylruthenium(II) complex: Disproportionation, chlorine dioxide formation and alcohol oxidation**

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## 1. Materials

All organic substrates were obtained from Sigma-Aldrich and purified according to literature methods.<sup>1</sup> Sodium chlorite was purchased from Acros Organic Chemicals as 80% technical grade and purified by recrystallization from water. The purity was determined to be 95% pure by iodometric titration and ion chromatography. *cis*-[Ru(2,9-Me<sub>2</sub>phen)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was synthesized according to a published procedure.<sup>2</sup> *d*<sup>12</sup>-cyclohexanol (98+ atom % D) and H<sub>2</sub><sup>18</sup>O (98 atom % <sup>18</sup>O) were purchased from Medical Isotopes and used as received.

## 2. Instrumentation

UV/Vis spectra and kinetics were recorded on an Agilent 8453 diode array spectrophotometer equipped with a temperature control cell holder. Ion chromatography was performed on a Dionex ICS-1600 liquid chromatograph equipped with a Dionex IonPac AS12A Analytical (4 × 200 mm) column. 2.7 mM Na<sub>2</sub>CO<sub>3</sub>/0.3 mM NaHCO<sub>3</sub> was used as eluent with a flow rate of 2.0 mL/min. Chromatography calibration standards were prepared in the 0.02–0.2 mM concentration range. Gas chromatographic analyses were performed on a HP5890 GC/FID equipped with a DB-FFAP (30 m × 0.25 mm i.d.) or HP-5MS (30 m × 0.25 mm i.d.) column. GC/MS measurements were carried out on a HP6890 gas chromatograph interfaced to a HP 5975 mass selective detector. Gas evolution was analyzed using a HP5890 GC/TCD equipped with a CP-Molsieve 5A (30 m × 0.32 mm i.d.) column. Electrospray ionization mass spectra (ESI/MS) were obtained on a

PE SCIEX API 365 mass spectrometer. The analyte solution was continuously infused with a syringe pump at a constant flow rate of 5  $\mu\text{L min}^{-1}$  into the pneumatically assisted electrospray probe with nitrogen as the nebulising gas.

### 3. Kinetic studies of the reaction of $\text{ClO}_2^-$ with $\text{cis}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2]^{2+}$

The concentrations of the sodium chlorite were at least in 10-fold excess of that of  $\text{cis}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2]^{2+}$ . The reaction progress was monitored by observing absorbance changes at 493 nm and 360 nm ( $\lambda_{\text{max}}$  of  $\text{cis}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2]^{2+}$  and  $\text{ClO}_2$ ). Pseudo-first-order rate constants,  $k_{\text{obs}}$ , were obtained by nonlinear least-squares fits of  $A_t$  versus time  $t$  according to the equation  $A_t = A_f + (A_0 - A_f) \exp(-k_{\text{obs}} t)$ , where  $A_0$  and  $A_f$  are the initial and final absorbance, respectively.

### 4. General procedure for catalytic oxidation of alcohols with $\text{ClO}_2^-$

Typically a solution containing 3.0 mmol substrate and 0.003 mmol  $\text{cis}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2](\text{PF}_6)_2$  in 3 mL phosphate buffer was prepared. The solution was treated with 0.3 mmol  $\text{NaClO}_2$ , and the mixture was stirred at 296 K for 1 hour. Product analysis and quantification were made by GC and GC/MS.

### 5. Kinetic isotope effects for cyclohexanol oxidation

Kinetic isotope effects were investigated by using an equimolar mixture of cyclohexanol and  $d^{12}$ -cyclohexanol as substrate. The organic products were quantified and identified by GC and GC/MS. The KIE value was obtained by taking the ratio of

the corresponding areas from GC measurements.

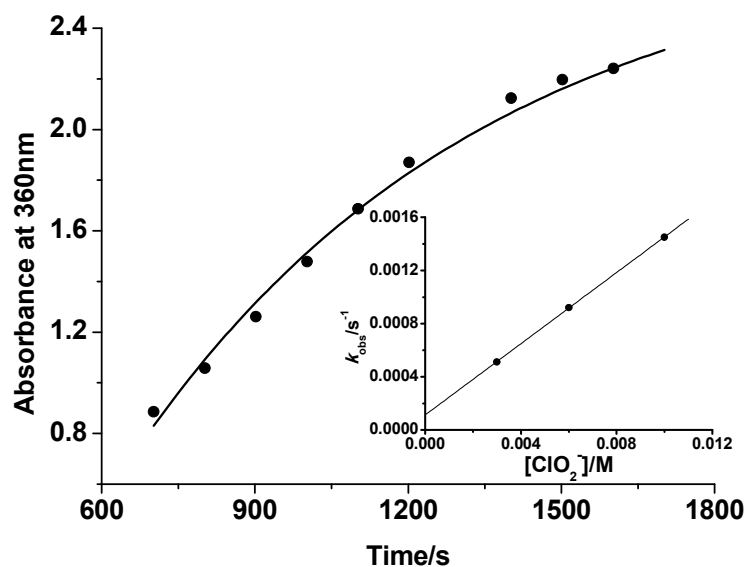
## 6. O<sub>2</sub> Evolution analysis

In a typical reaction, a deaerated solution of NaClO<sub>2</sub> (0.3 mmol) in 1.5 mL buffer solution was placed in a 10 mL one-neck round bottle flask under argon at 23 °C. The neck of the flask was sealed with a septum. A solution of deaerated *cis*-[Ru(2,9-Me<sub>2</sub>phen)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (0.003 mmol, 1.5 mL) was transferred by a needle through the septum into the NaClO<sub>2</sub> solution with vigorous stirring. 150 μL gas in the headspace was withdrawn after 3 h and analyzed by GC/TCD and GC/MS.

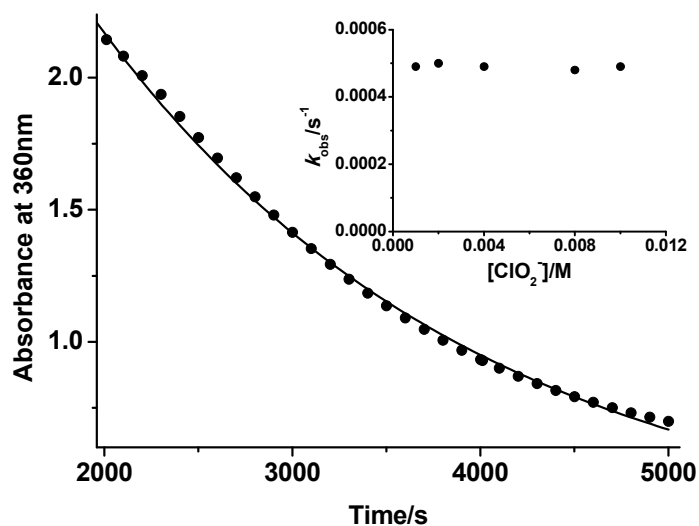
## 7. Cyclic voltammetry

Cyclic voltammetry (CV) was done on a CH Instrument Model 660C electrochemical station, using a glassy carbon working electrode, a platinum-wire counter electrode and a saturated calomel electrode (SCE).

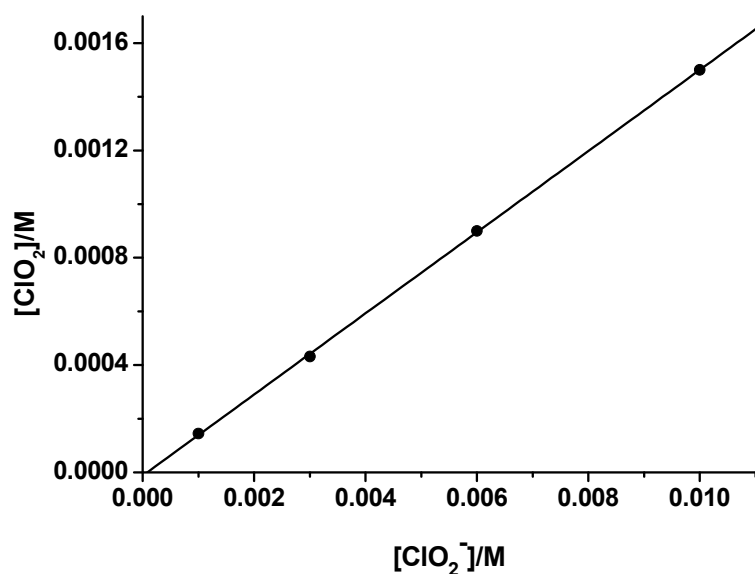
The CV of various *cis*-[Ru(L)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (L = substituted 2,2'-bipyridyl) complexes have been studied by Meyer<sup>3</sup> and Che<sup>4</sup>. The CV of *cis*-[Ru<sup>II</sup>(2,9-Me<sub>2</sub>phen)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in water at pH 6.8 (Fig. S5) shows a reversible couple at 0.37 V vs. SCE, which is assigned to [Ru<sup>III</sup>(OH)(OH<sub>2</sub>)]<sup>2+</sup>/[Ru<sup>II</sup>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>; an irreversible oxidation wave at 0.65 V which is assigned to [Ru<sup>IV</sup>(O)(OH)]<sup>+</sup>/[Ru<sup>III</sup>(OH)(OH<sub>2</sub>)]<sup>2+</sup>, and an irreversible oxidation wave at 0.93 V which is assigned to [Ru<sup>VI</sup>(O)<sub>2</sub>]<sup>2+</sup>/[Ru<sup>IV</sup>(O)(OH)]<sup>+</sup>. Similar electrochemical behavior was observed at pH 4.9. These assignments were made by reference to work on related complexes by Meyer and Che.



**Fig. S1** Kinetic trace and second-order fit for formation of ClO<sub>2</sub> at pH 4.9 ( $[\text{Ru}^{\text{II}}] = 1.0 \times 10^{-4}$  M at 298 K,  $I = 0.1$  M). Slope =  $(1.3 \pm 0.1) \times 10^{-1}$ , y-intercept =  $(1.1 \pm 0.1) \times 10^{-4}$ ,  $r = 0.999$ .

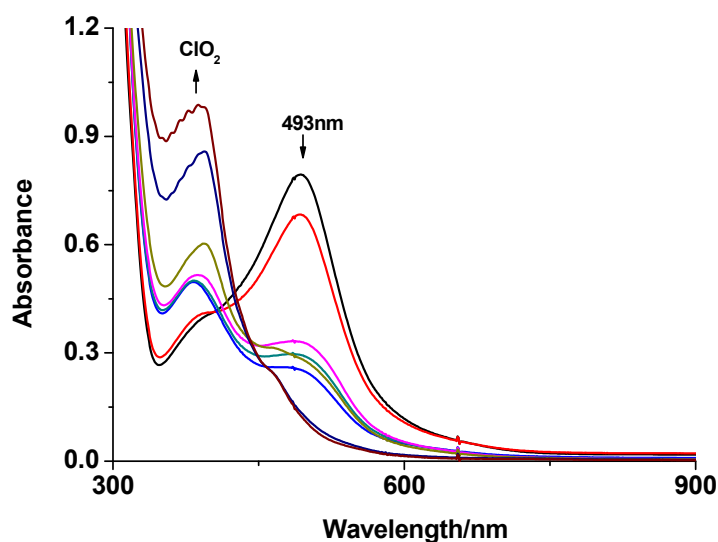


**Fig. S2** Kinetic trace and first-order fit for the decay of ClO<sub>2</sub> at 360 nm at pH 4.9 ( $[\text{Ru}^{\text{II}}] = 1.0 \times 10^{-4}$  M,  $[\text{ClO}_2^-] = 1.0 \times 10^{-2}$  M at 298 K,  $I = 0.1$  M).

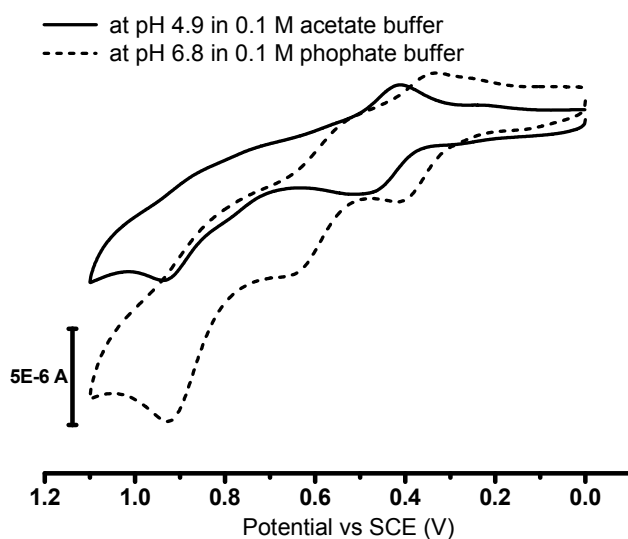


**Fig. S3** Plot of  $\text{ClO}_2$  generated from the reaction of  $\text{ClO}_2^-$  and  $\text{cis-}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2]^{2+}$  at pH 4.9 ( $[\text{Ru}^{\text{II}}] = 1.0 \times 10^{-4} \text{ M}$  at 298 K,  $I = 0.1 \text{ M}$ ).

Slope =  $(1.5 \pm 0.2) \times 10^{-1}$ , y-intercept =  $-(1.2 \pm 0.7) \times 10^{-5}$ ,  $r = 0.999$ .



**Fig. S4** Spectrophotometric changes for the reaction of  $\text{ClO}_2^-$  and  $\text{cis-}[\text{Ru}(\text{2,9-Me}_2\text{phen})_2(\text{OH}_2)_2]^{2+}$  at pH 6.8 ( $[\text{Ru}^{\text{II}}] = 1.0 \times 10^{-4} \text{ M}$ ,  $[\text{ClO}_2^-] = 1.0 \times 10^{-2} \text{ M}$  at 298 K,  $I = 0.1 \text{ M}$ , spectra were collected at 600 s intervals).



**Fig. S5** Cyclic voltammogram of *cis*-[Ru<sup>II</sup>(2,9-Me<sub>2</sub>phen)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.5 mM) at pH 4.9 in 0.1 M acetate buffer (solid) and at pH 6.8 in 0.1 M phosphate buffer (dashed). Scan rate = 50 mV s<sup>-1</sup>.

## References

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