Rapid catalytic water oxidation by a single site, Ru carbene catalyst

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Supporting Information
Figure S1. UV-vis spectra of 50 µM 2 in solution of different pHs before (black line) and after (red line) storing for 4 months.
**Figure S2.** Square wave voltammogram of 1 mM 2 at pH 1 (0.1 M HNO₃) at a glassy carbon electrode. Increment potential of each point, 0.004 V; square wave amplitude, 0.025 V; square wave frequency, 15 Hz.

**Figure S3.** Plots of $E_{1/2}$ vs pH for the Ru(III/II), Ru(IV/III), and Ru(V/IV) redox couples of 1 (a) and 2 (b). Buffer concentration, 0.1 M; electrode, GC; scan rate, 100 mV/s.
Figure S4. Cyclic voltammograms of 1 mM 2 at pH 7.45 in different concentration of H$_2$PO$_4^-$ /HPO$_4^{2-}$ buffer. Electrode, GC; scan rate, 100 mV/s. Ionic strength was maintained with added KNO$_3$. The positive shift of the potential for Ru(III$\rightarrow$II) reduction at [H$_2$PO$_4^-$/HPO$_4^{2-}$] < 0.03 M is due to local pH effects associated with water oxidation, 2H$_2$O $-$ 4e$^{-}$ $\rightarrow$ O$_2$ + 4H$^+$. For the cyan line of [H$_2$PO$_4^-$/HPO$_4^{2-}$] = 0 M, the pseudo pH is $\sim$6 and CV profile is almost the same as that at pH 1.

Figure S5. (a) Concentration dependence of cyclic voltammograms of 2 at pH 1 (0.1 M HNO$_3$). (b) Dependence of the electrocatalytic current at 1.72 V vs NHE on [Ru$^{II}$-OH$_2^{2+}$] (GC background subtracted). Electrode, GC; scan rate, 100 mV/s.
Figure S6. (a) Concentration dependence of cyclic voltammograms of 2 at pH 7.45 (0.1 M H₂PO₄⁻/HPO₄²⁻). (b) Dependence of the electrocatalytic current at 1.60 V vs NHE on [Ru⁺₋OH₂²⁺] (GC background subtracted). Electrode, GC; scan rate, 100 mV/s.

Figure S7. Square root of scan rate normalized cyclic voltammograms (i/ν₁/²) of 1 mM 2 at GC electrode. Solution, pH 1 (0.1 M HNO₃).
Figure S8. Square root of scan rate normalized cyclic voltammograms ($i/\nu^{1/2}$) of 1 mM 2 at GC electrode. Solution, pH 7.45 (0.1 M H$_3$PO$_4$/HPO$_4^{2-}$).

Figure S9. Solvent isotope effect of cyclic voltammograms of 1 mM 2 at (a) pH 1 (0.1 M HNO$_3$) and (b) pH 7.45 (0.1 M H$_3$PO$_4$/HPO$_4^{2-}$). Electrode, GC; scan rate, 100 mV/s.
Figure S10. Cyclic voltammograms of 1 mM 2 at pH 5 (0.036 M CH₃CO₂H-0.064 M CH₃CO₂Na). During the second cycle scan, the potential was held at 1.3 V for 5 min. Electrode, GC; scan rate, 100 mV/s.

Figure S11. Square root of scan rate normalized cyclic voltammograms (i/υ¹/²) of 1 mM 2 at GC electrode. Solution, pH 5 (0.36 M CH₃CO₂H-0.64 M CH₃CO₂Na, high buffer concentration).
**Figure S12.** Cyclic voltammograms of 1 mM 2 in solution of pH 5 with different concentration of base as indicated in the figure. (a) shows the anation effect become pronounced with increasing the base concentration; (b) shows the water oxidation is suppressed with increasing the base concentration due to the anation effect. Ionic strength was maintained with added KNO₃. Electrode, GC, scan rate, 100 mV/s.