Electronic Supplementary Information

for

Hydrogen Atom Abstraction Reactions Independent of C-H Bond Dissociation Energies of Organic Substrates: Significance of Oxidant-Substrate Adduct Formation

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Computational method

Gibbs energy calculations for the hydrogen-bonded adducts between **1** and hfp in the triplet state (Fig. 4) were carried out by using unrestricted density functional theory (UDFT) implemented in Gaussian 09.¹ For geometry optimizations the B3LYP method^{2,3} combined with the D3 dispersion correction⁴ and the solvent effect (PCM)⁵ were used. The stability of optimized geometries was confirmed with vibrational analyses, and no imaginary frequency was found. Thermal free energy corrections were taken into account in calculating the total energies. For the Ru atom, the SDD basis set⁶ with and for the H, C, N, and O atoms, the 6-31+G* basis set^{7,8} were used.

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Fig. S1 ¹H NMR spectra of oxidized products of 2-propanol as a substrate in the presence of **1** as the oxidant in D_2O . The arrow indicates the signal of the product. \times : DSS as an internal reference.



Fig. S2 (a) Spectral changes of every 2 min during oxidation of *n*PrOH in the presence of 1 (0.5 mM) in B.-R. buffer (pH 1.8, sample concentration: 0.15 M) at 298 K and (b) the time courses of the absorbance changes monitored at 500 nm (red) and 620 nm (blue).



Fig. S3 Pseudo-first-order kinetic analysis for oxidation reactions with complexes 1 (a), 2 (b), and 3 (c) as oxidants (0.5 mM) in B.-R. buffer (pH 1.8) at 298 K. The substrates were CH₃OH (filled circle, blue line), CD₃OH (filled square, red line), and CH₃OD (filled diamond, green line).

Fig. S4 van't Hoff plots for the pre-equilibrium processes of **1** (a), **2** (c), and **3** (e), and Eyring plots for the oxidation reactions of **1** (b), **2** (d), and **3** (f) in B.-R. buffer (pH 1.8). The substrates were CH₃OH (filled circle, blue line), CD₃OH (filled square, red line), and CH₃OD (filled diamond, green line).

Fig. S5 Pseudo first-order kinetic analysis for oxidation of 2-propanol with complexes 1 (a), 2 (b), and 3 (c) as oxidants (0.5 mM) in B.-R. buffer (pH 1.8) at 305 K (red), 297 K (purple), 289 K (green), and 281 K (blue).

Fig. S6 van't Hoff plots for the pre-equilibrium processes of **1** (a), **2** (c), and **3** (e), and Eyring plots for the oxidation reactions using **1** (b), **2** (d), and **3** (f) in B.-R. buffer (pH 1.8). The substrate was 2-propanol.

Fig. S7 A titration curve of the chemical shift change (black-filled circles) for the ¹⁹F signal of 1,1,1,3,3,3- hexafluoro-propan-2-ol (hfp) against the concentration of **1** (filled circle) and **2** (filled square) in D₂O (0.66 mM) acidified with HClO₄ to be pD 1.8. The red dotted line is the fitting curve based on eq S2. The blue-filled triangles display the changes of the chemical shifts for the ¹⁹F signal of hfp upon addition of $[Ru^{III}(bpy)_3](PF_6)_2$ in the absence of the Ru^{II}-OH₂ complexes as the starting material of **1** and **2**.

Fig. S8 A plot of $\ln(k_{\rm H}/k_{\rm D})$ ($k_{\rm H}$: the reaction rate of oxidation of CH₃OH, $k_{\rm D}$: the reaction rate of oxidation of CD₃OH) with **1** (filled circle, blue line), **2** (filled square, green line), and **3** (filled triangle, red line) against the inverse of temperature. The slopes of each the plot are 1470 for **1**, 1740 for **2** and 630 for **3**, respectively.

Fig. S9 ESI-MS spectrum of a μ -oxo Ru^{III}-dimer complex generated by dissolving 2 into neutral water and stirring for 1 h at room temperature (below, black) and the computer simulation (above, red).

Fig. S10 Pseudo-first-order kinetic analysis for oxidation reactions with **1** as the oxidant (0.5 mM) in B.-R. buffer (pH 1.8) at 298 K. The substrates were CH₃OH (a), 1-propanol (b), 2-propanol (c), 4-methylbenzyl alcohol (d), and sodium 4-ethylbenzenesulfonic acid (e). The equilibrium constants (K) of the adduct formation and the rate constant (k) of the oxidation are noted on each the graph.