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Photocatalytic Oxygenation of Sulfide and Alkenes by Trinuclear Ruthenium Clusters

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Supporting Information

ABSTRACT: Trinuclear Ru cluster photocatalysts that contain two Ru(II) photosensitizers and a Ru(II) reaction center are prepared, and their activity in the photocatalytic oxygenation of a sufide and alkenes is investigated. Photoirradiation (visible light) and the use of a Co salt ($[Co(NH_3)_5Cl]Cl_2$, as an electron acceptor) are found to be essential for these catalytic reactions. The O atom of the water solvent (pH 6.8) is transferred to the substrate by a stepwise electron transfer and deprotonation of an aqua ligand at the reaction center. Through these processes, the aqua ligand coordinated at the reaction center is converted to a Ru^V=O species, which is the active intermediate in the sulfide and alkene oxygenation.



1. INTRODUCTION

Utilization of clean and inexhaustible sunlight energy toward molecular transformation is attracting a great deal of attention, since it provides a new pathway for the synthesis of various materials without consuming limited oil resources.¹ Nowadays, many researchers devote much of their effort into development of highly active molecular catalysts, which can produce dihydrogen or dioxygen from abundantly present water,² because there is an urgent need to resolve future energy problems and realize artificial photosynthesis.³ In this work, ruthenium(II) trisdiimine complexes and their derivatives are used as photosensitizers to collect visible-light energy, because of their excellent photophysical properties;⁴ the collected energy is used to drive electron transfer reactions. Although only little attention has been paid to apply these systems for organic syntheses, the continuous pursuit of organic chemists for developing green reactions has led to rapid expansion in the use of photoredox catalysts.⁵ Recently, Hamelin's group reported light-driven sulfide oxygenation using water as the oxygen source; this reaction was catalyzed by a dyad of a ruthenium photosensitizer and a catalytic center linked by a 1,10phenanthroline-based nonconjugated linker.⁶ In this reaction, a high-valent Ru^{IV}=O is generated as the active species for oxygenation through a proton-coupled electron-transfer process, which is a new way to use light energy for the catalytic molecular transformation of organic compounds. Our group has also been working toward the development of catalytic organic transformation reactions driven by visible-light-active photocatalysts.⁷ For these studies, we synthesized various bridging ligands, which act as a linker between a photosensitizer and a reaction center.^{8,9} We also considered that electronic interactions via the bridging ligands will largely affect to the photoreactivities. 10

Previously, we developed a pyridine-substituted 2,2'bipyrimidine ligand (6-pyridyl-2,2'-bipyrimidine, pybpm) and synthesized a dinuclear ruthenium catalyst, [Ru(bpy)₂(pybpm)-Ru(bpy) (OH₂)]⁴⁺, linked by the pybpm ligand. Inspired by the work of Hamelin and Ménage,¹¹ the dinuclear ruthenium catalyst was investigated for sulfide oxygenation, and was found to show higher activity than the mixture of mononuclear ruthenium components.9 Based on these results, we extended this work to include trinuclear ruthenium cluster catalysts having stronger electronic conjugation between the metals. Normally, many multinuclear photocatalysts are designed by linking the mononuclear components with nonconjugated linkers; this is because it is a safe way to maintain the photochemical performance of each component. Several multinuclear catalysts have been designed for photocatalytic water oxidation,^{3a,12} alcohol oxidation,¹³ and sulfide and alkene oxygenation.^{6,11,14} In contrast, in this work, we designed highly conjugated trinuclear complexes that exhibit characteristic properties different from that expected from a combination of the mononuclear components. Here, we report synthesis of trinuclear catalysts containing two ruthenium photosensitizers and one ruthenium reaction center, which are linked by conjugated pybpm and/or bpm ligands, and their reactivities, with a focus on the characteristic properties of this electronically conjugated system.

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Scheme 1. Synthesis of Trinuclear Cluster Catalysts





2. RESULTS AND DISCUSSION

Syntheses. The trinuclear aqua complex with the bridging pybpm ligand **3-OH**₂ was synthesized as follows. First, $[Ru(bpy)_2(pybpm)]^{2+}$ (1) was treated by $RuCl_2(dmso)_4$ to obtain the dinuclear complex 2, which was subsequently treated with $[Ru(bpy)_2(bpm)]^{2+}$ (bpm = 2,2'-bipyrimidine) to give trinuclear the Ru complex 3-Cl. Chloride abstraction by a silver salt afforded the target aqua complex 3-OH₂ in a quantitative manner. Unlike the synthesis of 3-OH₂, the trinuclear complex with the two bridging bpm ligands (5-Cl) was synthesized by directly treating 4 with 2 equiv of *cis*-Ru(bpy)₂Cl₂·2H₂O. Subsequently, 5-Cl is quantitatively converted to the target aqua complex 5-OH₂ by reaction with a silver salt (see Scheme 1).

Both trinuclear Ru complexes 3-OH₂ and 5-OH₂ have been unambiguously characterized by nuclear magnetic resonance (NMR) and electrospray ionization-mass spectroscopy (ESI-MS) and elemental analyses.

Photocatalytic Oxygenation of Sulfides and Alkenes. Photocatalytic oxygenation of thioanisole by the trinuclear



Table 1. Photocatalytic	Oxygenation	of	Thioanisole	by
Ruthenium Catalysts ^a				

entry	catalyst	light	conversion ^{36h} [%]	TON ^b	quantum yield, Φ^c
1	3-OH ₂ (Ru ₃)	ON	73	366	0.10
2	5-OH ₂ (Ru ₃)	ON	68	340	f
3	6-OH ₂ (Ru ₂)	ON	77	384	0.086
4	$\begin{array}{l} \textbf{6-OH}_2 \ (\text{Ru}_2) \ + \\ [\text{Ru}(\text{bpy})_3] \text{Cl}_2 \end{array}$	ON	54	265	f
5	$\begin{array}{l} \textbf{7-OH}_2 \ (\text{Ru}) \ + \\ 2[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \end{array}$	ON	53 ^g	28 ^g	0.015
6	3-OH ₂ (Ru ₃)	OFF	0	0	f
7	d (no catalyst)	ON	6	31	f
8	3-OH ₂ (Ru ₃) ^{e} (with- out Co salt)	ON	0	0	f

^{*a*}Unless otherwise noted, the reaction was conducted with 0.2 mol % (20 μ M) of catalyst in phosphate buffered D₂O (pH 6.8, 0.067 M) with 2 equiv (vs substrate) of [Co(NH₃)₅Cl]Cl₂ for 36 h at 35 °C. ^{*b*}Turnover number for the sulfoxide formation. ^{*c*}Quantum yields were calculated by using a Si photodiode sensor and 435 nm monochromatic light. Details for the measurements are shown in Figures S17 and S18 in the Supporting Information. ^{*d*}Without catalyst. ^{*e*}Without [Co(NH₃)₅Cl]Cl₂. ^{*J*}Not measured. ^{*g*}See Figure S2 in the Supporting Information for the obtained products.

catalysts was tested, and its performance was compared with those of related species, such as the dinuclear catalyst $6-OH_2^{9}$ and the mononuclear catalyst $7-OH_2^{15}$ (see Figure 1, as well as

Table 1 and eq 1). The reactions were conducted in the presence of 0.2 mol % Ru catalyst (20 μ M) and 2 equiv (vs thioanisole) of the Co salt, [Co(NH₃)₅Cl]Cl₂ (a sacrificial oxidant), in phosphate-buffered water (pH 6.8, 0.067 M). The reaction vessel was kept at 35 °C in a water bath with vigorous stirring under degassed and visible-light-irradiated conditions (150 W Xe lamp, $\lambda > 420$ nm).

Under the above-mentioned conditions, thioanisole was converted to methyl phenyl sulfoxide (Figure S1 in the Supporting Information). All the catalysts except 7-OH₂ (described later) gave only the methyl phenyl sulfoxide as a single product.¹⁶ The trinuclear catalyst 3-OH, and dinuclear catalyst 6-OH, showed the highest activity, compared to the other catalysts. The other trinuclear catalyst $(5-OH_2)$ exhibited activity comparable to that of 3-OH₂ (entries 1 and 2 in Table 1). The activity of the dinuclear catalyst 6-OH₂ with additional photosensitizer unit ($[Ru(bpy)_3]^{2+}$) was lower than that without the photosensitizer (entries 3 and 4 in Table 1). The mononuclear catalyst $(7-OH_2)$ mixed with two equivalent of photosensitizer $([Ru(bpy)_3]^{2+})$ showed much less activity (entry 5 in Table 1). Although the conversion of thioanisole is comparable to the reaction by other trinuclear catalysts, yield of sulfoxide (turnover number, TON) was very low, because other side products such as diphenyl disulfide and bis(phenylthio)methane (see entry 5 in Table 1, and Figure S2 in the Supporting Information) is formed.¹⁷ Entries 6-8 in Table 1 clearly show that light, catalyst, and a Co salt are essential for the catalysis reaction. After the reaction catalyzed by 3-OH₂, the reaction mixture was checked by ESI-MS spectra, and detected the mass number of the trinuclear component, which supports the stability of the trinuclear catalyst throughout the reaction. Although photodissociation of the monodentate pyridine ligand often occurs,12b,18 it was confirmed that the pyridine ligand in 5-OH₂ was kept through the irradiation (λ > 420 nm) in D₂O for over 20 h (see Figures S3 and S4 in the Supporting Information):

Next, photocatalytic oxygenation reactions of various alkenes were tested under the same conditions (see Table 2 and eq 2, as well as Figures S5-S8 in the Supporting Information). Alkenes such as styrenes (entries 1 and 2 in Table 2) and *cis*-stilbene (entry 3 in Table 2) were converted to 2 mol (vs substrate) of

Table 2. Oxygenation of Alkenes^a



aldehydes or ketones via stepwise C=C bond cleavage (mentioned later). For example, cis-stilbene yielded 2 mol of benzaldehyde, and similarly, styrene yielded benzaldehyde and formaldehyde, with the latter being detected by ¹H NMR spectra. Determination and quantification of these aldehydes were done on the basis of ¹H NMR, gas chromatography (GC), and gas chromatography-mass spectroscopy (GCMS) spectral data. The reaction by trinuclear catalyst 3-OH₂ was also applicable to aliphatic alkenes, such as *cis*-2-decene, to yield the corresponding aldehydes, although reactivity and selectivity is low (entry 4 in Table 2). In addition to 1-octanal and other unidentified biproducts, a small amount of 1-heptanal and 1-hexanal was formed, probably due to the isomerization of the double bond of the starting compound or intermediate during the reaction.¹⁹ The higher activity of the trinuclear catalysts compared to the dinuclear and mononuclear catalysts is clearly observed (entries 2-4 in Table 2), even under the same Ru photosensitizer/Ru catalyst ratio ($Ru_{photo}/Ru_{cat} = 2:1$). In these reactions, trinuclear catalyst $5-OH_2$ showed activity comparable to that of $3-OH_2$. Although the mechanistic details of the C=C bond cleavage needed to give aldehydes has remained unclear, we detected correponding epoxides during the oxygenation of styrene, α -methylstyrene, and *cis*-stilbene (see eq 3, as well as

$$\underbrace{ \begin{array}{c} \begin{array}{c} \textbf{3-OH}_{2} (0.2 \text{ mol}\%, 20 \, \mu\text{M}) \\ \hline [\text{Co}(\text{NH}_{3})_{5}\text{CI}]\text{Cl}_{2} (2 \text{ eq.}) \\ \hline \textbf{phophate buffered H}_{2}\text{O} \\ (0.067M, \text{pH 6.8}) \\ 35 \,^{\circ}\text{C} \\ \mu_{V} (\lambda \geq 420 \, \text{nm}) \end{array}}_{67\%} \begin{array}{c} \textbf{H}_{3}\text{C} \\ \textbf{0.9\%} \\ \hline \textbf{0.9\%} \end{array} \right)$$
(3)

Figures S5, S6, and S7 in the Supporting Information).²⁰When the reaction with the corresponding intermediates such as styrene oxide and α -methylstyrene oxide was tested, the results

			conversion /% [TON of the main product] ^b			
entry	substrate	main product	3 (Ru ₃)	6 (Ru ₂)	7 (Ru ₁)	5 (Ru ₃)
					$+ 2 [Ru(bpy)_3]^{2+}$	
1		A A	41.2 [205]	42.0 [212]	17.6 [90]	50.8 [251]
1			(67.0 [332]) ^c	42.9 [212]	17.0[80]	50.8 [251]
2	\sim	\sim	58.8 [289]	44.1 [217]	26.0 [125]	54 ([2(()]
2	C ·	$\square \circ$	(71.9 [333]) ^c	(49.7 [249]) ^c	20.9 [135]	54.0 [200]
3	\bigcirc	2 ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	34.2 [41] ^d	21.2 [32] ^d	18.1 [8] ^e	36.7 [44]
4		0= ^H	24.2 [5.4]	11.1 [1.6]	g	9.6 [1.0]

^{*a*}Unless otherwise specified, the reaction was conducted under O_2 -free conditions with 0.2 mol % (20 μ M) of catalyst in phosphate buffered D_2O (pH 6.8, 0.067 M) with 2 equiv (vs substrate) of $[Co(NH_3)_5Cl]Cl_2$ for 36 h at 35 °C. ^{*b*}TON was calculated from the oxygenated products determined by GCMS, which data are calibrated with standard chemicals. ^{*c*}4 equiv of $[Co(NH_3)_5Cl]Cl_2$ vs substrate was added. ^{*d*}Benzophenone, stilbene oxide is also formed. ^{*e*}The main product was *trans*-stilbene. ^{*s*}Not performed.

indicate that diol was formed as the major product, together with the corresponding final product (benzaldehyde or acetophenone) (see eq 4, as well as Figures S9 and S10 in

$$\overset{3-\text{OH}_{2}}{\swarrow} (0.2 \text{ mol}\%, 20 \ \mu\text{M}) \\ \overset{[Co(NH_{3})_{5}\text{CI}]Cl_{2}(2 \ eq.)}{\underset{35 \ ^{\circ}\text{C}}{\overset{1.9\%}{\checkmark}} + \overset{OH}{\underset{1.9\%}{\checkmark}} + \overset{OH}{\underset{51\%}{\checkmark}} + \overset{OH}{\underset{1.9\%}{\checkmark}} + \overset{OH}{\underset{51\%}{\checkmark}} + \overset{OH}{\underset{1.9\%}{\checkmark}} + \overset{OH}{\underset{51\%}{\checkmark}} + \overset{OH}{\underset{1.9\%}{\checkmark}} + \overset{OH}{\underset{1.9\%}{\rightthreetimes}} + \overset{OH}{\underset{1.9\%}{\r}} + \overset{OH}{\underset{1.9\%}{\r} + \overset{OH}{\underset{1.9\%}{\r}} + \overset{OH}{\underset{1.9\%}{\r} + \overset{OH}{\underset{1.9\%}{\r}} + \overset{OH}{\underset{1.9\%}{\r} + \overset{OH}{\r} + \overset{OH}{\underset{1.9\%}{\r} + \overset{OH}{\underset{1.9\%}{\r} + \overset{OH}{\r} + \overset{OH}{\r} + \overset{OH}{\r} + \overset$$

the Supporting Information). Reaction of 2-phenyl-1,2propanediol gave acetophenone as a single product (see eq 5,



Scheme 2. Stepwise Oxygenation of Alkene to Aldehydes



Figure 2. Mass spectra (m/z) of the products (acetophenone) after photocatalytic oxygenation of α -methylstyrene (a) in phosphate buffered H₂¹⁶O, and (b) in phosphate buffered H₂¹⁸O.

as well as Figure S11 in the Supporting Information). Photocatalytic oxygenation of water-soluble styrene to give the corresponding benzaldehyde has been reported by the Kojima and Sun groups,²¹ but the precise mechanism has not been discussed. Based on these results, the oxygenation of alkenes proceeds via epoxide and diol (see Scheme 2). Several reactions of alcohols to give the corresponding aldehydes by Ru=O species have been reported by other groups,¹³ and it seems that the C–C bond is cleaved during the diol oxidation step, yielding the aldehydes.²²

In order to confirm the oxygen source of the product, labeling experiments were conducted for the photocatalytic oxygenation of α -methylstyrene in a phosphate buffered H₂¹⁸O (97% atom ¹⁸O). After the reaction, the product was isolated and analyzed by GCMS to determine the isotope distribution (eq 6, Figure 2).

When comparing the mass spectra shown in Figures 2a and 2b, the mass number of the product (acetophenone) in Figure 2b shows that the product contains mainly ¹⁸O, having the same fragment peaks as those in Figure 2a. The results prove that the source of O atom in the product is the solvent water.

Photophysical and Electrochemical Studies. The electronic absorption spectra for the trinuclear complexes **3-OH**₂ and **5-OH**₂ observed in DMF at room temperature are compared with those of the mononuclear and dinuclear components (6-OH₂, $[Ru(bpy)_2(bpm)]^{2+}$ and 1) (see Figure 3, as



Figure 3. Ultraviolet-visible (UV-vis) absorption spectra (room temperature, DMF solution).

Table 3. UV-vis Absorption Spectral Data in DMI	F (at Room
Temperature)	

complex	λ_{\max} [nm]	$\varepsilon ~[imes 10^5 ~\mathrm{M^{-1}~cm^{-1}}]$
3-OH ₂	426.5	0.33
	597	0.12
5-OH ₂	416.5	0.34
	591.0	0.11
6-OH ₂	428.5	0.26
	522.0	0.17
$[Ru(bpy)_2(pybpm)](BF_4)_2 (1)$	430	0.21
$[Ru(bpy)_2(bpm)](BF_4)_2$	429	0.21

well as Figure S12 in the Supporting Information and Table 3). Comparison of the spectra of the mononuclear and dinuclear complexes indicates that a new MLCT $(d_{\pi Ru} \rightarrow \pi^*_{pybpm})$ absorption band appears in the low-energy region (6-OH₂, $\lambda_{max} = 522 \text{ nm}$) as a result of dinucleation. For the absorption spectra of the trinuclear complex 5-OH₂, which possesses only bpm as



Figure 4. Cyclic voltammograms of (a) 1, $[Ru(bpm)](BF_4)_2$, 3-Cl, and 3-OH₂, (b) $[Ru(pybpm)Ru(bpy)(OH_2)](BF_4)_4$, $[Ru(bpm)Ru(pybpy)(OH_2)](BF_4)_4$, 3-OH₂, and 5-OH₂ in CH₃CN ($Ru = [(bpy)_2Ru]$, [complex] = 1 mM, $["Bu_4NBF_4] = 0.1 \text{ M}$, 100 mV/s, E vs Fc/Fc⁺).

1 able 4. Summary of Electrochemical Data in CH_2C
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	$E_{1/2}$ [V]			
complex	bpm/bpm•-	pybpm/pybpm•-	$\mathrm{Ru}_{\mathrm{cat}}^{\mathrm{II}}/\mathrm{Ru}_{\mathrm{cat}}^{\mathrm{III}}$	$\mathrm{Ru}_{\mathrm{photo}}^{\mathrm{II}}/\mathrm{Ru}_{\mathrm{photo}}^{\mathrm{III}}$
$[Ru(bpy)_2(pybpm)](BF_4)_2 (1)$		-1.39		0.99
$[Ru(bpy)_2(bpm)](BF_4)_2$	-1.39			1.03
$[Ru(pybpm)Ru(OH_2)(bpy)](BF_4)_4$ (6-OH ₂)		-0.86	1.04 ^b	1.30
$[Ru(bpm)Ru(OH_2)(tpy)](BF_4)_4$	-0.89		0.90 ^b	1.21
$[Ru(pybpm)Ru(Cl)(bpm)Ru](BF_4)_5$ (3-Cl)	-0.98	-0.82	1.01 ^b	1.27 ^c
$[Ru(pybpm)Ru(OH_2)(bpm)Ru](BF_4)_6$ (3-OH ₂)	-0.95	-0.80	1.18 ^b	1.25 ^c
$[Ru(bpm)Ru(OH_2)(py)(bpm)Ru](BF_4)_6 (5-OH_2)$	$-1.01, -0.82^{d}$		1.00 ^b	1.28^e

 a [complex] = 1 mM, [${}^{n}Bu_{4}NBF_{4}$] = 0.1 M, 100 mV/s, *E* vs Fc/Fc⁺. $Ru = [(bpy)_{2}Ru]$, $Ru_{cat} = Ru$ reaction center, $Ru_{photo} = Ru$ photoredox center. b Irreversible wave; anodic peak. ${}^{c}Redox$ potential of the two-electron process. d Irreversible wave; cathodic peak. ${}^{e}Quasi-reversible$ peak.

a bridging ligand, a new MLCT band based on the $d_{\pi Ru} \rightarrow \pi_{bpm}^*$ transition $(\lambda_{max} = 591 \text{ nm})^{11}$ is observed. On the other hand, the trinuclear complex **3-OH**₂ possesses a broad and wide MLCT band that stretches from 390 nm to 800 nm, because of the overlap of the two $d_{\pi Ru} \rightarrow \pi_{pybpm}^*$ and $d_{\pi Ru} \rightarrow \pi_{bpm}^*$ transitions. In this way, formation of the dinuclear and trinuclear clusters results in low-energy absorption bands below 500 nm, which suggest strong interactions between the metal fragments. Both trinuclear clusters show a dark green color, which is due to the above-mentioned low-energy absorption bands.

CV data measured in CH₃CN at room temperature (see Figure 4, as well as Figure S13 in the Supporting Information) are summarized in Table 4. A comparison of the CV data of the aqua complex (3-OH₂) with the corresponding chloride complex (3-Cl) reveals that the latter exhibits sharper peaks. Thus, for reliable assignment of the peaks of the aqua complexes, the CV spectrum of the 3-Cl is also shown (Figure 4a). A comparison of the redox potentials of the bridging ligands (BL/BL^{•-}), pybpm and bpm, reveals that reduction occurs at a slightly higher potential for pybpm than that for bpm.^{8,23,24} Thus, in the CV data of the trinuclear clusters with mixed bridging ligands, the redox wave (BL/BL^{•-}) with higher potential is assigned to pybpm (Figure 4a). The redox waves with the highest potential (~1.3 V) with high reversibility are not affected by the number of nuclei or bridging ligands, and the

wave can be assigned to the redox process of $Ru_{photo}^{II}/Ru_{photo}^{III}$. In the spectra of the trinuclear complexes **3-Cl**, **3-OH**₂, and **5-OH**₂, redox waves of $Ru_{cat}^{II}/Ru_{cat}^{III}$ are observed at ~1.0 V. The potential for **3-OH**₂ is higher than that of **5-OH**₂ (Figure 4b).

Mechanistic Studies. The redox potential of the Ru_{cat} center of 3-OH₂ is plotted in the range of pH 4–10, since the peaks become broader in the highly acidic (pH <2) region or the basic pH (pH >10) region (see the Poubiax diagram in Figure 5, as well as Figure S14 in the Supporting Information). From the plotted electrochemical data, two oxidation processes are observed: a one-electron one-proton process and a two-electron one-proton process. Thus, within this pH range, the Ru_{cat}^{II} –OH₂, Ru_{cat}^{III} –OH, and Ru_{cat}^{V} =O species can be formed through photoredox processes. It is interesting that, under the actual photocatalytic reaction conditions (pH 6.8), the high oxidation state Ru^{V} =O species can be generated at relatively low potential.

In order to confirm the active species of the catalytic oxygenation, we attempted chemical oxidation of the catalyst. $[Ru^{III}(bpy)_3](ClO_4)_3$ was selected as a one-electron oxidant, because it possesses suitable redox potential to oxidize the reaction center, but not the photoredox center. While up to 4.7 equiv of $[Ru^{III}(bpy)_3](ClO_4)_3$ was added to an CD_3CN solution of **3-OH**₂, the corresponding spectral changes were followed by UV-vis absorption (Figure 6), ¹H NMR

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Figure 5. Pourbaix diagram plotted in the range of pH 4–10.

(Figure S15 in the Supporting Information), and ESI-MS (Figure S16 in the Supporting Information) spectroscopies.

In the UV-vis absorption spectra (Figures 6 and 7), absorption changes at \sim 289 nm (Ru^{II}) and \sim 314 nm (Ru^{III}: oxidant)



Figure 6. UV-vis absorption spectral changes via the addition of oxidant $([Ru(bpy)_3]^{3+}$ in acetonitrile, at room temperature).



Figure 7. Spectral change in the UV-vis absorption spectra at 289 nm (Ru^{II}) and 314 nm (Ru^{III}) via the addition of $[Ru(bpy)_3]^{3+}(Ru^{III})$.

can be seen. When the amount of the added oxidant is below 3 equiv, an increase in the amount of Ru^{II} species is observed. In contrast, an increase in the amount of Ru^{II} is observed when the amount of the added oxidant exceeds 3 equiv. The increase

in Ru^{II} can be attributed to the formation of $[Ru^{II}(bpy)_3]^{2+}$ from the reduced oxidant, and the increase in Ru^{III} is due to the unreacted oxidant ($[Ru^{III}(bpy)_3]^{3+}$), as seen in the spectra. These results indicate that up to 3 equiv of $[Ru^{III}(bpy)_3]$ -(ClO₄)₃ are consumed via the three-electron oxidation of **3-OH**₂ to generate a Ru^V=O species (eq 7). After this, further addition of the one-electron reductant, Cp₂Fe, led to the disappearance of the absorption at 314 nm and an increase in the intensity of the absorption at 289 nm, supporting the assignment of both peaks. In addition, the MLCT band between 500 and 700 nm remained unchanged, indicating the stability of the trinuclear catalyst against decomposition during the redox processes. A similar result was obtained by a use of NOBF₄ as an oxidant (see Figure S19 in the Supporting Information).



In ¹H NMR spectra, a broad signal corresponding to the residual $[Ru^{III}(bpy)_3]^{3+}$ can be observed after the addition of over 3 equiv of the oxidant (see Figure S15); this result corroborates well with the change in the UV-vis absorption spectra. In the ESI-MS spectra, an intermediate $Ru^V=O$ peak was detected (see Figure S16).

Based on these results, a plausible reaction mechanism is depicted in Scheme 3. The reaction proceeds via the formation

Scheme 3. Plausible Reaction Mechanism



of Ru^{III}–OH and Ru^V=O species. Excitation of **3-OH**₂ induces Ru^{III}_{photo} formation by a redox process between Ru^{*}_{photo} and Co^{III} (eq (i), Scheme 3) and subsequent deprotonation produces 3^{III} –OH (paths (a) and (b)). Then, two cycles of the photoredox processes (eq (ii)) and deprotonation give the Ru^V=O species (paths (c)–(e)). The reaction between the

substrate and Ru^{V} =O gives an oxygenated product (sub=O), and reoxidation of Co^{II} to Co^{III} by 3^{III}-OH₂ regenerates the starting complex (eq (ii), Scheme 3).²⁵ In total, two equiv of the Co^{III} salt is consumed in one catalytic cycle. The characteristic feature of the mechanism is the formation of Ru^V=O, resulting in the high catalytic activities of oxygenation. Alkenes are oxidized by the Ru^V=O species to epoxides, diols, and then aldehydes via C-C bond cleavage, in a stepwise manner (Scheme 2). The facile formation of the Ru^V=O species is due to the presence of dicationic species in the same molecule. Thus, the photosensitizer units assist the intramolecular one-electron transfer process (eq (i)), and at the same time, helps to produce the Ru^V=O species. These results show the potential ability of the trinuclear cluster catalysts.

3. SUMMARY

In summary, we have synthesized trinuclear ruthenium cluster catalysts that contain two photoredox sites and one reaction center, and we have achieved photocatalytic oxygenation of sulfide and alkenes in neutral water media using these catalysts. Since these catalysts possess two dicationic photoredox units, $Ru^{V} = O$ with high oxidizability can be formed at relatively low potential, resulting in high activity, when compared to the corresponding intermolecular system. Alkenes were converted to 2 mol of aldehydes via the stepwise oxygenation of a C=Cdouble bond, followed by C-C bond cleavage. Investigation of the reaction mechanism revealed that the formation of the Ru^V=O species proceeds via the Ru^{III}-OH intermediate. The dual role of the photosensitizers is one of the key advantages of using trinuclear catalysts. The conjugated multinuclear system is a new approach to the catalyst design for various oxygenation reactions.

4. EXPERIMENTAL SECTION

General Procedures. Standard Schlenk and vacuum line techniques under N₂ atmosphere were employed for all the manipulations. Acetone (molecular sieves), acetonitrile (P_2O_5) , MeOH (Mg(OMe)₂), and EtOH $(Mg(OEt)_2)$, were treated with appropriate drying agents, distilled, and stored under N2. Dehydrated solvent was purchased from Kanto Chemical for Et₂O. Other solvents (dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and nitromethane) were purchased and used as received. The metal reagents, $\operatorname{RuCl}_2(\operatorname{dmso})_4^{26}$ [(bpy)₂Ru(bpm)]^{2+,27} cis-Ru(bpy)₂Cl₂·2H₂O,²⁸ (1),^{9,29} 6-OH₂,⁹ and 7were prepared according to the published procedures. Other OH₂,¹ organic chemicals were purchased and used as received. Standard phosphate buffer solutions at pH 6.8 (0.1 or 0.067 M) were prepared from the sodium phosphate monobasic and dibasic salts (KH₂PO₄/ Na₂HPO₄). ¹H and ¹³C NMR spectra were recorded on Bruker AVANCE-500, Bruker AVANCE-400, JEOL EX-270, JEOL JNM-400, and JEOL ECS-400 spectrometers. ESI-MS and GC-MS spectra were recorded on Bruker MicroTOF II, and Shimadzu GC-17A/QP5050 mass spectrometers, respectively. Solvents for NMR measurements were dried over molecular sieves, degassed, and stored under N2. UV-vis and steadystate emission spectra were obtained on a JASCO V-670 and Shimadzu RF-5300PC spectrometers, respectively. ESI-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo and Bruker micrOTOFII-SDT1 mass spectrometers. GC and GCMS chromatography was recorded on a Shimadzu GC-17A and QP5050 spectrometers. Electrochemical measurements were made with CH Instruments Electrochemical Analyzer Model 620B and Hokuto Denko HZ-5000 analyzers. In the following sections, ${}^{3}J_{\text{HH}}$ and ${}^{1}J_{\text{CH}}$ are abbreviated as J and J_{CH} , respectively.

General Photocatalytic Reactions. A total of 0.6 mL of a 0.1 mM solution of the catalyst in CH_3NO_2 was added in the reactor. After evaporation of the solvent, $[CoCl(NH_3)_5]Cl_2$ (15 mg, 60 μ mol) and 3 mL of 0.067 M sodium phosphate buffer (pH 6.8) H₂O solution were added. The resulting solution was degassed by freeze–pump–thaw

method and an organic substrate (30 μ mol) was then added under N₂ atmosphere. The system was sealed, and the resulting solution was exposed to the light produced by 150 W Xe lamp through a cut filter ($\lambda > 420$ nm) and stirred during the reaction. The reaction was followed by ¹H NMR and GC-MS, after appropriate time intervals.

Quantum Yield Measurements. A reaction solution containing Ru catalyst (20 μ M) in 5 mL of phosphate-buffered H₂O (0.067 M, pH 6.8) with thioanisole 10 mM and [Co(NH₃)₃Cl]Cl₂ sacrificial electron acceptor (20 mM) was prepared. Before light irradiation, the solution was degassed by a freeze–pump–thaw method in 20 mL of transparent Schlenk tube. Light-emitting diode (LED) monochromatic light (λ = 435 nm) was used as a light source, which consisted of an optical lens, to maintain incident light intensity. The number of photons absorbed by the solution was calculated by using a light power meter (StarLite, OPHIR Photonics Solutions, Ltd.) at λ = 435 nm. A plot of photon number (mmol) versus methyl phenyl sulfoxide product (mmol) exhibited a slope that indicated the quantum efficiency.

Electrochemistry. All cyclic voltammetry was performed in 1 mM of each Ru complex in acetonitrile by an electrochemical analyzer (model 620B, CH Instruments, Inc.) using a platinum working electrode (1.6 mm in diameter), a Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M tetrabutylammonium perchlorate in electrolyte solution), and a platinum wire counter electrode. Ferrocene was added to the solution as an internal standard.

For the trinuclear complex 3-OH₂, pH-dependent electrochemistry was done at pH 2–10 in water. Square wave voltammetry was measured using 1 mM 3-OH₂ in Britton–Robinson buffer 0.04 M (pH 2) with glassy carbon (diameter 1 mm) as a working electrode, Ag/AgCl (3 M NaCl aqueous solution) as a reference electrode, and platinum wire as a counter electrode. The solution was titrated by 0.2 M NaOH to a modified pH and an actual detected pH using a pH/ion meter (Laqua F-72, Horiba, Ltd.). Square wave voltammogram data were plotted versus pH, as shown in Figure S14 (Ag/AgCl vs NHE: +0.197 V). [Ru(bpy)₃]Cl₂ was used as an internal standard in aqueous solution $E(Ru^{II}/Ru^{III}) = 1.26$ V.

Preparation of 2.



A mixture of $[Ru(bpy)_2(pybpm)](BF_4)_2$ (1) (100 mg, 0.122 mmol) and *cis*(Cl), *fac*(S)-[RuCl₂(dmso-S)₃-(dmso-O)] (65.0 mg, 0.134 mmol) in EtOH-dmso (6.6 mL, 10:1 v/v) was refluxed for 36 h. After cooling to room temperature (RT), the solvent was evaporated and the residue was purified by recrystallization from CH₂Cl₂ containing 5% CH₃NO₂/ diethyl ether more than once to afford a blackish-brown solid (112 mg, 0.105 mmol, 86.0% yield). ¹H NMR (400 MHz, CD₃NO₂, RT, δ /ppm): 9.22–9.19 (m, 2 H, H_g and H_m), 8.63–8.57 (m, 5 H, H_D, H_D, 4 mH_i), 8.31–8.06 (m, 10 H, H_A or H_{A'}, H_d, H_{e'}, H_{b'} and H_k), 7.96–7.85 (m, 4 H, H_A or H_{A'}, H_i, and H_l), 7.55–7.46 (m, 4 H, H_B and H_{B'}), 2.96 (s, 1.5 H, Ru-*dmso*), 2.77 (s, 1.5 H, Ru-*dmso*), 2.64 (s, 1.5 H, Ru-*dmso*), 2.53 (s, 1.5 H, Ru-*dmso*). ESI-MS (*m*/*z*): 985.6 [M–BF₄]⁺ (calcd: 984.99). Anal. Calcd for C₃₅H₃₁B₂Cl₂F₈N₉ORu₂S, CH₂Cl₂: C, 37.36; H, 2.87; N, 10.89. Found: C, 37.67; H, 2.71; N, 11.09.

Preparation of **3-Cl**. [Ru(bpy)₂(pybpm)RuCl₂(dmso)](BF₄)₂ (2) (100 mg, 0.0932 mmol) and [Ru(bpy)₂(bpm)](BF₄)₂ (76.4 mg, 0.103 mmol) were dissolved in EtOH (6 mL) and refluxed for 36 h. NH₄BF₄ (100 mg, 0.954 mmol) was added after cooling to room temperature and the solution was stirred for 5 h. After the solvent was evaporated under reduced pressure, the reaction mixture was dissolved in CH₂Cl₂ containing 5% CH₃NO₂ and filtered through Celite to remove insoluble inorganic salts. The filtrate was concentrated and the residue was purified by recrystallization from CH₃NO₂/diethyl ether more than once to afford a blackish-green solid (141 mg, 0.0788 mmol, 84.5% yield). ¹H NMR (400 MHz, CD₃NO₂, RT, δ/ppm): 10.24–10.21 (m, 1 H), 10.16–10.14 (m, 1 H), 8.72–8.37 (m, 27 H), 8.35–7.90 (m, 38 H), 7.86–7.40 (m, 25 H), 7.22–7.07 (m, 2 H). ESI-MS (*m*/*z*): 1706.4 [M–BF₄]⁺ (calcd: 1706.12). Anal. Calcd

for $C_{61}H_{47}B_5ClF_{20}N_{17}Ru_3$, ${}^3/_2CH_3NO_2$, ${}^1/_2$ diethyl ether: C, 40.36; H, 2.97; N, 13.50. Found: C, 40.09; H, 2.73; N, 13.13. *Preparation of* **3-OH**₂. A mixture of $[Ru(bpy)_2(pybpm)RuCl-$

Preparation of **3-OH**₂. A mixture of $[Ru(bpy)_2(pybpm)RuCl-(bpm)Ru(bpy)_2](BF_4)_5$ (3-Cl) (120 mg, 0.0670 mmol), and AgBF₄ (23.9 mg, 0.118 mmol) in H₂O (6 mL) was refluxed for 3 h. After cooling to room temperature, the solvent was evaporated and the residue dissolved in CH₃NO₂ was filtered through Celite. The filtrate was concentrated and added excessive amounts of diethyl ether. After the resulting solid was washed with toluene and CH₂Cl₂, a blackish-green solid product was obtained from CH₃NO₂/diethyl ether (117 mg, 0.0628 mmol, 93.8% yield). ¹H NMR (400 MHz, CD₃NO₂, RT, δ/ppm): 10.02–9.98 (m, 1 H), 9.95–9.92 (m, 1 H), 8.71–8.40 (m, 28 H), 8.35–8.04 (m, 29 H), 8.00–7.84 (m, 10 H), 7.81–7.40 (m, 23 H), 7.20–7.06 (m, 2 H). ESI-MS (*m*/*z*): 1687.9 [M–BF₄]⁺ (calcd: 1688.16) (M = [(bpy)₂Ru^{II}(pybpm)Ru^{II}(OH) (bpm)Ru^{II}(bpy)₂](BF₄)₅). Anal. Calcd for C₆₁H₄₉B₆F₂₄N₁₇ORu₃. 3H₂O·2CH₃NO₂: C, 37.16; H, 3.02; N, 13.07. Found: C, 37.03; H, 2.69; N, 12.93.

Preparation of 4.



Synthesis of cis-Ru(bpm)₂Cl₂. 2,2'-Bipyrimidine (0.11 g, 0.67 mmol) was dissolved in DMSO/EtOH (1/9, 3 mL) and RuCl₂(dmso)₄ (0.1527 g, 0.32 mmol) was slowly added and refluxed for 5 h. After Celite filtration, the solvent of the filtrate was removed under vacuum. The obtained *cis*-Ru(bpm)₂Cl₂ was purified by Al₂O₃ column chromatography (¹/₉MeOH–CH₃NO₂). After recrystallization by CH₃NO₂/Et₂O twice, *cis*-Ru(bpm)₂Cl₂ was obtained as a brown solid (0.0604 g, 0.12 mmol, 39%). ¹H NMR (500 MHz, CD₃NO₂ RT, δ /ppm). 10.21 (dd, *J* = 5.7 and 2.1 Hz, 2 H, H_a), 9.08 (dd, *J* = 4.7 and 2.0 Hz, 2 H, H_c), 8.74 (dd, *J* = 4.6 and 1.8 Hz, 2 H, H_d), 8.17 (dd, *J* = 5.9 and 1.9 Hz, 2 H, H_f), 7.83 (t, *J* = 5.1 Hz, 2 H, H_b or H_e), 7.19 (t, *J* = 5.1 Hz, 2 H, H_b or H_e).



Excess pyridine was added to a cis-Ru(bpm)₂Cl₂ (0.0336 g, 0.06 mmol) MeOH (2 mL) solution, and the solution was refluxed for 12 h. After the solution was cooled to room temperature, NH₄BF₄ (0.0070 g, 0.07 mmol) was added and vigorously stirred for 3 h. The obtained product (4) was purified by Al₂O₃ column chromatography eluting with CH₃NO₂. Deep red crystal was deposited from recrystallization in CH₃NO₂/Et₂O (0.0336 g, 0.05 mmol, 85%). ¹H NMR (500 MHz, CD₃NO₂, room temperature (RT), δ /ppm): 10.17 (dd, J = 5.7 and 2.1 Hz, 1 H, H_a), 9.15 (dd, J = 4.7 and 1.9 Hz, 1 H, H_f), 9.11 (dd, J = 4.8 and 2.1 Hz, 1 H, H_c), 8.95 (dd, J = 5.7 and 2.0 Hz, 1 H, H_d), 8.91 (dd, J = 4.7 and 2.0 Hz, 1 H, H_{c'}), 8.88 (dd, J = 4.7 and 1.9 Hz, 1 H, H_f), 8.65 (s, 2 H, Ho), 8.50 (dd, J = 5.8 and 1.9 Hz, 1 H, Hd'), 8.14 (dd, J = 5.8 and 2.0 Hz, 1 H, H₂), 7.92 (t, J = 5.2 Hz, 1 H, H_{b}), 7.83 (tt, J = 7.7 and 1.3 H_{z} , 1 H, H_{p}), 7.77 (t, J = 5.3 Hz, 1 H, H_{e}), 7.41 (t, J = 5.3 Hz, 1 H, $H_{e'}$), 7.36 (t, J = 5.2 Hz, 1 H, $H_{h'}$), 7.83 (tt, J = 7.1 and 1.3 Hz, 1 H, H_m). ESI-MS (m/z): 531.8 [M-BF₄] (calcd: 531.9). Anal. Calcd for C₂₁H₁₇BClF₄N₉Ru·CH₃NO₂: C, 38.87; H, 2.97, N, 20.60. Found: C, 39.02; H, 2.90; N, 20.41.

Preparation of 5-Cl. Complex 4 (0.0479 g, 0.08 mmol) and cis-Ru(bpy)₂Cl₂·2H₂O (0.1497 g, 0.23 mmol) were refluxed in EtOH (3 mL) for 20 h. After cooled to RT, the solution was stirred with NH₄BF₄ 0.1043 g (1.00 mmol) for 3 h to obtain the product as a green powder. The product was washed with EtOH. The product was extracted by water and the water was removed before purified by recrystallization in MeOH/Et₂O (0.1088 g, 0.061 mmol, 78%). ¹H NMR (500 MHz, CD₃NO₂, RT, δ /ppm): 10.04–9.94 (m, 1 H), 9.08–8.84 (m, 2 H), 8.72–8.35 (m, 14 H), 8.28–7.99 (m, 11 H), 7.95–7.85 (m, 6 H), 7.79–7.62 (m, 5 H), 7.50–7.10 (m, 10 H). ESI-MS (*m*/*z*): 1706.87 [M–BF₄]⁺ (calcd: 1706.06). Anal. Calcd for C₆₁H₄₉B₅ClF₂₀N₁₇Ru₃·1.5CH₃NO₂·H₂O: C, 39.46; H, 2.94, N, 13.62. Found: C, 39.65; H, 2.84; N, 13.33.

Preparation of **5-OH**₂. Complex **5-CI** (0.0252 g, 0.01 mmol) and AgBF₄ (0.0160 g, 0.08 mmol) was dissolve in H₂O, and the solution was heated to 60 °C for 10 h. After reaction, water was removed and the obtained solid was dissolved in CH₃NO₂ to remove AgBF₄ salt through Celite filtration. Dark green solid powder was precipitated from CH₃NO₂/Et₂O-CH₂Cl₂ solution (0.0175 g, 0.01 mmol, 67%). ¹H NMR (500 MHz, CD₃NO₂, RT, δ /ppm): 9.98–9.84 (m, 1 H), 9.07–8.75 (m, 2 H), 8.66–8.37 (m, 15 H), 8.23–7.90 (m, 14 H), 7.84–7.42 (m, 16 H), 7.29–6.96 (m, 1 H). ESI-MS (*m*/*z*): 1688.6 [M–BF₄]⁺ (calcd: 1690.9) (M = [(bpy)₂Ru^{II}(bpm)Ru^{II}(OH) (py) (bpm)Ru^{II}(bpy)₂](BF₄)₅).

Anal. Calcd for $C_{61}H_{51}B_6F_{24}N_{17}ORu_3^{,1}.5CH_3NO_2^{,2}H_2O^{,}CH_2Cl_2^{,2}$ C, 36.76; H, 2.99; N, 12.49. Found: C, 36.42; H, 2.69; N, 12.19.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02518.

GC-MS data of the oxygenated products, ESI-MS, NMR, UV-vis absorption, differential pulse voltammograms, and square wave voltammograms data of compounds, related intermediates, and reagents used in the experiments. Details for quantum yield measurements, ORTEP diagram and IR data of the resultant Co salt. (PDF)

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Notes

The authors declare no competing financial interest.

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