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Redox Reactivity of a Mononuclear Manganese-Oxo Complex Binding Calcium Ion and Other Redox-Inactive Metal Ions

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ABSTRACT: Mononuclear nonheme manganese(IV)-oxo complexes binding calcium ion and other redox-inactive metal ions, $[(dpaq)Mn^{IV}(O)]^+-M^{n+}(1-M^{n+}, M^{n+} = Ca^{2+}, Mg^{2+}, Zn^{2+}, Lu^{3+}, Y^{3+}, Al^{3+} and Sc^{3+}) (dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-$ *N* $-quinolin-8-yl-acetamidate), were synthesized by reacting a hydroxomanganese(III) complex, <math>[(dpaq)Mn^{II}(OH)]^+$, with iodosylbenzene (PhIO) in the presence of redox-inactive metal ions (M^{n+}). The Mn(IV)-oxo complexes were characterized using various spectroscopic techniques. In reactivity studies, we observed contrasting effects of M^{n+} on the reactivity of 1- M^{n+} in redox reactions such as electron-transfer (ET), oxygen atom transfer (OAT), and hydrogen atom transfer (HAT) reactions. In the OAT and ET reactions, the reactivity order of 1- M^{n+} , such as 1-Sc³⁺ \approx 1-Al³⁺ > 1-Y³⁺ > 1-Lu³⁺ > 1-Zn²⁺ > 1-Ca²⁺, follows the Lewis acidity of M^{n+} bound to the Mn-O moiety; that is, the stronger is the Lewis acidity of M^{n+} , the higher becomes the reactivity of 1- M^{n+} . In sharp contrast, the reactivity of 1- M^{n+} in HAT reaction was reversed, giving the reactivity order of 1- $Ca^{2+} > 1$ - $Zn^{2+} > 1$ - $Lu^{3+} > 1$ - $Y^{3+} > 1$ - $Xl^{3+} \approx 1$ - Sc^{3+} ; that is, the higher is the Lewis acidity of M^{n+} the lower becomes the reactivity of 1- M^{n+} . The latter result implies that the Lewis acidity of M^{n+} bound to the Mn-O moiety can modulate the basicity of the metal-oxo moiety, thus influencing the HAT reactivity of 1- M^{n+} ; Cytochrome P450 utilizes the axial thiolate ligand to increase the basicity of iron-oxo moiety that enhances the reactivity of Compound I in C-H bond activation reactions.

INTRODUCTION

High-valent manganese-oxo complexes play pivotal roles as reactive intermediates in enzymatic reactions; one example is the water oxidation by the oxygen-evolving complex (OEC) in Photosystem II (PS II), where Ca^{2+} ion is an essential component for the dioxygen evolution in the catalytic water oxidation reaction.¹⁻⁵ The role of the Ca^{2+} ion, which is a redox-inactive metal ion, has been proposed to facilitate the O-O bond formation step occurring between a high-valent Mn(V)-oxo intermediate and an aqua (or hydroxide) ligand bound to the Ca^{2+} ion, although the exact role of the Ca^{2+} ion has yet to be clearly clarified.⁶⁻⁸

Recently, a large number of high-valent metal-oxo complexes bearing nonheme ligands have been successfully synthesized and characterized spectroscopically and/or structurally in biomimetic studies.9-²⁰ Their reactivities have also been investigated intensively in various oxidation reactions.⁹⁻²⁰ In addition, factors that modulate the reactivities and reaction mechanisms of the high-valent metal-oxo complexes have been the focus of current research.²¹⁻²⁶ For example, it has been shown that binding of redox-inactive metal ions, such as scandium ion (Sc³⁺), to nonheme metal-oxo complexes enhanced their reactivities greatly in oxygen atom transfer (OAT) and electrontransfer (ET) reactions.²²⁻²⁶ Further, enhancement of the oxidizing power of nonheme iron(IV)-oxo complexes in the presence of redox-inactive metal ions was shown to be correlated with the Lewis acidity of the redox-inactive metal ions.²⁵ In Mn-oxo complexes, binding of Sc^{3+} ion(s) to nonheme Mn(IV)-oxo complexes resulted in a large positive shift in the one-electron reduction potentials of the Mn(IV)-oxo complexes, thereby enhancing their reactivities in OAT and ET reactions but diminishing their reactivities in hydrogen atom transfer (HAT) reactions.²⁶ Goldberg and co-workers reported the influence of a redox-inactive Zn^{2+} ion on a valence tautomerization of a Mn(V)-oxo corrolazine complex and the change of the reactivity of the Mn(V)-oxo complex in ET and HAT reactions.²⁷ The redox-inactive metal ion effect has also been demonstrated in the catalytic oxidation of organic substrates by terminal oxidants, in which high-valent metal(IV)-oxo species binding Sc³⁺ ion was proposed as an active oxidant.²⁸

As alluded above, the effects of redox-inactive metal ions on the chemical properties of Mn-oxo complexes have merited significant interest due to the vital role of Ca2+ ion in OEC in PS II as well as the desire for the development of efficient catalytic oxidation systems. However, non-heme Mn(IV)-oxo complexes binding calcium ion and other redox-inactive metal ions other than Sc³⁺ have yet to be reported. Herein, we report the synthesis and characterization of Mn(IV)-oxo complexes binding a series of redox-inactive metal ions, $[(dpaq)Mn^{IV}(O)]^+-M^{n+}$ (1- M^{n+} , $M^{n+} = Ca^{2+}$, Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , Al^{3+} , and Sc^{3+}) (dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-*N*-quinolin-8-yl-acetamidate), by reacting a hydroxomanganese(III) complex, [(dpaq)Mn^{III}(OH)]⁺, with iodosylbenzene (PhIO) in the presence of redox-inactive metal ions (M^{n+}) (Scheme 1, reaction *a*). In the absence of M^{n+} , a bis(μ -oxo)dimanganese(III,IV) complex, [(dpaq)Mn^{III}(O)₂Mn^{IV}-(dpaq)]⁺, was produced (Scheme 1, reaction *b*). We also report the contrasting effects of redox-inactive metal ions (M^{n+}) on the redox reactivity of **1**- M^{n+} in OAT, ET, and HAT reactions (Scheme 1). Interestingly, we found that the reactivities of

Scheme 1. Effects of Redox-Inactive Metal Ions on the Synthesis and Reactivity of Mn(IV)–Oxo Complex



Scheme 2. The Ligand (H-dpaq) and the Mn(III) Complex, [(dpaq)Mn^{III}(OH)]⁺, Used in This Study



1-Mⁿ⁺ differed markedly in the OAT, ET, and HAT reactions, depending on the Lewis acidity of Mⁿ⁺ in 1-Mⁿ⁺. For example, as the Lewis acidity of Mⁿ⁺ increases, the reactivity of 1-Mⁿ⁺ becomes greater in the OAT and ET reactions (Scheme 1). In sharp contrast, 1-Mⁿ⁺ becomes a weaker oxidant in the HAT reaction as the Lewis acidity of Mⁿ⁺ increases (Scheme 1). The latter result implies that the Lewis acidity of Mⁿ⁺ modulates the reactivity of **1**-Mⁿ⁺ in abstracting hydrogen atom (H-atom) from substrate C-H bonds by controlling the basicity of metal-oxo moiety; it has been discussed in the communities of bioinorganic/biomimetic and biological chemistry that Cytochrome P450 enzymes utilize the axial thiolate ligand to modulate the basicity of iron-oxo moiety that influences the reactivity of Compound I in C-H bond activation reactions. To the best of our knowledge, the present study reports for the first time the synthesis of Mn(IV)-oxo complexes binding various redox-inactive metal ions, such as Ca²⁺, Mg²⁺, Zn²⁺, Lu³⁺, Y³⁺, Al³⁺, and Sc³⁺, which provides us with an excellent opportunity to investigate the redox-inactive metal ion effect on the chemical properties of high-valent metal-oxo species systematically.

RESULTS AND DISCUSSION

Synthesis and Characterization of $Mn^{IV}(O)-M^{n+}$. The starting $[(dpaq)Mn^{III}(OH)]^+$ complex was synthesized according to the literature methods (see Scheme 2 for the structures of the dpaq ligand and the $[(dpaq)Mn^{III}(OH)]^+$ complex; also see the X-ray crystal structure and ¹H NMR spectrum of $[(dpaq)Mn^{III}(OH)]^+$ (Supporting Information (SI), Figures S1 and S2);^{29,30} it has been reported very recently that the $[(dpaq)Mn^{III}(OH)]^+$ complex, is in equilibrium with a μ -oxodimanganese(III,III) complex, $[(dpaq)_2Mn^{III}_2(\mu-O)]^{2+,30b}$ When the solution of $[(dpaq)Mn^{III}(OH)]^+$ was reacted with PhIO in acetonitrile (MeCN) at 263 K, we observed the formation of a green-colored species with broad absorption bands at ~520 nm within 2 min (Figure 1a). The manganese product was



Figure 1. (a) Visible-NIR absorption spectral changes showing the formation of а bis(µ-oxo)dimanganese(III,IV) complex $([(dpaq)Mn^{III}(O)_2Mn^{IV}(dpaq)]^+)$ in the reaction $[(dpaq)Mn^{III}(OH)]^+$ (1.0 mM) and PhIO (0.50 mM) in the presence of H₂O (20 µL) in deaerated MeCN at 263 K. Inset shows the time course of the reaction monitored at 520 nm. (b) Visible-NIR absorption spectral changes showing the formation of $[(dpaq)Mn^{IV}(O)]^+$ - Sc^{3+} (1- Sc^{3+}) in the reaction of $[(dpaq)Mn^{III}(OH)]^+$ (0.50 mM) and PhIO (1.5 mM) in the presence of Sc(OTf)₃ (1.0 mM) in deaerated MeCN at 253 K. Inset shows the time course of the reaction monitored at 700 nm. (c) CSI-MS spectrum of 1-Sc³⁺. The peaks at 945.0 and 986.0 correspond to $[(dpaq)Mn^{IV}(O)]^+$ -Sc(OTf)₃ (calc. m/z =944.9) and $[(dpaq)Mn^{IV}(O)(CH_3CN)]^+-Sc(OTf)_3$ (calc. m/z =985.9), respectively. Insets show the observed isotope distribution patterns for 1-Sc³⁺-¹⁶O (left panel) and 1-Sc³⁺-¹⁸O (right panel); the 1-Sc3+_16O and 1-Sc3+_18O complexes were prepared by reacting $[(dpaq)Mn^{III}(OH)]^+$ (0.25 mM) with PhI¹⁶O (0.75 mM) and PhI¹⁸O (0.75 mM), respectively, in the presence of Sc(OTf)₃ (0.50 mM) in deaerated MeCN at 253 K. The percentage of ¹⁸O incorporation in 1- Sc^{3+} was determined to be 85(5)%.

identified as a dinuclear bis(μ -oxo)dimanganese complex,^{29a} [(dpaq)Mn^{III}(O)₂Mn^{IV}(dpaq)]⁺, by electron paramagnetic resonance (EPR) spectroscopy (SI, Figure S3); the yield of [(dpaq)Mn^{III}(O)₂Mn^{IV}(dpaq)]⁺ was determined to be ~90% by comparing the doubly integrated value of the EPR signal with that of the reference signal of 2,2-diphenyl-1-picrylhydrazyl radical (DPPH[•]) (SI, Figure S3).

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Scheme 3. DFT Optimized Structure of the Redox-Inactive Metal Ion (Sc³⁺)-Bound Mn(IV)–Oxo Complex (1-Sc³⁺)



[(dpaq)Mn^{IV}(O)]⁺-Sc(OTf)₃

Interestingly, when we reacted the solution of [(dpaq)Mn^{III}(OH)]⁺ containing redox-inactive metal ions, such as Sc(OTf)₃, with PhIO in MeCN at 253 K, we observed the formation of a green-colored species with two electronic absorption bands at 510 and 700 nm (Figure 1b); this intermediate is denoted as 1-Sc³⁺ (see Scheme 3 for the DFT-optimized schematic structure). 1-Sc³⁺ was metastable ($t_{1/2} \sim 1$ day at 253 K), allowing us to characterize it with cold-spray ionization time-of-flight mass spectrometry (CSI-MS) and EPR. The CSI-MS of 1-Sc³⁺ exhibits a prominent ion peak at a mass-to-charge (m/z) ratio of 945.0 (Figure 1c), whose mass distribution pattern corresponds and isotope to $[(dpaq)Mn(O)Sc(OTf)_3]^+$ (calc. m/z = 944.9). When the reaction was performed with isotopically labeled PhI¹⁸O, the mass peak at m/z = 945.0 shifted to m/z = 947.0, indicating that this intermediate possesses one oxygen atom. The EPR spectrum exhibits signals at $g_{\rm eff}$ = 5.4, 4.0 and 1.81 (SI, Figures S4 and S5), suggesting a high-spin S $= 3/2 \text{ Mn}^{\text{IV}} \text{ species.}^{26,31}$

1-Sc³⁺ was further characterized using Mn K-edge X-ray absorption spectroscopy (XAS). Figure 2a shows the comparison of X-ray absorption near edge structure (XANES) spectra for $[(dpaq)Mn^{III}(OH)]^+$ (blue line) and **1**-Sc³⁺ (red line). Shift in the edge position of 1-Sc³⁺, compared with $[(dpaq)Mn^{III}(OH)]^+$, indicates that the Mn oxidation state in 1-Sc3+ is higher than MnIII. Preedge structure characteristic for Mn^{IV} complexes^{31b} at ~6539 eV decreased in intensity, which is consistent with the binding of Sc³⁺ ion at Mn^{IV}=O fragment.^{26a,31b} Extended X-ray absorption fine structure (EXAFS) data for [(dpaq)Mn^{III}(OH)]⁺ and 1-Sc³⁺ are shown in Figure 2b. Fit results for both curves are provided in SI, Tables S1 and S2, and the comparisons of best-fit curve with Fourier transformed (FT) EXAFS of 1-Sc³⁺ is shown in SI, Figure S6. EXAFS analysis of 1-Sc³⁺ spectrum indicates the presence of a 1.68 Å Mn-O interaction, which is close to the result obtained with Sc3+ ion-bound $[(N4Py)Mn^{IV}(O)]^{2+} (N4Py = N, N-bis(2-pyridylmethyl)-N-bis(2-pyridylmethyl) - N-bis(2-pyridylmethyl) - N-bis(2-pyridylmethyl - N-bis(2-pyridylmethyl) - N-bis(2-pyridylmethyl) - N-bis(2-pyri$ pyridyl)methylamine) reported previously.^{26a} The EXAFS data also reveal a short Mn-Sc³⁺ distance (3.99 Å), which clearly indicates that Sc^{3+} ion binds to the Mn-O moiety in $1-Sc^{3+}$. Very recently, we have shown the binding of Sc^{3+} ion to the Mn(V)-oxo complex bearing a tetraamido macrocyclic ligand, [Mn^V(O)(TAML)]⁻;³² the binding site of the Sc³⁺ ion was proposed at the carbonyl group of the TAML ligand with the Mn-Sc³⁺ bond length of ~6.0 Å, whereas in the present case, we observed a shorter bond length of $Mn-Sc^{3+}$ (3.99 Å).



Figure 2. (a) Normalized Mn K-edge XANES spectra of $[(dpaq)Mn^{III}(OH)]^+$ (blue line) and **1**-Sc³⁺ (red line). (b) Fourier transformed EXAFS for $[(dpaq)Mn^{III}(OH)]^+$ (blue line) and **1**-Sc³⁺ (red line) (k = 3.5 – 10.9 Å⁻¹).

This result suggests the binding of the Sc³⁺ ion to the Mn-oxo moiety, not to the carbonyl group in the dpaq ligand.

We have also observed the formation of $1-M^{n+}$ binding a series of redox-inactive metal ions (M^{n+}), such as Ca^{2+} , Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , and Al^{3+} , in the reactions of $[(dpaq)Mn^{III}(OH)]^+$ (0.50 mM) with PhIO (1.5 mM) in the presence of $Ca(OTf)_2$ (200 mM), $Mg(OTf)_2$ (25 mM), $Zn(OTf)_2$ (5.0 mM), $Lu(OTf)_3$ (1.5 mM), $Y(OTf)_3$ (1.0 mM), and $Al(OTf)_3$ (1.0 mM) in MeCN at 253 K; those are denoted as $1-Ca^{2+}$, $1-Mg^{2+}$, $1-Zn^{2+}$, $1-Lu^{3+}$, $1-Y^{3+}$, and $1-Al^{3+}$, respectively. In the case of weak Lewis acidic redox-inactive metal ions, higher concentration of the redox-inactive metal ions is needed because the



Figure 3. UV-vis spectra of $[(dpaq)Mn^{IV}(O)]^+-M^{n+}(1-M^{n+};M^{n+}=Ca^{2+}, Mg^{2+}, Zn^{2+}, Lu^{3+}, Y^{3+}, Al^{3+} and Sc^{3+})$. **1**-Mⁿ⁺ were generated by reacting $[(dpaq)Mn^{III}(OH)]^+$ (0.50 mM) with PhIO (1.5 mM) in the presence of metal ions (Ca²⁺, 200 mM; Mg²⁺, 25 mM; Zn²⁺, 5.0 mM; Lu³⁺, 1.5 mM; Y³⁺, 1.0 mM; Al³⁺, 1.0 mM; Sc³⁺, 1.0 mM) in deaerated MeCN at 253 K.

acidity is not enough to obtain the product or prohibit the dimer formation. The UV-vis spectra of $1-M^{n+}$ ($M^{n+} = Ca^{2+}$, Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , and Al^{3+}) exhibit two absorption bands, such as 500 and 580 nm for $1-Ca^{2+}$, 500 and 580 nm for $1-Mg^{2+}$, 500 and 590 nm for $1-Zn^{2+}$, 510 and 684 nm for $1-Lu^{3+}$, 510 and 690 nm for $1-Y^{3+}$, and 510 and 695 nm for $1-Al^{3+}$ (see Figure 3). The metastable $1-M^{n+}$ intermediates ($t_{1/2} > 4h$ at 253 K) were further characterized using CSI-MS and EPR spectroscopic techniques (SI, Figures S4, S5, S7 and S8).

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The EPR spectra of $1-M^{n+}$ exhibit signals at $g_{eff} = 3.7$ and 1.96 for 1-Ca²⁺, 1-Mg², and 1-Zn²⁺ and $g_{\text{eff}} = 5.4$, 4.0 and 1.81 for 1-Y³⁺, 1-Lu³⁺, and 1-Al3+ (SI, Figures S4, S5 and S7), indicating that all 1-Mn+ are high-spin S = 3/2 Mn^{IV} species irrespective of the kind of M^{n+.26,31} The CSI-MS spectra of 1-Zn²⁺, 1-Lu³⁺, and 1-Y³⁺ exhibited prominent ion peaks at m/z = 815.1, 1075.1, and 989.0, respectively (SI, Figure S8); the mass and isotope distribution patterns of the ion peaks at m/z = 815.1, 1075.1, and 989.0 correspond to $[(dpaq)Mn^{IV}(O)Zn(OTf)_2]^+$ (calc. = 815.1), m/z $[(dpaq)Mn^{IV}(O)Lu(OTf)_3]^+$ (calc. m/z =1075.1), and $[(dpaq)Mn^{IV}(O)Y(OTf)_3]^+$ (calc. m/z = 988.9), respectively. We have also confirmed the oxidation state of 1-Zn²⁺ and 1-Lu³⁺ using Mn K-edge X-ray absorption spectroscopy (SI, Figure S9); in the XANES spectra of [(dpaq)Mn^{III}(OH)]⁺, 1-Zn²⁺, and 1-Lu³⁺, the shift in the edge position of 1-Mⁿ⁺, compared to [(dpaq)Mn^{III}(OH)]⁺, indicates that oxidation state of the Mn ion in $1-M^{n+}$ is higher than Mn^{III} , as shown in the case of $1-Sc^{3+}$ (Figure 2; vide supra). EXAFS analysis of 1-Lu³⁺ spectrum indicates the Mn-O and Mn-Lu³⁺ distances are 1.73 and 4.25 Å, respectively (SI, Table S3 and Figure S10). Based on the spectroscopic characterization discussed above, **1**- M^{n+} is assigned as $[(dpaq)Mn^{IV}(O)]^+$ binding a redox-inactive metal ion (M^{n+}) , $[(dpaq)Mn^{IV}(O)]^+-M^{n+}$ (1- M^{n+} ; $M^{n+} = Ca^{2+}$, Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , Al^{3+} , and Sc^{3+}).

Reactivity Studies of [(dpaq)Mn^{IV}(O)]⁺–Mⁿ⁺. In this section, we report the redox-inactive metal ion effects on the reactivities of the $[(dpaq)Mn^{IV}(O)]^+-M^{n+}(1-M^{n+})$ complexes in ET, OAT, and HAT reactions. It should be noted that the bis(μ -oxo)dimanganese(III,IV) complex, $[(dpaq)Mn^{II}(O)_2Mn^{IV}(dpaq)]^+$, produced by the oxidation of $[(dpaq)Mn^{III}(OH)]^+$ by PhIO in the absence of M^{n+} exhibited no reactivity towards thioanisole, cyclohexadiene and $[Fe^{II}(Me_2bpy)_3]^{2+}$ (SI, Figure S11).

(i) Redox Properties of 1-Mⁿ⁺. The one-electron reduction potential of 1-Mⁿ⁺, such as 1-Sc³⁺, was determined by performing the ET titration with tris(4-bromophenyl)amine (TBPA, Eox = 1.08 V vs SCE).^{33,34} When 1-Sc³⁺ was employed as an electron acceptor, efficient ET occurred from TBPA to 1-Sc³⁺ (Figure 4a), where the absorption band at 705 nm is assigned due to TBPA⁺⁺ (ε = 32,000 M⁻¹ cm⁻¹ at λ_{max} = 705 nm).³⁵ The ET from TBPA to **1**-Sc³⁺ was found to be in equilibrium, where the concentration of TBPA⁺ produced increased with increasing the initial concentration of TBPA, as shown in Figure 4b. The equilibrium constant (K_{et}) was determined to be 70 at 253 K by fitting the plot of [TBPA⁺⁺] vs [TBPA]₀ with the use of the ET equilibrium equations (eqs 7 – 9) in Experimental Section (Figure 4c). The one-electron reduction potential (E_{red}) of **1**-Sc³⁺ was determined to be 1.17 V vs SCE from the Ket value of 70 and the E_{ox} value of TBPA (1.08 V vs SCE) using the Nernst equation (eq $1).^{36}$

$$E_{\rm red} = E_{\rm ox} + (RT/F) \ln K_{\rm et} \tag{1}$$

The rate of ET from a coordinatively saturated metal complex, such as $[Fe^{II}(Me_2bpy)_3]^{2+}(Me_2bpy) = 4,4'-dimethyl-2,2'-bipyridine)$, to 1-



Figure 4. (a) Absorption spectra of TBPA⁺⁺ produced in electron transfer from TBPA (0 – 0.12 mM) to $1-\text{Sc}^{3+}$ (0.050 mM) in MeCN at 253 K. (b) Plot of concentration of TBPA⁺⁺ produced in ET from TBPA to $1-\text{Sc}^{3+}$ (0.050 mM) vs initial concentration of TBPA, [TBPA]₀. (c) Plot of $(a^{-1}-1)^{-1}$ vs $[1-\text{Sc}^{3+}]_0/a[(TBPA]_0 - 1 \text{ (where } a = [TBPA^{++}]/[TBPA]_0)$ to determine the equilibrium constant (K_{et}) of electron transfer from TBPA to $1-\text{Sc}^{3+}$ upon addition of TBPA to an MeCN solution of $1-\text{Sc}^{3+}$ at 253 K (see eq 9 in Experimental Section).

Table 1. Second-Order Rate Constants (k_{et} and k_{ox}) for Oxidation of $[Fe^{II}(Me_2bpy)_3]^{2+}$, Thioanisole, and CHD by 1-Mⁿ⁺ in Deaerated MeCN at 253 K

metal ion	$k_{ m et}$ or $k_{ m oxy}{ m M}^{-1}{ m s}^{-1}$		
	[Fe ^{II} (Me ₂ bpy) ₃] ²⁺	thioanisole	CHD
Ca ²⁺	$1.9(2) \times 10^{2}$	$5.8(5) \times 10^{-2}$	$1.3(1) \times 10^{-1}$
Mg ²⁺	$3.2(3) \times 10^2$	$1.5(1) \times 10^{-1}$	$1.0(1) \times 10^{-1}$
Zn ²⁺	$4.8(4) \times 10^2$	$4.7(4) \times 10^{-1}$	$7.1(6) \times 10^{-2}$
Lu ³⁺	$4.8(3) \times 10^3$	$7.4(5) \times 10^{-1}$	$2.3(2) \times 10^{-2}$
Y ³⁺	$6.0(5) \times 10^3$	$9.0(7) \times 10^{-1}$	$2.1(2) \times 10^{-2}$
Al ³⁺	$7.8(5) \times 10^3$	3.4(3)	$1.8(1) \times 10^{-2}$
Sc ³⁺	$8.4(7) \times 10^{3}$	2.2(2)	$1.6(1) \times 10^{-2}$

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Figure 5. (a) Visible-NIR absorption spectral change observed in the reaction of $1-Sc^{3+}$ (0.25 mM) with thioanisole (15 mM) in deaerated MeCN at 253 K. Inset shows time profile of absorbance at 700 nm. (b) Plot of pseudo-first-order rate constant (k_{obs}) vs the concentration of thioanisole for the reaction of $1-Sc^{3+}$ with thioanisole in MeCN at 253 K.

Sc³⁺ obeyed the first-order kinetics and the pseudo-first-order rate constant (k_1) was proportional to the concentration of $[Fe^{II}(Me_2bpy)_3]^{2+}$, affording the second-order rate constant (k_{et}) of 8.4 × 10³ M⁻¹ s⁻¹ in MeCN at 253 K for the ET from $[Fe^{II}(Me_2bpy)_3]^{2+}$ to 1-Sc³⁺ (SI, Figure S12a). Similarly, k_{et} values of ET from various one-electron donors (i.e., coordinatively saturated metal complexes, such as $[Fe^{II}(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), $[Fe^{II}(phen)_3]^{2+}$ (phen = 1,10-phenonthroline), and $[Ru^{II}(Me_2bpy)_3]^{2+}$) to 1-Sc³⁺ (vide infra) were determined and listed in SI, Table S4 (also see SI, Figure S12). The k_{et} values of ET from $[Fe^{II}(Me_2bpy)_3]^{2+}$ to other 1-Mⁿ⁺ were also determined and listed in Table 1 (also see SI, Figure S13).

(ii) Sulfoxidation Reaction by 1-Mⁿ⁺. Oxygen atom transfer (OAT) reactions by 1-Mⁿ⁺, such as 1-Sc³⁺, were performed using thioanisole derivatives as substrates in MeCN at 253 K. Upon addition of thioanisole to an MeCN solution of $1-Sc^{3+}$, the absorption band at 700 nm corresponding to 1-Sc³⁺ disappeared with the first-order decay kinetics profile (Figure 5a). Pseudo-first-order rate constants, determined by the first-order fitting of the kinetic data for the decay of 1-Sc³⁺, increased linearly with an increase in thioanisole concentration, giving the second-order rate constant (k_{ox}) of 2.2 M⁻¹ s⁻¹ at 253 K (Figure 5b). Similarly, the oxidation of other para-substituted thioanisoles (para-X-thioanisoles; X = OMe, Me, H, Cl, and Br) by 1- Sc^{3+} was also performed, and the second-order rate constants (k_{ox}), determined by the plots of pseudo-first-order rate constants vs concentrations of thioanisole derivatives (SI, Figure S14), were listed in SI, Table S5. The logarithm of k_{ox} values is linearly correlated with the one-electron oxidation potentials of para-X-thioanisoles (SI, Figure S15a), where the k_{ox} value increases as the electron-donating ability of the para-substituent increases.^{21,22} The slope of -15 in SI, Fig-



Figure 6. Driving force $(-\Delta G_{et})$ dependence of logarithm of rate constants (log k_{et}) of ET from one-electron donors [(1) [Fe^{II}(Me₂bpy)₃]²⁺, (2) [Fe^{II}(bpy)₃]²⁺, (3) [Fe^{II}(phen)₃]²⁺, and (4) [Ru^{II}(Me₂bpy)₃]²⁺] to **1**-Sc³⁺, and logarithm of rate constants (log k_{ox}) determined in the oxidation of substrates [(5) *p*-methylthioanisole, (6) thioanisole, (7) *p*-chlorothioanisole and (8) *p*-bromothioanisole, (9) xanthene, (10) DHA, and (11) CHD] by **1**-Sc³⁺ in MeCN at 253 K. The black and blue lines are drawn according to eq 2 with the λ values of 1.79 and 1.85 eV, respectively.

ure S15a indicates that electron transfer is involved in the rate-determining step (vide infra).^{24a,24d,26a} In addition, a plot of the logarithm of rate constant as a function of σ_p^+ shows a good Hammett correlation with a largely negative ρ value of –4.5 (SI, Figure S15b).

The product(s) formed in this reaction was analyzed using ESI-MS and EPR. Analysis of the Mn product by ESI-MS showed that a Mn^{III} species was formed as a major product with an impurity scale of Mn^{II} in the sulfoxidation reaction by $1-Sc^{3+}$ (SI, Figure S16a). In the EPR analysis, an impurity scale (< 1%) of Mn^{II} was observed (SI, Figure S16b), confirming that a Mn^{III} species was formed as the major product. It has been reported that (dpaq) Mn^{II} is not stable under certain circumstances and reacts with O₂ to form the $[(dpaq)Mn^{III}(OH)]^+$ complex.^{30a} The organic product analysis of the reaction solution revealed that methyl phenyl sulfoxide was formed quantitatively. It was confirmed that oxygen in methyl phenyl sulfoxide derived from the oxo group of $1-Sc^{3+}$, not from water, by using ¹⁸O-labeled $1-Sc^{3+}$ as shown in SI, Figure S17, as the case of anthracene oxidation by $1-Sc^{3+}$ to produce anthraquinone in which two oxygen atoms originated from the oxo group of $1-Sc^{3.37}$

The oxidation of thioanisole by other 1-Mⁿ⁺ was also performed in MeCN at 253 K (SI, Figure S18), and the second-order rate constants (k_{ox}) determined were listed in Table 1. The k_{ox} value increased with increasing the Lewis acidity of redox-inactive metal ions bound to the Mn^{IV}(O) moiety.^{23,38} Thus, the reactivity order of 1-Mⁿ⁺ in the oxidation of thioanisole (i.e., OAT reaction) was determined to be 1-Al³⁺ > 1-Sc³⁺ > 1-Y³⁺ > 1-Lu³⁺ > 1-Zn²⁺ > 1-Mg²⁺ > 1-Ca²⁺.

The dependence of logarithm of the second-order rate constants of ET(k_{t}) from electron donors to $1-Sc^{3+}$ (vide supra) on the ET driving force $[-\Delta G_{et}(eV) = e(E_{red} - E_{ox})]$ is shown in Figure 6, where the logarithm of the second-order rate constants (k_{ox}) of sulfoxidation of thioanisole derivatives by $1-Sc^{3+}$ is also plotted.^{22a} The driving force dependence of the ET rate constants is well fitted by the Marcus theory of outer-sphere electron transfer (eq 2),

$$k_{\rm et} = Z \exp[-(\lambda/4)(1 + \Delta G_{\rm et}/\lambda)^2/k_{\rm B}T$$
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Figure 7. (a) Plots of pseudo-first-order rate constant (*k*_{obs}) against substrate concentration to determine the second-order rate constants in the reactions of 1-Sc³⁺ with xanthene (black circle), DHA-*h*₄ (green circle), DHA-*d*₄ (red circle), and CHD (blue circle) in MeCN at 253 K. (b) Plots of pseudo-first-order rate constant (*k*_{obs}) against CHD concentration to determine the second-order rate constants (M⁻¹s⁻¹) in the reactions of 1-Mⁿ⁺ with CHD in MeCN at 253 K (see Table 1).

where Z is the collision frequency taken as 1×10^{11} M⁻¹ s⁻¹, λ is the reorganization energy of ET, $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature.³⁹ The best fit λ value of ET from metal complexes to $1-Sc^{3+}$ is 1.85 eV (blue line in Figure 6), which is similar to the best fit λ value (1.79 eV) of sulfoxidation of thioanisole derivatives by $1-Sc^{3+}$ (black line in Figure 6). Such an agreement strongly indicates that sulfoxidation of thioanisole derivatives by 1-Sc3+ proceeds via the rate-determining ET (vide supra). It should be noted that the λ values (1.79 and 1.85 eV) are significantly smaller than those of ET reactions of [(Bn-TPEN)Mn^{IV}(O)]²⁺-(Sc³⁺)₂ (Bn-TPEN N-benzyl-N,N,N-tris(2-pyridylmethyl)-1,2-dia-= minoethane; $\lambda = 2.12 \text{ eV}$) and $[(N4Py)Mn^{IV}(O)]^{2+}-(Sc^{3+})_2 (\lambda = 2.21)^{10}$ eV),^{26b} probably because of the more rigid structure of the dpaq ligand that contains a quinoline moiety. On the other hand, the reorganization energy of electron exchange between thioanisole and thioanisole radical cation was determined to be 0.80 eV from the rate constant of the electron exchange $(1 \times 10^7 \,\text{M}^{-1} \,\text{s}^{-1})^{40}$ using eq 2 when $\Delta G_{\rm et}$ =0. The observed reorganization energy of electron transfer from thioanisole to $1-Sc^{3+}$ ($\lambda = 1.79$ eV in Figure 6) is much larger than that of electron exchange between thioanisole and thioanisole radical cation (0.80 V). It should be noted that the observed reorganization energy (1.79 eV) is the average of the reorganization energy of electron exchange between thioanisole and thioanisole radical cation (0.80 eV) and that of electron exchange between $[(dpaq)Mn^{IV}(O)]^+$ -Sc³⁺ and $[(dpaq)Mn^{III}(O)]^+$ -Sc³⁺ (2.78 eV).

(iii) C-H Bond Activation by 1-Mⁿ⁺. The hydrogen atom (H-atom) abstraction reactions of 1-Mⁿ⁺, such as 1-Sc³⁺, with hydrocarbons having weak C-H bond dissociation energies (BDEs), such as xanthene (75.5 kcal mol⁻¹), dihydroanthracene (DHA; 77.0 kcal mol⁻¹), and 1,4-cyclohexadiene (CHD; 78.0 kcal mol⁻¹),⁴¹ were performed

in MeCN at 253 K. Addition of DHA to an MeCN solution of 1-Sc³⁺ resulted in the disappearance of the absorption band at 700 nm due to 1-Sc³⁺ (SI, Figure S19a). Pseudo-first-order rate constants, determined by the first-order fitting of the kinetic data for the decay of 1-Sc³⁺, increased linearly with an increase in DHA concentration, giving the second-order rate constant (k_{ox}) of 2.5 × 10⁻¹ M⁻¹ s⁻¹ at 253 K (Figure 7a). The C-H bond activation reactions were also investigated with other weak C-H bonds, such as xanthene and CHD. The second-order rate constants (k_{ox}) of 4.9 × 10⁻¹ and 1.6 × 10⁻² M⁻¹ s⁻¹ were determined in the oxidation of xanthene and CHD by 1-Sc³⁺, respectively (Figure 7a). As expected, the second-order rate constants decreased with an increase in the C-H BDEs of alkyl hydrocarbons, showing a correlation between the log k_{ox} values and the C-H BDEs of the substrates with a slope of -0.54 (SI, Figure S19b). The oxidation of DHA- h_4 and DHA- d_4 by **1**-Sc³⁺ was also investigated, affording the kinetic isotope effect (KIE) value of 2.3(1) (Figure 7a). These results indicate that the C-H bond activation of alkyl hydrocarbons by 1-Sc³⁺ occurs via an H-atom abstraction mechanism and the H-atom abstraction by **1**-Sc³⁺ is the rate-determining step.

The product(s) formed in the oxidation reactions was analyzed using ESI-MS and EPR spectroscopic techniques. Analysis of the Mn product by ESI-MS shows that an Mn^{III} species was formed as a major product with an impurity scale of Mn^{II} in the C-H bond activation reaction by $1-Sc^{3+}$ (SI, Figure S20a), as observed in the oxidation of thioanisole derivatives by $1-Sc^{3+}$ (vide supra). In the EPR analysis, a trace amount of Mn^{II} active signal was observed (SI, Figure S20b), confirming that a Mn^{III} species was the major product. The product analysis of the reaction solution of xanthene revealed that xanthone was formed as the sole product. In addition, by carrying out the oxidation of xanthene with the ¹⁸O-labeled $1-Sc^{3+}$ (SI, Figure S21).

The CHD was chosen as the C-H bond substrate to compare the oxidizing ability of $1-M^{n+}$ complexes in MeCN at 253 K. The second-order rate constants of $1-M^{n+}$ were determined and listed in Table 1 (see also Figure 7b). Interestingly, the k_{ox} values decreased with increasing the Lewis acidity of redox-inactive metal ions bound to the Mn-oxo moiety. Thus, the reactivity order of $1-M^{n+}$ in the oxidation of CHD (i.e., HAT reaction) is opposite to that obtained in the ET and OAT reactions by $1-M^{n+}$; that is, the reactivity order is $1-Ca^{2+} > 1-Mg^{2+} > 1-Zn^{2+} > 1-Lu^{3+} > 1-Y^{3+} > 1-Al^{3+} \ge 1-Sc^{3+}$ in the HAT reaction (vide infra). The reason why the reactivity order of $1-M^{n+}$ in HAT is opposite that in ET and OAT is discussed as follows.

There are two extreme mechanisms for hydrogen atom transfer (HAT) reactions. The first one is electron transfer, followed by proton transfer, referred to ET-PT. In this case, the HAT reactivity is in parallel with the ET reactivity. The other one is proton transfer followed by electron transfer (PT-ET), when the HAT reactivity is in parallel with the PT reactivity, which is opposite to the ET reactivity, because the stronger base for the PT reaction acts as the weaker electron acceptor for the ET reaction. A change of the mechanism between ET-PT and PT-ET was reported as a V-shaped Hammett plot for the HAT from *para*-substituted 2,6-di-tert-butylphenols to an imido manganese(V) corrole (tpfc)Mn^V(NTs) where tpfc = 5,10,15-tetrakis(pentafluoro-phenyl)corrole.⁴³ As the more withdrawing substituents are employed, the acidity of the phenolic proton increases to enhance the initial rate-determining proton transfer

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Figure 8. Plots of logarithm of the second-order rate constants in the oxidation (k_{ox}) of thioanisole (red line) and CHD (green line) by 1- M^{n+} and in the electron transfer (k_{et}) from $[Fe^{II}(Me_2bpy)_3]^{2+}$ (blue line) to 1- M^{n+} vs a quantitative measure of Lewis acidity of metal ions (ΔE).⁴² The ΔE value of the Al(OTf)₃ was determined using fluorescence maximum of 10-methylacridone (AcrCO)-Al(OTf)₃ complex (SI, Figure S22).^{42f}

from the phenolic proton to (tpfc)Mn^VNTs, followed by fast electron transfer.⁴³ When electron-donating substituents are employed, the rate-determining step is changed from PT-ET to ET-PT, exhibiting a V-shaped Hammett plot.⁴³ In most cases, however, ET and PT may occur in a concerted manner. In such a case, the HAT reactivity may be determined by the compensation between the ET and PT reactivity depending on the ET and PT driving force.⁴⁴ In the case of **1**-Mⁿ⁺, the HAT reactivity seems to be determined by the PT reactivity rather than the ET reactivity, because the stronger is the Lewis acidity of Mⁿ⁺ binding to the Mn^{IV}(O) moiety, the weaker is the basicity of the oxo group in the PT reaction. The decreased reactivity of a trivalent metal ion-bound Mn^{IV}(O) complex such as **1**-Sc(OTf)₃ as compared with a divalent metal ion-bound Mn^{IV}(O) complex such as **1**-Ca(OTf)₂ may also result from the steric effects of Sc(OTf)₃ that binds with the oxo moiety stronger than Ca(OTf)₂.

CONCLUSION

 $Mn^{IV}(O)$ Redox-inactive metal ion-bound complexes, $[(dpaq)Mn^{IV}(O)]^+-M^{n+}$ (1- M^{n+} ; $M^{n+} = Ca^{2+}$, Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , Al^{3+} and Sc^{3+}), were synthesized in the oxidation of a mononuclear hydroxomanganese(III) complex, [(dpaq)Mn^{III}(OH)]⁺, by PhIO in the presence of various metal triflates, $M^{n+}(OTf)_n$, whereas a bis- μ oxo dimer, $[(dpaq)Mn^{III}(O)_2Mn^{IV}(dpaq)]^+$, was formed in the absence of $M^{n+}(OTf)_n$. Although the bis(μ -oxo)dimanganese(III,IV) complex exhibited no reactivity in OAT and HAT reactions, 1-Mn+ oxidized thioanisoles and CHD efficiently via ET and HAT reactions, respectively. Interestingly, when the log k_{ox} values obtained in the OAT (e.g., thioanisole) and HAT (e.g., CHD) reactions as well as the log k_{et} values of ET (e.g., $[Fe^{II}(Me_2bpy)_3]^{2+})$ were plotted against a quantitative measure of Lewis acidity of metal ions (ΔE),⁴² the reactivity trends differed markedly (Figure 8). For example, the log k_{ox} values of the oxidation of thioanisole (red line in Figure 8), which proceeds via ET, and the log $k_{\rm et}$ values of ET of $[Fe^{II}(Me_2bpy)_3]^{2+}$ (blue line in Figure 8) increase with an increase in the Lewis acidity (ΔE), since the stronger is the Lewis acidity of the redox-inactive metal ions bound to the Mn-oxo moiety, the faster becomes ET to 1-Mⁿ⁺ due to the more positive shift in the one-electron reduction potentials of 1-Mⁿ⁺.^{21,22} The binding of metal ions to the

Scheme 4. Influence of Axial Ligand and Lewis Acid Metal Ion on the Basicity of the Oxo Ligand



one-electron reduced species of electron acceptors generally results in the large positive shift in the one-electron reduction potentials of electron acceptors. $^{\rm 8c,21,22,45,46}$

In the case of HAT reaction, however, the log k_{ox} values decrease as the Lewis acidity of the redox-inactive metal ions increases (green line in Figure 8). It has been reported previously that the basicity of the metal-oxo group determines the capability of high-valent metaloxo intermediates in abstracting H-atom from substrate C-H bonds. One notable example is the role of the thiolate ligand in Cytochrome P450 enzymes.⁴⁷ It has also been demonstrated in synthetic metaloxo complexes that the HAT reactivity of high-valent metal-oxo complexes increases as the axial ligand becomes a better electron donor (Scheme 4A).⁴⁸ In the present study, we have shown for the first time that the basicity of the metal-oxo group can be tuned by binding redox-inactive metal ions (Scheme 4B). For example, the Mn(IV)oxo group of **1**-Mⁿ⁺ binding Ca²⁺ (ΔE = 0.58 eV) is more basic than that binding Sc³⁺ (ΔE = 1.00 eV), resulted in showing a higher reactivity in the HAT reaction by $1-Ca^{2+}$ (green circles in Figure 8). In addition, based on the reactivity of 1-Mⁿ⁺ in the HAT reaction, we can predict that the basicity of the metal-oxo moiety for 1-Ca²⁺ is the highest and decreases in the order of $1-Ca^{2+} > 1-Mg^{2+} > 1-Zn^{2+} > 1$ - $Lu^{3+} > 1-Y^{3+} > 1-Al^{3+} > 1-Sc^{3+}$. Further investigation is underway to fully understand the redox-inactive metal ion effect on the basicity of metal-oxo moiety and the reactivity of metal-oxo species in HAT reactions.

EXPERIMENTAL SECTION

Materials. Commercially available chemicals were used without further purification unless otherwise indicated. 8-Aminoquinoline, bromoacetyl bromide, dipicolylamine, sodium carbonate, trifluromethanesulfonic acid, manganese powder, (diacetoxyiodo)benzene, sodium hydroxide, calcium triflate $(Ca(OTf)_2)$ $(OTf = SO_3CF_3)$, magnesium triflate $(Mg(OTf)_2)$, magnesium perchlorate $(Mg(ClO_4)_2)$, zinc triflate $(Zn(OTf)_2)$, scandium triflate $(Sc(OTf)_3)$, aluminium triflate $(Al(OTf)_3)$, yttrium triflate $(Y(OTf)_3)$, lutetium triflate $(Lu(OTf)_3)$ and acetonitrile were purchased from Aldrich chemical Co. 2,2-Diphenyl-1-picrylhydrazyl radical (DPPH[•]) was purchased from Wako Pure Chemicals (Osaka, Japan). H₂¹⁸O (95% ¹⁸O-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). Iodosylbenzene (PhIO)⁴⁹ and Mn^{II}(OTf)₂·2CH₃CN⁵⁰ were prepared by the literature method. The dpaq ligand (dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-Nquinolin-8-yl-acetamidate) was synthesized according to the previously reported methods.²⁹ PhI¹⁸O was prepared by the addition of $H_2^{18}O(140 \text{ mM}, 5 \mu\text{L})$ to the PhI¹⁶O (50 $\mu\text{L})$ in trifluoroethanol at 298 K and wait for 20 min for the exchange. Then use the PhI¹⁸O to synthesis the ¹⁸O-labeled **1**-Sc³⁺. The $[(dpaq)Mn^{III}(OH)](OTf)$ complex was synthesized by mixing the stoichiometric amounts of

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the dpaq ligand and $Mn(OTf)_2$ in an oxygen-saturated MeCN solution, followed by the addition of triethylamine.²⁹ The deuterated DHA- d_4 was synthesized by a literature method:⁵¹ DHA (0.50 g, 2.7 mmol) was reacted with NaH (0.20 g, 8.1 mmol) in DMSO- d_6 (3.0 mL) under an Ar atmosphere. The deep red solution was stirred at room temperature for 8 h and then quenched with D₂O (5.0 mL). The crude product was filtered and washed with copious amounts of distilled H₂O. Purity of >99% deuteration was confirmed by ¹H NMR.

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments or on a Hi-Tech Scientific (U.K.) SF-61 DX2 cryogenic stopped-flow spectrophotometer equipped with a Xe arc lamp and a KinetaScan diode array rapid scanning unit. The coldspray ionization time-of-flight mass (CSI-MS) spectral data were collected on a JMS-T100CS (JEOL) mass spectrometer equipped with the CSI source. Typical measurement conditions are as follows: Needle voltage, 2.2 kV; orifice 1 current, 50 - 500 nA; orifice 1 voltage, 0 to 20 V; ring lens voltage, 10 V; ion source temperature, 5°C; spray temperature, -40 °C. Electrospray ionization mass (ESI-MS) spectra were collected using Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 µL min⁻¹ using a syringe pump. The spray voltage was set at 4.7 kV while the capillary temperature was maintained at 80 °C. X-band EPR spectra were recorded at 5 K using X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperature was achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR measurements were as follows: microwave frequency = 9.647 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1×10^3 , modulation frequency = 100 kHz, time constant = 40.96 ms, and conversion time = 81.00 ms. EPR spectra were also recorded at 77 K with use of JEOL X-band spectrometer (JES-FA100). The spin amount of the bis-µ-oxo dimer produced in the reaction of [(dpaq)Mn^{III}(OH)]⁺ with PhIO in MeCN at 263 K was determined by the double integration of the EPR signal at 77 K, which was compared with that obtained from DPPH used as a reference. The gvalue was calibrated using the Mn²⁺ marker. The EPR spectra were recorded under non-saturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The experimental parameters for EPR measurements by JES-FA100 were as follows: microwave frequency = 9.028 GHz, microwave power = 1.0 mW, modulation amplitude = 3.0 G, modulation frequency = 100 kHz and time constant = 0.03 s. The product analyses were performed with an Agilent 6890N gas chromatograph (GC) and a FOCUS DSQ (dual-stage quadrupole) mass spectrometer (Thermo Finnigan, Austin, TX, USA) interfaced with a Finnigan FOCUS gas chromatograph (GC-MS). Product analysis of thioanisole oxidation was performed on High Performance Liquid Chromatography (HPLC, DIOMEX Pump Series P580) equipped with a variable wavelength UV-200 detector and Diacel OD-H column (4.6 mm × 25 cm). The fluorescence spectra were recorded using a four faced quartz cuvette (10 mm i.d.), which containing 10-methylacridone (AcrCO) with Al(OTf)₃ in deaerated MeCN at 298 K, was irradiated with monochromatic light of 430 nm from a Shimadzu RF-

5300PC fluorescence spectrophotometer with the excitation and emission slit widths are 2 nm.

Generation of $[(dpaq)Mn^{IV}(O)]^+-M^{n+}(OTf)_n$. $[(dpaq)Mn^{IV}(O)]^+-M^{n+}(OTf)_n$ (1- $M^{n+}; M^{n+} = Ca^{2+}, Mg^{2+}, Zn^{2+}, Lu^{3+}, Y^{3+}, Al^{3+}, and Sc^{3+})$ complexes were generated by adding iodosylbenzene (PhIO; 3 equiv dissolved in methanol/trifluoroethanol) into the solution of $[(dpaq)Mn^{II}(OH)]^+$ (0.50 mM) in the presence of $Ca(OTf)_2$ (200 mM), $Mg(OTf)_2$ (25 mM), $Zn(OTf)_2$ (5.0 mM), $Lu(OTf)_3$ (1.5 mM), $Y(OTf)_3$ (1.0 mM), $Al(OTf)_3$ (1.0 mM), and $Sc(OTf)_3$ (1.0 mM) in MeCN at 253 K, respectively. 1- M^{n+} species were also generated in the solvent mixture (i.e., MeCN/trifluoroethanol (v/v 1:1)). The characteristic peaks of 1- M^{n+} species were red-shifted as compared with those in MeCN (data are not shown).

XAS and EXAFS Measurements. X-ray absorption spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on bending magnet beamline 20 at electron energy 6 keV and average current of 100 mA. The radiation was monochromatized by a Si(110) crystal monochromator. The intensity of the X-rays was monitored by three ion chambers $(I_0, I_1, \text{ and } L)$ filled with 20% nitrogen and 80% helium and placed before the sample (I_0) and after the sample (I_1 and I_2). KMnO₄ powder was placed between I_1 and I_2 and its absorption was recorded with each scan for energy calibration. Plastic (Lexan) EXAFS sample holders (inner dimensions of 12 mm \times 2 mm \times 3 mm) filled with frozen solutions were inserted into a cryostat pre-cooled to 20 K. The samples were kept at 20 K in a He atmosphere at ambient pressure. Data were recorded as fluorescence excitation spectra using a 13-element energy-resolving detector. In order to reduce the risk of sample damage by X-ray defocused mode (beam size 1 × 2 mm) was used and no damage was observed. Shutter was synchronized with the scan software preventing exposure to X-rays in between scans and during spectrometer movements. Mn XAS energy was calibrated by the maximum of the pre-edge feature of the potassium permanganate powder XANES spectrum (6543.3 eV), which was placed between I_1 and L_2 ionization chambers. EXAFS scans with 5 eV steps in the pre-edge region (6437.67 - 6529.67 eV), 0.5 eV steps (6529.67 - 6637.67 eV) through the edge and 0.05 Å⁻¹ steps from k = 2.0 - 12 Å⁻¹ were used.

EXAFS Data Analysis. Athena software was used for data processing.⁵² Energy scale for each scan was normalized using potassium permanganate powder standard and scans for same samples were added. Data in energy space were pre-edge corrected, normalized, and background corrected. The processed data were converted to the photoelectron wave vector (k) space and weighted by k^3 . The electron wave number is defined as in eq 3,

$$k = \left[\left\{ 2m(E - E_0) \right\} / \eta^2 \right]^{1/2} \tag{3}$$

where E_0 is the threshold energy. *k*-space data were truncated near zero crossings and Fourier-transformed into *R*-space. Artemis software was used for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, or entire experimental spectrum was fitted. The individual Fourier peaks were isolated by applying a Hanning window. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8 program from the University of Washington. *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation (eq 4):⁵³

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{df_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda_j(k)}} \sin(2kR_j + \phi_{ij}(k))$$
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where N_j is the number of atoms in j^{th} shell; R_j is the distance between the absorbing atoms and the atoms in j^{th} shell; f_{effj} is the *ab initio* amplitude function for j, and $e^{-2\sigma_j^2 k^2}$ is Debye-Waller factor for shell j accounting for damping due to thermal and static disorder in the shell. The mean free path term ($e^{-2R_j/\lambda_j^2(k)}$) accounts for losses due to inelastic scattering. The oscillations in the EXAFS spectrum are reflected in the sin $(2kR_j + \varphi_{ij}(k))$ term, where $\varphi_{ij}(k)$ is the *ab initio* phase function for the shell j. So is an amplitude reduction factor. The EXAFS equation was used to fit experimental data using N, E_0 , R and σ^2 as variable parameters, while S_0 was kept fixed. The quality of fit was evaluated by R-factor: if R-factor is less than 2% then the fit is good enough. Reduced χ^2 was used to justify the addition of new absorberbackscatter shells.

Spectral Redox Titration for the ET Equilibrium Constant (K_{et}). Redox titration of ET from tri(4-bromophenyl)amine (TBPA) to 1-Sc³⁺ was examined with various concentrations of TBPA in MeCN at 253 K using a Hewlett Packard 8453 photodiode-array spectrometer with a quartz cuvette (path length = 1.0 cm). Typically, a deaerated MeCN solution of TBPA (0.00 – 0.12 mM) was added to a deaerated MeCN solution containing 1-Sc³⁺ (0.050 mM). The concentration of TBPA⁺⁺ was determined from the absorption band at λ = 705 nm (ε_1 = 3.2 × 10⁴ M⁻¹cm⁻¹), and 1-Sc³⁺ (ε_2 = 1.2 × 10³ M⁻¹cm⁻¹) using eq 5 derived from eq 6, where [1-Sc³⁺]₀ is the initial concentration of 1-Sc³⁺ and [1-Sc³⁺] = [1-Sc³⁺]₀ – [TBPA⁺⁺].

$$[TBPA^{+}] = (Abs_{705} - \varepsilon_2 [\mathbf{1} - Sc^{3+}]_0) / (\varepsilon_1 - \varepsilon_2)$$
(5)

$$Abs_{705} = \varepsilon_1 [TBPA^{++}] + \varepsilon_2 [1-Sc^{3+}]$$
(6)

The ε_1 value of TBPA⁺⁺ ($3.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) was confirmed by the standard authentic sample of tris(4-bromo-phenyl)ammoniumyl hexachloroantimonate, [(4-BrC₆H₄)₃N]-SbCl₆, in MeCN at 253 K. The expression used for determination of K_{et} was derived according to our previous work.⁵⁴ The equilibrium constant (K_{et}) in eq 1 is expressed by eq 7, from which eq 8 is derived,

$$K_{\text{et}} = [\text{TBPA}^{+}] [\text{Mn}^{\text{III}}(\text{O})\text{Sc}^{3+}] / [\text{TBPA}] [1-\text{Sc}^{3+}]$$
(7)

 $K_{\rm et}^{-1} = ([TBPA]_0 - [TBPA^{*+}])([1-Sc^{3+}]_0 - [TBPA^{*+}])/[TBPA^{*+}]^2$ $= ([TBPA]_0/[TBPA^{*+}] - 1) ([1-Sc^{3+}]_0/[(TBPA^{*+})] - 1)$ (8)

where $[Mn^{III}(O)Sc^{3+}] = [TBPA^{++}], [TBPA]_0 = [TBPA] + [TBPA^{++}],$ and $[\mathbf{1}-Sc^{3+}]_0 = [\mathbf{1}-Sc^{3+}] + [Mn^{III}(O)Sc^{3+}].$ $[\mathbf{1}-Sc^{3+}]_0$ and $[TBPA]_0$ are the initial concentrations of $[\mathbf{1}-Sc^{3+}]$, and [TBPA], respectively. Equation 9 is derived from eq 8, where $a = [TBPA^{++}]/[TBPA]_0$.

$$(a^{-1} - 1)^{-1} = K_{\text{et}} \left([1 - \text{Sc}^{3+}]_0 / a [\text{TBPA}]_0 - 1 \right)$$
(9)

The K_{et} value of 70 was determined from the slope of the linear plot between $(\alpha^{-1} - 1)^{-1}$ and $[1-\text{Sc}^{3+}]_0/\alpha$ [TBPA]₀ – 1 as shown in Figure 4c.

Kinetic Measurements. All the reactions were run in a 1-cm UV cuvette by monitoring UV-vis spectral changes of reaction solutions. First-order rate constants for the oxidation of substrates by $[(dpaq)Mn^{IV}(O)]^+$ - $M^{n+}(OTf)_n$ (1- M^{n+} ; $M^{n+} = Ca^{2+}$, Mg^{2+} , Zn^{2+} , Lu^{3+} , Y^{3+} , Al^{3+} , and Sc^{3+}) were determined under pseudo-first-order conditions (e.g., [substrate]/[1- M^{n+}] > 10) by fitting the decay of absorbance due to 1- M^{n+} in the ET, OAT and HAT reactions in MeCN at 253 K. The first-order plots were linear for three or more half-lives with the correlation coefficient of $\rho > 0.99$. In each case, it was confirmed that the rate constants derived from at least three independent measurements agreed within an experimental error of $\pm 10\%$. The pseudo-first-order rate constants increased proportionally with

the concentrations of substrates, from which second-order rate constants were determined.

Product Analysis. Products formed in the oxidation of thioanisole by $1-Sc^{3+}$ in MeCN at 253 K were analyzed by HPLC and GC-MS. Phenyl methyl sulfoxide was formed as a sole product in the oxidation of thioanisole by $1-Sc^{3+}$. Products formed in the oxidation of xanthene by $1-Sc^{3+}$ were analyzed by GC, and GC-MS. Quantitative analysis was performed by comparison against standard curves prepared with known authentic samples and using decane as an internal standard. In the reaction of $1-Sc^{3+}$ and xanthene, xanthone was obtained as sole product. The manganese products formed in the reaction of $1-Sc^{3+}$ with thioanisole and xanthene were analyzed by ESI-MS and EPR techniques. In both the reactions, Mn^{III} species were produced as a major product.

ASSOCIATED CONTENT

Supporting Information. Spectral and kinetic data (Figures S1 – S22) and EXAFS data (Tables S1 – S3) and kinetic data (Tables S4 and S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Askerka, M.; Brudvig, G. W.; Batista, V. S. The O₂-Evolving Complex of Photosystem II: Recent Insights from Quantum Mechanics/Molecular Mechanics (QM/MM), Extended X-Ray Absorption Fine Structure (EXAFS), and Femtosecond X-Ray Crystallography Data. *Acc. Chem. Res.* **2017**, *50*, 41. (b) Cox, N.; Pantazis, D. A.; Neese, F.; Lubitz, W. Biological Water Oxidation. *Acc. Chem. Res.* **2013**, *46*, 1588. (c) Shen, J.-R. The Structure of Photosystem II and the Mechanism of Water Oxidation in Photosynthesis. *Annu. Rev. Plant Biol.* **2015**, *66*, 23.

(2) (a) Suga, M.; Akita, F.; Sugahara, M.; Kubo, M.; Nakajima, Y.; Nakane, T.; Yamashita, K.; Umena, Y.; Nakabayashi, M.; Yamane, T.; Nakano, T.; Suzuki, M.; Masuda, T.; Inoue, S.; Kimura, T.; Nomura, T.; Yonekura, S.; Yu, L.-J.; Sakamoto, T.; Motomura, T.; Chen, J.-H.; Kato, Y.; Noguchi, T.; Tono, K.; Joti, Y.; Kameshima, T.; Hatsui, T.; Nango, E.; Tanaka, R.; Naitow, H.; Matsuura, Y.; Yamashita, A.; Yamamoto, M.; Nureki, O.; Yabashi, M.; Ishi-kawa, T.; Iwata, S.; Shen, J.-R. Light-Induced Structural Changes and the Site of O=O Bond Formation in PSII Caught by XFEL. *Nature* **2017**, *543*, 131. (b) Suga, M.; Akita, F.; Hirata, K.; Ueno, G.; Murakami, H.; Nakajima, Y.; Shimizu, T.; Yamashita, K.; Yamamoto, M.; Ago, H.; Shen, J.-R. Native Structure of Photosystem II at 1.95 Å Resolution Viewed by Femtosecond X-Ray Pulses. *Nature* **2015**, *517*, 99. (c) Umena, Y.; Kawakami, K.; Shen, J.-

R.; Kamiya, N. Crystal Structure of Oxygen-Evolving Photosystem II at a Resolution of 1.9 Å. Nature 2011, 473, 55.

(3) Young, I. D.; Ibrahim, M.; Chatterjee, R.; Gul, S.; Fuller, F. D.; Koroidov, S.; Brewster, A. S.; Tran, R.; Alonso-Mori, R.; Kroll, T.; Michels-Clark, T.; Laksmono, H.; Sierra, R. G.; Stan, C. A.; Hussein, R.; Zhang, M.; Douthit, L.; Kubin, M.; de Lichtenberg, C.; Vo Pham, L.; Nilsson, H.; Cheah, M. H.; Shevela, D.; Saracini, C.; Bean, M. A.; Seuffert, I.; Sokaras, D.; Weng, T-C.; Pastor, E.; Weninger, C.; Fransson, T.; Lassalle, L.; Bräuer, P.; Aller, P.; Docker, P. T.; Andi, B.; Orville, A. M.; Glownia, J. M.; Nelson, S.; Sikorski, M.; Zhu, D.; Hunter, M. S.; Lane, T. J.; Aquila, A.; Koglin, J. E.; Robinson, J.; Liang, M.; Boutet, S.; Lyubimov, A.Y.; Uervirojnangkoorn, M.; Moriarty, N. W.; Liebschner, D.; Afonine, P. V.; Waterman, D. G.; Evans, G.; Wernet, P.; 10 Dobbek, H.; Weis, W. I.; Brunger, A. T.; Zwart, P. H.; Adams, P. D.; Zouni, 11 A.; Messinger, J.; Bergmann, U.; Sauter, N. K.; Kern, J.; Yachandra, V. K.; 12 Yano, J. Structure of Photosystem II and Substrate Binding at Room Temperature. Nature 2016, 540, 453.

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2

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4

5

6

7

8

9

58 59

60

13 (4) (a) Zhang, C.; Chen, C.; Dong, H.; Shen, J.-R.; Dau, H.; Zhao, J. A 14 Synthetic Mn₄Ca-Cluster Mimicking the Oxygen-Evolving Center of Pho-15 tosynthesis. Science 2015, 348, 690. (b) Sun, L. A Closer Mimic of the Ox-16 ygen Evolution Complex of Photosystem II. Science 2015, 348, 635.

17 (5) (a) Yano, J.; Yachandra, V. Mn₄Ca Cluster in Photosynthesis: Where 18 and How Water is Oxidized to Dioxygen. Chem. Rev. 2014, 114, 4175. (b) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. Molecular Catalysts for 19 Water Oxidation. Chem. Rev. 2015, 115, 12974. (c) Young, K. J.; Brennan, 20 B. J.; Tagore, R.; Brudvig, G. W. Photosynthetic Water Oxidation: Insights 21 from Manganese Model Chemistry. Acc. Chem. Res. 2015, 48, 567. (d) 22 Najafpour, M. M.; Renger, G.; Hołyńska, M.; Moghaddam, A. N.; Aro, E.-23 M.; Carpentier, R.; Nishihara, H.; Eaton-Rye, J. J.; Shen, J.-R.; Allakhverdiev, 24 S. I. Manganese Compounds as Water-Oxidizing Catalysts: from the Natural Water-Oxidizing Complex to Nanosized Manganese Oxide Structures. 25 Chem. Rev. 2016, 116, 2886. (e) Davis, K. M.; Pushkar, Y. N. Structure of 26 the Oxygen Evolving Complex of Photosystem II at Room Temperature. J. 27 Phys. Chem. B2015, 119, 3492.

28 (6) (a) Najafpour, M. M.; Heidari, S.; Balaghi, S. E.; Hołyńska, M.; Sadr, 29 M. H.; Soltani, B.; Khatamian, M.; Larkum, A. W.; Allakhverdiev, S. I. Proposed Mechanisms for Water Oxidation by Photosystem II and Nanosized 30 Manganese Oxides. Biochim. Biophys. Acta 2017, 1858, 156. (b) Yamaguchi, 31 K.; Shoji, M.; Isobe, H.; Yamanaka, S.; Kawakami, T.; Yamada, S.; Katouda, 32 M.; Nakajima, T. Theory of Chemical Bonds in Metalloenzymes XXI. Pos-33 sible Mechanisms of Water Oxidation in Oxygen Evolving Complex of Pho-34 tosystem II. Mol. Phys. 2018, 116, 717. (c) Chen, C.; Li, Y.; Zhao, G.; Yao, 35 R.; Zhang, C. Natural and Artificial Mn₄Ca Cluster for the Water Splitting Reaction. ChemSusChem 2017, 10, 4403. (d) Pushkar, Y. N.; Yano, J.; Sauer, 36 K.; Boussac, A.; Yachandra, V. K. Structural Changes in the Mn₄Ca Cluster 37 and the Mechanism of Photosynthetic Water Splitting. Proc. Natl. Acad. Sci. 38 USA 2008, 105, 1879. (e) Pushkar, Y. N.; Davis, K. M.; Palenik, M. Model 39 of the Oxygen Evolving Complex Which is Highly Predisposed to O-O Bond 40 Formation. J. Phys. Chem. Lett. 2018, 9, 3525.

(7) (a) Kanady, J. S.; Tsui, E. Y.; Day, M. W.; Agapie, T. A Synthetic Model 41 of the Mn₃Ca Subsite of the Oxygen-Evolving Complex in Photosystem II. 42 Science 2011, 333, 733. (b) Tsui, E. Y.; Kanady, J. S.; Agapie, T. Synthetic 43 Cluster Models of Biological and Heterogeneous Manganese Catalysts for 44 O2 Evolution. Inorg. Chem. 2013, 52, 13833. (c) Tsui, E. Y.; Tran, R.; Yano, 45 J.; Agapie, T. Redox-Inactive Metals Modulate the Reduction Potential in 46 Heterometallic Manganese-Oxido Clusters. Nat. Chem. 2013, 5, 293.

47 (8) (a) Bang, S.; Lee, Y.-M.; Hong, S.; Cho, K.-B.; Nishida, Y.; Seo, M. S.; Sarangi, R.; Fukuzumi, S.; Nam, W. Redox-Inactive Metal Ions Modulate 48 the Reactivity and Oxygen Release of Mononuclear Non-Haem Iron(III)-49 Peroxo Complexes. Nat. Chem. 2014, 6, 934. (b) Lionetti, D.; Agapie, T. 50 How Calcium Affects Oxygen Formation. Nature 2014, 513, 495. (c) Bae, S. 51 H.; Lee, Y.-M.; Fukuzumi, S.; Nam, W. Fine Control of the Redox Reactivity 52 of a Nonheme Iron(III)-Peroxo Complex by Binding Redox-Inactive Metal Ions. Angew. Chem., Int. Ed. 2017, 56, 801. 53

(9) (a) Engelmann, X.; Monte-Pérez, I.; Ray, K. Oxidation Reactions with 54 Bioinspired Mononuclear Non-Heme Metal-Oxo Complexes. Angew. 55 Chem., Int. Ed. 2016, 55, 7632. (b) Ray, K.; Heims, F.; Schwalbe, M.; Nam, 56 W. High-Valent Metal-Oxo Intermediates in Energy Demanding Processes: 57 From Dioxygen Reduction to Water Splitting. Curr. Opin. Chem. Biol. 2015,

25, 159. (c) Ray, K.; Pfaff, F. F.; Wang, B.; Nam, W. Status of Reactive Non-Heme Metal-Oxygen Intermediates in Chemical and Enzymatic Reactions. J. Am. Chem. Soc. 2014, 136, 13942.

(10) (a) Kal, S.; Que, L., Jr. Dioxygen Activation by Nonheme Iron Enzymes with the 2-His-1-carboxylate Facial Triad That Generate High-Valent Oxoiron Oxidants. J. Biol. Inorg. Chem. 2017, 22, 339. (b) Puri, M.; Que, L., Jr. Toward the Synthesis of More Reactive S = 2 Non-Heme Oxoiron(IV) Complexes. Acc. Chem. Res. 2015, 48, 2443. (c) McDonald, A. R.; Que, L. Jr. High-Valent Nonheme Iron-Oxo Complexes: Synthesis, Structure, and Spectroscopy. Coord. Chem. Rev. 2013, 257, 414.

(11) (a) Chen, Z.; Yin, G. The Reactivity of the Active Metal Oxo and Hydroxo Intermediates and Their Implications in Oxidations. Chem. Soc. Rev. 2015, 44, 1083. (b) Yin, G. Understanding the Oxidative Relationships of the Metal Oxo, Hydroxo, and Hydroperoxide Intermediates with Manganese(IV) Complexes Having Bridged Cyclams: Correlation of the Physicochemical Properties with Reactivity. Acc. Chem. Res. 2013, 46, 483.

(12) Collins, T. J.; Ryabov, A. D. Targeting of High-Valent Iron-TAML Activators at Hydrocarbons and Beyond. Chem. Rev. 2017, 117, 9140.

(13) (a) Baglia, R. A.; Zaragoza, J. P. T.; Goldberg, D. P. Biomimetic Reactivity of Oxygen-Derived Manganese and Iron Porphyrinoid Complexes. Chem. Rev. 2017, 117, 13320. (b) Sahu, S.; Goldberg, D. P. Activation of Dioxygen by Iron and Manganese Complexes: A Heme and NonHeme Perspective. J. Am. Chem. Soc. 2016, 138, 11410. (c) Neu, H. M.; Baglia, R. A.; Goldberg, D. P. A Balancing Act: Stability Versus Reactivity of Mn(O) Complexes. Acc. Chem. Res. 2015, 48, 2754.

(14) (a) Sankaralingam, M.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. Amphoteric Reactivity of Metal-Oxygen Complexes in Oxidation Reactions. Coord. Chem. Rev. 2018, 365, 41. (b) Hong, S.; Lee, Y.-M.; Ray, K.; Nam, W. Dioxygen Activation Chemistry by Synthetic Mononuclear Nonheme Iron, Copper and Chromium Complexes. Coord. Chem. Rev. 2017, 334, 25. (c) Fukuzumi, S.; Kojima, T.; Lee, Y.-M.; Nam, W. High-Valent Metal-Oxo Complexes Generated in Catalytic Oxidation Reactions Using Water as an Oxygen Source. Coord. Chem. Rev. 2017, 333, 44.

(15) Nam, W. Synthetic Mononuclear Nonheme Iron-Oxygen Intermediates. Acc. Chem. Res. 2015, 48, 2415.

(16) (a) Cook, S. A.; Borovik, A. S. Molecular Designs for Controlling the Local Environments Around Metal Ions. Acc. Chem. Res. 2015, 48, 2407. (b) Cook, S. A.; Hill, E. A.; Borovik, A. S. Lessons from Nature: A Bio-Inspired Approach to Molecular Design. Biochemistry 2015, 54, 4167.

(17) (a) Garrido-Barros, P.; Gimbert-Suriñach, C.; Matheu, R.; Sala, X.; Llobet, A. How to Make an Efficient and Robust Molecular Catalyst for Water Oxidation. Chem. Soc. Rev. 2017, 46, 6088. (b) Sala, X.; Maji, S.; Bofill, R.; García-Antón, J.; Escriche, L.; Llobet, A. Molecular Water Oxidation Mechanisms Followed by Transition Metals: State of the Art. Acc. Chem. Res. 2014, 47, 504.

(18) (a) Ishizuka, T.; Kotani, H.; Kojima, T. Characteristics and Reactivity of Ruthenium-Oxo Complexes. Dalton Trans. 2016, 45, 16727. (b) Ishizuka, T.; Ohzu, S.; Kojima, T. Oxidation of Organic Substrates with Ru^{IV}=O Complexes Formed by Proton-Coupled Electron Transfer. Synlett 2014, 25, 1667.

(19) Lebedev, D.; Pineda-Galvan, Y.; Tokimaru, Y.; Fedorov, A.; Kaeffer, N.; Copéret, C.; Pushkar, Y. The Key Ru^V=O Intermediate of Site-Isolated Mononuclear Water Oxidation Catalyst Detected by In Situ X-Ray Absorption Spectroscopy. J. Am. Chem. Soc. 2018, 140, 451.

(20) (a) Pfaff, F. F.; Kundu, S.; Risch, M.; Pandian, S.; Heims, F.; Pryjomska-Ray, I.; Haack, P.; Metzinger, R.; Bill, E.; Dau, H.; Comba, P.; Ray, K. An Oxocobalt(IV) Complex Stabilized by Lewis Acid Interactions with Scandium(III) Ions. Angew. Chem., Int. Ed. 2011, 50, 1711. (b) Hong, S.; Pfaff, F. F.; Kwon, E.; Wang, Y.; Seo, M. S.; Bill, E.; Ray, K.; Nam, W. Spectroscopic Capture and Reactivity of a Low-Spin Cobalt(IV)-Oxo Complex Stabilized by Binding Redox-Inactive Metal Ions. Angew. Chem., Int. Ed. 2014, 53, 10403. (c) Wang, B.; Lee, Y.-M.; Tcho, W.-Y.; Tussupbayev, S.; Kim, S.-T.; Kim, Y.; Seo, M. S.; Cho, K.-B.; Dede, Y.; Keegan, B. C.; Ogura, T.; Kim, S. H.; Ohta, T.; Baik, M.-H.; Ray, K.; Shearer, J.; Nam, W. Synthesis and Reactivity of a Mononuclear Non-Haem Cobalt(IV)-Oxo Complex. Nat. Commun. 2017, 8, 14839.

59

60

(21) Nam, W.; Lee, Y.-M.; Fukuzumi, S. Tuning Reactivity and Mechanism in Oxidation Reactions by Mononuclear Nonheme Iron(IV)-Oxo Complexes. Acc. Chem. Res. 2014, 47, 1146.

2 (22) (a) Fukuzumi, S.; Ohkubo, K.; Lee, Y.-M.; Nam, W. Lewis Acid Cou-

3 pled Electron Transfer of Metal-Oxygen Intermediates. Chem.-Eur. J. 2015, 4

21, 17548. (b) Fukuzumi, S. Electron Transfer and Catalysis with High-Va-

5 lent Metal-Oxo Complexes. Dalton Trans. 2015, 44, 6696. (c) Fukuzumi, S.;

6 Ohkubo, K.; Morimoto, Y. Mechanisms of Metal Ion-Coupled Electron Transfer. Phys. Chem. Chem. Phys. 2012, 14, 8472. 7

(23) (a) Fukuzumi, S.; Morimoto, Y.; Kotani, H.; Naumov, P.; Lee, Y.-M.; 8 Nam, W. Crystal Structure of a Metal Ion-Bound Oxoiron(IV) Complex 9 and Implications for Biological Electron Transfer. Nat. Chem. 2010, 2, 756. 10 (b) Swart, M. A Change in the Oxidation State of Iron: Scandium Is Not 11 Innocent. Chem. Commun. 2013, 49, 6650. (c) Prakash, J.; Rohde, G. T.; 12 Meier, K. K.; Jasniewski, A. J.; Van Heuvelen, K. M.; Münck, E.; Que, L. Jr. Spectroscopic Identification of an Fe^{III} Center, Not Fe^{IV}, in the Crystalline 13 Sc-O-Fe Adduct Derived from [Fe^{IV}(O)(TMC)]²⁺. J. Am. Chem. Soc. 2015, 14 *137*, 3478.

15 (24) (a) Park, J.; Morimoto, Y.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. Metal 16 Ion Effect on the Switch of Mechanism from Direct Oxygen Transfer to 17 Metal Ion-Coupled Electron Transfer in the Sulfoxidation of Thioanisoles by a Non-Heme Iron(IV)-Oxo Complex. J. Am. Chem. Soc. 2011, 133, 5236. 18 (b) Park, J.; Morimoto, Y.; Lee, Y.-M.; You, Y.; Nam, W.; Fukuzumi, S. Scan-19 dium Ion-Enhanced Oxidative Dimerization and N-Demethylation of N,N-20 Dimethylanilines by a Non-Heme Iron(IV)-Oxo Complex. Inorg. Chem. 21 2011, 50, 11612. (c) Park, J.; Morimoto, Y.; Lee, Y.-M.; Nam, W.; Fukuzumi, 22 S. Proton-Promoted Oxygen Atom Transfer vs Proton-Coupled Electron 23 Transfer of a Non-Heme Iron(IV)-Oxo Complex. J. Am. Chem. Soc. 2012, 134, 3903. (d) Morimoto Y.; Park, J.; Suenobu, T.; Lee, Y.-M.; Nam, W.; 24 Fukuzumi, S. Mechanistic Borderline of One-Step Hydrogen Atom Trans-25 fer Versus Stepwise Sc3+-Coupled Electron Transfer from Benzyl Alcohol 26 Derivatives to a Non-Heme Iron(IV)-Oxo Complex. Inorg. Chem. 2012, 51, 27 10025. (e) Park, J.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. Brønsted Acid-Pro-28 moted C-H Bond Cleavage via Electron Transfer from Toluene Derivatives 29 to a Protonated Nonheme Iron(IV)-Oxo Complex with No Kinetic Isotope Effect. J. Am. Chem. Soc. 2013, 135, 5052. (f) Park, J.; Morimoto, Y.; Lee, 30 Y.-M.; Nam, W.; Fukuzumi, S. Unified View of Oxidative C-H Bond Cleav-31 age and Sulfoxidation by a Nonheme Iron(IV)-Oxo Complex via Lewis 32 Acid-Promoted Electron Transfer. Inorg. Chem. 2014, 53, 3618.

33 (25) Morimoto, Y.; Kotani, H.; Park, J.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. 34 Metal Ion-Coupled Electron Transfer of a Nonheme Oxoiron(IV) Complex: 35 Remarkable Enhancement of Electron-Transfer Rates by Sc3+. J. Am. Chem. Soc. 2011, 133, 403. 36

(26) (a) Chen, J.; Lee, Y.-M.; Davis, K. M.; Wu, X.; Seo, M. S.; Cho, K.-B.; 37 Yoon, H.; Park, Y. J.; Fukuzumi, S.; Pushkar, Y. N.; Nam, W. A Mononuclear 38 Non-Heme Manganese(IV)-Oxo Complex Binding Redox-Inactive Metal 39 Ions. J. Am. Chem. Soc. 2013, 135, 6388. (b) Yoon, H.; Lee, Y.-M.; Wu, X.; 40 Cho, K.-B.; Sarangi, R.; Nam, W.; Fukuzumi S.; Enhanced Electron-Transfer Reactivity of Nonheme Manganese(IV)-Oxo Complexes by Binding Scan-41 dium Ions. J. Am. Chem. Soc. 2013, 135, 9186. 42

(27) (a) Leeladee, P.; Baglia, R. A.; Prokop, K. A.; Ltifi, R.; de Visser, S. P.; 43 Goldberg, D. P. Valence Tautomerism in a High-Valent Manganese-Oxo 44 Porphyrinoid Complex Induced by a Lewis Acid. J. Am. Chem. Soc. 2012, 45 134, 10397. (b) Baglia, R. A.; Krest, C. M.; Yang, T.; Leeladee, P.; Goldberg, 46 D. P. High-Valent Manganese-Oxo Valence Tautomers and The Influence of Lewis/Brönsted Acids on C-H Bond Cleavage. Inorg. Chem. 2016, 55, 47 10800. 48

(28) (a) Chen, Z.; Yang, L.; Choe, C.; Lv, Z.; Yin, G. Non-Redox Metal Ion 49 Promoted Oxygen Transfer by a Non-Heme Manganese Catalyst. Chem. 50 Commun. 2015, 51, 1874. (b) Zhang, J.; Wei, W.-J.; Lu, X.; Yang, H.; Chen, 51 Z.; Liao, R.-Z.; Yin, G. Nonredox Metal Ions Promoted Olefin Epoxidation 52 by Iron(II) Complexes with H2O2: DFT Calculations Reveal Multiple Channels for Oxygen Transfer. Inorg. Chem. 2017, 56, 15138. (c) 53 Nodzewska, A.; Watkinson, M. Remarkable Increase in the Rate of the Cat-54 alytic Epoxidation of Electron Deficient Styrenes Through the Addition of 55 Sc(OTf)₃ to the MnTMTACN Catalyst. Chem. Commun. 2018, 54, 1461. 56 (d) Ho, C.-M.; Lau, T.-C. Lewis Acid Activated Oxidation of Alkanes by 57 Barium Ferrate. New J. Chem. 2000, 24, 587. 58

(29) (a) Sankaralingam, M.; Jeon, S. H.; Lee, Y.-M.; Seo, M. S.; Ohkubo, K.; Fukuzumi, S.; Nam, W. An Amphoteric Reactivity of a Mixed-Valent Bis(µoxo)dimanganese(III,IV) Complex Acting as an Electrophile and a Nucleophile. Dalton Trans. 2016, 45, 376. (b) Sankaralingam, M.; Lee, Y.-M.; Karmalkar, D. G.; Nam, W.; Fukuzumi, S. A Mononuclear Non-Heme Manganese(III)-Aqua Complex as a New Active Oxidant in Hydrogen Atom Transfer Reactions. J. Am. Chem. Soc. 2018, 140, 12695.

(30) (a) Wijeratne, G. B.; Corzine, B.; Day, V. W.; Jackson, T. A. Saturation Kinetics in Phenolic O-H Bond Oxidation by a Mononuclear Mn(III)-OH Complex Derived from Dioxygen. Inorg. Chem. 2014, 53, 7622. (b) Rice, D. B.; Jones, S. D.; Douglas, J. T.; Jackson, T. A. NMR Studies of a Mn^{III}-Hydroxo Adduct Reveal an Equilibrium Between Mn^{III}-Hydroxo and µ-Oxodimanganese(III,III) Species. Inorg. Chem. 2018, 57, 7825.

(31) (a) Yin, G.; McCormick, J. M.; Buchalova, M.; Danby, A. M.; Rodgers, K.; Day, V. W.; Smith, K.; Perkins, C. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. Synthesis, Characterization, and Solution Properties of a Novel Cross-Bridged Cyclam Manganese(IV) Complex Having Two Terminal Hydroxo Ligands. Inorg. Chem. 2006, 45, 8052. (b) Wu, X.; Seo, M. S.; Davis, K. M.; Lee, Y.-M.; Chen, J.; Cho, K.-B.; Pushkar, Y. N.; Nam, W. A Highly Reactive Mononuclear Non-Heme Manganese(IV)-Oxo Complex That Can Activate the Strong C-H Bonds of Alkanes. J. Am. Chem. Soc. 2011, 133, 20088. (c) Sawant, S. C.; Wu, X.; Cho, J.; Cho, K.-B.; Kim, S. H.; Seo, M. S.; Lee, Y.-M.; Kubo, M.; Ogura, T.; Shaik, S.; Nam, W. Water as an Oxygen Source: Synthesis, Characterization, and Reactivity Studies of a Mononuclear Nonheme Manganese(IV) Oxo Complex. Angew. Chem., Int. Ed. 2010, 49, 8190.

(32) Hong, S.; Lee, Y.-M.; Sankaralingam, M.; Vardhaman, A. K.; Park, Y. J.; Cho, K.-B.; Ogura, T.; Sarangi, R.; Fukuzumi, S.; Nam, W. A Manganese(V)-Oxo Complex: Synthesis by Dioxygen Activation and Enhancement of Its Oxidizing Power by Binding Scandium Ion. J. Am. Chem. Soc. 2016, 138, 8523.

(33) (a) Cias, P.; Slugovc, C.; Gescheidt, G. Hole Transport in Triphenylamine Based OLED Devices: From Theoretical Modeling to Properties Prediction. J. Phys. Chem. A 2011, 115, 14519. (b) Yurchenko, O.; Freytag, D.; zur Borg, L.; Zentel, R.; Heinze, J.; Ludwigs, S. Electrochemically Induced Reversible and Irreversible Coupling of Triarylamines. J. Phys. Chem. B 2012, 116, 30.

(34) The reported values vs NHE were converted to those vs SCE by subtracting 0.24 V; see: Fukuzumi, S.; Wong, C. L.; Kochi, J. K. Unified View of Marcus Electron Transfer and Mulliken Charge Transfer Theories in Organometallic Chemistry. Steric Effects in Alkylmetals as Quantitative Probes for Outer-Sphere and Inner-Sphere Mechanisms. J. Am. Chem. Soc. 1980, 102, 2928.

(35) (a) Amthor, S.; Noller, B.; Lambert, C. UV/Vis/NIR Spectral Properties of Triarylamines and Their Corresponding Radical Cations. Chem. Phys. 2005, 316, 141. (b) Vardhaman, A. K.; Lee, Y.-M.; Jung, J.; Ohkubo, K.; Nam, W.; S. Fukuzumi, Enhanced Electron Transfer Reactivity of a Nonheme Iron(IV)-Imido Complex as Compared to the Iron(IV)-Oxo Analogue. Angew. Chem., Int. Ed. 2016, 55, 3709.

(36) (a) Lee, Y.-M.; Kotani, H.; Suenobu, T.; Nam, W.; Fukuzumi, S. Fundamental Electron-Transfer Properties of Non-Heme Oxoiron(IV) Complexes. J. Am. Chem. Soc. 2008, 130, 434. (b) Fukuzumi, S. Electron-transfer Properties of High-Valent Metal-Oxo Complexes. Coord. Chem. Rev. 2013, 257, 1564.

(37) Sharma, N.; Jung, J.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. Multi-Electron Oxidation of Anthracene Derivatives by Nonheme Manganese(IV)-Oxo Complexes, Chem.-Eur. J. 2017, 23, 7125.

(38) Lee, Y.-M.; Bang, S.; Kim, Y. M.; Cho, J.; Hong, S.; Nomura, T.; Ogura, T.; Troeppner, O.; Ivanović-Burmazović, I.; Sarangi, R.; Fukuzumi, S.; Nam, W. A Mononuclear Nonheme Iron(III)-Peroxo Complex Binding Redox-Inactive Metal Ions. Chem. Sci. 2013, 4, 3917.

(39) (a) Marcus, R. A. Chemical and Electrochemical Electron-Transfer Theory. Annu. Rev. Phys. Chem. 1964, 15, 155. (b) Marcus, R. A. Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture). Angew. Chem., Int. Ed. Engl. 1993, 32, 1111.

(40) Balakumar, S.; Thanasekaran, P.; Rajagopal, S.; Ramaraj, R. Electron Transfer Reactions of Iron (III) - Polypyridyl Complexes with Organic Sulphides. Tetrahedron 1995, 51, 4801.

(41) Luo, Y.-R. *Handbook of bond dissociation energies in organic compounds*; CRC Press: New York, 2002.

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- (42) (a) Fukuzumi, S. Roles of Metal Ions in Controlling Bioinspired Electron-Transfer Systems. Metal Ion-Coupled Electron Transfer. Prog. Inorg. Chem. 2009, 56, 49. (b) Fukuzumi, S.; Ohkubo, K. Metal Ion-Coupled and Decoupled Electron Transfer. Coord. Chem. Rev. 2010, 254, 372. (c) Fukuzumi, S.; Patz, M.; Suenobu, T.; Kuwahara, Y.; Itoh, S. ESR Spectra of Superoxide Anion-Scandium Complexes Detectable in Fluid Solution. J. Am. Chem. Soc. 1999, 121, 1065.(d) Fukuzumi, S.; Ohkubo, K. Quantitative Evaluation of Lewis Acidity of the Metal Ions Derived from the g Values of ESR Spectra of Superoxide: Metal Ion Complexes in Relation to the Promoting Effects in Electron Transfer Reactions. Chem.-Eur. J. 2000, 6, 4532. (e) Ohkubo, K.; Menon, S. C.; Orita, A.; Otera, J.; Fukuzumi, S. Quantitative Evaluation of Lewis Acidity of Metal Ions with Different Ligands and Counterions in Relation to the Promoting Effects of Lewis Acids on Electron Transfer Reduction of Oxygen. J. Org. Chem. 2003, 68, 4720. (f) Fukuzumi, S.; Ohkubo, K. Fluorescence Maxima of 10-Methylacridone-Metal Ion Salt Complexes: A Convenient and Quantitative Measure of Lewis Acidity of Metal Ion Salts. J. Am. Chem. Soc. 2002, 124, 10270.
- (43) Zdilla, M. J.; Dexheimer, J. L.; Abu-Omar, M. M. Hydrogen Atom
 Transfer Reactions of Imido Manganese(V) Corrole: One Reaction with
 Two Mechanistic Pathways. *J. Am. Chem. Soc.* 2007, *129*, 11505.
- (44) (a) Osako, T.; Ohkubo, K.; Taki, M.; Tachi, Y.; Fukuzumi, S.; Itoh, S. 19 Oxidation Mechanism of Phenols by Dicopper-Dioxygen (Cu₂/O₂) Com-20 plexes. J. Am. Chem. Soc. 2003, 125, 11027. (b) Lee, J. Y.; Peterson, R. L.; 21 Ohkubo, K.; Garcia-Bosch, I.; Himes, R. A.; Woertink, J.; Moore, C. D.; Sol-22 omon, E. I.; Fukuzumi, S.; Karlin, K. D. Mechanistic Insights into the Oxida-23 tion of Substituted Phenols via Hydrogen Atom Abstraction by a Cupric-24 Superoxo Complex. J. Am. Chem. Soc. 2014, 136, 9925. (c) Wang, Y.; Sheng, J.; Shi, S.; Zhu, D.; Yin, G. Influence of the Net Charge on the Reactivity of 25 a Manganese(IV) Species: Leading to the Correlation of Its Physicochemi-26 cal Properties with Reactivity. J. Phys. Chem. C2012, 116, 13231. (d) Parsell, 27 T. H.; Yang, M.-Y.; Borovik, A. S. C-H Bond Cleavage with Reductants: Re-28 Investigating the Reactivity of Monomeric Mn^{III/IV}-Oxo Complexes and the 29 Role of Oxo Ligand Basicity. J. Am. Chem. Soc. 2009, 131, 2762. (45) (a) Kuss-Petermann, M.; Wenger, O. S. Exceptionally Long-Lived 30
- Photodriven Multi-Electron Storage Without Sacrificial Reagents. *Chem.- Eur. J.* 2017, 23, 10808. (b) Bonn, A. G.; Wenger, O. S. Photoinduced
 Charge Accumulation by Metal Ion-Coupled Electron Transfer. *Phys. Chem. Chem. Phys.* 2015, 17, 24001.

(46) Yuasa, J.; Suenobu, T.; Fukuzumi, S. Binding Modes in Metal Ion
Complexes of Quinones and Semiquinone Radical Anions: Electron-Transfer Reactivity. *ChemPhysChem* 2006, *7*, 942.

(47) (a) Green, M. T.; Dawson, J. H.; Gray, H. B. Oxoiron(IV) in Chloroperoxidase Compound II is Basic: Implications for P450 Chemistry. *Science* 2004, *304*, 1653. (b) Yosca, T. H.; Rittle, J.; Krest, C. M.; Onderko, E. L.; Silakov, A.; Calixto, J. C.; Behan, R. K.; Green, M. T. Iron(IV)Hydroxide pK_a and the Role of Thiolate Ligation in C-H Bond Activation by Cytochrome P450. *Science* 2013, *342*, 825. (c) Krest, C. M.; Silakov, A.; Rittle, J.;
Yosca, T. H.; Onderko, E. L.; Calixto, J. C.; Green, M. T. Significantly

Shorter Fe–S Bond in Cytochrome P450-I is Consistent with Greater Reactivity Relative to Chloroperoxidase. *Nat. Chem.* **2015**, *7*, 696. (d) Onderko, E. L.; Silakov, A.; Yosca, T. H.; Green, M. T. Characterization of a Selenocysteine-Ligated P450 Compound I Reveals Direct Link Between Electron Donation and Reactivity. *Nat. Chem.* **2017**, *9*, 623. (e) Yosca, T. H.; Ledray, A. P.; Ngo, J.; Green, M. T. A New Look at the Role of Thiolate Ligation in Cytochrome P450. *J. Biol. Inorg. Chem.* **2017**, *22*, 209.

(48) (a) Sastri, C. V.; Lee, J.; Oh, K.; Lee, Y. J.; Lee, J.; Jackson, T. A.; Ray, K.; Hirao, H.; Shin, W.; Halfen, J. A.; Kim, J.; Que, L. Jr.; Shaik, S.; Nam, W. Axial Ligand Tuning of a Nonheme Iron(IV)-Oxo Unit for Hydrogen Atom Abstraction. Proc. Natl. Acad. Sci. USA 2007, 104, 19181. (b) Fukuzumi, S.; Kotani, H.; Suenobu, T.; Hong, S.; Lee, Y.-M.; Nam, W. Contrasting Effects of Axial Ligands on Electron-Transfer Versus Proton-Coupled Electron-Transfer Reactions of Nonheme Oxoiron(IV) Complexes. Chem.-Eur. J. 2010, 16, 354. (c) Borovik, A. S. Role of Metal-Oxo Complexes in the Cleavage of C-H Bonds. Chem. Soc. Rev. 2011, 40, 1870. (d) Usharani, D.; Lacy, D. C.; Borovik, A. S.; Shaik, S. Dichotomous Hydrogen Atom Transfer vs Proton-Coupled Electron Transfer During Activation of X-H Bonds (X = C, N, O) by Nonheme Iron-Oxo Complexes of Variable Basicity. J. Am. Chem. Soc. 2013, 135, 17090. (e) Mandal, D.; Ramanan, R.; Usharani, D.; Janardanan, D.; Wang, B.; Shaik, S. How Does Tunneling Contribute to Counterintuitive H-Abstraction Reactivity of Nonheme Fe(IV)O Oxidants with Alkanes? J. Am. Chem. Soc. 2015, 137, 722. (f) Baglia, R. A.; Prokop-Prigge, K. A.; Neu, H. M.; Siegler, M. A.; Goldberg, D. A. Mn(V)(O) Versus Cr(V)(O) Porphyrinoid Complexes: Structural Characterization and Implications for Basicity Controlling H-Atom Abstraction. J. Am. Chem. Soc. 2015, 137, 10874. (g) Klein, J. E. M. N.; Mandal, D.; Ching, W.-M.; Mallick, D.; Que, L. Jr.; Shaik, S. Privileged Role of Thiolate as the Axial Ligand in Hydrogen Atom Transfer Reactions by Oxoiron(IV) Complexes in Shaping the Potential Energy Surface and Inducing Significant H-Atom Tunneling. J. Am. Chem. Soc. 2017, 139, 18705.

(49) Saltzman, H.; Sharefkin, J. G. In *Organic Syntheses*; Wiley: New York, 1973; Vol. V, pp 658.

(50) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. Trifluoromethanesulfonates and Trifluoromethanesulfonato-*O*Complexes. *Inorg. Synth.* **1990**, *28*, 70.

(51) Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. C-H Bond Activation by a Ferric Methoxide Complex: Modeling the Rate-Determining Step in the Mechanism of Lipoxygenase *J. Am. Chem. Soc.* **2002**, *124*, 83.

(52) Ravel, B.; Newville, M. J. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *Synchrot. Radiat.* **2005**, *12*, 537.

(53) Rehr, J. J.; Albers, R. C. Theoretical Approaches to X-Ray Absorption Fine Structure. *Rev. Mod. Phys.* **2000**, *72*, 621.

(54) Fukuzumi, S.; Kondo, Y.; Mochizuki, S.; Tanaka, T. Complex Formation Between NADH Model Compounds and Metalloporphyrins. *J. Chem. Soc., Perkin Trans.* 2 **1989**, 1753.

