

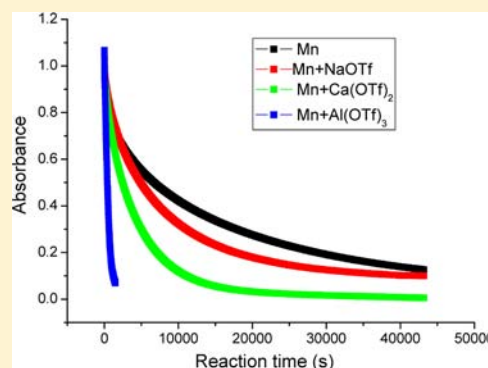
Lewis-Acid-Promoted Stoichiometric and Catalytic Oxidations by Manganese Complexes Having Cross-Bridged Cyclam Ligand: A Comprehensive Study

Lei Dong, Yujuan Wang, Yanzong Lv, Zhuqi Chen, Fuming Mei, Hui Xiong, and Guochuan Yin*

School of Chemistry and Chemical Engineering, Hubei Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, P.R. China

S Supporting Information

ABSTRACT: Redox-inactive metal ions have been recognized to be able to participate in redox metal-ion-mediated biological and chemical oxidative events; however, their roles are still elusive. This work presents how the redox-inactive metal ions affect the oxidative reactivity of a well-investigated manganese(II) with its corresponding manganese(IV) complexes having cross-bridged cyclam ligand. In dry acetone, the presence of these metal ions can greatly accelerate stoichiometric oxidations of triphenylphosphine and sulfides by the manganese(IV) complexes through electron transfer or catalytic sulfoxidations by the corresponding manganese(II) complexes with PhIO. Significantly, the rate enhancements are highly Lewis-acid strength dependent on added metal ions. These metal ions like Al^{3+} can also promote the thermodynamic driving force of the $\text{Mn}^{\text{IV}}\text{-OH}$ moiety to facilitate its hydrogen abstraction from ethylbenzene having a BDE_{CH} value of 85 kcal/mol, while it is experimentally limited to 80 kcal/mol for $\text{Mn}^{\text{IV}}\text{-OH}$ alone. Adding Al^{3+} may also improve the manganese(II)-catalyzed olefin epoxidation with PhIO. However, compared with those in electron transfer, improvements in hydrogen abstraction and electron transfer are minor. The existence of the interaction between Lewis acid and the manganese(IV) species was evidenced by the blue shift of the characteristic absorbance of the manganese(IV) species from 554 to 537 nm and by converting its EPR signal at $g = 2.01$ into a hyperfine 6-line signal upon adding Al^{3+} ($I = 5/2$). Cyclic voltammograms of the manganese(IV) complexes reveal that adding Lewis acid would substantially shift its potential to the positive direction, thus enhancing its oxidizing capability.



INTRODUCTION

Oxidations including hydrogen abstraction, oxygen transfer, and electron transfer are of most important biological and chemical processes in which the redox metal ions play significant roles.¹ In these redox metal-ion-mediated oxidations, the oxidation state of the metal ions generally changes frequently in the catalytic cycle. Among a variety of transition metal elements, iron, manganese, and copper dominate over the vast realm of redox catalysts in nature. Classical examples include the iron element in P450 enzymes and methane monooxygenases, manganese in Photosystem II and peroxidases, and copper in many copper oxidases.² To clarify related oxidation mechanisms, versatile inorganic models having synthetic ligands have been extensively explored; meanwhile, these metal complexes, including expanded metal ions like ruthenium and palladium, have also been widely applied in chemical catalytic oxidation studies.^{3,4} In general, the oxidative reactivities of these redox metal catalysts are modified through ligand designs due to their wide availability, and attention has seldom been paid on other factors such as the overall net charge of the active species.⁵

In addition to the redox-active metal ions which directly catalyze the oxidation reactions, the redox-inactive metal ions

may also be involved in these oxidation processes. The well-known examples include various metal ions that are frequently added to the redox metal oxide catalysts to modify their reactivities in heterogeneous oxidations, and in nature, Ca^{2+} also occurs in the Photosystem II center as one part of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster, even though its role still remains elusive.^{6,7} However, these redox-inactive metal ions are seldom utilized in the catalytic oxidations happening in liquid media, that is, homogeneous catalytic oxidations. In limited examples, Collins even found that certain Lewis acids like Zn^{2+} , Mg^{2+} , and Sc^{3+} could drive the oxygen atom transfer of their manganyl moiety ($\text{Mn}^{\text{V}}\equiv\text{O}$) species to triphenylphosphine, which is apparently a sluggish oxidant in the absence of Lewis acids.⁸ Lau demonstrated a series of Lewis-acid-activated stoichiometric oxidations of the C–H bond with MnO_4^- or FeO_4^- and FeCl_3 as Lewis-acid-accelerated catalytic alkane oxidation by $[\text{Os}^{\text{VI}}(\text{N})\text{Cl}_4]^-$.⁹ Fukuzumi and Nam found that Lewis acids like Sc^{3+} may substantially accelerate stoichiometric sulfide oxygenation by $\text{Fe}^{\text{IV}}(\text{N4Py})(\text{O})$; a similar acceleration effect was also observed in $\text{Mn}^{\text{IV}}(\text{N4Py})(\text{O})$ -mediated sulfoxidation

Received: February 11, 2013

Published: April 19, 2013



but not in hydrogen abstraction; in another example, they also observed that formation of the $\text{Sc}^{3+}\text{-O-Fe}^{\text{IV}}$ bridge in $\text{Fe}^{\text{IV}}(\text{TMC})(\text{O})$ complex may shift its one-electron reduction by ferrocene to two-electron reduction.¹⁰ Fukuzumi also extensively investigated the redox-inactive metal-ion-controlled electron transfer from electron donors to acceptors, named metal-ion-coupled electron transfer.¹¹ Also, Goldberg found that the redox-inactive Zn^{2+} can enhance the oxidizing ability of $(\text{TPB}_8\text{Cz})\text{Mn}^{\text{V}}\equiv\text{O}$ in electron transfer.¹² Notably, Borovik most recently found that Ca^{2+} may enhance reduction of dioxygen with their $[\text{Mn}^{\text{II}}\text{MST}]^-$ complexes.¹³

In the literature, the acceleration effects of the redox-inactive metal ions in oxidations are generally attributed to their linkages to the redox metal ions. In Collin's $\text{Mn}^{\text{V}}\equiv\text{O}$ complexes, binding of Li^+ or Zn^{2+} within the manganyl moiety was illustrated by the 15 cm^{-1} blue shift of the IR band of the $\nu(\text{Mn}^{\text{V}}\equiv\text{O})$ moiety from 939 to 954 cm^{-1} .⁸ Goldberg proposed that Zn^{2+} may interact with the $\text{Mn}^{\text{V}}\equiv\text{O}$ functional group in their $(\text{TPB}_8\text{Cz})\text{Mn}^{\text{V}}\equiv\text{O}$ complexes, which shifts the $\text{Mn}^{\text{V}}\equiv\text{O}$ functional group to an $\text{Mn}^{\text{IV}}=\text{OZn}^{2+}$ moiety, thus accelerating its electron transfer rate.¹² Lau rationalized their acceleration effects in C–H bond oxidation as the oxidant activation by formation of $[(\text{O})_3\text{Fe}^{\text{VI}}=\text{O}\rightarrow\text{M}^{n+}]$, $[(\text{O})_3\text{Mn}^{\text{VII}}=\text{O}\rightarrow\text{BF}_3]$, and $[\text{Cl}_4(\text{O})\text{Os}^{\text{VIII}}\equiv\text{N}\rightarrow\text{Fe}^{3+}]$ intermediates.⁹ The great acceleration of electron transfer in sulfide oxygenation observed by Fukuzumi was also attributed to formation of the plausible $[(\text{N4Py})\text{Fe}^{\text{III}}(\text{O})]^+-\text{nSc}^{3+}$ or binding of redox-inactive metal ions to the radical anion of electron acceptors in their metal-ion-coupled electron transfer processes.^{10a,11} These discoveries strongly imply that, as well as in heterogeneous oxidations, Lewis acid may participate in modulating the reactivity of the redox metal ions in liquid oxidation through its bridge or ligation with them. However, due to the fact that the examples reporting Lewis-acid-accelerated oxidations are still very limited until now, it is still unclear to which extent the Lewis acid could improve the traditional oxidations happening in liquid media. For example, (1) can Lewis acid accelerate all kinds of oxidations occurring in liquid media including electron transfer, oxygen transfer, and hydrogen abstraction? (2) Does Lewis acid improve the oxidizing capability of the active metal intermediate as well as accelerating its reaction rate? (3) Does Lewis acid accelerate catalytic oxidations mediated by these popular redox metal catalysts like manganese as well as those in stoichiometric oxidations? Clarifying these issues may help to understand how the redox-inactive metal ions participate in these redox metal-ion-mediated biological and chemical oxidations and benefit design of selective oxidation catalysts. In particular, compared with the oxidations happening in redox enzymes and on heterogeneous catalyst surfaces, the mechanisms of oxidations happening in liquid media are apparently easier to be clarified, which provides a convenient protocol to address the aforementioned issues through investigating how the redox-inactive metal ions affect the oxidative reactivities of a redox metal catalyst in liquid media.

Inspired by these preceding works, here we present an example of Lewis-acid-promoted stoichiometric and catalytic oxidations based on a well-developed manganese(II) catalyst having cross-bridged cyclam ligand, $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$ ($\text{Me}_2\text{EBC} = 4,11$ -dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]-hexadecane), with its corresponding manganese(IV) complexes to address these issues (Figure 1). Since the oxidative properties of this manganese catalyst have been extensively

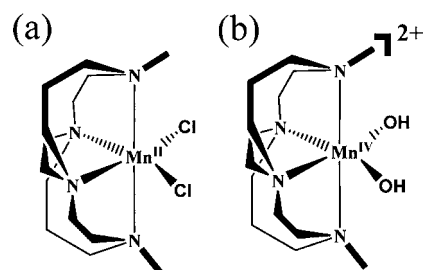


Figure 1. Structure of $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$ and corresponding $\text{Mn}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$.

studied,¹⁴ it would apparently benefit investigation of how and to which extent the Lewis acid can affect its oxidative properties. Our results reveal that the redox-inactive metal ions may greatly accelerate the oxidations proceeding by electron transfer with this manganese complex and improve its ability in electron transfer as well. The hydrogen abstraction ability of the manganese complexes can also be promoted by adding Lewis acids like Al^{3+} , but the efficiencies are very poor; similar slightly improved oxygen transfer efficiencies of this manganese complex were also observed in olefin epoxidation.

EXPERIMENTAL SECTION

The manganese(II) and corresponding manganese(IV) complexes, $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2$ and $\text{Mn}(\text{Me}_2\text{EBC})(\text{OH})_2(\text{PF}_6)_2$, were synthesized according to the literature.^{14b,f} Iodosobenzene was synthesized from iodosobenzene diacetate by following the reported procedures.¹⁵ Sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate ($\text{Mg}(\text{OTf})_2$), and scandium trifluoromethanesulfonate ($\text{Sc}(\text{OTf})_3$) came from Aladdin. Other trifluoromethanesulfonates including $\text{Ca}(\text{OTf})_2$, $\text{Al}(\text{OTf})_3$, $\text{Y}(\text{OTf})_3$, and $\text{Yb}(\text{OTf})_3$ came from a local chemical company. Benzyl phenyl sulfide, diphenyl sulfide, diphenyl sulfoxide, methyl phenyl sulfoxide, benzophenone, 2-phenylpropionaldehyde, tris(*m*-tolyl)phosphine, tris(*p*-fluorophenyl)phosphine, tris(*p*-chlorophenyl)phosphine, tris(*m*-methoxyphenyl)phosphine, and other reagents were purchased from Alfa Aesar. Acetone was dried with molecular sieves (3 Å) before use.

Kinetic data were collected on Analytikjena, specord 205, GC-MS analysis was performed on Agilent 7890A/5975C, and EPR experiments were conducted at 160 K on Bruker A200. Electrochemical data were collected on a CS Corrtest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as reference electrode. Electrochemical measurements were performed under nitrogen in dry acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

General Procedures for Lewis-Acid-Promoted Catalytic Sulfoxidation by the Manganese(II) Complexes. In 5 mL of dry acetone containing 0.1 M thioanisole, 0.33 mM manganese(II) complexes, and 0.33 mM Lewis acid, for example, $\text{Al}(\text{OTf})_3$, 0.6 mmol of PhIO was added to initialize the reaction. The reaction mixture was stirred in a water bath at 298 K for 4 h, and product analysis was performed by GC using the internal standard method. Control experiments using the manganese(II) complexes or Lewis acid alone as catalyst were carried out in parallel. In particular, GC-MS analysis was carried out for product identification of benzyl phenyl sulfide oxidation.

General Procedures for Lewis-Acid-Promoted Stoichiometric Sulfoxidation by the Manganese(IV) Complexes. In 5 mL of dry acetone solvent, 0.02 mmol of the manganese(IV) complexes, 0.02 mmol of $\text{Al}(\text{OTf})_3$, and 0.01 mmol of biphenyl sulfide were added. The resulting reaction mixture was stirred in a water bath at 293 K for 4 h, and product analysis was performed by GC using the internal standard method. Control experiments using the manganese(IV) complexes alone as oxidant were carried out in parallel. In particular, GC-MS analysis was carried out for product identification of benzyl phenyl sulfide oxidation.

General Procedures for Kinetic Measurement in Lewis-Acid-Promoted Triphenylphosphine Oxygenation by the Manganese(IV) Complexes. To determine the second-order kinetic rate constant of triphenylphosphine oxygenation by the manganese(IV) complexes in the presence of redox-inactive metal ions, oxygenations of triphenylphosphine (10, 20, 30, and 40 mM) were separately carried out with the manganese(IV) complexes (2 mM) and Lewis acid (2 mM), for example, Al(OTf)₃, in dry acetone at 293 K. The disappearance of the manganese(IV) species was monitored by a UV-vis spectrophotometer, and oxygenation kinetic data were collected. In each oxygenation reaction, the disappearance of the manganese(IV) species in a control experiment without triphenylphosphine was conducted in parallel. For calculations of the pseudo-first-order rate constants, corrections of the oxygenation kinetic curves were done by compensating for the disappearance of the manganese(IV) species in control experiments due to its instability. Kinetic experiments were performed at least in duplicate, and average kinetic data were used in the discussion.

In the Hammett plot, similar triarylphosphine oxygenation kinetics with the manganese(IV) complexes in the presence of Al(OTf)₃ was conducted for substrates including tris(*m*-tolyl)phosphine, tris(*p*-fluorophenyl)phosphine, tris(*p*-chlorophenyl)phosphine, and tris(*m*-methoxyphenyl)phosphine.

General Procedures for Lewis-Acid-Promoted Catalytic Olefin Epoxidation by the Manganese(II) Complexes. In 5 mL of dry acetone containing 0.1 M cyclohexene, 0.33 mM manganese(II) complexes, and 0.33 mM Al(OTf)₃, 0.6 mmol of PhIO was added to initialize the reaction. The reaction mixture was stirred in a water bath at 298 K for 14 h, and product analysis was conducted by GC using the internal standard method. Control experiments using the manganese(II) complexes or Al(OTf)₃ alone as catalyst were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in the discussion.

General Procedures for Lewis-Acid-Promoted Stoichiometric Hydrogen Abstraction by the Manganese(IV) Complexes. In 5 mL of dry acetone, 0.04 mmol of the manganese(IV) complexes, 0.04 mmol of Al(OTf)₃, and 0.02 mmol of ethylbenzene were added. The resulting reaction mixture was stirred in a water bath at 293 K for 48 h, and product analysis was conducted by GC using the internal standard method. Control experiments using the manganese(IV) complexes alone as oxidant were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in the discussion.

General Procedures for Lewis-Acid-Promoted Catalytic Hydrogen Abstraction by the Manganese(II) Complexes. In 5 mL of dry acetone containing 0.1 M ethylbenzene, 0.33 mM manganese(II) complexes, and 0.33 mM Al(OTf)₃, 0.6 mmol of PhIO was added to initialize the reaction. The reaction mixture was stirred in a water bath at 298 K for 48 h, and product analysis was conducted by GC using the internal standard method. Control experiments using the manganese(II) complexes or Al(OTf)₃ alone as catalyst were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in the discussion.

RESULTS AND DISCUSSION

Redox-Inactive Metal-Ion-Promoted Catalytic Sulfoxidation with the Manganese(II) Complexes. In previous studies it was found that stoichiometric sulfoxidation by the manganese(IV) complexes, Mn(Me₂MBC)(OH)₂(PF₆)₂, is very sluggish in acetone/water (ratio 4:1), while catalytic sulfoxidation by the corresponding manganese(II) complexes, Mn(Me₂MBC)Cl₂, is highly efficient when using H₂O₂ as oxidant.^{14p} These findings provide a basis for us to investigate how the redox-inactive metal ions serving as Lewis acid affect the catalytic sulfoxidation activity of the Mn(Me₂MBC)Cl₂ catalyst. To avoid potential interference from the hydroxyl radical and the solvation effect of water to the added redox-inactive metal ions due to use aqueous H₂O₂ as oxidant,

iodosylbenzene (PhIO) was selected as oxidant in the present studies, and reactions were performed in dry acetone. Results of catalytic oxygenation of thioanisole with Mn(Me₂MBC)Cl₂ catalyst in the presence of various Lewis acids are summarized in Table 1.

Table 1. Catalytic Oxygenation of Thioanisole by the Manganese(II) Complexes in the Presence of Redox-Inactive Metal Ions As Lewis Acid^a

additives	conversion (%) ^a	yield (%) ^a
	9.8	5.1
Na ⁺	27.5 (17.5)	6.8 (16.9)
Mg ²⁺	59.0 (10.2)	48.5 (2.7)
Ca ²⁺	46.7 (7.8)	42.7 (1.9)
Al ³⁺	97.1 (17.9)	95.4 (11.8)
Sc ³⁺	90.8 (16.7)	78.2 (8.5)
Y ³⁺	98.3 (11.5)	96.0 (3.9)
Yb ³⁺	94.8 (13.5)	57.1 (6.8)

^aThe data in parentheses represent control experiment without manganese(II) catalyst. ^aConditions: solvent acetone 5 mL, thioanisole 0.1 M, manganese(II) catalyst 0.33 mM, Lewis acid 0.33 mM, PhIO 0.6 mmol, 293 K, 4 h. Conversion is defined as (amount of substrate consumption)/(amount of substrate added) × 100%.

As shown in Table 1, without redox-inactive metal ions added, the manganese(II) complexes are capable of oxygenating thioanisole with PhIO as oxidant in dry acetone at 293 K; however, the catalytic efficiency is very poor. After 4 h reaction, only 9.8% of thioanisole was converted with 5.1% yield of methyl phenyl sulfoxide, representing 52% selectivity. Adding 1 equiv of metal ions such as Na⁺, Mg²⁺, Ca²⁺, Al³⁺, Sc³⁺, Y³⁺, and Yb³⁺ to the catalytic solution would greatly improve the catalytic efficiency. Adding Na⁺ remarkably improves thioanisole oxidation with 27.5% conversion, but the yield of sulfoxide is still poor (6.8%). In the presence of Ca²⁺, which has biological importance, conversion of thioanisole can be improved up to 46.7% with 42.7% yield of sulfoxide in 4 h, representing 91.4% of selectivity on sulfoxide, while Ca²⁺ alone can only provide 7.8% conversion with 1.9% yield. Using Al³⁺ as additive provides 95.4% yield with 97.1% conversion, representing 98.2% selectivity on sulfoxide, while Al³⁺ alone gives only 11.8% yield with 17.9% conversion. In the case of using synthesized pure manganese(IV) complexes plus Al³⁺ as catalyst it provides 88.7% yield with 92.0% conversion, representing 96.4% selectivity on sulfoxide, very similar to that of using manganese(II) complexes plus Al³⁺. Similarly, using Y³⁺ provides 98.3% conversion with 96.0% yield, representing 97.7% selectivity on sulfoxide, while Y³⁺ alone only provides 11.5% conversion with 3.9% yield. In complementary experiments, adding more Lewis acid would further accelerate the oxygenation rate but leads to the lower selectivity to sulfoxide. For example, adding 4 equiv of Ca(OTf)₂, 51.1% yield of sulfoxide can be obtained with 74.6% conversion of thioanisole in 4 h, representing 68.5% selectivity on sulfoxide, much lower than that of using 1 equiv of Ca²⁺ (91.4%). In the case of Al³⁺, adding 4 equiv of Al(OTf)₃, PhIO oxidant can be depleted in 0.5 h with only 62.8% yield of sulfoxide and 86.4% of conversion achieved, also indicating the decreased selectivity (72.7%) on sulfoxide.

Apparently, the greatly improved catalytic activity of the manganese(II) catalyst by adding redox-inactive metal ions cannot be attributed to simple addition of using manganese(II)

catalyst and these metal ions separately but strongly suggests that the synergistic effect occurs between the manganese(II) catalyst and the Lewis acid in oxygenation. Notably, the added metal ions having higher positive charge demonstrate better efficiency in promoting the catalytic efficiency of the manganese(II) catalyst. For example, the yield of sulfoxide increases along the series of the positive charge from 1+, 2+, to 3+ of the added Lewis acid. For example, from Na^+ to Mg^{2+} and then to Al^{3+} , the yield of sulfoxide increases from 6.8% to 48.5% and then to 95.4%. The catalytic kinetics further disclosed the acceleration effect of Lewis acid on the manganese(II) complexes mediated sulfoxidations (Figure 2). Without Lewis

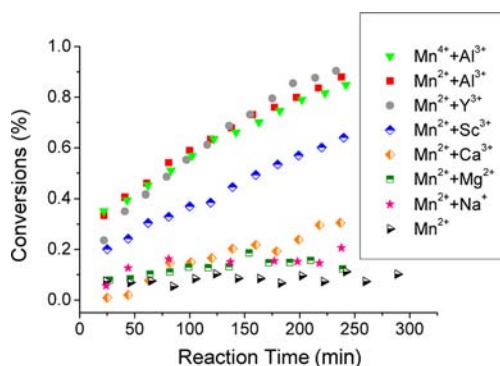


Figure 2. Lewis-acid-accelerated oxygenation kinetics by the manganese(II) catalyst. Conditions: solvent acetone 5 mL, thioanisole 0.1 M, manganese(II) catalyst 0.33 mM, Lewis acid 0.33 mM, PhIO 0.6 mmol, 293 K, 4 h.

acid added, catalytic oxygenation by the manganese(II) catalyst is very sluggish, while adding 1 equiv of Lewis acid would apparently accelerate the oxygenation rate of the manganese(II) catalyst. Consistent with the improved yields as shown in Table 1, the acceleration effect increases along the series of charge 1+, 2+, and 3+ of the added metal ions, and typically, Y^{3+} and Al^{3+} demonstrate the highest acceleration effect. In addition, using synthesized pure manganese(IV) complexes with Al^{3+} generates an identical kinetic curve to that of the manganese(II) complexes with Al^{3+} . Together with the catalytic efficiency aforementioned, it suggests that the catalyst precursor does not affect the acceleration effect of added Lewis acid.

Benzyl phenyl sulfide is a unique substrate for sulfide oxygenation. In a common oxygen atom transfer process it provides benzyl phenyl sulfoxide as the dominant oxygenation product.¹⁶ In the case of the reaction proceeding by electron transfer in which a sulfur cation radical would occur as the intermediate, C–S bond cleavage products including benzaldehyde, thiophenol, and phenyl disulfide may occur with minor sulfoxide product formation.¹⁷ Unlike using H_2O_2 as oxidant which provides dominant sulfoxide as product in previous studies,^{14p} in this work, the manganese(II) catalyst alone provides only 6.1% yield of benzyl phenyl sulfoxide with 47.6% conversion when using PhIO as oxidant. Adding Al^{3+} to the reaction system gives 19.9% yield of sulfoxide with 95.1% conversion, while Al^{3+} alone as catalyst produces only 0.6% yield with 4.2% conversion. Furthermore, GC-MS analysis revealed the occurrence of dominant C–S bond cleavage products including benzaldehyde, benzenethiol, phenyl disulfide, 1,2-diphenylethane, and S-phenyl benzenesulfonothioate, etc., clearly supporting catalytic sulfoxidation proceeding by electron transfer (see Figure S20, Supporting Information).

Redox-Inactive Metal-Ion-Promoted Stoichiometric Sulfoxidation by the Manganese(IV) Complexes.

Although catalytic sulfoxidations by the manganese(II) catalyst demonstrated high efficiencies, as reported earlier, the synthesized pure manganese(IV) complexes alone, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2(\text{PF}_6)_2$, are incapable of oxidizing sulfides like diphenyl sulfide and thioanisole to their corresponding sulfoxides in acetone/water (ratio 4:1).^{14p} Here, the influence of the redox-inactive Al^{3+} was investigated for stoichiometric oxygenation of various sulfides by the manganese(IV) complexes, and the results are summarized in Table 2. In dry acetone, the synthesized manganese(IV) species

Table 2. Lewis-Acid-Promoted Stoichiometric Oxygenation of Sulfides by the Manganese(IV) Complexes^a

substrate	product	yield (%) ^b
thianthrene	thianthrene monooxide	53.2 (9.7)
diphenyl sulfide	diphenyl sulfoxide	15.4 (4.3)
thioanisole	methyl phenyl sulfoxide	23.9 (6.7)
benzyl phenyl sulfide	benzyl phenyl sulfoxide	1.9 (0.6)

^aConditions: solvent acetone, manganese(IV) complexes 4 mM, $\text{Al}(\text{OTf})_3$ 4 mM, substrate 2 mM, 293 K, 4 h. ^bYield is based on sulfide conversion, and data in parentheses come from control experiments without $\text{Al}(\text{OTf})_3$ added.

has the characteristic absorbance occurring at 554 nm which is identical to that in acidic acetone/water solution,^{14k} indicating that, here, the manganese(IV) species still remains two hydroxide functional groups (see Figure S1, Supporting Information, and Figure 6). In the control experiments, the manganese(IV) complexes alone cannot efficiently oxidize these sulfides in dry acetone. Without Al^{3+} added, stoichiometric oxygenations of thianthrene, diphenyl sulfide, and thioanisole by the manganese(IV) complexes provide only 9.7%, 4.3%, and 6.7% yield of the corresponding sulfoxides in 4 h at 293 K, respectively. Upon adding 1 equiv of $\text{Al}(\text{OTf})_3$, the oxygenation efficiency of the manganese(IV) species was improved significantly, providing 53.2%, 15.3%, and 23.9% yield of the sulfoxides, respectively. Apparently, the presence of redox-inactive metal ions like Al^{3+} would greatly promote the oxidizing ability of the manganese(IV) complexes for sulfide oxidation.

Using benzyl phenyl sulfide as substrate for stoichiometric oxygenation provides similar mechanistic information as well as that in catalytic sulfoxidation. In the presence of 1 equiv of Al^{3+} , benzyl phenyl sulfide as substrate provides only 1.9% yield of sulfoxide product with 50.8% conversion while the manganese(IV) complexes alone gives only 0.6% yield of sulfoxide with 8.0% conversion. GC-MS analysis of products also confirmed the occurrence of dominant C–S cleavage products including benzenethiol, phenyl disulfide, 1,2-diphenylethane, and S-phenyl benzenesulfonothioate as well as those in catalytic oxygenation by the manganese(II) complexes plus Al^{3+} (see Figure S21, Supporting Information). Taken together, these results provide clear evidence to support that sulfide oxygenation proceeds by electron transfer rather than direct oxygen atom transfer in this manganese(IV) complexes plus Lewis-acid-mediated sulfoxidations, and adding Lewis acid would greatly enhance its ability in electron transfer. Remarkably, when oxygenations were carried out in acetone/water (4:1), adding Lewis acid like Al^{3+} does not generate any improvement on sulfoxidation. For example, in diphenyl sulfide and

thioanisole oxidations, 1 equiv of $\text{Al}(\text{OTf})_3$ with the manganese(IV) complexes in acetone/water (4:1) can only provide less than 1.5% yield of diphenyl sulfoxide or methyl phenyl sulfoxide, which is identical to that using the manganese(IV) complexes alone. Apparently, the presence of water may block the interaction between Al^{3+} and the manganese(IV) species due to its solvation effect on the Al^{3+} cation (*vide infra*); thus, the acceleration effect does not occur in acetone/water mixture.

Kinetics of Redox-Inactive Metal-Ion-Promoted Stoichiometric Triphenylphosphine Oxygenation by the Manganese(IV) Complexes. The kinetics of triphenylphosphine oxygenation by the manganese(IV) complexes in dry acetone further disclosed the acceleration effect of adding these redox-inactive metal ions as Lewis acid. After adding manganese(IV) complexes to the dry acetone solution containing triphenylphosphine the purple color of the manganese(IV) species gradually turns to the colorless manganese(II) species with formation of triphenylphosphine oxide as reported previously.^{14k} In the presence of 1 equiv of $\text{Al}(\text{OTf})_3$, stoichiometric oxidation of triphenylphosphine with manganese(IV) complexes could provide 85.2% yield of triphenylphosphine oxide. In particular, adding redox-inactive metal ions to the reaction mixture would substantially accelerate the oxygenation rate, and the corresponding kinetic results are summarized in Table 3. Without redox-inactive

Table 3. Second-Order Rate Constants of Redox-Inactive Metal-Ion-Promoted Triphenylphosphine Oxygenation by the Manganese(IV) Complexes^a

additives	k_2 ($\text{M}^{-1}\text{s}^{-1}$)	relative rate
	$(1.6 \pm 0.026) \times 10^{-3}$	1
Na^+	$(3.2 \pm 0.014) \times 10^{-3}$	2
Mg^{2+}	$(3.8 \pm 0.018) \times 10^{-3}$	2.4
Ca^{2+}	$(6.8 \pm 0.027) \times 10^{-3}$	4.2
Yb^{3+}	$(1.4 \pm 0.019) \times 10^{-2}$	8.8
Y^{3+}	$(2.8 \pm 0.035) \times 10^{-2}$	18
Sc^{3+}	$(3.6 \pm 0.11) \times 10^{-2}$	23
Al^{3+}	$(4.2 \pm 0.13) \times 10^{-2}$	26

^aConditions: solvent acetone, triphenylphosphine 10, 20, 30, and 40 mM, manganese(IV) complexes 2 mM, trifluoromethanesulfonate of redox-inactive metal ions 2 mM, 293 K.

metal ions added, the second-order rate constant (k_2) for triphenylphosphine oxygenation by the manganese(IV) species alone is $(1.6 \pm 0.026) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ in dry acetone at 293 K. Adding 1 equiv of Na^+ improves k_2 to $(3.2 \pm 0.014) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, representing a doubled oxygenation rate, and they are $(3.8 \pm 0.018) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for Mg^{2+} and $(6.8 \pm 0.027) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for Ca^{2+} , representing 2–4-fold rate enhancements. Using strong Lewis acids like Yb^{3+} , Y^{3+} , Sc^{3+} , and Al^{3+} would greatly accelerate the oxygenation rate of the manganese(IV) species. For example, adding 1 equiv of Sc^{3+} or Al^{3+} may generate a 23- or 26-fold rate increase, and the corresponding k_2 values are $(3.6 \pm 0.11) \times 10^{-2}$ and $(4.2 \pm 0.13) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Apparently, with the positive charge of added redox-inactive metal ions increasing from 1+ to 3+, the acceleration effect becomes more and more sensitive as those observed in sulfoxidation (*vide supra*). For example, from Na^+ to Mg^{2+} and then to Al^{3+} , the rate enhancement changes from 2- to 2.4- and then to 26-fold with the charge increasing from 1+ to 2+ and then to 3+. Figure 3 clearly displays their different

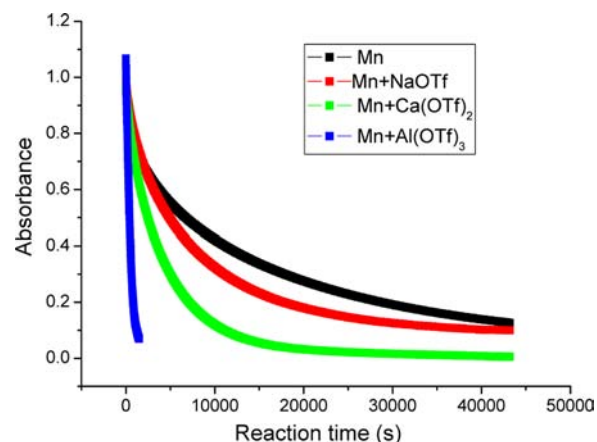


Figure 3. Oxygenation kinetics for triphenylphosphine with the manganese(IV) complexes in the absence/presence of Lewis acid. Conditions: solvent acetone, triphenylphosphine 40 mM, manganese(IV) complexes 2 mM, trifluoromethanesulfonate of redox-inactive metal ions 2 mM, 293 K.

rates in triphenylphosphine oxygenation. These metal ions, including Na^+ , Mg^{2+} , and Al^{3+} , occur in the same third row of the periodic table; with their positive charge increasing from 1+ to 2+ and then to 3+, their ionic radii decreases from 1.18 to 0.89 and then to 0.535 Å, indicating their Lewis-acid strength increases along the series of Na^+ , Mg^{2+} , and Al^{3+} .¹⁸ Obviously, the oxygenation rate increases along the series of the Lewis-acidity strength of added redox-inactive metal ions. Consistent with this, with the ionic radii increasing along the series of Al^{3+} (0.535 Å), Sc^{3+} (0.87 Å), and Y^{3+} (1.019 Å) which have identical 3+ overall charge,¹⁸ their acceleration in oxygenation rate decreases along the identical series from 26- to 23- and then to 18-fold.

As demonstrated in Figure 4, increasing the ratio of Lewis-acid/Mn(IV) would further accelerate the oxygenation rate of

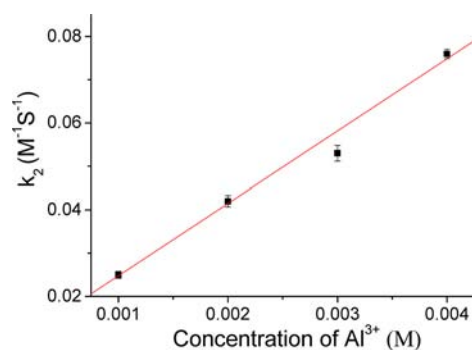


Figure 4. Influence of Al^{3+} concentration on triphenylphosphine oxygenation by the manganese(IV) complexes. Conditions: solvent acetone, triphenylphosphine 20 mM, Mn(IV) complexes 2 mM in acetone, 293 K.

triphenylphosphine. For example, in the absence of Lewis acid, the k_2 value for oxygenation by the manganese(IV) species is $(1.6 \pm 0.026) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, while they are $(4.2 \pm 0.13) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ in the presence of 1 equiv of Al^{3+} ion and $(7.6 \pm 0.11) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ in the presence of 2 equiv of Al^{3+} , representing 26- and 48-fold oxygenation rate increase, respectively. Due to the great influence of the $\text{Al}(\text{III})/\text{Mn}(\text{IV})$ ratio on the oxygenation rate, further increasing the ratio leads to a too fast oxygenation rate which cannot be accurately

measurable by UV–vis spectrophotometry. Accordingly, the saturation behavior on the concentration of Al^{3+} cannot be observed here.

In previous studies, it was revealed that triarylphosphine oxygenation by $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ proceeds by electron transfer and increasing the overall positive net charge of the manganese(IV) species through protonation to generate $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH}(\text{OH}_2))^3+$ would substantially accelerate its oxygenation rate by 10–20-fold.^{14k,q} To clarify the Lewis-acid-promoted oxygenation mechanism of the manganese(IV) species, the substituent effect of triphenylphosphine oxygenation was investigated with *p*-F-, *p*-Cl-, *m*-CH₃-, and *m*-OCH₃-substituted triarylphosphines and triphenylphosphine itself as substrates, and the corresponding Hammett plot is displayed in Figure 5. The obtained slope of the Hammett plot ($\rho = -0.65$

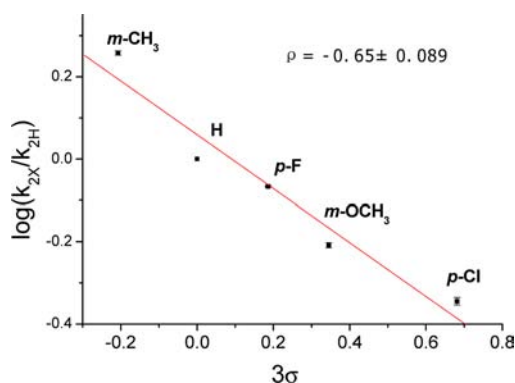


Figure 5. Hammett plot for oxygenation of triarylphosphines by the manganese(IV) complexes (2 mM) with $\text{Al}(\text{OTf})_3$ (2 mM) in acetone at 293 K.

± 0.089) is almost identical to the value in the earlier study with Bronsted-acid-accelerated oxidation ($\rho = -0.697$) in which oxygenation proceeds by electron transfer.^{14k} Therefore, the presence of the Lewis acid may significantly accelerate triphenylphosphine oxygenation but not change the oxygenation mechanism, for example, from electron transfer to direct oxygen transfer. In the literature, Fukuzumi and Nam observed that in the Sc^{3+} -accelerated thioanisole oxygenation by $\text{Fe}^{\text{IV}}(\text{N4Py})(\text{O})$ adding Sc^{3+} would shift the oxygenation mechanism from the direction oxygen transfer to metal-coupled electron transfer, and the reaction could be accelerated up to 100-fold.¹⁹ These findings apparently suggest that adding Lewis acid would substantially accelerate the redox-active metal-ion-mediated electron transfer rate, and enhancement is highly Lewis-acid strength dependent.

Redox-Inactive Metal-Ion-Participated Catalytic Olefin Epoxidation with the Manganese(II) Complexes.

Olefin epoxidation is a classic probe to investigate oxygen transfer reactions.²² Previous studies reveal that neither $\text{Mn}^{\text{IV}}=\text{O}$ nor $\text{Mn}^{\text{IV}}-\text{OH}$ is capable of epoxidizing olefin, while catalytic epoxidation with H_2O_2 proceeds by a Lewis-acid pathway having a $\text{Mn}^{\text{IV}}-\text{OOH}$ moiety serving as the active intermediate.^{14d,e} Here, quantitative treatment of the manganese(IV) complexes plus Al^{3+} with olefins, for example, cyclohexene and styrene, does not provide any epoxide product as well as using the manganese(IV) complexes alone, indicating that the oxygen transfer capability of the Mn(IV) species, which have two hydroxide rather than oxo ligands (see Figure 1b), may not be enhanced by adding Lewis acid. In the case of using PhIO as oxidant, catalytic epoxidation of cyclohexene is also

sluggish using either manganese(II) complexes alone or manganese(II) complexes plus Al^{3+} as catalyst. After reaction for 14 h at 298 K, manganese(II) catalyst alone provides $5.5 \pm 0.2\%$ yield of epoxide while manganese(II) complexes plus Al^{3+} gives $12.9 \pm 0.4\%$ yield. A control experiment using Al^{3+} alone gives only $3.9 \pm 0.1\%$ yield of epoxide as well as that of using PhIO alone without catalyst ($3.3 \pm 0.1\%$). Thus, Al^{3+} as Lewis acid has demonstrated its capability to accelerate catalytic epoxidation by the manganese(II) catalyst, although its efficiency is still poor. In Collins's studies, they even found that their manganyl moiety ($\text{Mn}^{\text{V}}=\text{O}$) plus Mg^{2+} or Sc^{3+} does not epoxidize olefin like 2,3-dimethyl-2-butene but provides hydrogen abstraction products when using *tert*-butylhydroperoxide as oxidant, whereas the manganyl moiety alone does catalyze olefin epoxidation.⁸ In common olefin epoxidation by an oxygen rebound mechanism, the active oxygen is transferred from the redox metal oxo functional group to the double bond of olefin.²³ Here, the manganese(IV) species has two hydroxide ligands which is incapable of transferring oxygen to olefin in quantitative treatment. The detailed mechanism is not fully understood for the Al^{3+} improved catalytic epoxidation by the manganese(II) catalyst. In the literature, PhIO adducts of the manganese(III) and manganese(V) complexes were independently proposed by Collman and Goldberg as active intermediates in olefin epoxidation, where the manganese species serve as Lewis acid.²⁴ Here, since neither synthesized manganese(IV) complexes alone nor manganese(IV) complexes plus Al^{3+} is incapable of epoxidizing olefins in the absence of PhIO, one may similarly suspect that catalytic epoxidation by this manganese(II) catalyst with PhIO oxidant may proceed by a Lewis-acid mechanism in which the PhIO adduct of the manganese(IV) species serves as the key active intermediate as well as those in Collman and Goldberg's epoxidations, and interaction of Al^{3+} cation with the manganese(IV) species may enhance its Lewis-acid strength, thus improving its epoxidation efficiency.

Redox-Inactive Metal-Ion-Promoted Stoichiometric and Catalytic Hydrogen Abstractions by the Manganese Complexes.

In addition to electron transfer and oxygen transfer, hydrogen abstraction is one of the most important processes in oxidations.^{4d,20} As reported earlier, the hydrogen abstraction ability of the manganese(IV) species, including $\text{Mn}^{\text{IV}}-\text{OH}$ and $\text{Mn}^{\text{IV}}=\text{O}$ moieties, is experimentally limited to the C–H bond of 80 kcal/mol or less in acetone/water (4:1).^{14g} Here, in dry acetone in which the functional group of the manganese(IV) complexes exists as the $\text{Mn}^{\text{IV}}-\text{OH}$ moiety (vide supra), the manganese(IV) species alone demonstrates a similar hydrogen abstraction ability to that in acetone/water, that is, it is also incapable of abstracting a hydrogen atom from diphenyl methane (82 kcal/mol) and ethylbenzene (85 kcal/mol). However, it was found that adding Al^{3+} to the synthesized manganese(IV) complexes could improve the hydrogen abstraction capability of the $\text{Mn}^{\text{IV}}-\text{OH}$ moiety, even though its efficiency is modest. For example, in the presence of 2 equiv of the manganese(IV) complexes and Al^{3+} in relation to ethylbenzene in dry acetone, stoichiometric hydrogen abstraction from ethylbenzene provides $2.8 \pm 0.1\%$ yield of acetophenone with $0.8 \pm 0.1\%$ yield of 1-phenylethanol at 298 K, whereas the manganese(IV) species alone is definitely inactive, demonstrating improved hydrogen abstraction capability in the presence of Lewis acid. The low yields of the oxidized products from ethylbenzene are due to the fact that adding Al^{3+} would reduce the stability of the Mn(IV) species

sharply (see Figure S19, Supporting Information), while the hydrogen abstraction rate by the Mn(IV)–OH functional group is very slow.¹⁴ⁱ In catalytic hydrogen abstraction using PhIO as oxidant, manganese(II) catalyst plus Al(OTf)₃ gives 3.4 ± 0.3% yield of acetophenone with 1.5 ± 0.4% yield of 1-phenylethanol in 48 h at 298 K, while in the control experiments, manganese(II) catalyst alone gives 1.9 ± 0.1% yield of acetophenone with 0.6 ± 0.1% yield of 1-phenylethanol and Al³⁺ alone provides 0.7 ± 0.1% and 0.2 ± 0.02% yield of acetophenone and 1-phenylethanol, respectively. In the absence of metal ions, PhIO as oxidant alone also gives 0.3 ± 0.02% yield of acetophenone with 0.1 ± 0.03% yield of 1-phenylethanol. Under identical catalytic conditions, diphenylmethane as substrate gives 5.6 ± 0.1% yield of benzophenone with 1.3 ± 0.02% yield of diphenylmethanol using manganese(II) complexes plus Al³⁺ as catalyst. Apparently, in comparison with oxygenation of triphenylphosphine and sulfides through electron transfer, the acceleration effect of Lewis acid is very poor in catalytic hydrogen abstraction. However, combined data from stoichiometric and catalytic oxidations still support the fact that adding Lewis acid may promote the thermodynamic driving force of the Mn^{IV}–OH moiety, for example, to facilitate its hydrogen abstraction from ethylbenzene having a BDE_{CH} value of 85 kcal/mol, whereas it is experimentally limited to 80 kcal/mol for the Mn^{IV}–OH moiety alone.

Certainly, compared with the corresponding active metal oxo moiety, i.e. Mⁿ⁺=O, the redox metal hydroxo moiety generally demonstrates a relatively low rate in hydrogen abstraction. For example, the Mn^{IV}=O moiety in this Mn^{IV}(Me₂EBC) complex demonstrates above 40-fold faster rate than the corresponding Mn^{IV}–OH moiety, while their thermodynamic driving forces in hydrogen abstraction are very similar (84.3 vs 83.0 kcal/mol).¹⁴ⁱ In addition, Fujii found that the Mn^{IV}=O moiety in the Mn^{IV}(Salen) complexes demonstrates more than 1000-fold faster rate than the corresponding Mn^{IV}–OH in hydrogen abstraction from substituted phenols with very similar oxidizing power (84.2 vs 83.1 kcal/mol), and Que also reported that the Fe^{IV}=O group in Fe^{IV}(β-BPNCN) complexes abstracts hydrogen atom by 100-fold faster than does the corresponding Fe^{IV}–OH.²¹ Notably, Fukuzumi and Nam recently observed that, in contrast to electron transfer, the Mn^{IV}(N4Py)(O) complex itself demonstrates about 180-fold faster rate than the Mn^{IV}(N4Py)O plus Sc³⁺ in hydrogen abstraction. However, in FeCl₃-promoted cyclohexane oxidation with [Os^{VI}(N)Cl₄][−] catalyst and *tert*-butylhydroperoxide oxidant, Lau observed that FeCl₃ could sharply accelerate cyclohexane oxidation with TON up to 7500.^{9b} The proposed key active intermediate is [Cl₄(O)Os^{VIII}≡N→Fe³⁺] species in which ligation of Fe³⁺ to the N≡Os^{VIII} group in [Cl₄(O)Os^{VIII}(N)] may promote the oxidizing power of the Os^{VIII}=O functional group. Here, although adding Al³⁺ can enhance the thermodynamic driving force of the manganese(IV) species in hydrogen abstraction, due to the intrinsic properties of the Mn^{IV}–OH moiety, its hydrogen abstraction rate does not accelerate as remarkably as that in electron transfer.

Interaction between the Redox-Inactive Metal Ions and the Manganese(IV) Species. Reaction data from electron transfer, oxygen transfer, and hydrogen abstraction as presented above have strongly implied that there exists a synergic effect between the manganese(IV) species and the added redox-inactive metal ions in oxidations. Evidence to display the interaction between the manganese(IV) species and Al³⁺ first comes from its UV–vis spectra. As shown in Figure 6,

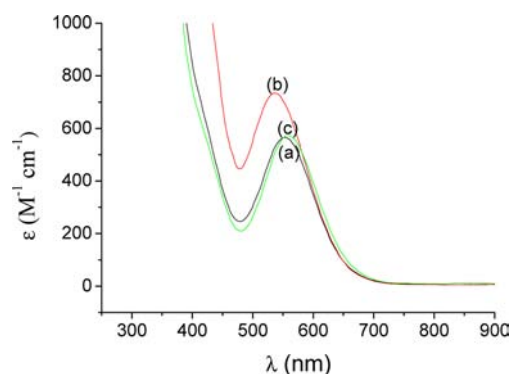


Figure 6. UV–vis spectra of the manganese(IV) complexes (1 mM) in dry acetone (a, black), manganese(IV) complexes (1 mM) plus Al(OTf)₃ (1 mM) in dry acetone (b, red), and manganese(IV) complexes (1 mM) plus Al(OTf)₃ (1 mM) in acetone/water (4:1) (c, green).

in dry acetone, the manganese(IV) species has a characteristic absorbance at $\lambda_{\max} = 554$ nm with a ϵ value of $563 \text{ M}^{-1} \text{ cm}^{-1}$, which supports the fact that the manganese(IV) species still retains two hydroxide ligands as those in previous studies,^{14k,q} while adding 1 equiv of Al³⁺ generates a blue shift of the characteristic manganese(IV) absorbance having λ_{\max} at 537 nm with an enhanced ϵ value of $734 \text{ M}^{-1} \text{ cm}^{-1}$. In the spectrum titration experiments, it was also observed that successive small additions of Al³⁺ to the acetone solution of the manganese(IV) complexes would cause the continuous blue shift of its characteristic absorbance, and a saturation behavior could be observed, implying binding of the Al³⁺ cation to the manganese(IV) species (see Figure S1, Supporting Information). As described above, in acetone/water (ratio 4:1) there is no acceleration effect observed for Lewis-acid-promoted sulfide oxygenation. Here, as shown in Figure 6, in contrast to the spectrum in dry acetone, the absorbance of the manganese(IV) species plus Al³⁺ in acetone/water (4:1) is identical to that of the manganese(IV) species alone, indicating that there is no interaction occurring between the Mn(IV) species and Al³⁺ due to the solvation effect of water, consistent with the fact that no acceleration effect was observed in oxygenation. In complementary experiments, using 1 equiv of NaOTf in place of Al(OTf)₃ yields a similar spectrum with that of the manganese(IV) species alone in dry acetone, and adding 3 equiv of NaOTf does not change the spectrum too much, supporting it being Al³⁺ rather than OTf[−] that interacts with the manganese(IV) species to cause its obvious blue shift. Similar blue shifts were also observed by adding other Lewis acids, including Sc³⁺, Y³⁺, Yb³⁺, Mg²⁺, and Ca²⁺, and the strong Lewis acid makes an obvious blue shift (see Figure S2, Supporting Information).

Therefore, the blue shift of the characteristic absorbance of the manganese(IV) species with enhanced ϵ value in Figure 6 apparently suggests that there exists an interaction between the Mn(IV) species and the Al³⁺ cation. Unfortunately, attempts to obtain the X-ray crystal structure of such intermediate failed due to its instability. Since in neutral to acidic solution the manganese(IV) complexes would dominantly exist as manganese(IV) species having two hydroxide ligands, Mn^{IV}(Me₂EBC)(OH)₂²⁺ (see Figure 1b), a plausible style for their interaction would be that Al³⁺ binds to the Mn(IV) species through its Mn^{IV}–OH group to form the μ -O-bridged Mn^{IV}–O–Al³⁺ species. Binding of Al³⁺ with Mn(IV) species was further supported by EPR experiments (Figure 7). In previous

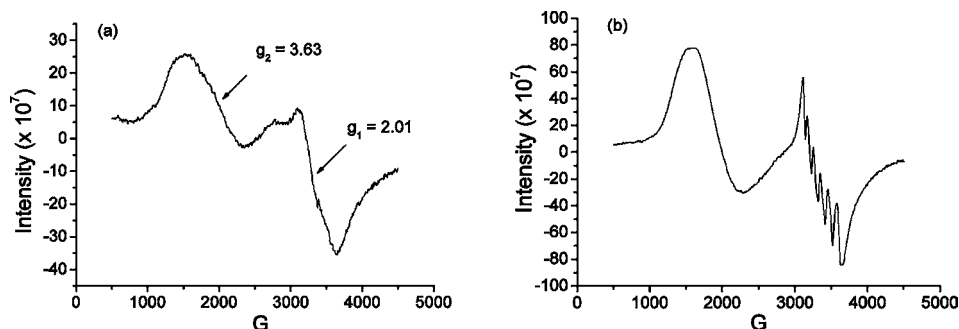


Figure 7. EPR spectra of (a) the manganese(IV) complexes and (b) the manganese(IV) complexes plus $\text{Al}(\text{OTf})_3$ in dry acetonitrile at 160 K.

studies, $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ alone has the characteristic signals of the monomeric manganese(IV) species with g values of 3.41 and 1.96 at 77 K.^{14f} Here, at 160 K, it demonstrates two EPR signals at 3.63 and 2.01, very similar to those at 77 K. Adding 1 equiv of Al^{3+} , which has $I = 5/2$, causes the g signal at 2.01 of the manganese(IV) species converted into a hyperfine 6-line signal, clearly indicating formation of the $\text{Mn}(\text{IV})\text{--O--Al}^{3+}$ unit.²⁵ Binding of the Al^{3+} cation to the manganese(IV) species may increase its overall positive net charge, thus causing the blue shift of the characteristic absorbance, and as a result reflected in reactivity, the electron transfer rate has been greatly accelerated. The similar charge-promoted electron transfer has also been observed in oxygenation of triphenylphosphine by protonation of the $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})_2^{2+}$ species to generate $\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{OH})(\text{OH}_2)^{3+}$.^{14k} Also, linkages of Zn^{2+} to $(\text{TPB}_8\text{Cz})\text{Mn}^{\text{V}}\equiv\text{O}$ and Sc^{3+} to $\text{Fe}^{\text{IV}}(\text{N4Py})(\text{O})$ all enhanced their abilities in electron transfer as reported in the literature.^{10,12} Intrinsically, binding of Lewis acid to the redox metal oxo functional group generates a similar effect as that through protonation, that is, both protocols increase the overall net charge of the redox metal ion with the increase of its redox potential, thus accelerating its electron transfer rate.

The influences of the Sc^{3+} and Al^{3+} ions on the redox potential of the manganese(IV) species are illustrated in Figure 8. In dry acetone without Lewis acid, the redox potential of the $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ couple is +0.47 V (vs SCE), while in the presence of 4 equiv of Sc^{3+} , it shifts 0.25 V to the positive direction (from +0.47 V to +0.72 V (vs SCE)), corresponding to 55.6-fold rate enhancement in oxygenation with a k_2 value of $(8.9 \pm 0.27) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. According to the Marcus cross relation, a

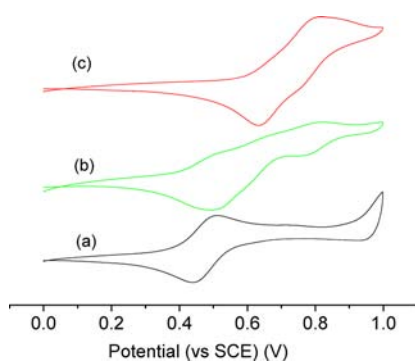


Figure 8. Cyclic voltammograms of the manganese(IV) complexes in the absence/presence of Lewis acid. Conditions: solvent dry acetonitrile, manganese(IV) complexes 2 mM, tetrabutylammonium perchlorate 0.1 M, (a) no additives, (b) $\text{Al}(\text{OTf})_3$ 0.8 mM, (c) $\text{Sc}(\text{OTf})_3$ 8 mM, under nitrogen.

difference of 0.25 V in potential could predict a 130-fold rate difference in other things being equal.^{26,27} Here, the experimentally observed 55.6-fold rate enhancement represents a significant portion of the factor of 130 predicted. The peak separation becoming large upon adding Lewis acid can be attributed to the reversibility of the $\text{Mn}(\text{IV})/\text{Mn}(\text{III})$ couple turning worse. In the case of Al^{3+} , due to its possible influence on the electrode surface, the reversibility of the $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ couple is not good upon adding $\text{Al}(\text{OTf})_3$, and adding more Al^{3+} would make the reversibility even worse; however, it still reveals a positive shift of its potential. For example, in the presence of only 0.4 equiv of Al^{3+} ion, its cathodic peak has shifted to +0.50 V (vs SCE), while without Lewis acid added it is +0.47 V (vs SCE). In the literature, Fukuzumi even observed a potential shift of $\text{Fe}^{\text{IV}}(\text{N4Py})(\text{O})$ by +0.84 V to the positive direction from +0.51 to +1.35 V by adding Sc^{3+} , and significantly, its stoichiometric thioanisole oxidation demonstrates above 10^8 -fold acceleration enhancement in the presence of 100 equiv of Sc^{3+} .^{10a}

In particular, it is worth noting that adding Ca^{2+} can accelerate the oxygenation rate of the manganese(IV) species as well as other redox-inactive metal ions. In nature, Ca^{2+} has special biological importance. In the water oxidation center of Photosystem II it contains a $\text{Mn}_4\text{O}_5\text{Ca}$ diamond cluster as the key unit for oxygen evolution.²⁸ Although the oxygen evolution mechanism has been partially elucidated, the role of Ca^{2+} still remains elusive.²⁹ On the basis of the artificial $[\text{Mn}_4\text{O}_4]^{6+}$ and $[\text{Mn}_3\text{CaO}_4]^{6+}$ models, Agepie suggests that the presence of Ca^{2+} in the cubane may modulate the redox potential of the manganese moieties, thus facilitating access of the high oxidation state (+4) of the manganese for efficient oxygen evolution.³⁰ In the presence of Ca^{2+} , Borovik also found that it may accelerate dioxygen reduction by their $\text{Mn}(\text{II})$ complexes.¹³ Here, we also observed that the presence of Ca^{2+} may accelerate the oxygenation rate of the manganese(IV) species through electron transfer. For example, adding 1 equiv of Ca^{2+} may accelerate the electron transfer by 4.2-fold, which predicts a difference of 74 mV in potential according to the Marcus cross relation with other things being equal.^{26,27} These findings may provide new clues for understanding the role of Ca^{2+} in the water oxidation process in Photosystem II, for example, accelerating the electron transfer rate in oxygen evolution as well as its role revealed here.

CONCLUSIONS

Using well-studied manganese complexes having cross-bridged cyclam ligand, this work investigated the influences of the redox-inactive metal ions on the oxidative reactivities of the redox metal ions in electron transfer, oxygen transfer, and

hydrogen abstraction. Available data reveal that adding redox-inactive metal ions would greatly accelerate the electron transfer rate of the manganese(IV) complexes in sulfoxidations and triphenylphosphine oxygenation, and its ability in electron transfer was also promoted as well. Similar accelerations have also been found in catalytic sulfide oxidations with the corresponding manganese(II) complexes as catalyst and PhIO as oxidant. Significantly, the improved efficiency in electron transfer is highly dependent on the Lewis-acid strength of the added metal ions. Compared with those in electron transfer, oxygen transfer and hydrogen abstraction efficiencies of the manganese complexes in stoichiometric and/or catalytic oxidations are just slightly improved by adding redox-inactive metal ions. However, the thermodynamic driving force of the manganese(IV) species in hydrogen abstraction has been obviously promoted. The improved oxidizing capability of the manganese(IV) species has been attributed to its interaction with the added redox-inactive metal ions through the plausible $Mn^{IV}-O-Al^{3+}$ bridge, which increases the overall net charge of the manganese(IV) species, thus increasing its redox potential. The comprehensive study demonstrated here on the influences of the redox-inactive metal ions on the stoichiometric and catalytic oxidations of these manganese complexes may provide new clues to the best understanding of their roles in versatile biological and chemical oxidations and benefit the rational design of novel oxidation catalysts.

■ ASSOCIATED CONTENT

Supporting Information

UV-vis spectra of the manganese(IV) complexes with different Lewis acid in dry acetone; detailed kinetic data for oxygenations of triphenylphosphine and substituted triarylphosphine by manganese(IV) complexes in the presence of Lewis acid; GC-MS graphs of the C-S cleavage products of benzyl phenyl sulfide in quantitative and catalytic oxidations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gyin@hust.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 20973069 and 21273086). GC-MS analysis was performed in the Analytical and Testing Center of Huazhong University of Science and Technology.

■ REFERENCES

- (1) (a) In *Active oxygen in biochemistry*; Valentine, J. S., Foote, C. S., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: UK, 1995. (b) In *Metal-oxo and Metal-peroxo Species in Catalytic oxidations*; Meunier, B., Ed.; Springer: Berlin, Germany, 2000. (c) Yin, G. *Coord. Chem. Rev.* **2010**, *254*, 1826.
- (2) (a) In *Cytochrome P450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York, 1986. (b) Tinberg, C. E.; Lippard, S. J. *Acc. Chem. Res.* **2011**, *44*, 280. (c) Dismukes, G. C.; Brimblecombe, R.; Felton, G. A. N.; Pryadun, R. S.; Sheats, J. E.; Spiccia, L.; Swiegers, G. F. *Acc. Chem. Res.* **2009**, *42*, 1935. (d) Mure, M. *Acc. Chem. Res.* **2004**, *37*, 131.
- (3) (a) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 522. (b) Costas, M.; Chen, K.; Que, L., Jr. *Coord. Chem. Rev.* **2000**, *200–202*, 517. (c) Kim, E.;

Chufan, E. E.; Kamaraj, K.; Karlin, K. D. *Chem. Rev.* **2004**, *104*, 1077. (d) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 3981.

(4) (a) In *Biomimetic oxidations catalyzed by transition metal complexes*; Meunier, B., Ed.; Imperial College Press: Singapore, 2000. (b) In *Modern oxidation methods*; Bäckvall, J. E., Ed.; Wiley-VCH: New York, 2004. (c) In *Ruthenium in organic synthesis*; Murahashi, S. I., Ed. Wiley-VCH: New York, 2004. (d) In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, S. A., Ed.; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004. (e) Murahashi, S.; Zhang, D. *Chem. Soc. Rev.* **2008**, *37*, 1490. (f) Sheldon, R. A.; Arends, I. W. C. E.; Ten, B. G.; Dijkman, A. *Acc. Chem. Res.* **2002**, *35*, 774.

(5) (a) Liang, Z.; Nocek, J. M.; Kurnikov, I. V.; Beratan, D. N.; Hoffman, B. M. *J. Am. Chem. Soc.* **2000**, *122*, 3552. (b) Hunter, C. L.; Lloyd, E.; Eltis, L. D.; Rafferty, S. P.; Lee, H.; Smith, M.; Mauk, A. G. *Biochemistry* **1997**, *36*, 1010. (c) Reid, L. S.; Taniguchi, V. T.; Gray, H. B.; Mauk, A. G. *J. Am. Chem. Soc.* **1982**, *104*, 7516. (d) Reid, L. S.; Mauk, A. G. *J. Am. Chem. Soc.* **1982**, *104*, 841.

(6) (a) Grasselli, R. K. *Top. Catal.* **2002**, *21*, 79. (b) Gluhoi, A. C.; Lin, S. D.; Nieuwenhuys, B. E. *Catal. Today* **2004**, *90*, 175. (c) Wachs, I. E.; Deo, G.; Jehng, J. M.; Kim, D. S.; Hu, H. *ACS Symp. Ser.* **1996**, *638*, 292.

(7) (a) Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99. (b) Rivalta, I.; Brudvig, G. W.; Batista, V. S. *Curr. Opin. Chem. Biol.* **2012**, *16*, 11. (c) Noguchi, T. *Photosynth. Res.* **2007**, *91*, 59.

(8) Miller, C. G.; Gordon-Wylie, S. W.; Horwitz, C. P.; Strazisar, S. A.; Peraino, D. K.; Clark, G. R.; Weintraub, S. T.; Collins, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 11540.

(9) (a) Du, H.; Lo, P.; Hu, Z.; Liang, H.; Lau, K.; Wang, Y.; Lam, W. W. Y.; Lau, T. *Chem. Commun.* **2011**, *47*, 7143. (b) Yiu, S.; Man, W.; Lau, T. *J. Am. Chem. Soc.* **2008**, *130*, 10821. (c) Lam, W. W. Y.; Yiu, S.; Lee, J. M. N.; Yau, S. K. Y.; Kwong, H.; Lau, T.; Liu, D.; Lin, Z. *J. Am. Chem. Soc.* **2006**, *128*, 2851. (d) Yiu, S.; Wu, Z.; Mak, C.; Lau, T. *J. Am. Chem. Soc.* **2004**, *126*, 14921. (e) Ho, C.; Lau, T. *New J. Chem.* **2000**, *24*, 587. (f) Lau, T.; Wu, Z.; Bai, Z.; Mak, C. *J. Chem. Soc., Dalton Trans.* **1995**, *4*, 695. (g) Lau, T.; Mak, C. *J. Chem. Soc., Chem. Commun.* **1993**, *9*, 766.

(10) (a) Morimoto, Y.; Kotani, H.; Park, J.; Lee, Y.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *133*, 403. (b) Chen, J.; Lee, Y.; Davis, K. M.; Wu, X.; Seo, M. S.; Cho, K.; Yoon, H.; Park, Y. J.; Fukuzumi, S.; Pushkar, Y. N.; Nam, W. *J. Am. Chem. Soc.* **2013**, DOI: [dx.doi.org/10.1021/ja312113p](https://doi.org/10.1021/ja312113p). (c) Fukuzumi, S.; Morimoto, Y.; Kotani, H.; Naumov, P.; Lee, Y.; Nam, W. *Nat. Chem.* **2010**, *2*, 756.

(11) (a) Fukuzumi, S.; Ohkubo, K.; Morimoto, Y. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8472. (b) Fukuzumi, S.; Ohkubo, K. *Coord. Chem. Rev.* **2010**, *254*, 372.

(12) Leeladee, P.; Baglia, R. A.; Prokop, K. A.; Latifi, R.; de Visser, S. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 10397.

(13) Park, Y. J.; Ziller, J. W.; Borovik, A. S. *J. Am. Chem. Soc.* **2011**, *133*, 9258.

(14) (a) Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Busch, D. H.; Alcock, N. W. *Chem. Commun.* **1998**, *16*, 1675. (b) Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Buchalova, M.; Perkins, C. M.; Alcock, N. W.; Kahol, P. K.; Raghunathan, A.; Busch, D. H. *J. Am. Chem. Soc.* **2000**, *122*, 2512. (c) Hubin, T. J.; McCormick, J. M.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **2001**, *40*, 435. (d) Yin, G.; Buchalova, M.; Danby, A. M.; Perkins, C. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 17170. (e) Yin, G.; Buchalova, M.; Danby, A. M.; Perkins, C. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *Inorg. Chem.* **2006**, *45*, 3467. (f) 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.; Busch, D. H. *Inorg. Chem.* **2006**, *45*, 8052. (g) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2007**, *129*, 1512. (h) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *Inorg. Chem.* **2007**, *46*, 2173. (i) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2008**, *130*, 16245. (j) Xu, A.; Xiong, H.; Yin, G. J.

- Phys. Chem. A* **2009**, *113*, 12243. (k) Xu, A.; Xiong, H.; Yin, G. *Chem.—Eur. J.* **2009**, *15*, 11478. (l) Chattopadhyay, S.; Geiger, R. A.; Yin, G.; Busch, D. H.; Jackson, T. A. *Inorg. Chem.* **2010**, *49*, 7530. (m) Yin, G.; Danby, A. M.; Day, V.; Roy, S. B.; Carter, J.; Scheper, W. M.; Busch, D. H. *J. Coord. Chem.* **2011**, *64*, 4. (n) Shi, S.; Wang, Y.; Xu, A.; Wang, H.; Zhu, D.; Roy, S. B.; Jackson, T. A.; Busch, D. H.; Yin, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 7321. (o) Yin, G.; Roy, S. B.; Danby, A. M.; Day, V.; Carter, J.; Scheper, W. M.; Busch, D. H. *J. Inclusion Phenom. Macrocyclic Chem.* **2011**, *71*, 311. (p) Wang, Y.; Shi, S.; Zhu, D.; Yin, G. *Dalton Trans.* **2012**, *41*, 2612. (q) Wang, Y.; Sheng, J.; Shi, S.; Zhu, D.; Yin, G. *J. Phys. Chem. C* **2012**, *116*, 13231. (r) Wang, Y.; Shi, S.; Wang, H.; Zhu, D.; Yin, G. *Chem. Commun.* **2012**, *48*, 7832. (s) Yin, G. *Acc. Chem. Res.* **2013**, *46*, 483.
- (15) Saltzman, H.; Sharefkin, J. G. *Org. Synth.* **1963**, *43*, 60.
- (16) (a) Linden, A. A.; Johansson, M.; Hermanns, N.; Baeckvall, J. J. *Org. Chem.* **2006**, *71*, 3849. (b) Sun, J.; Zhu, C.; Dai, Z.; Yang, M.; Pan, Y.; Hu, H. *J. Org. Chem.* **2004**, *69*, 8500. (c) Donnoli, M. I.; Superchi, S.; Rosini, C. *J. Org. Chem.* **1998**, *63*, 9392. (d) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *J. Org. Chem.* **1990**, *55*, 1323. (e) Kerber, W. D.; Ramdhanie, B.; Goldberg, D. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 3718.
- (17) (a) Glass, R. S. *Top. Curr. Chem.* **1999**, *205*, 1. (b) Li, Z.; Kutateladze, A. G. *J. Org. Chem.* **2003**, *68*, 8236. (c) Baciocchi, E.; Del Giacco, T.; Giombolini, P.; Lanzalunga, O. *Tetrahedron* **2006**, *62*, 6566. (d) Penenory, A. B.; Argueello, J. E.; Puiatti, M. *Eur. J. Org. Chem.* **2005**, *1*, 114.
- (18) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
- (19) Park, J.; Morimoto, Y.; Lee, Y.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *133*, 5236.
- (20) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471. (b) Conley, B. L.; Tenn, W. J., III; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A., III; Periana, R. A. *J. Mol. Catal. A: Chem.* **2006**, *251*, 8. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. (d) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (e) Arndtsen, B. A.; Bergman, R.; Mobley, A.; Peterson, T. *Acc. Chem. Res.* **1995**, *28*, 154. (f) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (g) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (h) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (i) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441.
- (21) (a) Fiedler, T.; Que, L., Jr. *Inorg. Chem.* **2009**, *48*, 11038. (b) Kurahashi, T.; Kikuchi, A.; Tosha, T.; Shiro, Y.; Kitagawa, T.; Fujii, H. *Inorg. Chem.* **2008**, *47*, 1674. (c) Kurahashi, T.; Kikuchi, A.; Shiro, Y.; Hada, M.; Fujii, H. *Inorg. Chem.* **2010**, *49*, 6664. (d) Goldsmith, C. R.; Stack, T. D. P. *Inorg. Chem.* **2006**, *45*, 6048. (e) Goldsmith, C. R.; Cole, A. P.; Stack, T. D. P. *J. Am. Chem. Soc.* **2005**, *127*, 9904.
- (22) (a) Mirafzal, G. A.; Kim, T.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 10968. (b) Adam, W.; Roschmann, K. J.; Saha-Moeller, C. R.; Seebach, D. *J. Am. Chem. Soc.* **2002**, *124*, 5068. (c) Kim, T.; Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 7653. (d) Adam, W.; Roschmann, K. J.; Saha-Moeller, C. R.; Seebach, D. *J. Am. Chem. Soc.* **2002**, *124*, 5068. (e) McGown, A. J.; Kerber, W. D.; Fujii, H.; Goldberg, D. P. *J. Am. Chem. Soc.* **2009**, *131*, 8040. (f) Wang, S. H.; Mandimutsira, B. S.; Todd, R.; Ramdhanie, B.; Fox, J. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2004**, *126*, 18. (g) Nam, W.; Lim, M. H.; Lee, H. J.; Kim, C. *J. Am. Chem. Soc.* **2000**, *122*, 6641. (h) Lee, K. A.; Nam, W. *J. Am. Chem. Soc.* **1997**, *119*, 1916.
- (23) (a) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928. (b) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269.
- (24) (a) Fox, J. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2004**, *126*, 18. (b) Collman, J. P.; Zeng, L.; Brauman, J. I. *Inorg. Chem.* **2004**, *43*, 2672.
- (25) Bershov, L. V.; Gaite, J. M.; Hafner, S. S.; Rager, H. *Phys. Chem. Miner.* **1983**, *9*, 95.
- (26) (a) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. (b) Marcus, R. A. *Angew. Chem., Int. Ed.* **1993**, *32*, 1111. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (d) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (e) Bolton, J. R.; Archer, M. D. In *Electron Transfer in Inorganic, Organic, and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1991; Vol. 228, p 7. (f) Alberly, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.
- (27) (a) Yoder, J. C.; Roth, J. P.; Gussenhoven, E. M.; Larsen, A. S.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 2629. (b) Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363. (c) Mayer, J. M. *Acc. Chem. Res.* **2011**, *44*, 36.
- (28) Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S. *Science* **2004**, *303*, 1831.
- (29) (a) Vrettos, J. S.; Brudvig, G. W. *Oxygen evolution. Comprehensive Coordination Chemistry II*; Elsevier Ltd. Oxford, UK, 2004; Vol. 8, p 507. (b) Najafpour, M. M. *J. Photochem. Photobiol. B* **2011**, *104*, 111. (c) Suzuki, H.; Sugiura, M.; Noguchi, T. *J. Am. Chem. Soc.* **2009**, *131*, 7849. (d) Ruettinger, W.; Yagi, M.; Wolf, K.; Bernasek, S.; Dismukes, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 10353. (e) Jenson, D. L.; Barry, B. A. *J. Am. Chem. Soc.* **2009**, *131*, 10567.
- (30) Kanady, J. S.; Tsui, E. Y.; Day, M. W.; Agapie, T. *Science* **2011**, *333*, 733.