

# Contrasting Effects of Axial Ligands on Electron-Transfer Versus Proton-Coupled Electron-Transfer Reactions of Nonheme Oxoiron(IV) Complexes

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**Abstract:** The effects of axial ligands on electron-transfer and proton-coupled electron-transfer reactions of mononuclear nonheme oxoiron(IV) complexes were investigated by using  $[\text{Fe}^{\text{IV}}(\text{O})(\text{tmc})(\text{X})]^{n+}$  (**1-X**) with various axial ligands, in which tmc is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and X is  $\text{CH}_3\text{CN}$  (**1-NCCH<sub>3</sub>**),  $\text{CF}_3\text{COO}^-$  (**1-OOCCF<sub>3</sub>**), or  $\text{N}_3^-$  (**1-N<sub>3</sub>**), and ferrocene derivatives as electron donors. As the binding strength of the axial ligands increases, the one-electron reduction potentials of **1-X** ( $E_{\text{red}}$ , V vs. saturated calomel electrode (SCE)) are more negatively shifted by the binding of the more electron-donating axial ligands in the order of **1-NCCH<sub>3</sub>** (0.39) > **1-OOCCF<sub>3</sub>** (0.13) > **1-N<sub>3</sub>** (-0.05 V).

Rate constants of electron transfer from ferrocene derivatives to **1-X** were analyzed in light of the Marcus theory of electron transfer to determine reorganization energies ( $\lambda$ ) of electron transfer. The  $\lambda$  values decrease in the order of **1-NCCH<sub>3</sub>** (2.37) > **1-OOCCF<sub>3</sub>** (2.12) > **1-N<sub>3</sub>** (1.97 eV). Thus, the electron-transfer reduction becomes less favorable thermodynamically but more favorable kinetically with increasing donor ability of the axial ligands. The net effect of the axial ligands is the deceleration of the

electron-transfer rate in the order of **1-NCCH<sub>3</sub>** > **1-OOCCF<sub>3</sub>** > **1-N<sub>3</sub>**. In sharp contrast to this, the rates of the proton-coupled electron-transfer reactions of **1-X** are markedly accelerated in the presence of an acid in the opposite order: **1-NCCH<sub>3</sub>** < **1-OOCCF<sub>3</sub>** < **1-N<sub>3</sub>**. Such contrasting effects of the axial ligands on the electron-transfer and proton-coupled electron-transfer reactions of nonheme oxoiron(IV) complexes are discussed in light of the counterintuitive reactivity patterns observed in the oxo transfer and hydrogen-atom abstraction reactions by nonheme oxoiron(IV) complexes (Sastri et al. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 19 181–19186).

**Keywords:** axial ligands • bioinorganic chemistry • electron transfer • enzyme models • iron

## Introduction

High-valent metal–oxo species play essential roles as reactive intermediates in a variety of enzymatic and catalytic oxidation reactions.<sup>[1,2]</sup> In particular, the activation of C–H bonds of organic substrates by high-valent metal–oxo species is of fundamental importance not only in biological reactions but also in industrial processes.<sup>[1,2]</sup> The key initial step in the C–H bond activation is considered to be electron ( $e^-$ ) transfer, hydrogen-atom (H-atom) transfer, or hydride ( $\text{H}^-$ ) transfer.<sup>[3–5]</sup> Electron transfer is often suggested as the rate-determining step or as a sequential electron- and proton-transfer pathway in H-atom transfer reactions.<sup>[6–9]</sup> There has also been extensive discussions as to whether hydride transfer occurs in a stepwise manner by sequential electron–proton–electron transfer ( $e^- + \text{H}^+ + e^-$ ) or one-step transfer of a hydride ion ( $\text{H}^-$ ) by a concerted pathway.<sup>[10–16]</sup> Thus, the knowledge of electron-transfer properties of high-valent metal–oxo species is essential not only in understand-

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ing the electron-transfer reactions, but also in clarifying the mechanisms of hydrogen- and hydride-transfer reactions. However, the fundamental electron-transfer properties of high-valent metal–oxo species have yet to be scrutinized mainly because of the thermal instability and high reactivity of high-valent metal–oxo species in nature.<sup>[17]</sup> In this context, mononuclear nonheme oxoiron(IV) intermediates, the structural and spectroscopic characterization of which has been well established recently,<sup>[18,19]</sup> have merited attention owing to their thermal stability.

The nature of axial ligands *trans* to the iron–oxo moiety was found to play a significant role in controlling reactivities of nonheme oxoiron(IV) complexes in oxo-transfer (O-transfer) processes to PPh<sub>3</sub> and H-atom abstraction from phenol O–H and alkyl aromatic C–H bonds recently.<sup>[20]</sup> More interestingly, the oxoiron(IV) complexes showed opposite reactivity trends in the O-transfer and H-abstraction reactions, depending on the axial ligands.<sup>[20b,d,e,f]</sup> For example, [Fe<sup>IV</sup>(O)(tmc)(X)]<sup>n+</sup> (**1-X**), in which *tmc* is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and X is CH<sub>3</sub>CN (**1-NCCH<sub>3</sub>**), CF<sub>3</sub>COO<sup>-</sup> (**1-OOCCF<sub>3</sub>**), or N<sub>3</sub><sup>-</sup> (**1-N<sub>3</sub>**), exhibited the reactivity order of **1-NCCH<sub>3</sub>** > **1-OOCCF<sub>3</sub>** > **1-N<sub>3</sub>** in O-transfer reactions, whereas the opposite reactivity order, that is **1-NCCH<sub>3</sub>** < **1-OOCCF<sub>3</sub>** < **1-N<sub>3</sub>**, was observed in H-atom abstraction reactions.<sup>[20d]</sup> These results indicate that **1-X** exhibits a dichotomic reactivity pattern; in O-transfer reactions, **1-X** behaves as an electrophile, whereby electron-donating axial ligands diminish the oxidative reactivity, whereas **1-X** behaves in a contrary manner in H-atom transfer reactions, in which electron-donating axial ligands enhance the reactivity of the oxoiron(IV) species.<sup>[20d]</sup> The latter result is counterintuitive because the more electron-rich oxoiron(IV) species should be less reactive in electrophilic C–H activation reactions. Similarly, it has been proposed recently that the role of the thiolate axial ligand of cytochrome P450 and chloroperoxidase is to increase the reactivity of oxoiron(IV) porphyrin  $\pi$ -cation radicals in H-abstraction reactions, by reducing the reduction potential of the high-valent iron center and increasing the basicity of the oxoiron(IV) group due to the strong electron donation by the thiolate ligand.<sup>[21]</sup>

Recently, we have reported fundamental electron-transfer properties (i.e., reorganization energies and one-electron reduction potentials) of nonheme oxoiron(IV) complexes, including **1-NCCH<sub>3</sub>**, by examining the thermodynamics and kinetics of the electron-transfer reactions with a series of electron donors.<sup>[22]</sup> As part of our ongoing efforts to understand the axial-ligand effects on the chemical properties of nonheme oxoiron(IV) complexes, we investigated herein the axial-ligand effects on the electron-transfer and proton-coupled electron-transfer reactions of the oxoiron(IV) species. In the former reactions, the driving-force dependence on the electron-transfer rate of nonheme oxoiron(IV) complexes is analyzed in light of the Marcus theory of electron transfer,<sup>[23]</sup> leading us to evaluate the reorganization energies and one-electron reduction potentials of nonheme oxoiron(IV) complexes bearing different axial ligands. In the latter reac-

tions, the axial ligand effects on the proton-coupled electron-transfer reactions from a series of ferrocene derivatives to **1-X** complexes were investigated in the presence of perchloric acid (HClO<sub>4</sub>), to provide a mechanistic insight into the relation between the proton-coupled electron-transfer and the hydrogen-atom-transfer reactions. We have found that there are significant axial-ligand effects on the electron-transfer and proton-coupled electron-transfer reactions of nonheme oxoiron(IV) complexes, such that the electron-donating axial ligand retards the electron-transfer reaction, whereas the rate of the proton-coupled electron-transfer is accelerated by the binding of an electron-donating axial ligand. Thus, the present study provides valuable mechanistic insight into the axial-ligand effects on the reactivities of nonheme oxoiron(IV) complexes in oxidation reactions.

## Results and Discussion

**Axial ligand effect on the electron-transfer reduction of [Fe<sup>IV</sup>(O)(tmc)(X)]<sup>n+</sup>:** The addition of axial ligands (N<sub>3</sub><sup>-</sup> and CF<sub>3</sub>COO<sup>-</sup>) to a reaction solution of **1-NCCH<sub>3</sub>** resulted in the change of the absorption spectrum of **1-NCCH<sub>3</sub>** (Figure 1), which indicates that the CH<sub>3</sub>CN ligand was sub-

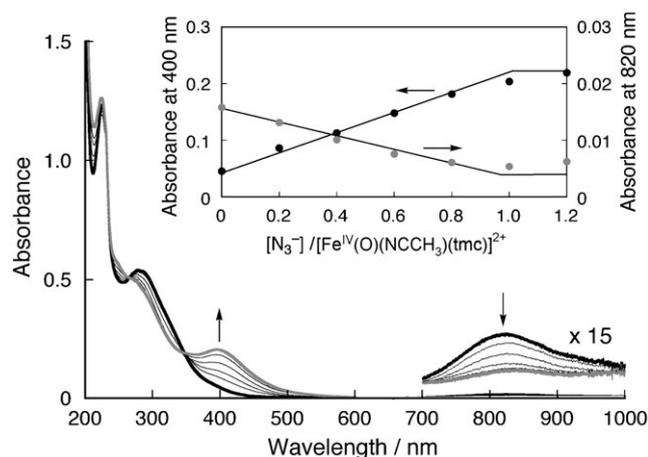
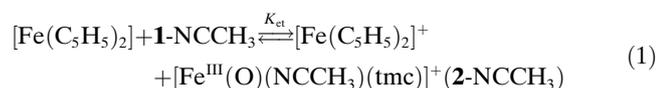


Figure 1. UV/Vis spectral changes of **1-NCCH<sub>3</sub>** upon the addition of N<sub>3</sub><sup>-</sup> to the solution of **1-NCCH<sub>3</sub>** ( $6.0 \times 10^{-5}$  M) at 298 K. Inset shows the spectral titrations monitored at 400 and 820 nm for the formation of **1-N<sub>3</sub>** and the decay of **1-NCCH<sub>3</sub>**, respectively.

stituted by the anionic ligands.<sup>[20a,b,d]</sup> The spectral titration experiments demonstrate that around one equivalent of the axial ligands was enough to replace the CH<sub>3</sub>CN ligand of **1-NCCH<sub>3</sub>** to give **1-N<sub>3</sub>** and **1-OOCCF<sub>3</sub>** (see inset of Figure 1), which indicates that the anionic ligands bind to the iron(IV) center strongly. Further, when N<sub>3</sub><sup>-</sup> was added to the solution of **1-OOCCF<sub>3</sub>**, the formation of **1-N<sub>3</sub>** was observed (data not shown). In contrast, we did not observe the formation of **1-OOCCF<sub>3</sub>** upon the addition of CF<sub>3</sub>COO<sup>-</sup> to the solution of

**1-N<sub>3</sub>** (data not shown). Thus, the binding strength of axial ligands to the iron(IV) center turns out to be in the order of  $N_3^- > CF_3COO^- > CH_3CN$ .

The electron-transfer reduction of **1-X** bearing different axial ligands was investigated by using a series of ferrocene derivatives as one-electron reductants in  $CH_3CN$ . The electron transfer from ferrocene,  $[Fe(C_5H_5)_2]$  ( $E_{ox} = 0.37$  V vs. saturated calomel electrode (SCE)), to **1-NCCH<sub>3</sub>** in  $CH_3CN$  is in equilibrium, see Equation (1).



in which the final concentration of  $[Fe(C_5H_5)_2]^+$  produced in the electron-transfer reaction increases with the increase in the initial  $[Fe(C_5H_5)_2]$  concentration. The equilibrium constant,  $K_{et}$ , in Equation (1) was determined to be 2.0 at 298 K.<sup>[22]</sup> The one-electron reduction potential,  $E_{red}$ , of **1-NCCH<sub>3</sub>** was then calculated from the  $K_{et}$  value and the  $E_{ox}$  value of  $[Fe(C_5H_5)_2]$  (0.37 V vs. SCE), by using the Nernst equation in Equation (2), to be 0.39 V versus SCE.

$$E_{red} = E_{ox} + (RT/F)\ln K_{et} \quad (2)$$

The <sup>1</sup>H NMR spectrum of  $[Fe^{III}(O)(NCCH_3)(tmc)]^+$  (**2-NCCH<sub>3</sub>**), generated by the one-electron reduction of **1-NCCH<sub>3</sub>**, was measured in  $CD_3CN$  at 298 K.<sup>[22]</sup> The large line broadening of the <sup>1</sup>H NMR spectrum indicates that there is only one species as a product (i.e., **2-NCCH<sub>3</sub>**) and that there are no peaks due to the corresponding  $Fe^{II}$  ( $S=2$ ) or  $Fe^{IV}$  complex ( $S=1$ ).<sup>[22]</sup> Based on the chemical shift of the tetramethylsilane (TMS) peak in the presence of **2-NCCH<sub>3</sub>** in comparison with the TMS peak in the inner capillary tube (77.3 Hz), the spin state of the resulting  $Fe^{III}$  complex was determined to be  $S=3/2$  by the Evans method.<sup>[22,24,25]</sup> This spin state  $S=3/2$  was also confirmed by the ESR spectrum of  $[Fe^{III}(O)(tmc)]^+$  at 77 K.<sup>[22]</sup>

In contrast to the case of **1-NCCH<sub>3</sub>**, no electron transfer occurred from  $[Fe(C_5H_5)_2]$  to **1-N<sub>3</sub>**. When  $[Fe(C_5H_5)_2]$  was replaced by a stronger one-electron reductant, octamethylferrocene ( $[Fe(C_5Me_4H)_2]$ ,  $E_{ox} = -0.04$  V vs. SCE), electron transfer from  $[Fe(C_5Me_4H)_2]$  to **1-N<sub>3</sub>** became energetically plausible to oxidize  $[Fe(C_5Me_4H)_2]$  as shown in Figure 2. The absorption at 760 nm due to  $[Fe(C_5Me_4H)_2]^+$  increases, accompanied by the decay in absorption at 400 nm due to **1-N<sub>3</sub>** in Figure 2. The time profile of  $[Fe(C_5Me_4H)_2]^+$  (see the inset of Figure 2) obeys first-order kinetics with exhibiting two-step processes at a 1:1 ratio (**1-NCCH<sub>3</sub>/1-N<sub>3</sub>**), which consist of the fast step due to **1-NCCH<sub>3</sub>** and the slow step due to **1-N<sub>3</sub>** (left panel of inset of Figure 2). This indicates that there is no axial ligand exchange between **1-NCCH<sub>3</sub>** and **1-N<sub>3</sub>** at the time scale of electron transfer.

The electron transfer from  $[Fe(C_5Me_4H)_2]$  to **1-N<sub>3</sub>** is also in equilibrium as shown in Equation (3). The final concentration of  $[Fe(C_5Me_4H)_2]^+$  increases with the increase of the initial concentration of  $[Fe(C_5Me_4H)_2]$  (Figure 3). The equi-

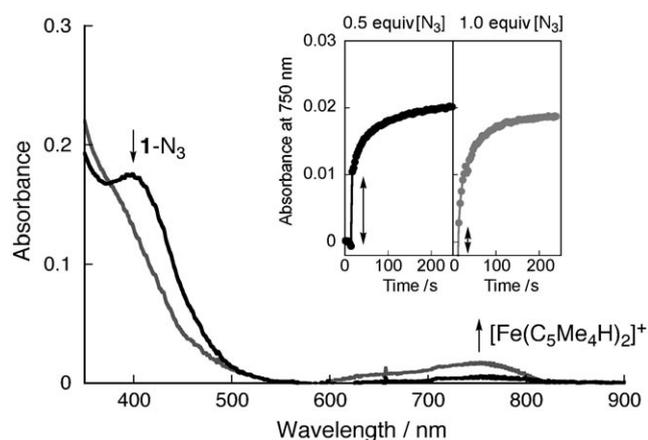


Figure 2. Spectral changes observed in the reaction of **1-N<sub>3</sub>** ( $6.0 \times 10^{-5}$  M) with  $[Fe(C_5Me_4H)_2]$  ( $2.0 \times 10^{-3}$  M) in deaerated MeCN at 298 K. Inset: Time profiles of absorption changes at  $\lambda = 760$  nm for the formation of  $[Fe(C_5Me_4H)_2]^+$  in the reactions of a mixture of **1-NCCH<sub>3</sub>/1-N<sub>3</sub>** 1:1 (left panel) and **1-N<sub>3</sub>** (right panel).

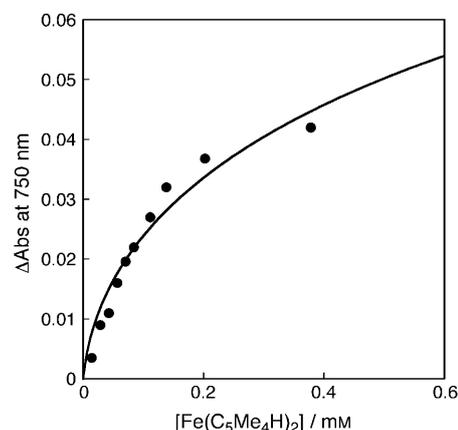
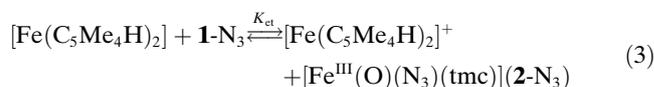


Figure 3. Plot of absorbance at 760 nm due to  $[Fe(C_5Me_4H)_2]^+$  produced in the electron-transfer equilibrium between  $[Fe(C_5Me_4H)_2]$  and **1-N<sub>3</sub>** ( $1.7 \times 10^{-4}$  M) in deaerated MeCN at 298 K versus initial concentration of  $[Fe(C_5Me_4H)_2]$ .

librium constant ( $K_{et}$ ) in Equation (3) was determined to be 1.0 at 298 K (Figure 3, —).



The  $E_{red}$  value of  $-0.05$  V versus SCE for **1-N<sub>3</sub>** was then calculated from the  $K_{et}$  value and the  $E_{ox}$  value of  $[Fe(C_5Me_4H)_2]$  ( $-0.04$  V vs. SCE) by using the Nernst equation in Equation (2). This value agrees well with the value ( $-0.05$  V) obtained from the negative shift ( $-0.44$  V) of the one-electron reduction peak potential of **1-N<sub>3</sub>** as compared with that of **1-NCCH<sub>3</sub>** (see Figure S1 in the Supporting Information).<sup>[26]</sup> Although there was no appropriate one-electron reductant available for the redox titration of **1-OOCCF<sub>3</sub>**, the  $E_{red}$  value was evaluated to be 0.13 V versus

SCE from the negative shift ( $-0.26$  V) of the one-electron reduction peak potential of **1**-OOCFF<sub>3</sub> as compared with that of **1**-NCCH<sub>3</sub> (see Figure S1 in the Supporting Information). Thus, the coordination of electron-rich anionic axial ligands, N<sub>3</sub><sup>-</sup> and CF<sub>3</sub>COO<sup>-</sup>, results in a negative shift of the one-electron reduction potential of **1**-NCCH<sub>3</sub>.

The rate of electron transfer from [Fe(C<sub>5</sub>Me<sub>4</sub>H)] to **1**-N<sub>3</sub> was determined from the decrease in the absorption band at 850 nm due to **1**-N<sub>3</sub> or the increase in the absorption band at 760 nm due to [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>]<sup>+</sup>. Similarly, the electron-transfer rates were determined with other ferrocene derivatives (e.g., [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]) and oxoiron(IV) complexes bearing different axial ligands, such as **1**-NCCH<sub>3</sub>, **1**-OOCFF<sub>3</sub>, and **1**-N<sub>3</sub>. The electron-transfer rates obeyed pseudo-first-order kinetics when a large excess of [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>] was used. The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) increased linearly with increasing concentrations of ferrocene derivative. The second-order rate constants ( $k_{\text{et}}$ ) were determined from the slopes of linear plots of  $k_{\text{obs}}$  versus concentrations of ferrocene derivatives. The  $k_{\text{et}}$  values thus obtained are listed in Table 1, together with the  $E_{\text{ox}}$  values of ferrocene derivatives, the  $E_{\text{red}}$  values of oxoiron(IV) complexes with different axial ligands, and the driving force of electron transfer ( $-\Delta G_{\text{et}} = e(E_{\text{red}} - E_{\text{ox}})$  in eV).

The driving-force dependence of the rate constants of electron transfer from ferrocene derivatives to oxoiron(IV) complexes with different axial ligands in MeCN at 298 K is shown in Figure 4, in which the  $\log k_{\text{et}}$  values are plotted against the  $-\Delta G_{\text{et}}$  values. Each curve is well fitted by the solid line in Figure 4 in light of the Marcus theory of adiabatic outer-sphere electron transfer [Eq. (4)].

$$k_{\text{et}} = Z \exp[-(\lambda/4)(1 + \Delta G_{\text{et}}/\lambda)^2/k_{\text{B}}T] \quad (4)$$

in which  $Z$  is the collision frequency taken as  $1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ,  $\lambda$  is the reorganization energy of electron transfer,  $k_{\text{B}}$  is the Boltzmann constant, and  $T$  is the absolute temperature.<sup>[10,15]</sup> The  $\lambda$  values thus obtained by Equation (4) are listed in

Table 1. Oxidation potentials ( $E_{\text{ox}}$ ) of ferrocene derivatives, reduction potentials ( $E_{\text{red}}$ ) of oxoiron(IV) complexes, rate constants ( $k_{\text{et}}$ ), and driving force ( $-\Delta G_{\text{et}}$ ) for electron transfer from ferrocene derivatives to oxoiron(IV) complexes with different axial ligands in deaerated MeCN at 298 K.

Electron donor	$E_{\text{ox}}$ [V vs. SCE]	Oxoiron(IV) complex	$E_{\text{red}}$ [V vs. SCE]	$k_{\text{et}}$ [M <sup>-1</sup> s <sup>-1</sup> ]	$-\Delta G_{\text{et}}$ [eV]
1 ferrocene	0.37	<b>1</b> -NCCH <sub>3</sub>	0.39	$1.4 \times 10$	0.02
		<b>1</b> -OOCFF <sub>3</sub>	0.13	— <sup>[a]</sup>	-0.24
		<b>1</b> -N <sub>3</sub>	-0.05	— <sup>[a]</sup>	-0.42
2 <i>n</i> -amylferrocene	0.31	<b>1</b> -NCCH <sub>3</sub>	0.39	$3.9 \times 10$	0.08
		<b>1</b> -OOCFF <sub>3</sub>	0.13	— <sup>[a]</sup>	-0.18
		<b>1</b> -N <sub>3</sub>	-0.05	— <sup>[a]</sup>	-0.36
3 dimethylferrocene	0.26	<b>1</b> -NCCH <sub>3</sub>	0.39	$1.0 \times 10^2$	0.13
		<b>1</b> -OOCFF <sub>3</sub>	0.13	— <sup>[a]</sup>	-0.13
		<b>1</b> -N <sub>3</sub>	-0.05	— <sup>[a]</sup>	-0.31
4 octamethylferrocene	-0.04	<b>1</b> -NCCH <sub>3</sub>	0.39	$2.7 \times 10^4$	0.43
		<b>1</b> -OOCFF <sub>3</sub>	0.13	$3.2 \times 10^3$	0.17
		<b>1</b> -N <sub>3</sub>	-0.05	$3.7 \times 10^2$	-0.01
5 decamethylferrocene	-0.08	<b>1</b> -NCCH <sub>3</sub>	0.39	$6.3 \times 10^4$	0.47
		<b>1</b> -OOCFF <sub>3</sub>	0.13	$1.3 \times 10^4$	0.21
		<b>1</b> -N <sub>3</sub>	-0.05	$1.6 \times 10^3$	0.03

[a] No reaction.

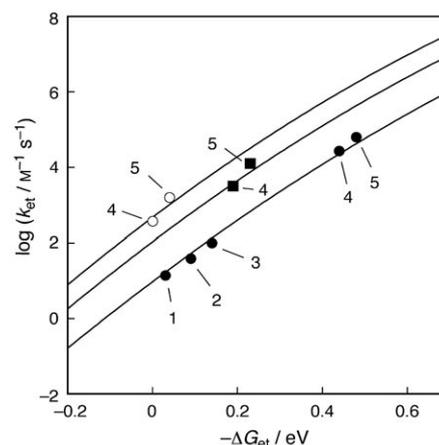


Figure 4. Driving-force dependence of rate constants ( $\log k_{\text{et}}$ ) for ET from ferrocene derivatives (1: ferrocene, 2: *n*-amylferrocene, 3: 1,1'-dimethylferrocene, 4: octamethylferrocene, 5: decamethylferrocene) to oxoiron(IV) complexes (●: **1**-NCCH<sub>3</sub>, ■: **1**-OOCFF<sub>3</sub>, ○: **1**-N<sub>3</sub>) bearing different axial ligands in deaerated MeCN at 298 K.

Table 2, together with the  $E_{\text{red}}$  values of oxoiron(IV) complexes.

The data in Table 2 clearly show that as the  $E_{\text{red}}$  value is more negatively shifted (i.e., X = CH<sub>3</sub>CN (0.39) > CF<sub>3</sub>COO<sup>-</sup> (0.13) > N<sub>3</sub><sup>-</sup> (-0.05 V)), the  $\lambda$  value of **1**-X becomes smaller (i.e., X = CH<sub>3</sub>CN (2.37) > CF<sub>3</sub>COO<sup>-</sup> (2.12) > N<sub>3</sub><sup>-</sup> (1.97 eV)).

Table 2. Reduction potentials ( $E_{\text{red}}$ ) of oxoiron(IV) complexes and reorganization energy ( $\lambda$ ) for electron transfer from ferrocene derivatives to oxoiron(IV) complexes with different axial ligands in deaerated MeCN at 298 K.

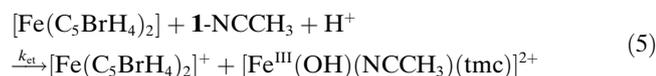
Oxoiron(IV) complex	$E_{\text{red}}$ [V vs. SCE]	$\lambda$ [eV]
<b>1</b> -NCCH <sub>3</sub>	$0.39 \pm 0.01$ <sup>[a,c]</sup>	$2.37 \pm 0.04$ <sup>[c]</sup>
<b>1</b> -OOCFF <sub>3</sub>	$0.13 \pm 0.01$ <sup>[b]</sup>	$2.12 \pm 0.04$
<b>1</b> -N <sub>3</sub>	$-0.05 \pm 0.01$ <sup>[a]</sup>	$1.97 \pm 0.04$

[a] Determined from the spectral redox titration. [b] Determined from CV. [c] Taken from reference [22].

Thus, coordination of a strongly binding and electron-donating axial ligand lowers the one-electron reduction potential and decreases the reorganization energy of the oxoiron(IV) species. The latter phenomenon is interpreted from the fact that the strong binding of an electron-rich axial ligand may result in the smaller structural change in the electron-transfer reactions of nonheme oxoiron(IV) species. Such a decrease in the reorganization energy in electron-transfer reactions has previously been reported in the

electron-transfer oxidation of iron(III) porphyrins in the presence of a strong axial ligand, which causes significant acceleration of the rate of the electron-transfer oxidation.<sup>[27]</sup> In the case of the electron-transfer reduction of the oxoiron(IV) complexes, the strong binding of the axial ligand makes the electron transfer more difficult thermodynamically due to the negative shift of the one-electron reduction potential, but the intrinsic kinetic barrier of electron transfer is lowered by the decrease in the reorganization energy of electron transfer.

**Axial ligand effect on the proton-coupled electron-transfer reduction of  $[\text{Fe}^{\text{IV}}(\text{O})(\text{tmc})(\text{X})]^{n+}$ :** As predicted by the positive value of the free energy change in the electron-transfer reactions, no electron transfer occurs from 1,1'-dibromoferrrocene ( $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$ ,  $E_{\text{ox}}=0.70$  V vs. SCE) to 1-NCCH<sub>3</sub> ( $E_{\text{red}}=0.39$  V vs. SCE) in MeCN at 298 K. Interestingly, addition of HClO<sub>4</sub> to a reaction solution of  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  and 1-NCCH<sub>3</sub> results in electron transfer from  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  to 1-NCCH<sub>3</sub> that leads to the formation of  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]^+$  and  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$  in Equation (5).



The electron-transfer rates obey pseudo-first-order kinetics in a large excess of  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$ . The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) increase linearly with increasing concentration of  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$ . The  $k_{\text{obs}}$  values also increase linearly with an increase in HClO<sub>4</sub> concentration (Figure 5a).

The addition of HClO<sub>4</sub> to 1-NCCH<sub>3</sub> also results in a large positive shift of the one-electron reduction peak potential from 0.00 V versus SCE in the absence of HClO<sub>4</sub> to +0.18 V versus SCE in the presence of HClO<sub>4</sub> (15 mM) at the sweep rate of 0.10 V s<sup>-1</sup> (see Figure S2 in the Supporting Information). No protonation of 1-NCCH<sub>3</sub> occurs in the presence of HClO<sub>4</sub>, judging from no spectral change of 1-NCCH<sub>3</sub> in the presence of HClO<sub>4</sub>. In such a case, the large positive shift of the one-electron reduction peak in Figure S2 (Supporting Information) should result from the protonation of the one-electron-reduced species (2-NCCH<sub>3</sub>), affording  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$ . Since no electron transfer occurs from  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  to 1-NCCH<sub>3</sub> in the absence of acid, electron transfer from  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  to 1-NCCH<sub>3</sub> must be coupled with the protonation of 2-NCCH<sub>3</sub>. This is regarded as proton-coupled electron transfer (PCET),<sup>[28]</sup> and the proposed PCET cycle is depicted in Scheme 1. The existence of  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$  was suggested by the stepwise addition of one equivalent of  $[\text{Fe}(\text{C}_5\text{Me}_5)_2]$  and HClO<sub>4</sub> to 1-NCCH<sub>3</sub> (see Figure S3 in the Supporting Information).<sup>[29]</sup> Although there is no spectral change between  $[\text{Fe}^{\text{III}}(\text{O})(\text{NCCH}_3)(\text{tmc})]^+$  and  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$ , the ESR spectrum shows the clear appearance of the high-spin state at  $g=8.2$  due to the formation of  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$  (see Figure S4 in the Supporting Informa-

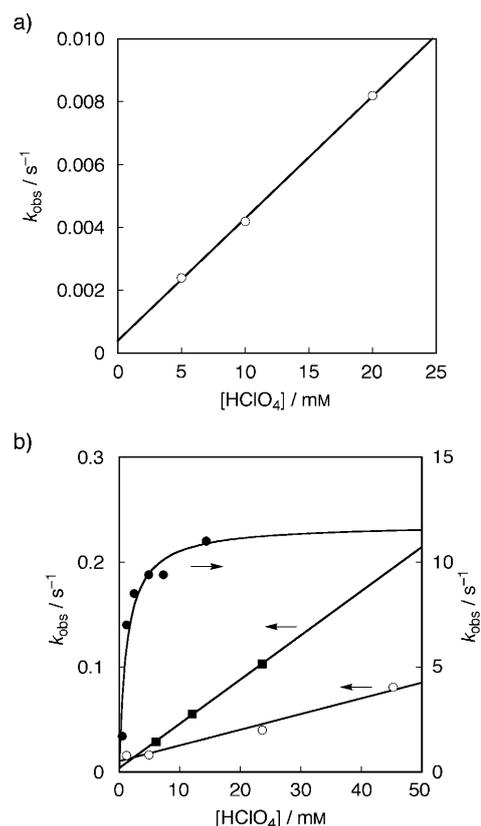
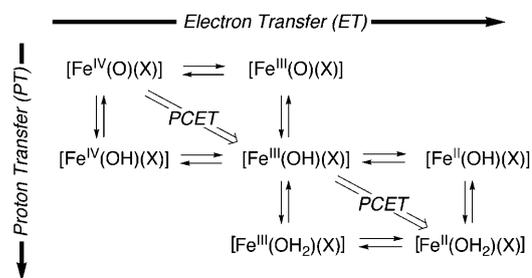


Figure 5. Plot of the rate constants ( $k_{\text{obs}}$ ) of proton-coupled electron transfer a) from  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  ( $3.0 \times 10^{-3}$  M) to 1-NCCH<sub>3</sub> and b) from  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  ( $3.0 \times 10^{-3}$  M) to nonheme oxoiron(IV) complexes ( $1.0 \times 10^{-4}$  M), 1-NCCH<sub>3</sub> (○), 1-OOCCF<sub>3</sub> (■), and 1-N<sub>3</sub> (●), in the presence of HClO<sub>4</sub> in MeCN at 298 K versus concentration of HClO<sub>4</sub>.



Scheme 1. PCET cycle of  $[\text{Fe}^{\text{IV}}(\text{O})(\text{tmc})(\text{X})]^{n+}$ . Charge is omitted for clarity.

tion).<sup>[30]</sup> Under the pseudo-first-order conditions in the presence of HClO<sub>4</sub>, however,  $[\text{Fe}^{\text{III}}(\text{OH})(\text{NCCH}_3)(\text{tmc})]^{2+}$  was not detected in the two-electron reduction of 1-NCCH<sub>3</sub> with  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]$  to yield  $[\text{Fe}^{\text{II}}(\text{OH}_2)(\text{tmc})]^{2+}$  and two equivalents of  $[\text{Fe}(\text{C}_5\text{BrH}_4)_2]^+$ .

The effect of axial ligands on the PCET process was also examined in electron transfer from  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  to 1-N<sub>3</sub> and 1-OOCCF<sub>3</sub> in the presence of acid in CH<sub>3</sub>CN. The results are shown in Figure 5b. Although electron transfer does not occur from  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  to 1-N<sub>3</sub> in the absence of HClO<sub>4</sub> in

CH<sub>3</sub>CN at 298 K (vide supra), the addition of HClO<sub>4</sub> to a reaction solution of [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] and **1**-N<sub>3</sub> results in electron transfer from [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to **1**-N<sub>3</sub>, as observed in the reaction of **1**-NCCH<sub>3</sub>. To our surprise, the rate of electron transfer of **1**-N<sub>3</sub> with the same concentration of HClO<sub>4</sub> is much faster than that of **1**-NCCH<sub>3</sub> (Figure 5b). This is in sharp contrast with the electron-transfer reactions of **1**-X, which were performed in the absence of HClO<sub>4</sub>, when the *k*<sub>et</sub> values of electron transfer from [Fe(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>] and [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] to **1**-N<sub>3</sub> are much smaller than the corresponding value of **1**-NCCH<sub>3</sub> (Table 1). However, such enhancement of electron transfer is observed only when HClO<sub>4</sub> is added last. When HClO<sub>4</sub> is added first to the solution of **1**-N<sub>3</sub>, the axial ligand is protonated. As a result, the rates of electron transfer from [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to **1**-N<sub>3</sub> and from [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to **1**-NCCH<sub>3</sub> become the same. This indicates that the PCET reaction occurs faster than the protonation of N<sub>3</sub><sup>-</sup> when the reaction is carried out in the presence of HClO<sub>4</sub>.

The *k*<sub>obs</sub> value of PCET from [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to **1**-N<sub>3</sub> increases with increasing concentration of HClO<sub>4</sub>, exhibiting a saturation behavior as shown by closed circles in Figure 5b. Such a saturation behavior of *k*<sub>obs</sub> on [HClO<sub>4</sub>] suggests that the oxoiron(IV) complex is protonated in the presence of the N<sub>3</sub><sup>-</sup> axial ligand prior to electron transfer. When the CH<sub>3</sub>CN ligand is replaced by CF<sub>3</sub>COO<sup>-</sup>, the *k*<sub>obs</sub> value of PCET from [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to **1**-OOCF<sub>3</sub> is greater than the corresponding *k*<sub>obs</sub> value of **1**-NCCH<sub>3</sub> at the same concentration of HClO<sub>4</sub>, but smaller than that of **1**-N<sub>3</sub> as shown by closed squares in Figure 5b, in which the *k*<sub>obs</sub> increases linearly with increasing concentration of HClO<sub>4</sub>.

## Conclusion

The effects of axial ligands on electron transfer from ferrocene derivatives to [Fe<sup>IV</sup>(O)(tmc)(X)]<sup>n+</sup> (**1**-X) (X = CH<sub>3</sub>CN, CF<sub>3</sub>COO<sup>-</sup>, or N<sub>3</sub><sup>-</sup>) were investigated to understand the electron-transfer properties of nonheme oxoiron(IV) complexes, such as one-electron reduction potentials and reorganization energies of electron transfer. As the electron-donating ability of the axial ligands (i.e. X = CH<sub>3</sub>CN < CF<sub>3</sub>COO<sup>-</sup> < N<sub>3</sub><sup>-</sup>) increases, the one-electron reduction potentials of **1**-X are shifted to the negative direction (i.e. *E*<sub>red</sub> = **1**-NCCH<sub>3</sub> (0.39) > **1**-OOCF<sub>3</sub> (0.13) > **1**-N<sub>3</sub> (-0.05 V)) and the reorganization energies of electron transfer become smaller (i.e. λ = **1**-NCCH<sub>3</sub> (2.37) > **1**-OOCF<sub>3</sub> (2.12) > **1**-N<sub>3</sub> (1.97 eV)). The binding of an electron-donating axial ligand (e.g. N<sub>3</sub><sup>-</sup>) to an iron(IV) center results in the deceleration of the rates of electron transfer from ferrocene derivatives to nonheme oxoiron(IV) complexes (i.e. the order of reaction rates in ET reactions = **1**-NCCH<sub>3</sub> > **1**-OOCF<sub>3</sub> > **1**-N<sub>3</sub>) and the remarkable acceleration of the rates of proton-coupled electron transfer in the presence of acid owing to the enhanced protonation of the oxoiron(IV) and oxoiron(III) complexes (i.e. the order of reaction rates in PCET reactions = **1**-NCCH<sub>3</sub> < **1**-OOCF<sub>3</sub> < **1**-N<sub>3</sub>). Such contrasting effects of axial ligands on the ET and PCET reactions of nonheme ox-

oiron(IV) complexes resemble the counterintuitive reactivity patterns observed in the O-transfer and H-atom abstraction reactions.<sup>[20]</sup> The reactivity order of **1**-NCCH<sub>3</sub> > **1**-OOCF<sub>3</sub> > **1**-N<sub>3</sub> observed in the O-transfer reactions<sup>[20d]</sup> is the same as that observed in the ET reactions. Such reactivity orders in the O-transfer and ET reactions are rationalized by the electron richness of the oxoiron(IV) species that is governed by the electron-donating ability of the axial ligands. Thus, an oxoiron(IV) species with a more electron-donating axial ligand becomes more electron-rich, thereby showing a low reactivity in electrophilic O-transfer reactions and giving a slow reaction rate in ET reactions.

The inverted reactivity order of **1**-NCCH<sub>3</sub> < **1**-OOCF<sub>3</sub> < **1**-N<sub>3</sub> observed in the H-atom abstraction reactions is the same as that determined in the PCET reactions. The enhanced reactivity of **1**-X bearing an electron-donating axial ligand in the H-atom abstraction reactions was previously rationalized by a decreased triplet–quintet gap with the more electron-donating axial ligand, which increases the contribution of the much more reactive quintet state and enhances the overall reactivity.<sup>[20d,f,30]</sup> However, the enhanced reactivity of **1**-X bearing an electron-donating axial ligand can be also rationalized by an increased basicity of the oxygen of the oxoiron(IV) complexes,<sup>[21]</sup> which increases the PCET reactivity if the H-atom abstraction proceeds by the PCET process. In any case, the present study has clearly demonstrated that the electron-donating axial ligand enhances the PCET reactivity of oxoiron(IV) complexes in the presence of acid despite the retarding effect on the electron-transfer reduction without an acid.

## Experimental Section

**Materials:** Commercially available reagents, such as ferrocene, *n*-amylferrocene, 1,1'-dibromoferrocene, *p*-chloranil, sodium iodide (Tokyo Chemical Industry), 1,1'-dimethylferrocene (Aldrich), octamethylferrocene (STREM), and dexamethylferrocene (Wako Pure) had the best available purity and were used without further purification unless otherwise noted. Acetonitrile (MeCN) was dried according to the literature procedures and distilled under Ar prior to use.<sup>[31]</sup> Preparation and handling of air-sensitive materials were done under an inert atmosphere either on a Schlenk line or in a glove box. The sodium salt of *p*-chloranil radical anion (Cl<sub>4</sub>Q<sup>-</sup>) was synthesized according to the literature procedure.<sup>[32]</sup> Iodosylbenzene (PhIO) was prepared by a literature method.<sup>[33]</sup> Nonheme oxoiron(IV) complexes, [Fe<sup>IV</sup>(O)(tmc)(X)]<sup>n+</sup>, were prepared by reacting [Fe<sup>II</sup>(tmc)(X)]<sup>n+</sup> (0.5 mM) with PhIO (1.2 equiv, 0.6 mM) in CH<sub>3</sub>CN at ambient temperature.<sup>[18a,20,22]</sup>

**Spectral redox titration:** Electron transfer from ferrocene to **1**-NCCH<sub>3</sub> (1.7 × 10<sup>-4</sup> M) was examined from the spectral change in the presence of various concentrations of ferrocene (0.5 × 10<sup>-4</sup>–6.0 × 10<sup>-4</sup> M) at 298 K by using a Hewlett Packard 8453 spectrophotometer with a quartz cuvette (path length = 10 mm). Typically, a deaerated MeCN solution of ferrocene (6.0 × 10<sup>-4</sup> M) was added by means of a microsyringe to a deaerated MeCN solution containing **1**-NCCH<sub>3</sub> (1.7 × 10<sup>-4</sup> M). The concentration of the ferrocenium ion was determined from the absorption band at λ<sub>max</sub> = 615 nm (ε = 5 × 10<sup>2</sup> M<sup>-1</sup> cm<sup>-1</sup>).<sup>[34]</sup> The ε value of the ferrocenium ion was confirmed by the electron-transfer oxidation of ferrocene with [Ru<sup>III</sup>(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (bpy = 2,2'-bipyridine).<sup>[35]</sup>

**Kinetic measurements:** Kinetic measurements were performed on a UNISOKU RSP-601 stopped-flow spectrometer equipped with a MOS-type

highly sensitive photodiode array or a Hewlett Packard 8453 spectrophotometer at 298 K. Rates of electron transfer from ferrocene derivatives to **1-X** were monitored by the rise and decay of absorption bands due to ferrocenium ions and **1-X**, respectively. All kinetic measurements were carried out under pseudo-first-order conditions in which concentrations of ferrocene derivatives were maintained at a more than 10-fold excess of **1-X**.

**Electrochemical measurements:** All electrochemical measurements were carried out under an Ar atmosphere. Electrochemical measurements were performed on a ALS630B electrochemical analyzer in deaerated MeCN containing 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum or gold working electrode (surface area of 0.3 mm<sup>2</sup>) and a platinum wire as a counter electrode. The platinum and gold working electrodes (BAS) were routinely polished with BAS polishing alumina suspension and rinsed with acetone and MeCN before use. The measured potentials were recorded with respect to an Ag/AgNO<sub>3</sub> (0.01 M) reference electrode. All potentials (vs Ag/Ag<sup>+</sup>) were converted to values versus SCE by adding 0.29 V.<sup>[36]</sup>

**ESR measurements:** The sodium salt of *p*-chloranil radical anion (Cl<sub>4</sub>Q<sup>-</sup>) or [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (1 equiv) was added to a reaction solution of [Fe<sup>IV</sup>(O)(tmc)]<sup>2+</sup> (8.0 × 10<sup>-3</sup> M) in MeCN, at room temperature. The resulting solution in the quartz ESR tube (3.0 mm i.d.) was frozen at 77 K. The ESR spectrum was taken on a JEOL X-band spectrometer (JES-RE1XE) under nonsaturating microwave power conditions (1.0 mW) operating at 9.2025 GHz. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio (S/N) of the observed spectrum (modulation width, 20 G; modulation frequency, 100 kHz). The *g* values were calibrated by using an Mn<sup>2+</sup> marker.

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- of  $[\text{Fe}^{\text{III}}(\text{O})(\text{tmc})]^+$  with the use of the Evans method,<sup>24</sup> because the oxidized product ( $\text{Cl}_4\text{O}$ ) is diamagnetic (see reference [22]).
- [26] A new reduction peak appears at  $-0.26$  V by the addition of  $\text{CF}_3\text{COO}^-$  to the solution of **1**-NCCH<sub>3</sub>, and the reduction peak of **1**-NCCH<sub>3</sub> is completely converted to the negatively shifted reduction peak by the addition of  $\text{CF}_3\text{COO}^-$  (1 equiv). The latter result indicates that  $\text{CF}_3\text{COO}^-$  (1 equiv) is enough to replace the  $\text{CH}_3\text{CN}$  ligand. Further, the observation of two reduction peaks when less than 1 equiv of  $\text{CF}_3\text{COO}^-$  was present in the solution of **1**-NCCH<sub>3</sub> indicates that there is no axial ligand exchange between **1**-NCCH<sub>3</sub> and **1**-OOCF<sub>3</sub> (see Figure S1a in the Supporting Information). Similar results were obtained in the reaction of **1**-NCCH<sub>3</sub> and  $\text{N}_3^-$  (see Figure S1b in the Supporting Information). The observation of the larger negative potential shift by the  $\text{N}_3^-$  coordination (**1**-N<sub>3</sub>, 0.44 V) than that of the  $\text{CF}_3\text{COO}^-$  coordination (**1**-OOCF<sub>3</sub>, 0.26 V) is rationalized by greater electron-donation of the  $\text{N}_3^-$  ligand than the  $\text{CF}_3\text{COO}^-$  ligand.
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