

## Biomimetic Hydrocarbon Oxidation Catalyzed by Nonheme Iron(III) Complexes with Peracids: Evidence for an Fe<sup>V</sup>=O Species

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**Abstract:** Mononuclear nonheme iron(III) complexes of tetradentate ligands containing two deprotonated amide moieties, [Fe(Me<sub>2</sub>bpb)Cl(H<sub>2</sub>O)] (**3a**) and [Fe(bpc)Cl(H<sub>2</sub>O)] (**4a**), were prepared by substitution reactions involving the previously synthesized iron(III) complexes [Et<sub>3</sub>NH][Fe(Me<sub>2</sub>bpb)Cl<sub>2</sub>] (**3**) and [Et<sub>3</sub>NH][Fe(bpc)Cl<sub>2</sub>] (**4**). Complexes **3a** and **4a** were characterized by IR and elemental analysis, and complex **3a** also by X-ray crystallography. Nonheme iron(III) complexes **3**, **3a**, **4**, and **4a** catalyze olefin epoxidation and alcohol oxidation on treatment with *m*-chloroperbenzoic acid. Pairwise com-

parisons of the reactivity of these complexes revealed that the nature of the axial ligand (Cl<sup>-</sup> versus H<sub>2</sub>O) influences the yield of oxidation products, whereas an electronic change in the supporting chelate ligand has little effect. Hydrocarbon oxidation by these catalysts was proposed to involve an iron(V) oxo species which is formed on heterolytic O–O bond cleavage of an iron acylperoxo intermediate (FeOO-

C(O)R). Evidence for this iron(V) oxo species was derived from KIE (*k<sub>H</sub>*/*k<sub>D</sub>*) values, H<sub>2</sub><sup>18</sup>O exchange experiments, and the use of peroxyphenylacetic acid (PPAA) as the peracid. Our results suggest that an Fe<sup>V</sup>=O moiety can form in a system wherein the supporting chelate ligand comprises a mixture of neutral and anionic nitrogen donors. This work is relevant to the chemistry of mononuclear nonheme iron enzymes that are proposed to oxidize organic substrates via reaction pathways involving high-valent iron oxo species.

**Keywords:** epoxidation · homogeneous catalysis · iron · oxidation · oxo ligands

### Introduction

There is currently much interest in the chemistry of mononuclear nonheme high-valent iron oxo species (Fe<sup>IV</sup>=O or Fe<sup>V</sup>=O), as they have been identified and/or implicated in the catalytic cycles of a number of mononuclear nonheme

iron enzymes which activate dioxygen.<sup>[1]</sup> For example, an oxoiron(IV) intermediate was recently identified in the catalytic cycle of Fe<sup>II</sup>- and  $\alpha$ -ketoglutarate-dependent oxygenases.<sup>[2]</sup> A mononuclear Fe<sup>V</sup>=O species has been proposed to carry out stereospecific alkane hydroxylation and alkene *cis*-dihydroxylation reactions in Rieske dioxygenases.<sup>[3]</sup> Of relevance to these biological oxidants, a number of synthetic systems containing tetra- or pentadentate amine/pyridine-containing ligands have been used to generate Fe<sup>IV</sup>=O species, as indicated by spectroscopic and/or structural studies.<sup>[4]</sup> An iron(V) oxo species has been proposed to form on treatment of TPA-ligated (TPA = tris(2-pyridylmethyl)amine) iron complexes with H<sub>2</sub>O<sub>2</sub>, with evidence for its formation coming from <sup>18</sup>O labeling studies and analysis of oxidation products.<sup>[5a–c]</sup> Very recently, Que, Munck, Collins, and co-workers reported the formation of an Fe<sup>V</sup> oxo complex of a tetraamido macrocyclic ligand (TAML). This complex, which is formed on treatment of an Fe<sup>III</sup> precursor with *m*-chloroperbenzoic acid (MCPBA), oxidizes thioanisole, styrene, and cyclooctene.<sup>[6]</sup>

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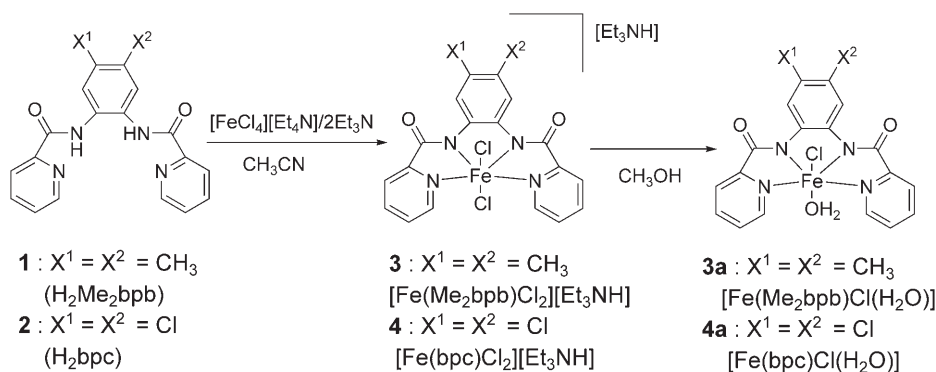
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Olefin epoxidation by heme iron catalysts in the presence of MCPBA is well established and involves an Fe<sup>IV</sup>=O porphyrin cation radical intermediate.<sup>[7]</sup> To date, there are only three mononuclear nonheme iron complexes that are capable of promoting alkene epoxidation in combination with MCPBA.<sup>[6,8]</sup> In this regard, while a TPA-ligated iron complex is an efficient catalyst for olefin epoxidation and *cis*-dihydroxylation with H<sub>2</sub>O<sub>2</sub> as oxidant,<sup>[5]</sup> this complex does not catalyze olefin epoxidation in the presence of MCPBA.<sup>[9]</sup>

As part of our efforts to model mononuclear nonheme iron enzymes, we are exploring the chemistry of nonheme iron complexes of bis-carboxamide donor ligands. As these ligands have an overall dianionic charge (via deprotonation of the two amide moieties) they might be expected to stabilize high oxidation state iron complexes. We now report the synthesis and characterization of iron(III) complexes of two bis-carboxamide ligands, as well as the catalytic olefin epoxidation and alcohol oxidation chemistry of these complexes on treatment with MCPBA. Importantly, mechanistic studies on the hydrocarbon oxidation reactions promoted by these complexes provide evidence for the involvement of an iron(V) oxo species.

## Results and Discussion

We previously reported the synthesis and characterization of the iron(III) complexes **3** and **4** (Scheme 1) which are supported by the 4,5-dimethyl-1,2-bis(2-pyridine-2-carboxami-



Scheme 1. Synthesis of iron(III) complexes.

do)benzene (H<sub>2</sub>Me<sub>2</sub>bpb, **1**) and 4,5-dichloro-1,2-bis(2-pyridine-2-carboxamido)benzene (H<sub>2</sub>bpc, **2**) chelate ligands, respectively.<sup>[10,11]</sup> Both ligands are tetradentate, leaving two available sites for chloride coordination. It has been proposed that the chloride ligands can be substituted by H<sub>2</sub>O.<sup>[12]</sup> Indeed, stirring **3** and **4** in wet methanol afforded aqua iron complexes [Fe(Me<sub>2</sub>bpb)Cl(H<sub>2</sub>O)] (**3a**) and [Fe(bpc)Cl(H<sub>2</sub>O)] (**4a**).<sup>[13]</sup> The X-ray structure of **3a** is shown in Figure 1. Details of X-ray data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. In **3a**, the four nitrogen atoms of the

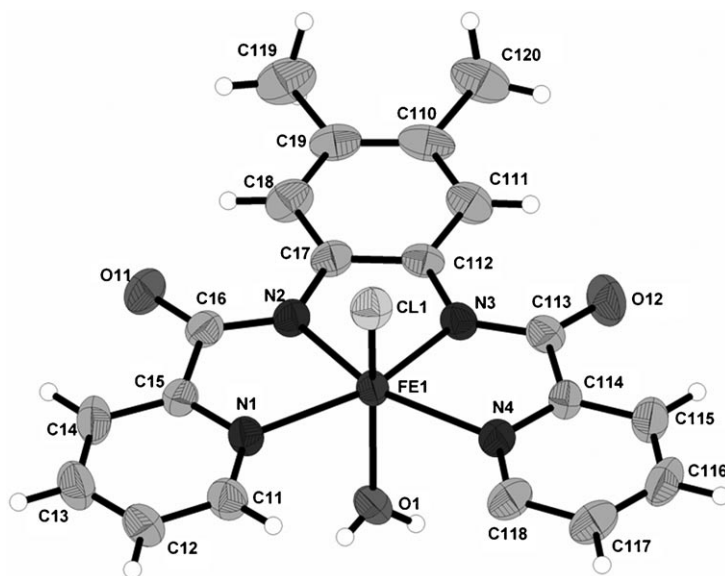


Figure 1. Crystal structure of **3a**. Ellipsoids are drawn at the 50% probability level. Methanol solvent molecule was omitted for clarity.

Me<sub>2</sub>bpb<sup>2-</sup> ligand, a chloro ligand, and a water molecule are coordinated to the iron(III) center. The two Fe–N<sub>amide</sub> distances (2.018(3) and 2.036(3) Å) are shorter than the Fe–N<sub>py</sub> distances (2.136(3) and 2.158(3) Å). The Fe–Cl distance is 2.334(1) Å and the Fe–O(water) distance is 2.064(3) Å. The Cl–Fe–O(water) angle of 152.82(10)° is more acute than the Cl–Fe–Cl angle in [Et<sub>3</sub>NH][Fe(Me<sub>2</sub>bpb)Cl<sub>2</sub>] (156.59(3)°).<sup>[10]</sup> The amide C–O bond lengths of the Me<sub>2</sub>bpb<sup>2-</sup> ligand are 1.233(4) and 1.227(4) Å.

We have investigated the oxidative reactivity of **3**, **3a**, **4**, and **4a** with olefins and alcohols in the presence of *m*-chloroperbenzoic acid (MCPBA). *m*-Chloroperbenzoic acid (0.02 mmol) was added to a mixture of substrate (0.2 mmol), iron complex (0.001 mmol), and solvent (1 mL, CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1). This mixture was stirred for

10 min at room temperature. We confirmed that direct substrate oxidation by MCPBA was negligible (it took place over a period of 10–60 min), whereas oxygen-transfer reactions catalyzed by the iron complexes occur in less than three minutes after the addition of MCPBA. Reactions with olefins in the presence of **3** resulted predominantly in the formation of epoxides (Table 3). For example, cyclic olefins such as cyclopentene, cycloheptene, and cyclooctene were oxidized to the corresponding epoxides in good yield (Table 3, entries 1–3). The terminal olefin 1-octene was less efficiently oxidized to 1-octene epoxide under these condi-

Table 1. Crystal data and structure refinement for  $[\text{Fe}(\text{Me}_2\text{bpb})\text{Cl}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{OH}$  (**3a**).

empirical formula	$\text{C}_{21}\text{H}_{22}\text{ClFeN}_4\text{O}_4$
formula weight	485.73
$T$ [K]	293(2)
$\lambda$ [Å]	0.71073
crystal system, space group	monoclinic, $P2_1/a$
$a$ [Å]	10.969(1)
$b$ [Å]	12.500(1)
$c$ [Å]	15.710(1)
$\alpha$ [°]	90.00
$\beta$ [°]	97.34(1)
$\gamma$ [°]	90.00
$V$ [Å <sup>3</sup> ]	2136.4(3)
$Z$	4
$\rho_{\text{calc}}$ [Mg m <sup>-3</sup> ]	1.510
absorption coefficient [mm <sup>-1</sup> ]	0.867
$F(000)$	1004
crystal size [mm]	0.10 × 0.20 × 0.15
reflections collected/unique data/restraints/parameters	4430/4194 [ $R(\text{int})=0.0343$ ]
GOF on $F^2$	1.031
final $R$ indices [ $I > 2\sigma(I)$ ]	$R1=0.0423$ , $wR2=0.0971$
$R$ indices (all data)	$R1=0.1077$ , $wR2=0.1135$
largest difference peak and hole	0.315 and $-0.384 \text{ e Å}^{-3}$

Table 2. Selected bond lengths [Å] and angles [°] for  $[\text{Fe}(\text{Me}_2\text{bpb})\text{Cl}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{OH}$  (**3a**).

Fe1–N3	2.018(3)	Fe1–N2	2.036(3)
Fe1–O1	2.064(3)	Fe1–N1	2.136(3)
Fe1–N4	2.158(3)	Fe1–Cl1	2.3339(10)
O11–C16	1.233(4)	O12–C113	1.227(4)
N3–Fe1–N2	78.19(11)	N3–Fe1–O1	98.65(12)
N2–Fe1–O1	98.97(12)	N3–Fe1–N1	155.22(11)
N2–Fe1–N1	77.46(11)	O1–Fe1–N1	80.68(12)
N3–Fe1–N4	77.55(10)	N2–Fe1–N4	155.55(11)
O1–Fe1–N4	81.69(11)	N1–Fe1–N4	126.35(10)
N3–Fe1–Cl1	102.76(8)	N2–Fe1–Cl1	103.16(8)
O1–Fe1–Cl1	151.82(10)	N1–Fe1–Cl1	87.27(8)
N4–Fe1–Cl1	85.24(8)		

Table 3. Hydrocarbon oxidation by MCPBA with iron catalysts in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1/1) at room temperature.<sup>[a]</sup>

Entry	Substrate	Product	<b>3</b>	<b>3a</b>	<b>4</b>	<b>4a</b>
1	cyclopentene	epoxide	44.9 ± 1.4	66.8 ± 0.3	48.5 ± 1.3	71.7 ± 1.5
2	cycloheptene	epoxide	59.8 ± 1.7	80.5 ± 1.8	49.5 ± 0.8	81.9 ± 0.9
3	cyclooctene	epoxide	48.8 ± 0.1	67.5 ± 1.7	48.2 ± 3.6	72.6 ± 3.4
4	1-octene	epoxide	14.3 ± 0.4	16.9 ± 0.5	15.6 ± 0.1	21.9 ± 0.6
5	cyclohexene	epoxide	42.1 ± 1.2	65.3 ± 0.9	47.5 ± 3.7	65.9 ± 2.5
2-cyclohexene-1-ol		5.0 ± 0.2	4.1 ± 0.5	5.9 ± 0.1	3.8 ± 0.1	
2-cyclohexenone		5.5 ± 0.2	4.9 ± 0.1	4.7 ± 1.3	4.5 ± 0.1	
6	1,2-dihydronaphthalene	epoxide	30.5 ± 0.5	36.4 ± 1.2	27.2 ± 3.5	38.5 ± 2.1
naphthalene		5.4 ± 0.1	5.7 ± 0.2	4.5 ± 0.4	3.0 ± 1.3	
(ol+one) <sup>[b]</sup>		9.3 ± 0.7	8.2 ± 0.5	9.2 ± 1.1	11.2 ± 0.4	
7	<i>cis</i> -2-octene	<i>cis</i> -oxide	46.6 ± 1.8	56.9 ± 1.2	38.6 ± 0.8	72.5 ± 3.5
<i>trans</i> -oxide		6.2 ± 0.6	5.0 ± 0.1	5.2 ± 0.1	2.4 ± 0.4	
8	<i>trans</i> -2-octene	<i>trans</i> -oxide	41.0 ± 2.2	47.7 ± 1.3	30.1 ± 0.1	57.7 ± 0.1
9	<i>cis/trans</i> -2-octene	<i>cis/trans</i> -oxide	1.7	1.6	2.3	1.6
10	cyclohexanol	cyclohexanone	51.5 ± 0.8	66.8 ± 1.0	67.4 ± 2.0	81.0 ± 1.8
11	benzyl alcohol	benzaldehyde ( $k_{\text{H}}/k_{\text{D}}$ )	49.7 ± 1.0 (3.3 ± 0.3)	67.3 ± 1.5 (3.0 ± 0.3)	72.0 ± 0.7 (3.0 ± 0.1)	88.2 ± 2.5 (2.8 ± 0.2)

[a] See Experimental Section for details. [b] Abbreviations ol and one denote 1,2-dihydronaphthalen-2-ol and naphthalene-2(1*H*)-one, respectively.

tions (Table 3, entry 4). In the reaction involving cyclohexene, small amounts of allylic oxidation products such as cyclohexenol and cyclohexenone were formed, that is, Fenton-type oxidation reactions were only minimally involved in the olefin epoxidation reactions. Studies of the oxidation of 1,2-dihydronaphthalene produced similar results to cyclohexene, albeit the desaturated product naphthalene was also generated. *cis*-2-Octene was used to probe the stereochemistry of the reaction, and *cis*-2-octene oxide was produced as the major species (46.6%) along with a small amount of *trans*-2-octene oxide (6.2%). This result indicates that the catalytic epoxidation reaction occurs with approximately 77% stereochemical retention (Table 3, entry 7). *trans*-2-Octene was oxidized exclusively to *trans*-2-octene oxide. In a competition experiment involving *cis*- and *trans*-2-octene, *cis*-2-octene was found to be approximately twice as reactive as *trans*-2-octene, and this implies a reactivity preference for *cis* over *trans* (Table 3, entry 9). The remaining three iron complexes (**3a**, **4**, and **4a**) displayed similar results. However, complexes **3a** and **4a**, which have an axial aqua ligand, afforded higher overall yields of oxidation products (Table 3). These combined results indicate that while the axial ligand in the Fe<sup>III</sup> complex influences the yield of oxidation products, electronic perturbation ( $\text{CH}_3$  versus Cl) of the chelate ligand shows little effect.

Alcohols were also converted efficiently to the corresponding carbonyl compounds (Table 3, entries 10 and 11). Cyclohexanol was oxidized to cyclohexanone, and benzyl alcohol to benzaldehyde. For solutions containing a low concentration of benzyl alcohol, the product benzaldehyde underwent further oxidation to benzoic acid (data not shown).

Kinetic isotope effects (KIE) have been used as a mechanistic probe in alkane hydroxylation reactions catalyzed by both iron-containing enzymes and model complexes.<sup>[14]</sup> To gain insight into the nature of the oxidizing species in the alcohol oxidation reactions catalyzed by **3**, **3a**, **4**, and **4a**, we performed intermolecular competition reactions involving benzyl alcohol and  $[\text{D}_7]$ benzyl alcohol. The KIE for benzal-

dehyde formation by **3** and MCPBA was determined to be  $3.3 \pm 0.3$  (Table 3), which is the same as that of a hydrogen abstraction reaction catalyzed by a high-valent heme iron oxo species ( $3.2 \pm 0.3$ ).<sup>[14d]</sup> Based on this result, we propose that the reactive species responsible for alcohol oxidation in our catalytic system may be a high-valent iron oxo species that is produced following O–O bond cleavage of acylperoxy intermediate FeOOC(O)R. Analogous results were obtained for complexes **3a**, **4**, and **4a** (Table 3, entry 11).

Additional evidence for the involvement of a high-valent iron oxo species in the alcohol oxidation reactions was derived from <sup>18</sup>O labeling experiments. It has been shown that high-valent metal oxo species will exchange their terminal oxo moiety with labeled water (H<sub>2</sub><sup>18</sup>O), and this approach has been previously used to provide evidence for high-valent metal oxo intermediates in metal-mediated oxygen-transfer reactions.<sup>[15]</sup> We examined the epoxidation of cyclohexene by **3** and MCPBA in the presence of an approximately 25-fold excess of H<sub>2</sub><sup>18</sup>O relative to the substrate. As shown in Table 4, the cyclohexene oxide product contained

Table 4. Percentage of <sup>18</sup>O incorporated from H<sub>2</sub><sup>18</sup>O into cyclohexene oxide formed during cyclohexene oxidation by MCPBA and iron catalysts.<sup>[a]</sup>

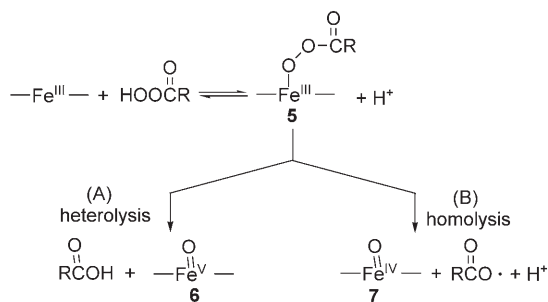
Entry	Catalyst	Amount of cyclohexene [mol]	Amount of MCPBA [mol]	Amount of H <sub>2</sub> <sup>18</sup> O [mol]	Amount of <sup>18</sup> O in cyclohexene oxide [%]
1	<b>3</b>	0.02	0.01	0.556	5.2 ± 0.9
2	<b>3a</b>	0.02	0.01	0.556	3.0 ± 1.0
3	<b>4</b>	0.02	0.01	0.556	8.9 ± 1.5
4	<b>3</b>	0.01	0.005	1.111	12.0 ± 1.4
5	<b>3a</b>	0.01	0.005	1.111	10.5 ± 2.0
6	<b>4</b>	0.01	0.005	1.111	17.3 ± 1.7

[a] See Experimental section for details.

5.2% of <sup>18</sup>O derived from H<sub>2</sub><sup>18</sup>O (Table 4, entry 1). A control experiment with cyclohexene oxide in H<sub>2</sub><sup>18</sup>O under the same conditions showed no incorporation. Additional experiments revealed that increasing the amount of labeled water resulted in a higher degree of <sup>18</sup>O incorporation in the epoxide product (compare entries 1 and 4, Table 4). The dependence of <sup>18</sup>O incorporation on the concentration of labeled water can be explained by the relative rates of oxygen-atom transfer and oxygen exchange, as has been previously described.<sup>[15]</sup> These results suggest that a high-valent iron oxo species may be the reactive moiety for substrate oxidation, as has been proposed for other catalytic systems.<sup>[15]</sup> However, the relatively low degrees of <sup>18</sup>O incorporation (5.2–8.9%, entries 1–3 in Table 4) in these labeling experiments suggest that an acylperoxy species (FeOOC(O)R) may also be able to directly epoxidize the olefin. While the latter scenario cannot be ruled out, we favor the involvement of a high-valent iron oxo species, because the degree of <sup>18</sup>O incorporation increases to 17% on increasing the amount of H<sub>2</sub><sup>18</sup>O present. The rate of oxygen-atom exchange between a nonheme iron oxo species and H<sub>2</sub><sup>18</sup>O has been reported to be slow.<sup>[15d]</sup> Notably, complex **4**, which is

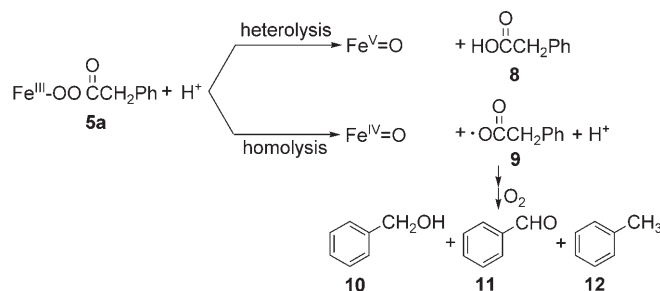
supported by the chlorine-containing bpc<sup>2-</sup> ligand, undergoes a higher degree of oxygen exchange than **3**, which is supported by the Me<sub>2</sub>bpb<sup>2-</sup> ligand (compare entries 1 and 3, and 4 and 6, respectively, in Table 4). This is similar to reactivity exhibited by heme model systems.<sup>[15c]</sup>

Based on our results, the most plausible mechanism for the formation of the reactive species responsible for hydrocarbon oxidation involves either a heterolytic (pathway A) or homolytic (pathway B) O–O bond cleavage of a coordinated peracid anion (**5**) to produce an Fe<sup>V</sup>=O (**6**) or Fe<sup>IV</sup>=O (**7**) species (Scheme 2). To determine whether the iron acyl-



Scheme 2. Plausible mechanism for formation of the reactive species.

peroxy intermediate FeOOC(O)Ph (**5**) decomposes by heterolysis or homolysis, we used peroxyphenylacetic acid (PPAA) as a mechanistic probe, as the use of PPAA to distinguish homolytic versus heterolytic cleavage of the peracid O–O bond is well established.<sup>[16]</sup> When the O–O bond of the coordinated anion of PPAA is cleaved homolytically, an acyloxyl radical (**9**) is generated (Scheme 3). This acyloxyl



Scheme 3. Product distribution of O–O bond cleavage of PPAA with iron complexes.

radical undergoes rapid β-scission (diffusion-controlled rate ca. 10<sup>9</sup> s<sup>-1</sup>) to give benzyl alcohol (**10**), benzaldehyde (**11**), and toluene (**12**). In contrast, heterolytic cleavage of the coordinated anion of PPAA yields phenylacetic acid (PAA, **8**). In cyclohexene oxidation catalyzed by **3** and PPAA, phenylacetic acid was the predominant degradation product of the oxidant (86.5% based on PPAA; entry 1 in Table 5).<sup>[17]</sup> Analogous results were obtained for **3a**, **4**, and **4a**. These results indicate that heterolytic O–O bond cleavage occurs to



Table 5. Yield of products derived from peroxyphenylacetic acid (PPAA) mediated by iron catalysts in the presence of cyclohexene.<sup>[a]</sup>

Entry	Catalyst	Heterolysis		Homolysis		Oxidation products <sup>[b]</sup>		
		<b>8</b>	<b>10</b>	<b>11</b>	<b>12</b>	oxide	ol	one
1	<b>3</b>	86.5 ± 4.0	7.0 ± 0.1	3.5 ± 0.1	-	28.5 ± 1.0	4.5 ± 0.2	4.3 ± 0.4
2	<b>3a</b>	85.2 ± 6.0	9.5 ± 0.5	4.0 ± 0.5	-	36.3 ± 1.0	8.2 ± 0.1	6.4 ± 0.1
3	<b>4</b>	83.7 ± 6.0	7.2 ± 0.5	3.8 ± 0.1	-	29.8 ± 1.8	4.5 ± 0.3	4.8 ± 0.5
4	<b>4a</b>	84.0 ± 6.0	9.4 ± 0.3	3.9 ± 0.2	-	44.2 ± 1.5	8.2 ± 0.5	6.8 ± 0.1

[a] See Experimental Section for details. [b] oxide, ol, and one denote cyclohexene oxide, cyclohexenol, and cyclohexenone, respectively.

produce high-valent Fe<sup>V</sup>=O species in the reactions involving these iron complexes and peracids. To our knowledge, this is only the second example of an Fe<sup>V</sup>=O species that can be generated in nonheme iron complexes by using a peracid as the oxidant.<sup>[6]</sup> Interestingly, the supporting chelating ligand in these systems is dianionic, whereas in the previously reported complex generated from a peracid the Fe<sup>V</sup> oxo moiety is supported by a tetraanionic macrocyclic ligand.<sup>[6]</sup> Our work provides evidence that complexes having a mixed-donor environment comprising both neutral and anionic nitrogen donors can afford Fe<sup>V</sup>=O species that are relevant to the proposed active oxidant in nonheme Rieske dioxygenases.

## Conclusion

We have found that mononuclear nonheme iron(III) complexes supported by chelate ligands having two deprotonated amide moieties are capable of catalyzing olefin epoxidation and alcohol oxidation on treatment with peracids. The active oxidant in these systems was proposed to be an Fe<sup>V</sup>=O species, as indicated by KIE ( $k_H/k_D$ ) and H<sub>2</sub><sup>18</sup>O exchange experiments, as well as the use of PPAA as an oxidant. This Fe<sup>V</sup>=O species is relevant to intermediates postulated in the mechanisms of dioxygen-activating mononuclear nonheme iron enzymes such as Rieske dioxygenases. Comparison of the results presented herein with those recently reported by others<sup>[5,6]</sup> reveals the important role that the structure of the supporting chelating ligand plays in influencing the formation of high-valent iron oxo species. Our future work will focus on 1) further exploring the biologically relevant reactivity of the iron(III) complex/MCPBA systems, and 2) obtaining spectroscopic evidence for the Fe<sup>V</sup>=O species described herein.

## Experimental Section

**Materials:** Olefins, cyclohexanol, benzyl alcohol, [D<sub>7</sub>]benzyl alcohol, dichloromethane, acetonitrile, MCPBA (65%), and H<sub>2</sub><sup>18</sup>O (95% <sup>18</sup>O enrichment) were purchased from Aldrich Chemical Co. and were used without further purification. Peroxyphenylacetic acid (PPAA) was synthesized according to the literature method.<sup>[16]</sup>

**Instrumentation:** Products of olefin epoxidation, alcohol oxidation, and <sup>18</sup>O incorporation by cyclohexene oxide were analyzed on a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with a Hewlett-Pack-

ard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with an FID detector using a 30 m capillary column (Hewlett-Packard, HP-1, HP-5, and Ultra 2). Elemental analyses (C, H, N) were carried out on an EA1108 instrument (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets.

**Synthesis of iron complexes:** [Et<sub>3</sub>NH][Fe(Me<sub>2</sub>bpb)Cl<sub>2</sub>] (**3**) and [Et<sub>3</sub>NH][Fe(bpc)Cl<sub>2</sub>] (**4**) were obtained from a previous study.<sup>[10]</sup> For the synthesis of [Fe(Me<sub>2</sub>bpb)Cl(H<sub>2</sub>O)] (**3a**), **3** (300 mg) was dissolved in methanol. After the solution was stirred for 30 min, dark green microcrystals that precipitated were collected by filtration, washed with methanol, and air-dried. Yield: 219 mg (73%). IR (KBr):  $\tilde{\nu}$  = 1614 (ν(C=O)) cm<sup>-1</sup>. Elemental analysis (%) calcd for **3a** (C<sub>21</sub>H<sub>22</sub>ClFeN<sub>2</sub>O<sub>4</sub>, 485.73): C 51.92, H 4.57, N 11.54; found: C 52.02, H 4.57, N 11.56. [Fe(bpc)Cl(H<sub>2</sub>O)] (**4a**) was obtained by a similar procedure. Yield: 126 mg (42%).  $\tilde{\nu}$  = 1638 (ν(C=O)) cm<sup>-1</sup>. Elemental analysis (%) calcd for **4a** (C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>FeN<sub>2</sub>O<sub>3</sub>, 492.93): C 43.72, H 2.45, N 11.33; found: C 43.66, H 2.59, N 11.53.

**X-ray analysis:** Dark brown plate crystals of **3a** suitable for crystallographic analysis were obtained from CH<sub>3</sub>OH/diethyl ether. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 Mach3 diffractometer equipped with a monochromator in the MoK $\alpha$  ( $\lambda$  = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. Final cell parameters were obtained from least-squares fit to 25 reflections in the range 9.40 ≤  $\theta$  ≤ 12.32°. Intensities were corrected for Lorentzian and polarization effects but not for absorption. The crystal structure was determined by direct methods and Fourier techniques. All calculations were performed on an IBM Pentium computer using SHELXS-97 and SHELXL-97,<sup>[18]</sup> and atomic scattering factors for all non-hydrogen atoms were supplied by SHELXS-97. All hydrogen atoms except for those of a water molecule were placed in calculated positions. The crystallographic data are listed in Table 1, and selected bond lengths and angles in Table 2.

CCDC-619186 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Catalytic hydrocarbon oxidation on treatment of iron complexes with MCPBA:** MCPBA (0.02 mmol) was added to a mixture of substrate (0.2 mmol), iron complex (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1, 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate, and average product yields based on MCPBA are presented. In the competitive reaction of *cis*-2-hexene and *trans*-2-hexene, the amount of each substrate was 0.1 mmol.

**KIE study on the oxidation of benzyl alcohol by iron complexes and MCPBA:** To improve the accuracy of measuring the amount of deuterated benzyl alcohol product, a 1:6 mixture of benzyl alcohol and deuterated benzyl alcohol was used. MCPBA (0.02 mmol) was added to a mixture of benzyl alcohol (0.1 mmol), deuterated benzyl alcohol (0.6 mmol), iron complex (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1, 1 mL). The mixture was stirred for 10 min at room temperature. The reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate, and the average KIE values are presented.

**H<sub>2</sub><sup>18</sup>O experiments:** MCPBA (0.005–0.01 mmol) was added to a mixture of cyclohexene (0.01–0.02 mmol), iron complex (0.001 mmol), and H<sub>2</sub><sup>18</sup>O (10–20 μL, 95% <sup>18</sup>O enriched, Aldrich Chemical Co.) in dried CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (1/1, 1 mL). The reaction mixture was stirred for 3 min at room temperature and then directly analyzed by GC/MS. The <sup>16</sup>O and <sup>18</sup>O compositions were determined by the relative abundance of mass peaks at  $m/z$  99 for [<sup>16</sup>O]cyclohexene oxide and  $m/z$  101 for [<sup>18</sup>O]cyclohexene oxide.

All reactions were run at least in triplicate, and the average values are presented.

**Analysis of O–O bond cleavage products by iron complexes with PPAA:** PPAA (0.02 mmol) was added to a mixture of substrate (0.2 mmol), iron complex (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1, 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate, and the average product yields based on PPAA are presented.

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