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An Iron(III)–Monoamidate Complex Catalyst for Selective Hydroxylation of Alkane C–H Bonds with Hydrogen Peroxide**

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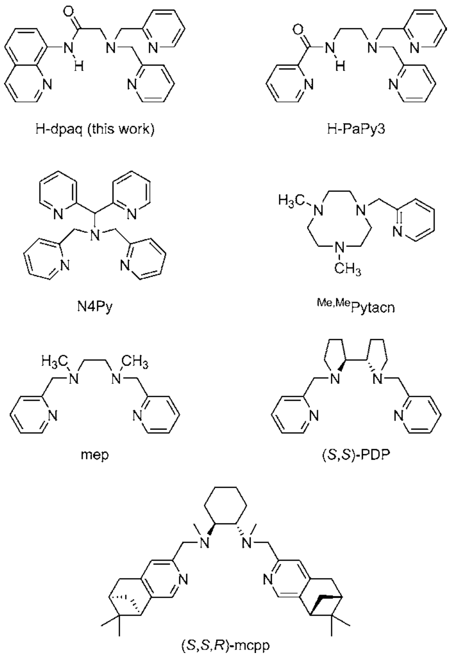
Development of catalysts for the selective hydroxylation of inert C–H bonds is an important research objective.[1–4] Significant progress toward this goal has been made in recent decades by using biologically inspired iron catalysts and hydrogen peroxide.[5–11] H_2O_2 is the most ideal oxidant from an atom-economy viewpoint, however, it is generally difficult to use as an oxidant for iron-catalyzed selective oxidations because it easily decomposes to hydroxyl radicals, thus resulting in an undesirable oxidation.[12,13] Despite this difficulty, recent studies showed that mononuclear iron complexes with two *cis*-oriented labile coordination sites can afford considerably high selectivity in alkane hydroxylation with H_2O_2.[14–19] It has been reported that acetic acid is required to increase the selectivity to synthetically useful levels in these hydroxylations.[15,19] The specific role of acetic acid has not yet been clarified, but it is believed that it facilitates the heterolytic scission of the O–O bond of a $Fe^{III}OOH$ species by acting as an acid catalyst.[20,21] Very recently, Costas and co-workers reported that Fe^{II}–^{Me,Me}Pytacn (^{Me,Me}Pytacn = 1-(2′-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, Scheme 1) also catalyzes selective hydroxylation of alkane C–H bonds when H_2O_2 is used without an acid additive,[17] and also observed the formation of an iron(V)–oxo-hydroxo species as an oxidant by mass spectroscopy.[22]



Scheme 1. Structures of the supporting ligands.

Herein, we report an Fe^{III}–dpaq complex (**1**; dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-*N*-quinolin-8-yl-acetamidate, Scheme 1) that can catalyze the selective hydroxylation of inert C–H bonds by using H_2O_2 as the oxidant. The crystal structure of **1** (Figure 1) shows a slightly distorted octahedral iron(III) center, which contains a pentadentate dpaq ligand, and an aqua ligand in *trans* position to the nitrogen atom of the amidate moiety of dpaq. In our strategy, the aqua ligand is replaced by H_2O_2 to form an $Fe^{III}OOH$ species, in which electron donation from the amidate ligand to the iron center promotes the generation of a formally Fe^{V}oxo species through the heterolytic scission of the O–O bond (Scheme 2), since the anionic amidate ligand should stabilize the high-valent Fe^{V}oxo species.

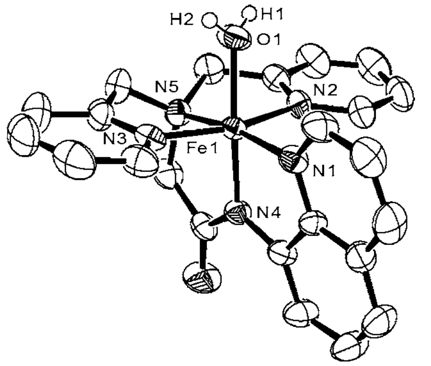


Figure 1. Ortep (50% probability) diagram of the cation of **1**. The counter anion and the hydrogen atoms, with the exception of H1 and H2, are omitted for clarity. Selected bond lengths [Å]: Fe1–N1 1.976(3), Fe1–N2 1.975(3), Fe1–N3 1.987(3), Fe1–N4 1.857(3), Fe1–N5 1.980(3), Fe1–O1 1.963(3).

We first performed the cyclohexane oxidation in acetonitrile at room temperature. H_2O_2 was added to a reaction vessel under air over a period of 30 minutes by using a syringe pump. The reaction gave cyclohexanol (A) and cyclohexanone (K) with an A/K ratio of 11.3:1. Formation of hydroxyl radicals should decrease the A/K ratio to about 1:1 through

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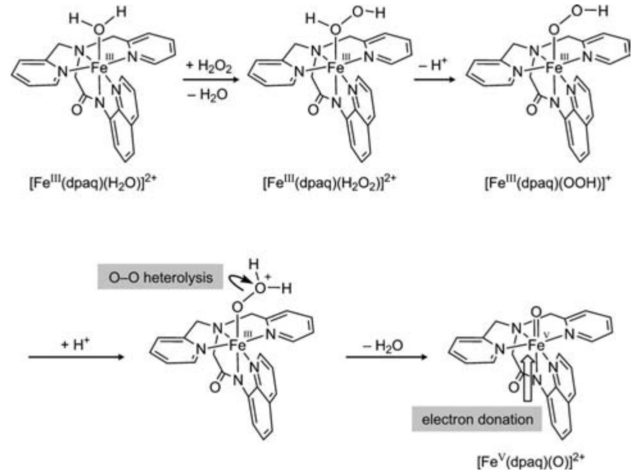


Scheme 2. Formation of the Fe^{V}oxo species from complex **1**.

Table 1: Oxidation of cyclohexane with CmOOH catalyzed by iron complexes.[a]

Entry	Catalyst	Alcohol[b]	Ketone[b]	A/K[c]	CmOH/PhCOMe
1	**1**	10	1.0	10	17.8:1 (9.2:1)[e]
2	**1**[d]	10	6.2	1.6	1.7:1 (2.0:1)[e]
3	**2**	4.8	4.3	1.1	1.8:1 (1.6:1)[e]
4	**3**	3.9	3.5	1.1	1:81.3 (1:99)[e]

[a] Catalyst/CmOOH/cyclohexane = 1:20:1000 in CH_3CN at RT. CmOOH was added over a period of 30 min by using a syringe pump. [b] Turnover number (mol of product/mol of iron). [c] A = cyclohexanol, K = cyclohexanone. [d] Catalyst/2,4,6-collidine/CmOOH/cyclohexane = 1:1:20:1000. [e] Values in parentheses are the ratio of CmOH:PhCOMe obtained after the reaction of an iron complex with equimolar amounts of CmOOH for 35 min without cyclohexane (catalyst/CmOOH = 1:1, no cyclohexane). In the absence of iron complexes, 0.9% of CmOH and 4% of PhCOMe were produced under the current conditions.

a Russell-type termination mechanism, which involves long-lived carbon centered radicals and molecular dioxygen.[23] The A/K ratio was not changed under an N_2 atmosphere (A/K = 11.4:1). Furthermore, the distribution of the products over time showed that the A/K ratio was initially 36:1 and then gradually decreased to 11:1 (see Figure S1 in the Supporting Information). These results indicate the formation of cyclohexanone by further oxidation of cyclohexanol and not through the Russell-type termination mechanism involving hydroxyl radicals. Thus, these results suggest the generation of metal-based oxidants through O–O bond heterolysis of an Fe^{III}OOH species. To validate this observation, we conducted catalytic oxidation of cyclohexane using other oxidants, including *m*-chloroperoxybenzoic acid (*m*CPBA), methyl 2-iodosylbenzoate (IBX ester),[24] *tert*-butyl hydroperoxide, and cumene hydroperoxide (CmOOH, Cm = $C(CH_3)_2C_6H_5$). The obtained A/K ratios were nearly identical, regardless of the oxidant that was used (Table S1). This result suggests the generation of a common metal-based oxidant, probably a formally iron(V)oxo species, because *m*CPBA and IBX ester would be expected to transfer an oxo group to the iron(III) center of **1**.

When CmOOH was used as the oxidant for cyclohexane oxidation, cumene alcohol (CmOH) was obtained as a major product with trace amounts of acetophenone (PhCOMe; CmOH/PhCOMe ≈ 18:1). Similar CmOH/PhCOMe ratios were obtained without cyclohexane (Table 1). CmOOH has been frequently used as a mechanistic probe to clarify the cleavage manner of the O–O bond, because the O–O heterolysis of M–OOCm (M = metal) affords CmOH, whereas O–O homolysis gives PhCOMe through β scission of a cumyloxyl radical.[25–27] The fact that CmOH was obtained as the major product in the cyclohexane oxidation with CmOOH strongly suggests that the O–O bond of Fe^{III}OOCm is predominantly cleaved in a heterolytic manner to give a formally Fe^{V}oxo species.

The above-mentioned results suggest that the reaction of **1** with H_2O_2 gives the corresponding Fe^{V}oxo species through O–O bond heterolysis of an Fe^{III}OOH species, which was further supported by cold-spray-ionization mass spectroscopy (CSI-MS). The positive-ion CSI-MS spectrum of the reaction mixture of **1** with 50 equivalents of H_2O_2 in CH_3CN at 273 K showed an ion signal at a mass-to-charge (*m*/*z*) ratio of 471.1, the mass and isotope distribution pattern of which were consistent with the chemical formula of $[Fe^{III}(dpaq)(OOH)]^+$ (calculated *m*/*z* = 471.1; Figure S2). When $H_2{}^{18}O_2$ was used, the position of the ion signal changed to 475.1 (shift of four mass units). These results unequivocally indicate the formation of a H_2O_2 adduct of [Fe(dpaq)] by mixing **1** and H_2O_2 in CH_3CN. More importantly, the CSI-MS analysis of the solution also showed a weak ion signal at *m*/*z* ratio of 553.0. The mass and isotope distribution pattern were consistent with the chemical formula of $\{[Fe^{V}(dpaq)(O)](ClO_4)\}^+$ (calculated *m*/*z* = 553.1), the signal position of which shifted to 555.1 (shift of two mass units) when $H_2{}^{18}O_2$ was used (Figure S2). These results suggest the formation of an Fe^{V}oxo species by mixing **1** and H_2O_2 in CH_3CN. It has been reported that Fe^{III}OOH species can be easily prepared by mixing mononuclear nonheme Fe^{II} complexes with H_2O_2,[28] but Fe^{V}oxo species have been observed only in a few cases.[22,29,30]

The reaction of **1** with H_2O_2 affords Fe^{III}OOH and a proton, and the O–O bond heterolysis gives an Fe^{V}oxo species and a water molecule (Scheme 2). In the last step, the distal oxygen atom of the Fe^{III}OOH species should be protonated to afford the water molecule. In order to examine whether the protonation is essential for the O–O bond heterolysis, we conducted cyclohexane oxidation by H_2O_2 in the presence of an equimolar mixture of **1** and 2,4,6-collidine, which is a strong base with a pK_a value of 14.7 in CH_3CN.[31,32] As a result, the A/K ratio reduced to 1.3:1. Furthermore, the reaction of **1** with CmOOH in the presence of 2,4,6-collidine gave significant amounts of PhCOMe, and the CmOH/PhCOMe ratio reduced from 9.2 to 2.0 (Table 1, entries 1 and 2). These results suggest that the amidate coordination of Fe–dpaq itself is not enough to accomplish the O–O bond heterolysis. In other words, the proton facilitates O–O bond heterolysis in collaboration with the amidate ligation. In this sense, it can be noted that Fe^{III}dpaq performs heme-enzyme-type chemistry based on the "push–pull" concept.[33]

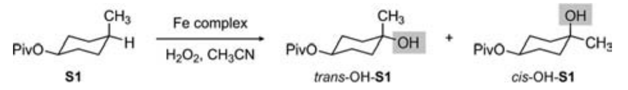
Interestingly, it has been reported that the structurally related monoamidate iron(III) complex Fe^{III}–$PaPy_3$ (**2**;

$PaPy_3$ = *N*,*N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-carboxamidate, Scheme 1) has poor selectivity in alkane oxidation with H_2O_2.[34] To determine the cause of this difference in selectivity, we conducted the same reaction using **2** instead of **1**. The A/K ratio in cyclohexane oxidation with H_2O_2 reduced to 1.1 (Table S2, entry 3). Cyclohexane oxidation with CmOOH gave products derived from CmOOH in a CmOH/PhCOMe ratio of 1.8, and cyclohexanol and cyclohexanone in an A/K ratio of 1.1 (Table 1, entry 3). In addition, when Fe^{II}–N4Py (**3**; N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine, Scheme 1), which lacks an amidate ligand, was used as a control, the A/K ratio became about 1:1 and PhCOMe was a major product derived from CmOOH (Table 1, entry 4). This result agrees with the previous report that **3** promotes O–O homolysis.[35] Thus, it is evident that the pentadentate monoamidate supporting ligands dpaq and $PaPy_3$ tend to facilitate the heterolysis of the O–O bond, but the neutral pentadentate supporting ligand N4Py does not facilitate it. Furthermore, the dpaq ligand promotes the heterolysis more efficiently than the $PaPy_3$ ligand. The measured Fe^{II}/Fe^{III} redox potential of **1** is lowered by 0.24 V compared to that of **2**, thus indicating that the dpaq ligand is a better electron donor than the $PaPy_3$ ligand (Figure S3). Density functional calculations also support this conclusion (Figure S4). The difference in electron donation abilities of **1** and **2** may in part explain the observed difference between **1** and **2**, although further studies will need to clarify the mechanism that better electron donor ligands induce the heterolysis of the O–O bond.

Determination of the intermolecular kinetic isotope effect (KIE) for cyclohexane and $[D_{12}]$-cyclohexane is a useful method for evaluating the capability of oxidants to discriminate between alkane C–H bonds with different strengths. The KIE determined by using a mixture of cyclohexane and $[D_{12}]$-cyclohexane with various molar ratios (from 1:1 to 1:6) was 3.9 (Figure S5). Adamantane has also been used to evaluate the discrimination ability of oxidants; in this case, it is used to examine the ability to discriminate between secondary and tertiary C–H bonds with bond dissociation energies of 100.2 and 96.2 $kcal\,mol^{-1}$, respectively.[36] The oxidation of adamantane with H_2O_2 in the presence of **1** gave products in a 3°/2° ratio of 18.8.[37] These high selectivities (KIE and 3°/2° values for **1**) are comparable to or even higher than those reported for iron complexes with two *cis*-oriented labile coordination sites (Tables S2 and S3). These results demonstrate high selectivity of the oxidant derived from the reaction of **1** with H_2O_2.

Another criterion for selective hydroxylation of C–H bonds with respect to tertiary C–H bonds concerns stereoselectivity; that is, whether hydroxylation occurs with inversion or retention of configuration. We chose *cis*-4-methylcyclohexyl-1-pivalate (**S1**) as a substrate to evaluate the capability of **1** to hydroxylate tertiary C–H bonds with retention of configuration (RC). The Fe^{III}–dpaq complex **1** catalyzed the hydroxylation of **S1** at the 4 position with high RC selectivity (94 %), in which RC selectivity is the fraction of *trans* conformers of 4-hydroxylated products. Chen and White reported a profitable effect of acetic acid on RC selectivity in the oxidation of **S1** with H_2O_2 catalyzed by Fe^{II}–mep (**4**; mep = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine) and Fe^{II}–(*S*,*S*)-PDP (**5**; (*S*,*S*)-PDP = 2-[{(*S*)-2[((*S*)-1-pyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl}-methyl]-pyridine, Scheme 1). Acetic acid increased RC selectivity from 56 % (in the absence of acetic acid) to 92 % and from 60 % to 90 % with **4** and **5**, respectively.[15] However, in the case of **1**, use of acetic acid as an additive did not improve RC selectivity (Table 2, entry 2).

Table 2: Regioselective hydroxylation of *cis*-4-methylcyclohexyl-1-pivalate.



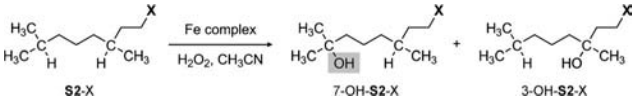
Entry	Catalyst	AcOH	Yield [%][c]	Conv. [%][d]	RC [%][e]	Ref.
1	**1**[a]	–	38	40	94	this work
2	**1**[a]	0.5 equiv	23	25	90	this work
3	**4**[b]	–	7	12	56	[15]
4	**4**[b]	0.5 equiv	26	41	92	[15]
5	**5**[b]	–	14	15	60	[15]
6	**5**[b]	0.5 equiv	38	42	90	[15]

[a] Catalyst/H_2O_2/substrate = 1:100:120 in CH_3CN at RT. The oxidant was added over a period of 30 min by using a syringe pump. [b] Catalyst/H_2O_2/substrate = 1:20:24 in CH_3CN at RT. [c] (mol of *trans*-OH-S1)/(mol of S1) × 100. [d] Conversion efficiency of S1. [e] {*trans*-OH-S1/(*trans*-OH-S1 + *cis*-OH-S1)} × 100.

Chen and White also reported that **5** catalyzes the regioselective hydroxylation of 1-substituted derivatives of 3,7-dimethyloctane (**S2**), in which two tertiary carbon atoms that are electronically different owing to the substituted group X (X = H, OAc, and Br) are present.[15] Subsequently, Costas and co-workers reported an improvement in turnover numbers for the same reaction using a sterically crowded version of an iron complex, Fe^{II}–(*S*,*S*,*R*)-mcpp (**6**; (*S*,*S*,*R*)-mcpp = *N*,*N*′-dimethyl-*N*,*N*′-bis[(*R*)-[4,5]-pineno-2-pyridylmethyl][(1*S*,2*S*)-1,2-cyclohexanediamine], Scheme 1).[19] Note that both **5** and **6** were used in the presence of acetic acid and the reactions were repeated two or three times to improve the conversion efficiency (Table 3, entries 4–9). Surprisingly, **1** gave products for three derivatives of **S2** with a moderate conversion efficiency and better selectivity, even after a single reaction. In the case of X = Br, **1** hydoxylated the C–H bond at the 7 position 15 times more selective than that at the 3 position, which is slightly better than the reported selectivities for **5** and **6** (Table 3, entries 3, 6, and 9). Thus, although **1** does not have two *cis*-oriented labile coordination sites as other iron catalysts for selective alkane hydroxylation do, it exhibits high regioselectivity for hydroxylation of alkane C–H bonds. More interestingly, the derivative with X = H was slightly more favorably hydroxylated at the 7 position than at the 3 position, although both **5** and **6** did not show any preference for the hydroxylation site (Table 3, entries 1, 4, and 7). This preference might be caused by greater steric hindrance around the iron-oxo group of **1** than those of **5** and **6**, as can be estimated from the crystal structures of their parent complexes.[15,19]

This study illustrates the uniqueness of the pentadentate monoamidate Fe^{III} complex, Fe^{III}–dpaq, in the catalysis of the

Table 3: Regioselective hydroxylation of 1-substituted 3,7-dimethyloctane.



Entry	Catalyst	X=	Repetition	Yield [%]	7-OH /3-OH	Ref.
1	**1**[a]	H	×1	39	3:2	this work
2		OAc	×1	53	9:1	this work
3		Br	×1	38	15:1	this work
4	**5**[b]	H	×3	48	1:1	[15]
5		OAc	×3	43	5:1	[15]
6		Br	×3	39	9:1	[15]
7	**6**[c]	H	×2	35	1:1	[19]
8		OAc	×2	49	5:1	[19]
9		Br	×2	51	7:1	[19]

[a] Catalyst/H_2O_2/substrate = 1:100:120 in CH_3CN at RT. The oxidant was added over a period of 30 min by using a syringe pump.
[b] 3×(Catalyst/H_2O_2/substrate/AcOH = 1:24:20:10) in CH_3CN at RT.
[c] 2×(Catalyst/H_2O_2/substrate/AcOH = 1:120:100:50) in CH_3CN at RT.

hydroxylation of inert alkane C–H bonds by H_2O_2 with a high level of selectivity and without an acid additive. To the best of our knowledge, Fe^{III}–dpaq is the first example of mononuclear nonheme Fe^{III} complex catalysts for selective hydroxylation of C–H bonds with H_2O_2. In our opinion, as a selective oxidation catalyst with H_2O_2 Fe^{III}–dpaq is superior to the reported Fe^{II} complexes with two *cis*-oriented labile coordination sites for the following reasons. 1) Fe^{III}–dpaq can afford the corresponding Fe^{V}oxo species through the formation of Fe^{III}OOH. On the other hands, Fe^{II} complexes must be oxidized first to the corresponding Fe^{III} species by H_2O_2 (0.5 equiv) prior to their entry into a catalytic cycle comprising Fe^{III} and Fe^{V}oxo species (Scheme 3). The oxidation step of Fe^{II} to Fe^{III} should generate some oxidants. 2) In terms of selective oxidations, a sole oxidant is desirable to be generated in reacting systems. Fe–dpaq satisfies this criterion by giving $[Fe^{V}(O)(dpaq)]^{2+}$ as a sole oxidant for the hydroxylation of C–H bonds. In the case of Fe^{V}oxo species supported by tetradentate ligands, however, exogenous ligands L′, such as acetate, would coordinate to Fe^{V}oxo species to give Fe^{V}oxo(L′) species. Thus, the reactivity of the Fe^{V}oxo species would be influenced by the coordination of L′. In these points, the catalytic system of Fe^{III}dpaq is simpler and more suitable for selective oxidation than those of iron(II) complexes with two *cis*-oriented labile coordination sites. We believe that the strategy to use Fe^{III} complexes supported by pentadentate monoamidate ligands for selective oxidations by H_2O_2 should contribute to the further development of bio-inspired "green" catalysts.

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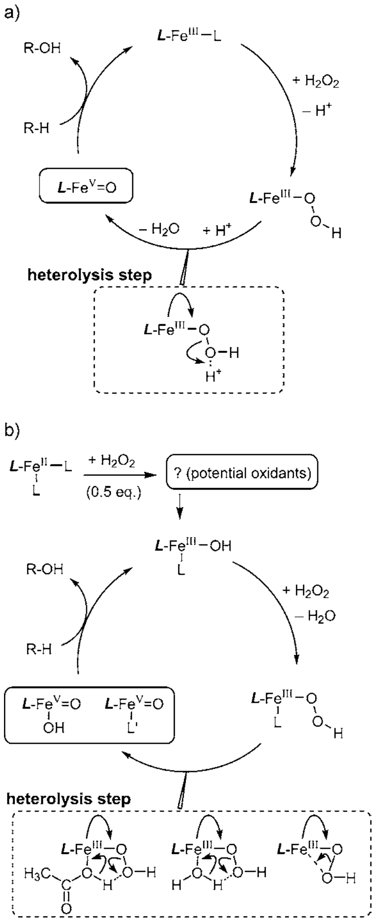

Scheme 3. Catalytic cycles of hydroxylation with a) Fe^{III}–dpaq, and b) an Fe^{II} complex with two *cis*-oriented labile sites.

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[37] The 3°/2° ratio is derived from the amount of 1-adamantanol divided by the amounts of 2-adamantanol and 2-adamantanone and multiplied by 3 to correct for the higher number of secondary C−H bonds.

[38] CCDC 867530 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.