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Anionic Ligand Effect on the Nature of Epoxidizing Intermediates in Iron Porphyrin Complex-Catalyzed Epoxidation Reactions

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We have studied an anionic ligand effect in iron porphyrin complex-catalyzed competitive epoxidations of *cis*- and *trans*-stilbenes by various terminal oxidants and found that the ratios of *cis*- to *trans*-stilbene oxide products formed in competitive epoxidations were markedly dependent on the ligating nature of the anionic ligands. The ratios of *cis*- to *trans*-stilbene oxides obtained in the reactions of Fe(TPP)X (TPP = *meso*-tetraphenylporphinato dianion and X^- = anionic ligand) and iodosylbenzene (PhIO) were 14 and 0.9 when the X^- of Fe(TPP)X was Cl^- and $CF_3SO_3^-$, respectively. An anionic ligand effect was also observed in the reactions of an electron-deficient iron(III) porphyrin complex containing a number of different anionic ligands, Fe(TPFPP)X [TPFPP = *meso*-tetrakis-(pentafluorophenyl)porphinato dianion and X^- = anionic ligand], and various terminal oxidants such as PhIO, *m*-chloroperoxybenzoic acid (*m*-CPBA), tetrabutylammonium oxone (TBAO), and H_2O_2. While high ratios of *cis*- to *trans*-stilbene oxides were obtained in the reactions of iron porphyrin catalysts containing ligating anionic ligands such as Cl^- and OAc^-, the ratios of *cis*- to *trans*-stilbene oxide were low in the reactions of iron porphyrin complexes containing nonligating or weakly ligating anionic ligands such as SbF_6^-, $CF_3SO_3^-$, and ClO_4^-. When the anionic ligand was NO_3^-, the product ratios were found to depend on terminal oxidants and olefin concentrations. We suggest that the dependence of the product ratios on the anionic ligands of iron(III) porphyrin catalysts is due to the involvement of different reactive species in olefin epoxidation reactions. That is, high-valent iron(IV) oxo porphyrin cation radicals are generated as a reactive species in the reactions of iron porphyrin catalysts containing nonligating or weakly ligating anionic ligands such as SbF_6^-, $CF_3SO_3^-$, and ClO_4^-, whereas oxidant–iron(III) porphyrin complexes are the reactive intermediates in the reactions of iron porphyrin catalysts containing ligating anionic ligands such as Cl^- and OAc^-.

Introduction

Elucidation of the nature of reactive intermediates responsible for oxygen atom transfer in catalytic oxygenations of hydrocarbons by cytochromes P450 and their iron porphyrin models is of continuing interest in the fields of biological, bioinorganic, and oxidation chemistry.[1,2] It has been believed for a long time that high-valent iron(IV) oxo porphyrin cation radicals **2** are the sole reactive species capable of oxygenating hydrocarbons. However, recent studies suggested that oxidant–iron(III) porphyrin complexes **1** also are able to oxygenate hydrocarbons prior to the formation of **2** and that the involvement of **1** and **2** as reactive intermediates is controlled by factors such as the presence of threonine in the active site of cytochromes P450 and the solvent system of iron porphyrin models.[3,4]

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It has been shown very recently that anionic ligands of iron(III) porphyrin complexes play an important role in the catalytic oxygenation of hydrocarbons by H_2O_2, in which the yields of oxygenated products were markedly dependent on the anionic ligands of the iron(III) porphyrin catalysts.[5] The anionic ligand effect was also observed in the reactions of iron(III) porphyrin complexes with *m*-chloroperoxybenzoic acid (*m*-CPBA) and iodosylbenzene (PhIO),[6] where two different oxoiron(IV) porphyrin complexes were generated, depending on the anionic ligands of the iron(III) porphyrins. Adam and co-workers also reported that the oxidation of olefins by M^{III}(salen)X (M = Mn and Cr) complexes and PhIO was significantly influenced by the counterions, X^-, of the metal salen catalysts.[7] More recently, the anionic ligand effect has been observed in non-porphyrin iron complex-catalyzed oxidation reactions by H_2O_2, in which the oxidation of ligand and external substrates and the yields of oxygenated products were significantly affected by the counterions of the iron catalysts.[8] Therefore, the aforementioned results indicate that the catalytic activities of metal complexes of porphyrin, salen, and non-porphyrin ligands are dependent on the simple anionic ligands or counterions of the metal complexes. In the present study, we demonstrate that the nature of the reactive intermediates responsible for oxygen atom transfer in iron(III) porphyrin-catalyzed epoxidation reactions is controlled by the simple anionic ligands of iron(III) porphyrin complexes and suggest that two epoxidizing intermediates such as **1** and **2** are generated, depending on the ligating nature of the anionic ligands.

Results and Discussion

We have shown recently that competitive epoxidations of *cis*- and *trans*-olefins are a useful mechanistic probe to distinguish the nature of reactive intermediates in the catalytic epoxidation of olefins by iron porphyrin complexes containing nonbulky *ortho*-substituents on the phenyl groups of the porphyrin ring.[4d] Therefore, to investigate the effect of anionic ligands of iron(III) porphyrin complexes on the nature of epoxidizing intermediates, we carried out the competitive epoxidations of *cis*- and *trans*-stilbenes with iron(III) porphyrin complexes containing nonbulky *ortho*-substituents on the phenyl groups of the porphyrin ligands and different anionic ligands. We first explored the anionic ligand effect in the epoxidation of olefins by Fe(TPP)X (TPP = *meso*-tetraphenylporphinato dianion and X^- = anionic ligand) and PhIO (eq 1). Groves and co-workers reported previously that the reaction of Fe(TPP)Cl and PhIO with a mixture of *cis*- and *trans*-stilbene yielded *cis*-stilbene oxide 15 times more than *trans*-stilbene oxide and suggested that the preference of *cis*-stilbene over *trans*-stilbene in the competitive epoxidation reaction was due to a severe steric interaction between the phenyl groups of *trans*-stilbene and those of the porphyrin ligand of the oxoiron(IV) porphyrin cation radical intermediate, $(TPP)^{+\bullet}Fe^{IV}{=}O$, generated in the reaction of Fe(TPP)Cl and PhIO.[9] The results in Table 1 show that the reaction of Fe(TPP)Cl and PhIO indeed yielded *cis*-stilbene oxide predominantly and that the ratio of *cis*- to *trans*-stilbene oxide was 14 ± 2, as Groves and co-workers reported previously.[9a] However, when the competitive epoxidation was carried out with the Fe(TPP)X complex containing a different anion such as triflate ($CF_3SO_3^-$), the product ratio of *cis*- to *trans*-stilbene oxide was dramatically changed from 14 to 0.9 under the identical reaction conditions (Table 1). Because the formation of isomerized products (e.g., the formation of *trans*-stilbene oxide in the epoxidation of *cis*-stilbene) would result in giving false product ratios in the competitive epoxidation reactions, control reactions were carried out with *cis*-stilbene and *trans*-stilbene individually in the catalytic epoxidation reactions by Fe(TPP)(CF_3SO_3) and PhIO under the reaction conditions employed. The control reactions showed only a small amount of isomerized *trans*-stilbene oxide formation in the epoxidations of *cis*-stilbene and no formation of *cis*-stilbene oxide in the epoxidations of *trans*-stilbene (Supporting Information, Table S1). The results of the control reactions demonstrate unambiguously that the

Table 1. Anionic Ligand Effect Observed in the Competitive Epoxidation of *cis*- and *trans*-Stilbenes by Fe(TPP)X and PhIO[a,b]

Fe(TPP)Cl			Fe(TPP)(CF_3SO_3)		
yield[c] (%)			yield[c] (%)		
cis[d]	*trans*[d]	ratio of *cis* to *trans*	*cis*[d]	*trans*[d]	ratio of *cis* to *trans*
56 ± 4	4 ± 1	14 ± 2	26 ± 3	28 ± 3	0.9 ± 0.2

[a] Detailed experimental procedures were described in the part Catalytic Competitive Epoxidations in the Experimental Section. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] The yields of products and the ratios of *cis*- to *trans*-stilbene oxides were the same when the reactions were carried out in CH_2Cl_2.[9] [c] Based on the amounts of PhIO added. [d] *cis* and *trans* stand for *cis*-stilbene oxide and *trans*-stilbene oxide, respectively.

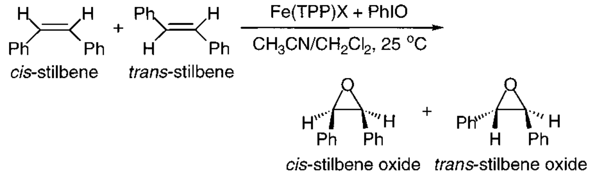

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Table 2. Ratios of *cis*- to *trans*-Stilbene Oxide Products Obtained in the Relative Reactivity Studies of *cis*- and *trans*-Stilbenes with Fe(TPFPP)X Complexes and Various Terminal Oxidants[a–c]

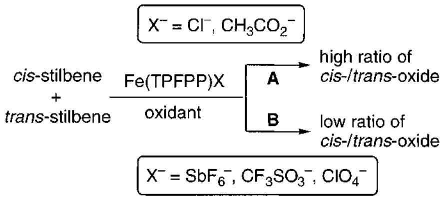
	ratio of *cis* to *trans* products for the following X^- of Fe(TPFPP)X					
oxidant	Cl^-	$CH_3CO_2^-$	NO_3^-	SbF_6^-	$CF_3SO_3^-$	ClO_4^-
PhIO	13 ± 2 (66:5)	13 ± 2 (66:5)	6.9 ± 0.7 (55:8)	1.5 ± 0.3 (32:20)	1.2 ± 0.3 (31:26)	1.4 ± 0.3 (34:24)
m-CPBA	7.0 ± 0.8 (77:11)	5.8 ± 0.7 (76:13)	4.3 ± 0.3 (68:16)	0.8 ± 0.2 (28:36)	0.9 ± 0.2 (35:37)	0.8 ± 0.1 (30:36)
TBAO	5.9 ± 0.6 (47:8)	5.3 ± 0.6 (42:8)	0.8 ± 0.1 (14:18)	0.8 ± 0.1 (19:24)	0.7 ± 0.1 (13:20)	0.7 ± 0.1 (13:19)
H_2O_2	nd[d]	nd[d]	0.9 ± 0.1 (18:20)	0.8 ± 0.1 (28:35)	0.8 ± 0.1 (24:30)	0.8 ± 0.1 (25:31)

[a] Detailed experimental procedures were described in the part Catalytic Competitive Epoxidations in the Experimental Section. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Numbers in parentheses are the yields (%) of *cis*-stilbene oxide and *trans*-stilbene oxide based on moles of oxidant used; the error is within ±10% of the state values. Only trace amounts of benzaldehyde were produced in all of the reactions. [c] Controlled reactions showed at most only trace amounts of isomerized *trans*-stilbene oxide formation in the epoxidations of *cis*-stilbene and no formation of *cis*-stilbene oxide in *trans*-stilbene epoxidations (data not shown). Another control experiment performed with *m*-CPBA in the absence of an iron porphyrin catalyst gave the *cis*- to *trans*-stilbene oxide ratio 0.8 ± 0.1. In the absence of the iron porphyrin catalysts, only trace amounts of oxide products were produced in all of the reactions except in the *m*-CPBA reaction. [d] Not determined because of the formation of only trace amounts of epoxide products in the epoxidation of olefins by Fe(TPFPP)X ($X^- = Cl^-$ and OAc^-) and H_2O_2.[5]

formation of *trans*-stilbene oxide was the result of the epoxidation of *trans*-stilbene, not the result of the isomerization of *cis*-stilbene, in the competitive epoxidation reaction.

Because we found that the ratios of *cis*- to *trans*-stilbene oxide products were significantly affected by the simple anionic ligands of Fe(TPP)X complexes, a more detailed anionic ligand effect was investigated by carrying out the competitive epoxidation of *cis*- and *trans*-stilbenes with an electron-deficient iron(III) porphyrin complex containing a number of different anionic ligands, Fe(TPFPP)X (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphinato dianion and X^- = anionic ligand), and with various terminal oxidants such as PhIO, *m*-CPBA, TBAO (tetrabutylammonium oxone),[10] and H_2O_2 in a solvent mixture of CH_3CN and CH_2Cl_2 at room temperature. The Fe(TPFPP)X complex containing nonbulky fluoro-substituents on the phenyl groups of the porphyrin ligand has been shown to be an efficient and robust catalyst in oxygenation reactions. As the results show in Table 2, when Fe(TPFPP)X complexes containing ligating anionic ligands such as Cl^- and OAc^- were used as a catalyst, high ratios of *cis*- to *trans*-stilbene oxide products were obtained in the reactions of PhIO, *m*-CPBA, and TBAO (Scheme 1, pathway A). In contrast, the ratios of *cis*- to *trans*-stilbene oxide were low in the reactions of Fe(TPFPP)X complexes containing nonligating or weakly ligating anionic ligands such as SbF_6^-, $CF_3SO_3^-$, and ClO_4^- (Scheme 1, pathway B).[11] These results indicate that the product ratios were significantly affected by the simple anionic ligands of Fe(TPFPP)X, as we have observed in the reactions of Fe(TPP)X and PhIO. Another intriguing observation that we made was the dependence of the product ratios on the terminal oxidants when the anionic ligand of Fe(TPFPP)X was NO_3^-. The ratios of *cis*- to *trans*-stilbene oxide were relatively high, such as 6.9 and 4.3 in the reactions of PhIO and *m*-CPBA, respectively, whereas a low ratio of ~0.8 was obtained when TBAO and H_2O_2 were used as terminal oxidants (Table 2, see data in the column of NO_3^-).

Scheme 1



Then, why are the ratios of *cis*- to *trans*-stilbene oxide products significantly dependent on the simple anionic ligands of iron(III) porphyrin complexes? This phenomenon may be explained with the generation and involvement of more than one epoxidizing intermediate, depending on the anionic ligands of iron(III) porphyrin catalysts in the competitive epoxidation reactions (e.g., a high-valent iron(IV) oxo porphyrin cation radical and oxidant–iron porphyrin complexes).[4c] If a high-valent iron(IV) oxo porphyrin cation radical (i.e., $(Porp)^{+\bullet}Fe^{IV}(O)(X)$) is generated as a common reactive species in all of the reactions and the different product ratios are resulted from the anionic ligand effect on the reactivity of the high-valent iron(IV) oxo porphyrin cation radical intermediate (e.g., $(Porp)^{+\bullet}Fe^{IV}(O)(Cl)$ vs $(Porp)^{+\bullet}Fe^{IV}(O)(CF_3SO_3)$),[12] then the ratio of *cis*- to *trans*-stilbene oxide should be independent of the identity of terminal oxidants. However, the ratios were different with different terminal oxidants, as shown in the reactions of Fe(TPFPP)(NO_3) with PhIO, *m*-CPBA, TBAO, and H_2O_2 (Table 2, see data in the column of NO_3^-), suggesting that more than one reactive species is generated as a reactive species responsible for oxygen atom transfer in the olefin epoxidation reactions.[13] Other supporting evidence for the involvement of two different epoxidizing intermediates is that the product ratios obtained in the competitive epoxidation by Fe(TPFPP)(NO_3) and *m*-CPBA were dependent on the concentration of olefinic substrates. As the amounts of *cis*- and *trans*-stilbene substrates present in the reaction solution decreased, the ratios

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(11) In the case of iron(III) porphyrin complexes containing nonligating or weakly ligating ligands such as SbF_6^-, $CF_3SO_3^-$, and ClO_4^-, the solvent CH_3CN binds to the iron ion as an axial ligand.

(12) Gross and co-workers demonstrated unambiguously that the reactivity and stability of high-valent iron(IV) oxo porphyrin cation radicals are significantly affected by the anionic axial ligands of the intermediates: (a) Gross, Z.; Nimri, S. *Inorg. Chem.* **1994**, *33*, 1731. (b) Gross, Z. *J. Biol. Inorg. Chem.* **1996**, *1*, 368. (c) Czarnecki, K.; Nimri, S.; Gross, Z.; Proniewicz, L. M.; Kincaid, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 2929. (d) Gross, Z.; Nimri, S.; Barzilay, C. M.; Simkhovich, L. *J. Biol. Inorg. Chem.* **1997**, *2*, 492.

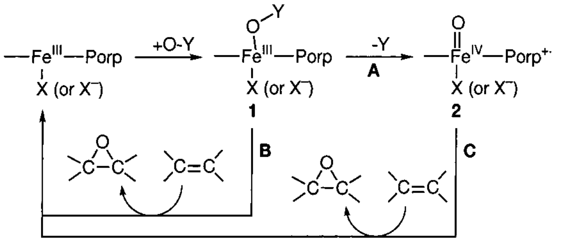
(13) One of the reviewers strongly argued against our suggestion that the different ratios of *cis*- to *trans*-stilbene oxide products are the result of the generation of two different epoxidizing intermediates depending on the anionic ligands of iron(III) porphyrin complexes. This reviewer suggested that the different product ratios may be the result of the anionic ligand effect on the reactivity of a common high-valent iron(IV) oxo porphyrin cation radical $X–Fe^{IV}(Porp)^{+\bullet}(O)$ and not the result of the involvement of two different reactive species.

Table 3. Effect of Substrate Concentration on the Ratio of *cis*- to *trans*-Stilbene Oxide Products in the Competitive Epoxidation of *cis*- and *trans*-Stilbenes by Fe(TPFPP)(NO_3) and *m*-CPBA[a]

	amount of substrate (mmol)			
	0.2	0.05	0.01[c]	0.0025[d]
ratio of *cis*-oxide/*trans*-oxide	4.3 ± 0.3	3.2 ± 0.3	2.1 ± 0.2	1.5 ± 0.2
(*cis*-oxide/*trans*-oxide)[b]	(68:16)	(64:20)	(57:27)	(46:30)

[a] Detailed experimental procedures were described in the part Catalytic Competitive Epoxidations in the Experimental Section. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Numbers in parentheses are the yields (%) of *cis*-stilbene oxide and *trans*-stilbene oxide based on moles of *m*-CPBA used; the error is within ±10% of the state values. *cis*-Oxide and *trans*-oxide stand for *cis*-stilbene oxide and *trans*-stilbene oxide, respectively. [c] The amount of *m*-CPBA added was 2×10^{-3} mmol. [d] The amount of *m*-CPBA added was 1×10^{-3} mmol.

Scheme 2



of *cis*- to *trans*-stilbene oxide products gradually decreased (Table 3). The dependence of the product ratios on the concentration of olefinic substrates suggests that there are competitive reaction pathways between the formation of **2** from **1** (Scheme 2, pathway A) and the oxygen atom transfer from **1** to olefins (Scheme 2, pathway B). In the presence of large amounts of olefinic substrates, **1** has more chance to transfer its oxygen to olefins prior to the formation of **2** (Scheme 2, pathway B), resulting in giving a high ratio of *cis*- to *trans*-stilbene oxide products.[14] In contrast, as the amounts of substrates in the reaction solution decrease, the *cis*- to *trans*-stilbene oxide ratio becomes lower (Table 3), demonstrating that **2** becomes a major epoxidizing intermediate when small amounts of olefinic substrates are present in reaction solution (Scheme 2, pathway A followed by pathway C).[15] On the basis of the results discussed above, we suggest that the Fe(TPFPP)X complexes containing ligating anionic ligands such as Cl^- and OAc^- generate **1** as an epoxidizing intermediate, whereas **2** becomes the reactive species when nonligating or weakly ligating anionic ligands such as SbF_6^-, $CF_3SO_3^-$, and ClO_4^- are the counterions of the iron porphyrin complex.[16] When the anionic ligand of Fe(TPFPP)X is NO_3^-, both **1** and **2** are involved as epoxidizing intermediates depending on the terminal oxidants and olefin concentration. Furthermore, the results of Fe(TPFPP)X complexes lead us to question whether the preference of *cis*-stilbene over *trans*-stilbene observed in the competitive epoxidation reaction by Fe(TPP)Cl and PhIO is due to a steric interaction between the phenyl groups on the porphyrin ligand of the $(TPP)^{+\bullet}Fe^{IV}{=}O$ intermediate and the phenyl groups of *trans*-stilbene.[9] Different from the previous suggestion of Groves and co-workers, we propose that the active species generated in the reaction of Fe(TPP)Cl and PhIO is not a $(TPP)^{+\bullet}Fe^{IV}{=}O$ complex but, possibly, a PhIO−Fe(TPP) complex[4b,d,17] and that the preference of *cis*-stilbene over *trans*-stilbene results from the steric repulsion between the phenyl groups of *trans*-stilbene and the bulky oxidant (i.e., PhIO) bound to the PhIO−Fe(TPP) complex.[4e]

Then, what is the role of the anionic ligands in giving different reactive epoxidizing intermediates? We have suggested previously that anionic ligands bound to an iron(III) ion may influence the electronic nature of oxidant−iron porphyrin intermediate **1**, affecting the oxidizing power and/or lifetime of the intermediate.[4c,5,6] Therefore, to understand whether the anionic ligand effect correlates with the electron-donating ability of anionic ligands, we performed the competitive epoxidations of *cis*- and *trans*-stilbenes with Fe(TPFPP)X ($X^- = Cl^-$ and $CF_3SO_3^-$) complexes in the presence of an imidazole such as 5-chloro-1-methylimidazole (5-Cl-1-MeIm)[18,19] because it has been well documented that the reactivities of metalloporphyrins are significantly affected by the binding of imidazoles as axial ligands.[20] We also showed recently that the presence of 5-Cl-1-MeIm in the catalytic epoxidation of olefins by iron(III) porphyrin complexes and H_2O_2 markedly increases the yields of epoxide products in aprotic solvent and suggested that the role of the imidazole decelerates the O−O bond cleavage of an iron(III) hydroperoxide porphyrin (or H_2O_2−iron(III) porphyrin adduct).[21] The results in Table 4 show that the

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(14) It has been suggested previously that when **1** is an epoxidizing intermediate, the ratio of *cis*- to *trans*-stilbene oxide products becomes high as a result of the steric effect of the oxidant bound to an iron porphyrin because the approach of *trans*-stilbene to **1** is highly restricted by the steric repulsion between the phenyl groups of *trans*-stilbene and the bulky oxidant bound to the iron ion.[4e]

(15) The ratios of *cis*- to *trans*-stilbene oxides formed in the competitive epoxidations by in situ generated $(TPFPP)^{+\bullet}Fe^{IV}{=}O(X)$ ($X^- = SbF_6^-$, $CF_3SO_3^-$, and ClO_4^-) complexes were determined to be 0.8 ± 0.2 (see the part Stoichiometric Competitive Epoxidations in the Experimental Section for detailed reaction procedures).[4d] However, the preparation of **2** with Fe(TPFPP)X ($X^- = Cl^-$ and OAc^-) complexes was not successful;[5] therefore, the *cis*- to *trans*-stilbene oxide ratio with $(TPFPP)^{+\bullet}Fe^{IV}{=}O(X)$ ($X^- = Cl^-$ and OAc^-) complexes was not determined.

(16) The ratios obtained in the PhIO reactions were a little bit higher than those obtained in the reactions of *m*-CPBA, TBAO, and H_2O_2 when the anionic ligands of Fe(TPFPP)X were SbF_6^-, $CF_3SO_3^-$, and ClO_4^- (see Table 2). The results may show that $(TPFPP)^{+\bullet}Fe^{IV}(O)(X)$ is generated as the major reactive species in the PhIO reaction, but a small amount of PhIO−Fe(TPFPP)(X) adduct is also involved as another reactive oxidant in the epoxidation reaction, resulting in giving a little bit higher number in the PhIO reactions.

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Table 4. Effect of 5-Cl-1-MeIm on the Competitive Epoxidation of *cis*- and *trans*-Stilbenes by Fe(TPFPP)X and Various Terminal Oxidants[a−c]

	Fe(TPFPP)Cl		Fe(TPFPP)(CF_3SO_3)	
	presence of 5-Cl-1-MeIm		presence of 5-Cl-1-MeIm	
oxidant	no	yes	no	yes
PhIO	13 ± 2 (66:5)	5.0 ± 0.6 (55:11)	1.2 ± 0.3 (31:26)	4.5 ± 0.6 (54:12)
m-CPBA	7.0 ± 0.8 (77:11)	10 ± 1 (89:9)	0.9 ± 0.2 (35:37)	9 ± 1 (81:9)
TBAO	5.9 ± 0.6 (47:8)	7 ± 1 (35:5)	0.7 ± 0.1 (13:20)	6 ± 1 (30:5)

[a] Reaction conditions:[20] oxidant (0.1 mmol) was added to a stirred solution containing Fe(TPFPP)X (1.0×10^{-3} mmol) and equal amounts of *cis*- and *trans*-stilbenes (1 mmol each) in a solvent mixture (1 mL) of CH_3CN and CH_2Cl_2 (1:1) at room temperature. After the reaction mixture was stirred for 30 min, the resulting solution was directly analyzed by HPLC. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Numbers in parentheses are the yields (%) of *cis*-stilbene oxide and *trans*-stilbene oxide based on moles of oxidant used; the error is within ±10% of the state values. Only trace amounts of benzaldehyde were produced in all of the reactions. [c] Controlled reactions showed at most only trace amounts of isomerized *trans*-stilbene oxide formation in the epoxidations of *cis*-stilbene and no formation of *cis*-stilbene oxide in *trans*-stilbene epoxidations (data not shown).

ratios of *cis*- to *trans*-stilbene oxide were not greatly affected by the presence of 5-Cl-1-MeIm in the reactions of Fe(TPFPP)Cl (see the column of Fe(TPFPP)Cl in Table 4), whereas the product ratios obtained in the reactions of Fe(TPFPP)(CF_3SO_3) were markedly changed upon the addition of 5-Cl-1-MeIm (see the column of Fe(TPFPP)(CF_3SO_3) in Table 4). The high ratios of *cis*- to *trans*-stilbene oxide products obtained in the latter reactions indicate that **1** became the reactive epoxidizing species when the competitive reactions were carried out in the presence of 5-Cl-1-MeIm.[21] Moreover, the product ratios obtained in the reactions of Fe(TPFPP)Cl and Fe(TPFPP)(CF_3SO_3) were identical within experimental errors to those in the presence of 5-Cl-1-MeIm, indicating that the anionic ligand effect disappears when the iron porphyrin complexes such as Fe(TPFPP)Cl and Fe(TPFPP)(CF_3SO_3) bind the same axial ligand (i.e., 5-Cl-1-MeIm). On the basis of the results discussed above, we propose that the electron-donating ability of the anionic ligands of iron(III) porphyrin complexes is an important factor in controlling the nature of reactive epoxidizing intermediates.[22]

Last, the anionic ligand effect was investigated with other metalloporphyrin complexes such as Cr(TPFPP)X and Mn(TPFPP)X ($X^- = Cl^-$ and $CF_3SO_3^-$) by carrying out the competitive epoxidations of *cis*- and *trans*-stilbenes with PhIO. As the results show in Table 5, the ratios of *cis*- to *trans*-stilbene oxides were high in the reactions of both Cr(TPFPP)Cl and Cr(TPFPP)(CF_3SO_3), indicating that there is no anionic ligand effect in the reactions of Cr(TPFPP)X and PhIO. In the reactions performed with manganese(III) porphyrin complexes, the ratio was slightly higher when X^- of Mn(TPFPP)X was Cl^- than when X^- of Mn(TPFPP)X was $CF_3SO_3^-$. We therefore conclude that, among the metalloporphyrins tested in this study, the reactivity of iron(III) porphyrin complexes is the most significantly affected by the anionic ligands.

In summary, we have shown here that the product ratios in iron(III) porphyrin complex-catalyzed competitive epoxidations of *cis*- and *trans*-stilbenes were markedly influenced by the simple anionic ligands of iron porphyrin complexes. This anionic ligand effect shows that the electron-donating ability of anionic ligands is an important factor in controlling the nature of reactive epoxidizing intermediates. In addition to the anionic ligand effect, other factors such as the identity of terminal oxidants and the concentration of organic substrates play a role in determining the nature of epoxidizing intermediates. Our future studies will be directed toward investigating the anionic ligand effect in oxidation reactions by metal complexes of nonporphyrin ligands.

Experimental Section

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

Materials. Dichloromethane (anhydrous) and acetonitrile (anhydrous) were obtained from Aldrich Chemical Co. and dried with CaH_2 prior to use. All chemicals obtained from Aldrich were the best available purity and were used without further purification unless otherwise indicated. H_2O_2 (30% aqueous) and $KHSO_5$ (oxone) were purchased from Aldrich. PhIO was prepared from iodobenzene diacetate by a literature method.[23] TBAO was prepared according to literature procedures, and the purity of TBAO was determined to be 34 ± 2%.[24] *m*-CPBA purchased from Aldrich Chemical Co. was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. Fe(TPP)Cl and Fe(TPFPP)Cl were purchased from Aldrich. Fe(TPFPP)(CH_3CO_2), Cr(TPFPP)Cl, and Mn(TPFPP)Cl were obtained from Mid-Century Chemicals. M(Porp)X complexes were prepared by stirring equimolar amounts of M(Porp)Cl complexes with AgX salts followed by filtering through a 0.45-μM filter. The resulting solution was used immediately for further studies. The purity of the iron(III) porphyrins purchased and prepared for reactions was examined by ^1H NMR in a solvent mixture of CD_3CN (0.03 mL) and CD_2Cl_2 (0.47 mL). ^1H NMR data (δ, ppm) of pyrrole H: Fe(TPP)Cl, 81.4; Fe(TPP)(CF_3SO_3), 33.2; Fe(TPFPP)Cl, 81.7; Fe(TPFPP)(CH_3CO_2), 83.0; Fe(TPFPP)(NO_3), 75.3; Fe(TPFPP)(SbF_6), 40.4; Fe(TPFPP)(CF_3SO_3), 56.6; Fe(TPFPP)(ClO_4), 38.2.

Table 5. Ratios of *cis*- to *trans*-Stilbene Oxide Products Formed in the Competitive Epoxidations of *cis*- and *trans*-Stilbenes by Various Metalloporphyrin Complexes and PhIO[a]

	Cr(TPFPP)X		Mn(TPFPP)X		Fe(TPFPP)X	
	$X^- = Cl^-$	$X^- = CF_3SO_3^-$	$X^- = Cl^-$	$X^- = CF_3SO_3^-$	$X^- = Cl^-$	$X^- = CF_3SO_3^-$
ratio of *cis*-oxide/*trans*-oxide (*cis*-oxide/*trans*-oxide)[b]	15 ± 2 (61:4)	14 ± 2 (42:3)	7.9 ± 0.9 (53:8)	4.6 ± 0.5 (55:12)	13 ± 2 (66:5)	1.2 ± 0.3 (31:26)

[a] Reaction conditions were the same as those described in the part Catalytic Competitive Epoxidations in the Experimental Section except that M(TPFPP)X complexes were used as a catalyst. [b] Numbers in parentheses are the yields (%) of *cis*-stilbene oxide and *trans*-stilbene oxide based on moles of PhIO added; the error is within ±10% of the state values. *cis*-Oxide and *trans*-oxide stand for *cis*-stilbene oxide and *trans*-stilbene oxide, respectively.

Instrumentation. Product analyses were performed on a Thermo Separation Products P2000 equipped with a variable wavelength UV-200 detector. Products were separated on a Waters Symmetry C18 reverse phase column (4.6 mm × 250 mm), eluted first with 50% methanol in water for 15 min and then with 85% methanol in water for 10 min at a flow rate of 1 mL/min. Detection was made at 215 and 254 nm. UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Low-temperature UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer equipped with an *Optostat* variable-temperature liquid-nitrogen cryostat (Oxford Instruments). ^{1}H NMR spectra were recorded on a Bruker AM 250, and chemical shifts are reported relative to residual hydrogen in the deuterated solvents.

Catalytic Competitive Epoxidations. Reactions were performed at ambient temperature under argon atmosphere. In general, oxidant (7.5×10^{-3} mmol, diluted in 20 μL of CH_3CN for the reactions of *m*-CPBA and TBAO; 5×10^{-2} mmol for PhIO reactions) was added to a stirred solution containing an iron porphyrin complex (1.5×10^{-3} mmol) and equal amounts of *cis*- and *trans*-stilbenes (0.2 mmol each) in a solvent mixture (0.5 mL) of CH_3CN and CH_2Cl_2 (1:1) at room temperature. In H_2O_2 reactions, oxidant (3×10^{-2} mmol, diluted in 50 μL of CH_3CN) was slowly added over a period of 20 min to the reaction solution. The reaction mixture was stirred for 10 min in the reactions of *m*-CPBA, TBAO, and H_2O_2 or for 30 min in PhIO reactions, and the resulting solution was directly analyzed by HPLC. The yields of products were determined by comparison with standard curves of known authentic samples. Because it is possible that the anionic ligand of Fe(Porp)X is exchanged with another anion derived from oxidants (e.g., *m*-chlorobenzoate from *m*-chloroperbenzoic acid), UV−vis spectra of reaction solutions were taken before and after the addition of oxidants to the reaction solutions (Supporting Information, Figure S1; UV−vis spectra of Fe(TPFPP)Cl and Fe(TPFPP)(CF_3SO_3) as a representative of the spectra of all other reactions).[25]

Stoichiometric Competitive Epoxidations. Oxoiron(IV) porphyrin cation radicals, $(TPFPP)^{+\bullet}Fe^{IV}{=}O(X)$ ($X^- = PF_6^-$, SbF_6^-, $CF_3SO_3^-$, and ClO_4^-), were prepared by reacting Fe(TPFPP)X (1×10^{-3} mmol) with 1.2 equiv of *m*-CPBA (1.2×10^{-3} mmol) in a solvent mixture (0.5 mL) of CH_3CN and CH_2Cl_2 (1:1) at −40 °C. The formation and stability of the intermediates were confirmed by taking low-temperature UV−vis spectra of the green solutions. Then, a mixture of *cis*- and *trans*-stilbenes (1.5×10^{-2} mmol each) in CH_2Cl_2 (0.2 mL) was injected into the reaction solution containing the in situ generated $(TPFPP)^{+\bullet}Fe^{IV} = O(X)$ (1×10^{-3} mmol) at −40 °C, and the reaction mixture was directly analyzed by HPLC. The sum of the yields of *cis*-stilbene oxide and *trans*-stilbene oxide products was 50 ± 10% on the basis of the amounts of $(TPFPP)^{+\bullet}Fe^{IV} = O(X)$ prepared.

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Supporting Information Available: Table S1 contains data of the control reactions of the epoxidations of *cis*-stilbene and *trans*-stilbene by Fe(TPP)(CF_3SO_3) and PhIO. Figure S1 shows the UV−vis spectra of Fe(TPFPP)Cl and Fe(TPFPP)(CF_3SO_3) taken before and after the addition of *m*-CPBA to the reaction solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) It has been reported that the use of small amounts of *m*-CPBA (∼4 equiv) does not cause the replacement of the anionic ligand bound to the iron(III) ion by *m*-chlorobenzoate derived from *m*-CPBA: Czarnecki, K.; Proniewicz, L. M.; Fujii, H.; Kincaid, J. R. *J. Am. Chem. Soc*. **1996**, *118*, 4680. Because we only used 5 equiv of *m*-CPBA in the catalytic competitive epoxidation reactions, we suggest that most of the iron(III) porphyrin complexes retain their original anionic ligands (see Figure S1 in the Supporting Information). Other supporting evidence for this assertion is that if anionic ligands of iron porphyrin complexes (e.g., Fe(TPFPP)(CF_3SO_3)) are replaced by *m*-chlorobenzoate in the reactions of *m*-CPBA, then the product ratios should be similar to those obtained in the reactions of Fe(TPFPP)(CH_3CO_2) containing acetate as an anionic ligand because the binding properties of acetate and *m*-chlorobenzoate should be similar. However, this is not the case as shown in Table 2; therefore, we conclude that most of the iron(III) porphyrin complexes retain their original anionic ligands under the reaction conditions employed in this study.