

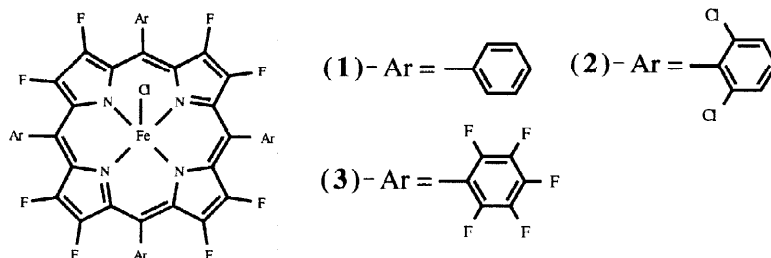
 **β -Octafluoro-*meso*-tetraarylporphyrin Iron Complexes as Catalysts for Monooxygenation Reactions**Emmanuel Porhiel,^a Arnaud Bondon^{a*} and Jacques Leroy^b^a Laboratoire de Chimie Organométallique et Biologique, CNRS et Université de Rennes 1, 35042 Rennes cedex, France.^b Ecole Normale Supérieure, Département de Chimie, associé au CNRS, 24 rue Lhomond, 75231 Paris cedex 05, France.

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Abstract: The stability and catalytic activity of the β -octafluoro-*meso*-tetraarylporphyrin iron complexes for cyclooctene epoxidation, cyclohexane and benzene hydroxylation by hydrogen peroxide and iodosylbenzene are studied. The results are compared to those obtained for the β -hydrogenated analogues.

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Synthetic iron and manganese porphyrins have been widely studied as oxygenation catalysts (i.e. hydroxylation and epoxidation) with various oxygen sources.¹⁻³ Electron-withdrawing substituents on the β -positions and/or *meso*-aryl groups have greatly improved their catalytic properties.⁴⁻⁸ We⁹ and others¹⁰ have recently described the synthesis of the β -octafluoro-tetraarylporphyrin free bases and their Zn^{II} complexes. Previous results of Tsuchiya and Seno¹¹ on "Teflon" porphyrins were attractive but the lack of characterization of these porphyrins (except erratic Soret absorption bands) made these results highly questionable. We report herein the first reliable results on the stability to oxidation and catalytic activity of these complexes.¹²

Scheme Structure of the β -octafluoroporphyrins iron complexes used as catalysts.

The robustness of iron porphyrins was studied at room temperature under ambient air with an oxidant to catalyst ratio of 100:1, the results being reported in Table 1. With PhIO, the introduction of fluorine on the β -positions resulted in an improvement in stability, consistent with the positive shifts in the oxidation potentials induced by β -octafluorination of TPPZn complex.¹⁰ This relation cannot apply to the comparison of **3** with **6**, since this later compound has already been described as a complex exhibiting a high and unusual stability.^{8,13} However, with H₂O₂, a decrease of the stability of the β -fluorinated complexes is observed as compared to the parent β -H analogues. This decrease can be related to a high reactivity of the β -fluorinated positions in the case of the homolytic cleavage of H₂O₂ or a nucleophilic attack of H₂O₂ on the highly electrodeficient porphyrin.

Table 1. Stability of the iron porphyrins to oxidants.

Hemin	Decrease in Soret absorbance (%)		Hemin	Decrease in Soret absorbance (%)	
	PhIO ^a	H ₂ O ₂ ^b		PhIO ^a	H ₂ O ₂ ^b
Fe(β -F ₈ TPP)Cl (1)	87	100	Fe(TPP)Cl (4)	100	100
Fe(β -F ₈ TDCPP)Cl (2)	3	54	Fe(TDCPP)Cl (5)	9	28
Fe(β -F ₈ TPFPP)Cl (3)	58	100	Fe(TPFPP)Cl (6)	4	93

^a Iron porphyrin in dichloromethane (2 mmol dm⁻³) was mixed with PhIO (100 eq.) at 25°C for 15 min. ^b H₂O₂ was added at once (100 eq., 3% in CH₃CN) to the iron porphyrin (2 mmol dm⁻³) in CH₂Cl₂-CH₃CN (1:1).

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Then we investigated the catalytic activity of the iron porphyrins with a substrate:PhIO:catalyst ratio of 100:100:1 and cyclooctene:H₂O₂:catalyst ratio of 100:300:1 (Table 2). Again high activities of Fe(TPFPP)Cl^{6,8} made the comparison with the complex **3** uneasy. Nevertheless, with PhIO, both cyclohexane and cyclooctene conversions were clearly improved by the presence of β -fluorine atoms. In contrast, with H₂O₂, the β -fluorination did not increase the efficiency of these catalysts, which remained poorly active for epoxidation, with the exception of **6**. Even the robust catalyst **5** was only slightly efficient.

Table 2. Hydroxylation and epoxidation by PhIO and H₂O₂ catalyzed by various iron porphyrins.

Catalyst	Reaction and product/turnovers (per 1.5 h)			
	Cyclohexane	Cyclooctene	Cyclooctene	Benzene
	+PhIO ^a	+PhIO ^a	+H ₂ O ₂ ^b	+H ₂ O ₂ ^c
	Cyclohexanol	Epoxide	Epoxide	Phenol
Fe(β -F ₈ TPP)Cl (1)	1	61	2.9	(0) ^d
Fe(β -F ₈ TDCPP)Cl (2)	32	81	3	(0) ^d
Fe(β -F ₈ TPFPP)Cl (3)	14	71	4,1	2
Fe(TPP)Cl (4)	(0) ^d	32	2.2	(0) ^d
Fe(TDCPP)Cl (5)	11	72	11	(0) ^d
Fe(TPFPP)Cl (6)	35	83	62	(0) ^d

^a Substrate:PhIO:catalyst = 100:100:1 in CH₂Cl₂ (catalyst 2 mmol dm⁻³), at room temp. Yields were determined by GC and based on starting substrate. ^b Cyclooctene:H₂O₂:iron porphyrin = 100:300:1 in CH₂Cl₂-CH₃CN (1:1) (catalyst 2 mmol dm⁻³), at room temp. H₂O₂ was progressively added (6 additions of 0.5 molar equivalents relative to cyclooctene). Yields were based on starting cyclooctene. ^c Conditions from ref. 11, catalyst at 1 mmol dm⁻³, turnovers per 2 h. ^d Not detectable.

The reported hydroxylation of benzene¹¹ was also reexamined. Whereas at 10⁻⁴ mol dm⁻³ in catalyst, phenol is not detected for any iron porphyrins, at 10⁻³ mol dm⁻³ the "Teflon" porphyrin **3** is the only one able to produce phenol to 2 turnovers in 2 hours.

In conclusion, these preliminary results reveal the capability of fluorine β -substitution to enhance the robustness and catalytic efficiency with PhIO as an oxidant for both epoxidation and hydroxylation. With H₂O₂, the β -fluorinated complexes are less stable, however, the higher reactivity of the iron-oxo intermediate might be associated with the phenol formation by the "Teflon" iron porphyrin.

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