Electrochemistry and Spectroelectrochemistry of σ-Bonded Iron(III) Porphyrins with Nonplanar Porphyrin Rings. Reactions of (OETPP)Fe(R) and (OETPP)FeCl, Where R = C_6H_5, C_6F_4H, or C_6F_5 and OETPP Is the Dianion of 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraphenylporphyrin

Karl M. Kadish*,[1a] **Eric Van Caemelbecke**,[1a] **Francis D'Souza**,[1a] **Craig J. Medforth**,[1b] **Kevin M. Smith**,[1b] **Alain Tabard**,[1c] **and Roger Guilard***,[1c]

Department of Chemistry, University of Houston, Houston, Texas 77204-5641, Department of Chemistry, University of California, Davis, California 95616, and LIMSAG, UMR 9953, Université de Bourgogne, Faculté des Sciences "Gabriel", 6 Boulevard Gabriel, 21100 Dijon, France

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A variety of nonplanar σ-bonded phenyl- and (fluorophenyl)iron(III) porphyrins are characterized as to their electrochemical and spectroscopic properties in nonaqueous media. The investigated compounds are represented as (OETPP)Fe(R), where R = C_6H_5, C_6F_4H, or C_6F_5 and OETPP is the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin. All three porphyrins contain a low-spin Fe(III) central metal ion and in the case of (OETPP)Fe(C_6F_5) and (OETPP)Fe(C_6F_4H) provide the first examples of low-spin iron σ-bonded (fluorophenyl)porphyrins. The site of electron transfer was assigned on the basis of the spectroscopic and electrochemical data for these compounds and by comparison with a related (OETPP)In(C_6H_5) derivative which was also synthesized and characterized. Comparisons of the results on (OETPP)Fe(R) are also made to data on earlier reported (OEP)Fe(R) derivatives where R = C_6H_5, C_6F_4H or C_6F_5, the latter two of which contain high-spin Fe(III) as compared to the low-spin (OEP)Fe(C_6H_5) species. (OETPP)Fe(C_6H_5) undergoes three one-electron oxidations to give a Fe(IV) π dication species. Our results show, for the first time, that the spin state of the iron(III) porphyrin is not a key factor which governs migration of the axial ligand of the electrooxidized species as has previously been proposed.

Introduction

A number of studies dealing with substrate activation by cytochrome P-450 have shown the formation of σ-bonded iron(III) alkyl or aryl intermediates during metabolic reduction of polyhalogenated compounds.[2−13] A variety of naturally occurring[3,14] and synthetic metalloporphyrins[12,15−34] containing σ-bonded alkyl or aryl axial ligands have been synthesized and studied in order to elucidate mechanistic details of the biological reactions. The one-electron chemical or electrochemical oxidation of synthetic σ-bonded iron(III) porphyrins may lead to

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(1) (a) University of Houston. (b) University of California (Davis). (c) Université de Bourgogne (Dijon).

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compounds in an iron(IV) oxidation state but this will depend in large part upon the nature of the axial ligand. For example, phenyl σ-bonded complexes of the type (P)Fe(C_6H_5) where P is the dianion of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP) or octaethyltetraphenylporphyrin (OETPP) can be chemically[33,34] or electrochemically[15,33] oxidized at the metal center to give $[(P)Fe^{IV}(C_6H_5)]^+$. However, a similar reaction may not occur for the C_6F_5 or C_6F_4H σ-bonded Fe(III) derivatives with the OEP or TPP macrocycles as evidenced by the fact that these complexes appear to be electrooxidized at the porphyrin π-ring system rather than at the metal center.[30]

All known five-coordinate (P)Fe(C_6F_5) and (P)Fe(C_6F_4H) complexes contain high-spin iron(III) while five-coordinate (P)-Fe(C_6H_5) either contains low-spin iron(III)[15] or exists in a spin-equilibrium[30] depending upon the specific porphyrin macrocycle. A migration of the σ-bonded axial ligand occurs after the first one-electron oxidation of (P)Fe(C_6H_5) (P = OEP or TPP)[15] or after the second one-electron oxidation of (OETPP)Fe(C_6H_5),[33] and this contrasts with (P)Fe(C_6F_5) and (P)Fe(C_6F_4H), both of which are stable on the cyclic voltammetry or controlled potential electrolysis time scale after electrooxidation by one or two electrons.[30] It was suggested that the difference in behavior between the phenyl and fluorophenyl σ-bonded compounds might be related to different sites of electron transfer or the different spin states of the initial Fe(III) porphyrin.[30] This is investigated in the present paper which reports the detailed electrochemistry of (OETPP)In(C_6H_5), (OETPP)Fe(C_6H_5), and (OETPP)Fe(R), where R = C_6F_4H or C_6F_5 and OETPP is the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin.

The investigated compounds are also of special interest with respect to examining how the saddle-shaped porphyrin ring and the iron(III) spin state may be related to the observed electrochemistry. (OETPP)Fe(C_6H_5) is low-spin[33] as are (OETPP)-Fe(C_6F_4H) and (OETPP)Fe(C_6F_5) which are the first examples of low-spin five-coordinate fluorophenyl σ-bonded porphyrins. Thus, a comparison of electrochemical data for the three nonplanar low-spin OETPP derivatives to those of the relatively planar low-spin (OEP)Fe(C_6H_5) and high-spin (OEP)Fe(C_6F_4H) and (OEP)Fe(C_6F_5) complexes should provide an opportunity to investigate directly how the spin state affects the redox potentials and site of electron transfer. It should also give information on how the planarity of the macrocycle may relate to the electrochemistry.

(OETPP)Zn,[35] (OETPP)Ni,[36] and (OETPP)FeCl[36] have saddle-shaped macrocycles, and this should also be the case for (OETPP)Fe(C_6H_5) and (OETPP)Fe(C_6F_4H) which would be in contrast to all previously investigated σ-bonded iron(III) metalloporphyrins, which are relatively planar.[37] It is known that nonplanar porphyrins are easier to oxidize than planar ones as was demonstrated for (OETPP)Zn,[35,38] (OETPP)Ni,[36] and (Br_x-TPP)M (where x varies from 0 to 8 and M = Fe[39] or H_2[40]), but very little is known as to how nonplanarity of the macrocycle will affect the site of electron transfer and the related formation of an iron(III) porphyrin π cation radical or an iron(IV) species from a neutral iron(III) metalloporphyrin.

(OETPP)Fe(C_6H_5) is the only monomeric iron(III) porphyrin known to undergo three reversible one-electron oxidations,[33] and we initially believed that the difference in redox behavior for this compound as compared to all other Fe(III) porphyrins could be due to its nonplanar conformation as well as to the higher basicity of the OETPP macrocycle. In order to now examine this point, the electrochemistry of (OETPP)FeCl was also investigated for comparison with the literature data on (OEP)FeCl and (TPP)FeCl.

Experimental Section

Chemicals. Benzonitrile (PhCN) was obtained from Aldrich Chemical Co. and distilled over P_2O_5 under vacuum prior to use. Absolute dichloromethane (CH_2Cl_2) obtained from Fluka Chemika was used without further purification and stored over molecular sieves. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use. Free base (OETPP)-H_2 was prepared from benzaldehyde and 3,4-diethylpyrrole following a literature procedure.[38] Iron was inserted using ferrous chloride tetrahydrate in DMF as described earlier.[36] (OETPP)InCl was obtained by metalation of the corresponding free base (OETPP)H_2 using literature methods.[41,42]

Synthesis of (OETPP)In(C_6H_5) and (OETPP)Fe(R), Where R = C_6H_5, C_6F_4H, or C_6F_5. The (OETPP)M(R) complexes where M = In or Fe were prepared by reacting an aryl Grignard reagent with (OETPP)-MCl according to literature procedures.[30,43,44]

(OETPP)Fe(C_6H_5): UV−visible (C_6H_6) λ_{max} (nm) ($10^{-3}\epsilon$, M^{-1} cm^{-1}) 432 (105.7), 550 (11.6, broad absorption); ^1H NMR (C_6D_6 from $SiMe_4$ at 294 K) δ (ppm) 14.39, 12.66, −0.74, −2.40 (16 H, α-CH_2), 7.51, 6.66, 5.42, 5.20, 4.29 (20 H, phenyl-H_{por}), 1.22 (12 H, β-CH_3), 0.39 (12 H, β′-CH_3), −89.14 (2 H, *o*-$H_{axial\ ligand}$), 2.09 (2 H, *m*-$H_{axial\ ligand}$), −30.87 (1 H, *p*-$H_{axial\ ligand}$); ESR (toluene at 4 K) $g_x = 1.86$, $g_y = 2.23$, $g_z = 2.69$.

(OETPP)Fe(C_6F_4H): UV−visible (C_6H_6) λ_{max} (nm) ($10^{-3}\epsilon$, M^{-1} cm^{-1}) 323 (41.7), 428 (106.1), 558 (12.3, broad absorption); ^1H NMR (C_6D_6 from $SiMe_4$ at 294 K) δ (ppm) 17.88, 16.43, 2.25, −1.71 (16H, α-CH_2), 8.26, 6.89, 5.66, 5.19, 4.78 (20 H, phenyl-H_{por}), 1.24 (12 H, β-CH_3), 0.42 (12 H, β′-CH_3), −21.16 (1 H, *p*-$H_{axial\ ligand}$); ^{19}F NMR (in C_6D_6 using $CFCl_3$ as external reference at 294 K) δ (ppm) −12.2, −194.4 ($F_{axial\ ligand}$); ESR (in toluene at 4 K) $g_x = 1.86$, $g_y = 2.27$, $g_z = 2.62$.

(OETPP)Fe(C_6F_5): UV−visible (C_6H_6) λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1}) 327 (41.7), 427 (104.3), 557 (12.4, broad absorption); ^1H NMR (C_6D_6 from $SiMe_4$ at 294 K) δ (ppm) 18.73, 17.10, 5.32, −0.07 (16 H, α-CH_2), 8.36, 6.02, 5.59, 4.93 (20 H, phenyl-H_{por}), 1.27 (12 H, β-CH_3), 0.41 (12 H, β′-CH_3); ^{19}F NMR (in C_6D_6 using $CFCl_3$ as external reference at 294 K) δ (ppm) 112.1, −52.2, −141.6 ($F_{axial\ ligand}$); ESR (in toluene at 4 K) $g_x = 1.85$, $g_y = 2.26$, $g_z = 2.54$.

(OETPP)In(C_6H_5): UV−visible (C_6H_6) λ_{max} (nm) ($10^{-3}\epsilon$, M^{-1} cm^{-1}) 379 (39.8), 450 (sh), 472 (297.1), 616 (8.13), 671 (7.7); ^1H NMR (C_6D_6 from $SiMe_4$ at 294 K) δ (ppm) 8.29, 8.11, 7.40 (20 H, phenyl-H_{por}), 2.93, 2.70, 2.43, 2.14 (16 H, α-CH_2), 0.76, 0.56 (24 H, β-CH_3), 3.45 (2 H, *o*-$H_{axial\ ligand}$), 5.92 (2 H, *m*-$H_{axial\ ligand}$), 6.16 (1 H, *p*-$H_{axial\ ligand}$).

Instrumentation. ^1H and ^{19}F NMR spectra were recorded at 400 MHz on a Bruker WM 400 spectrometer at the CSMUB ("Centre de Spectrométrie Moléculaire de l'Université de Bourgogne"). ESR spectra were recorded in toluene on a Bruker ESP 300 spectrometer equipped with an Oxford Instruments cryostat. The *g* values were measured with respect to diphenylpicrylhydrazyl ($g = 2.0036 \pm 0.0003$). Electronic absorption spectra were recorded on a Varian Cary 1 or an IBM Model 9430 spectrophotometer.

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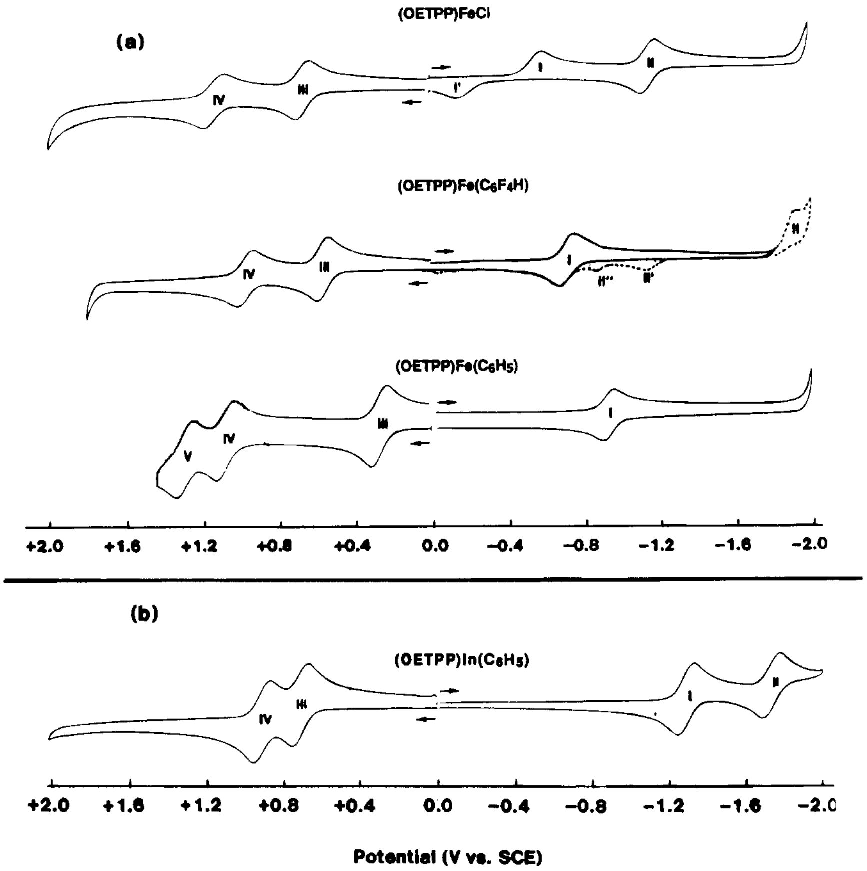

Figure 1. Cyclic voltammograms of (a) (OETPP)FeCl, (OETPP)Fe(C_6F_4H), and (OETPP)Fe(C_6H_5) and (b) (OETPP)In(C_6H_5) in PhCN, containing 0.1 M TBAP. The scan rate was 0.1 V/s for all compounds except (OETPP)Fe(C_6H_5) where it was 0.3 V/s.

Cyclic voltammetry was carried out with an EG&G Model 173 potentiostat or an IBM Model EC 225 voltammetric analyzer. Current−voltage curves were recorded on a EG&G Princeton Applied Research Model RE-0151 X-Y recorder. A three electrode system was used and consisted of a glassy carbon button working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). This reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

Spectroelectrochemical experiments were performed at a platinum thin-layer electrode whose design has been described previously.[45] The potentials were applied and monitored with an EG&G Model 173 potentiostat. Time-resolved UV−visible spectra were recorded with a Tracor Northern Model 6500 rapid scan spectrophotometer/multichannel analyzer.

Results and Discussion

Electroreduction in PhCN. Cyclic voltammograms of (OETPP)FeCl, (OETPP)Fe(C_6F_4H), and (OETPP)Fe(C_6H_5) in PhCN, 0.1 M TBAP are illustrated in Figure 1a, while the voltammogram of (OETPP)In(C_6H_5) is shown in Figure 1b and a summary of potentials is given in Table 1. All four compounds undergo four one-electron transfer reactions which are labeled as processes I and II for reductions and processes III−V for oxidation.

(OETPP)Fe(C_6H_5) undergoes a single one-electron reduction and three one-electron oxidations, while the other four compounds undergo two one-electron reductions and two one-electron oxidations within the potential range of the solvent. The first reduction of (OETPP)FeCl (process I) is irreversible in that it is coupled to a following chemical reaction leading to a product which is reoxidized to the starting compound at potentials positive of those for the original reduction (process I′ in Figure 1). This gives a voltammogram whose shape is similar to voltammograms described in the literature for reduction and reoxidation of a variety of (P)FeX derivatives in nonaqueous media.[46] The second reduction of (OETPP)FeCl is reversible and located at $E_{1/2} = -1.17$ V. The electrochemical behavior of this compound is similar upon reduction to what has been reported for (TPP)FeCl and (OEP)FeCl (see Table 1),[46] and this suggests a similar type of reactivity for all three chloroiron(III) porphyrins, independent of the macrocycle.

Table 1. Half-Wave Potentials (V vs SCE) for Oxidation and Reduction of (P)M(R) or/and (P)MCl Complexes, Where M = Fe or In and R = C_6H_5, C_6F_4H, or C_6F_5 in PhCN or CH_2Cl_2 Containing 0.1 or 0.2 M Supporting Electrolyte

				oxidation			reduction	
metal	solvent	axial ligand	porphyrin	3rd	2nd	1st	1st	2nd
Fe	PhCN	C_6H_5	OETPP[a]	+1.31	+1.06	+0.27	−0.93	
			OEP[b]		+1.30	+0.48	−0.93	
			TPP[b]		+1.43	+0.61	−0.70	
		C_6F_4H	OETPP[a]		+0.97	+0.56	−0.72	−1.91[d]
			OEP[c]		+1.14	+0.79	−0.64	−1.28
			TPP[c]		+1.32	+0.86	−0.45	−1.06
		C_6F_5	OETPP[a]		+0.80	+0.56	−0.70	−1.86[d]
			OEP[c]		+1.18	+0.87	−0.59	−1.30
			TPP[c]		+1.38	+0.94	−0.42	−1.06
		Cl^-	OETPP[a]		+1.12	+0.66	−0.60	−1.17
			OEP[c]			+1.08	−0.54	−1.26
			TPP[c]			+1.14	−0.39	−1.09
In	PhCN	C_6H_5	OETPP[a]		+0.90	+0.70	−1.28	−1.73
	CH_2Cl_2		OEP[e]		+1.15	+0.79	−1.47	
	CH_2Cl_2		TPP[e]		+1.44	+0.94	−1.22	−1.62

[a] This work. [b] Reference 15. [c] Reference 31. [d] E_{pc} at 0.1 V/s. [e] Reference 43.

The first reduction of (OETPP)Fe(C_6F_4H) occurs at $E_{1/2} = -0.72$ V and is reversible when the initial negative potential scan is terminated at values positive of −1.8 V (solid line).

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Table 2. Maximum Absorbance Wavelengths (λ_{max}) and Corresponding Molar Absortivities (ϵ) of $[(OETPP)M(R)]^n$ Complexes, Where M = Fe or In and $n = 0, -1, +1$, or $+2$ in PhCN, 0.2 M TBAP

compd	oxidn state	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})[a]				
(OETPP)Fe(C_6H_5)	neutral			435 (103)	535 (10)	
	singly reduced	323 (34)	375 (38)	449 (66)	574 (17)	718 (4)
	singly oxidized	357 (29)		426 (97)	538 (13)	
(OETPP)Fe(C_6F_4H)	neutral	324 (30)	429 (72)		559 (8)	
	singly reduced			443 (69)	568 (14)	
	singly oxidized		400 (sh)	421 (66)		
	doubly oxidized	337 (50)		475 (sh)		
(OETPP)In(C_6H_5)	neutral		387 (40)	473 (261)	611 (17)	670 (19)
	singly reduced			475 (66)	506 (62)	
	singly oxidized		399 (44)	469 (73)		
	doubly oxidized	342 (42)	414 (37)	475 (27)		

[a] sh = shoulder.

Under these conditions, the peak-to-peak separation, $|E_{pa} - E_{pc}|$, is equal to 70 mV and the anodic-to-cathodic peak current ratio, i_{pa}/i_{pc}, is equal to 1.0 at a scan rate of 100 mV/s. This suggests the diffusion-controlled addition of only one electron and the absence of any coupled chemical reactions on the cyclic voltammetric time scale. The second reduction of (OETPP)Fe(C_6F_4H) (process II) is irreversible and occurs at $E_{pc} = -1.91$ V for a scan rate of 100 mV/s. Reversal of the scan at potentials negative of this reduction results in two new anodic oxidation peaks (labeled as II′ and II″ in Figure 1a) located at $E_{pa} = -1.10$ and -0.84 V.

(OETPP)Fe(C_6H_5) and (OETPP)In(C_6H_5) differ from the other two compounds in Figure 1 in that only reversible electrode reactions are obtained with no evidence for loss of the σ-bonded ligand after electroreduction. (OETPP)Fe(C_6H_5) is reduced in a single step at $E_{1/2} = -0.93$ V, while (OETPP)In(C_6H_5) undergoes two reversible one-electron additions located at $E_{1/2} = -1.28$ and -1.73 V. The single reduction of (OETPP)Fe(C_6H_5) is located at the same half-wave potential as for reduction of (OEP)Fe(C_6H_5) (see Table 1), but this is not the case for (OETPP)In(C_6H_5) where $E_{1/2}$ for the first reduction is positively shifted by 190 mV as compared to $E_{1/2}$ for the first ring-centered electroreduction of (OEP)In(C_6H_5) in CH_2Cl_2 ($E_{1/2} = -1.47$ V).

Stability and Site of Electroreduction in σ-Bonded Complexes. Earlier electrochemical studies showed that the singly and doubly reduced forms of (P)Fe(C_6F_5) and (P)Fe(C_6F_4H) are both unstable when OEP and TPP are the porphyrin macrocycles and that both the electroreduced anionic compounds undergo a rapid dissociation of the σ-bonded axial ligand.[30-32] The liberated ligand then reacts with trace water from the solvent to produce a mixture of (P)Fe(OH) and $[(P)Fe]_2O$, as has been demonstrated for five σ-bonded complexes with different porphyrin rings.[31] The liberated C_6F_4H ligand of electroreduced (OETPP)Fe(C_6F_4H) also seems to react with trace water in solution since the E_{pa} of process II′ matches exactly the measured E_{pa} for the first one-electron reduction of (OETPP)FeOH, a species which was generated *in situ* by addition of 1 equiv TBAOH to (OETPP)FeCl.[47] However, no μ-oxo dimer is generated due to the nonplanar saddle conformation of the OETPP macrocycle and the only other porphyrin product seems to be $(OETPP)Fe^{II}$, as evidenced by the fact that the E_{pa} of process II′ is almost identical with the anodic peak potential for reoxidation of electroreduced (OETPP)FeCl (see process II in Figure 1), thus indicating the generation of $[(OETPP)Fe^{I}]^-$ in solution after the second one-electron reduction of (OETPP)Fe(C_6F_4H).

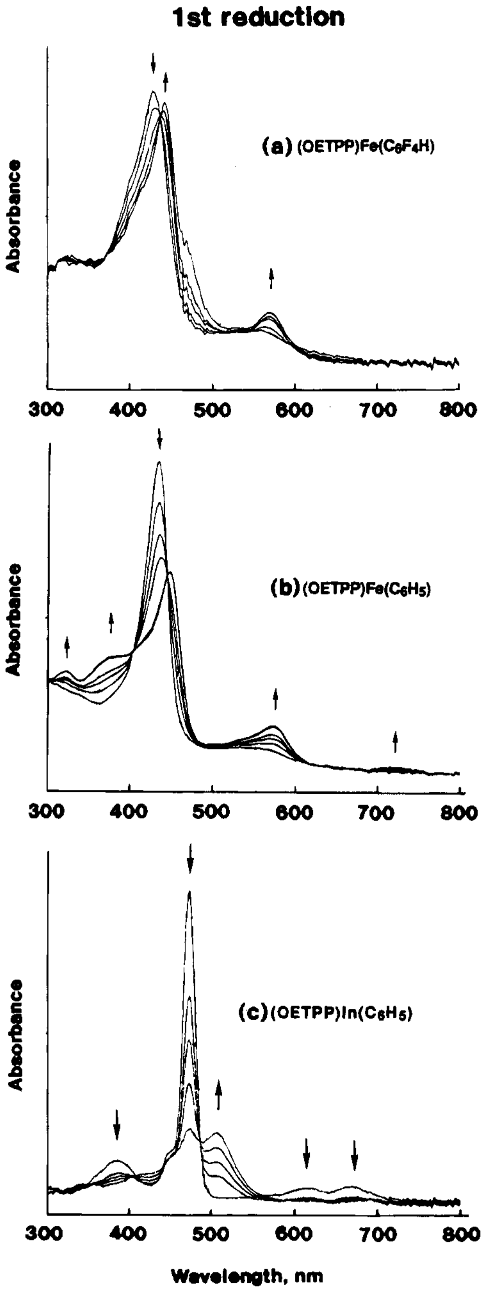

Figure 2. Time-resolved UV–visible thin-layer spectral changes during the one-electron reduction of (a) (OETPP)Fe(C_6F_4H), (b) (OETPP)Fe(C_6H_5), and (c) (OETPP)In(C_6H_5) in PhCN, 0.2 M TBAP.

It was suggested that the first one-electron reduction of (P)Fe(C_6F_5) and (P)Fe(C_6F_4H) occurs at the metal center,[30] and the UV–visible spectroelectrochemical data obtained during electroreduction of (OETPP)Fe(C_6F_4H) (Figure 2a) seem to bear

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(47) Addition of $\approx$1.0 equiv of (TBA)OH to a benzonitrile solution of (OETPP)FeCl results in the disappearance of process I and the appearance of a new cathodic peak at $E_{pc} = -1.07$ V coupled with a reoxidation peak at $E_{pa} = -0.83$ V, both of which are due to electrogenerated (OETPP)FeOH.

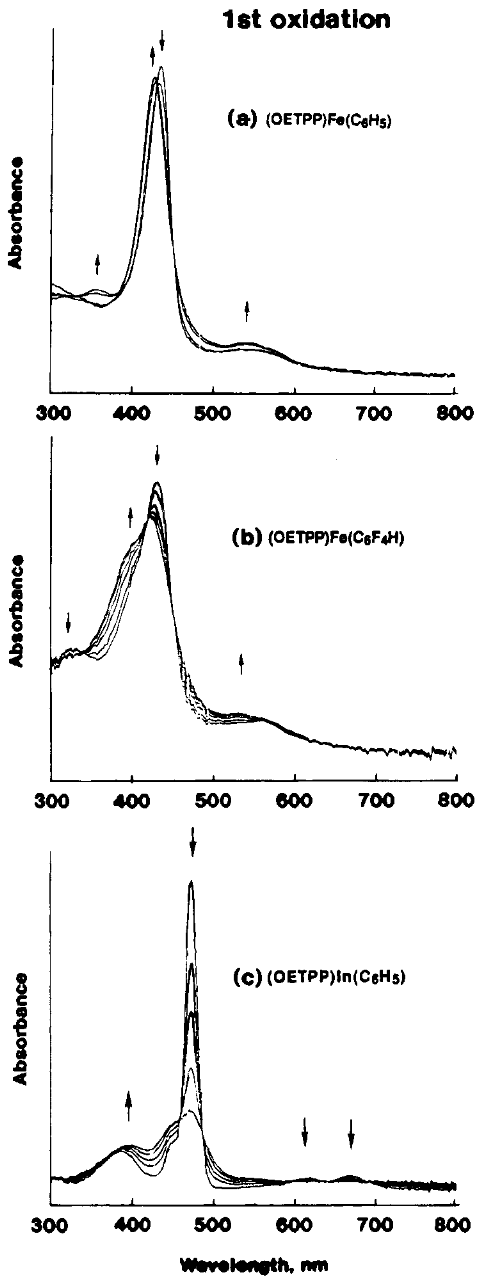

Figure 3. Time-resolved UV–visible thin-layer spectral changes during the first one-electron oxidation of (a) (OETPP)Fe(C_6H_5), (b) (OETPP)Fe(C_6F_4H), and (c) (OETPP)In(C_6H_5) in PhCN, 0.2 M TBAP.

this out. The Soret band of the neutral complex decreases slightly in intensity during controlled potential reduction at −1.00 V (see Table 2), and it also red shifts by 14 nm from the 429 nm band of the neutral compound. At the same time, the visible band at 559 nm increases in magnitude and shifts to 568 nm upon reduction. The spectrum after complete electrolysis has no major band between 600 and 800 nm, thus suggesting the lack of a porphyrin π anion radical and the formation of an iron(II) derivative with an uncharged porphyrin ring, i.e., $[(\mathrm{OETPP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{C_6F_4H})]^-$.

In contrast, the spectrum of $[(\mathrm{OETPP})\mathrm{In}(\mathrm{C_6H_5})]^-$ (Figure 2c) can clearly be assigned to a porphyrin π anion radical. The bands of the neutral compound at 473, 611, and 670 nm all decrease in intensity during the first one-electron reduction while a new absorption band grows in at 506 nm. Similar spectral features are observed upon reduction of several porphyrins containing main group central metal ions, and this has been used to imply the generation of a porphyrin π anion radical.[46]

Finally, the spectral changes obtained during controlled-potential reduction of (OETPP)Fe(C_6H_5) (Figure 2b) are intermediate between those for reduction of (OETPP)Fe(C_6F_4H), where the reaction occurs at the metal, and those for reduction of (OETPP)In(C_6H_5), where the reaction occurs at the porphyrin π ring system. The Soret band of the initial (OETPP)Fe(C_6H_5) complex decreases in intensity and red shifts from 435 to 449 nm during formation of the singly reduced species. At the same time, an intense band at 574 nm and a weaker band at 718 nm grow in, suggesting formation of an iron(II) species having some π anion radical character.[32,48] The singly-reduced $[(\mathrm{OETPP})\mathrm{Fe}(\mathrm{C_6H_5})]^-$ product is quite stable on the spectroelectrochemical time scale, and the spectrum of (OETPP)Fe(C_6H_5) could be fully regenerated by switching the applied potential back to 0.0 V.

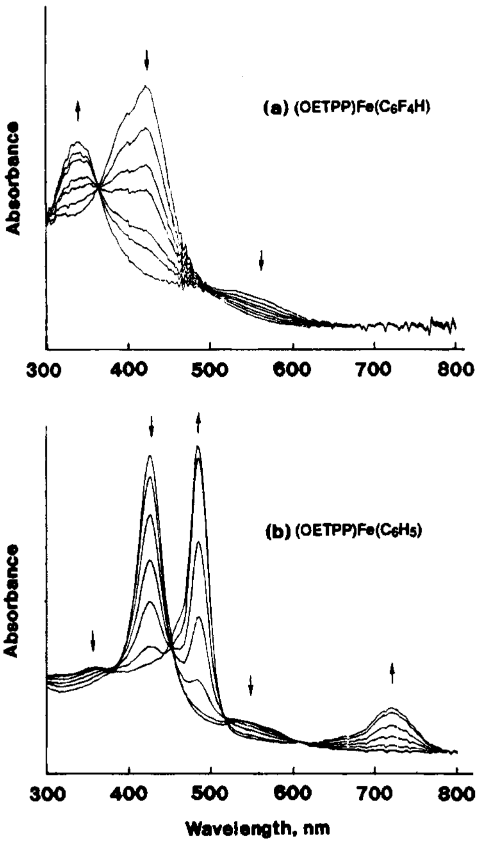

Figure 4. Time-resolved UV–visible thin-layer spectral changes during the second one-electron oxidation of (a) (OETPP)Fe(C_6F_4H) and (b) (OETPP)Fe(C_6H_5) in PhCN, 0.2 M TBAP.

Electrooxidation in PhCN. Half-wave potentials for oxidation of (OETPP)FeCl and the four OETPP σ-bonded complexes are listed in Table 1 along with related values for the OEP and TPP σ-bonded complexes containing the same axial ligands. OETPP is the most basic of the three porphyrin macrocycles, and it was expected that potentials for oxidation of these derivatives should all be shifted negatively with respect to $E_{1/2}$ values for oxidation of the related OEP and TPP complexes. This is indeed the case, with the exact magnitude of the shift depending upon both the type of axial ligand and the site of electron transfer.

The first oxidation of (OETPP)Fe(C_6H_5) occurs at $E_{1/2} = 0.27$ V and, to date, is the most facile oxidation ever seen for a σ-bonded iron(III) porphyrin. Spectroelectrochemical and ^{1}H NMR studies on the singly oxidized species unambiguously prove that the first oxidation of (OETPP)Fe(C_6H_5) generates an Fe(IV) species in solution while the second and third oxidations lead to an iron(IV) π-cation radical and dication, respectively.[33]

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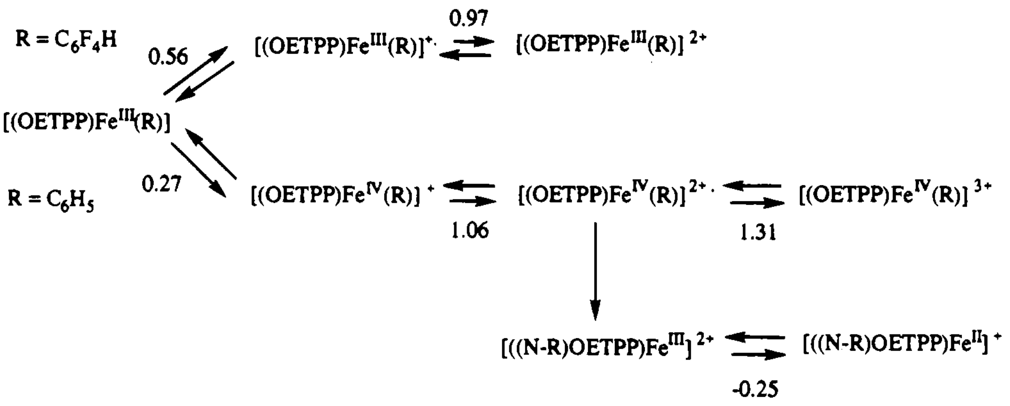
(48) Fuhrhop, J.-H. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; pp 593–623.

Scheme 1



The difference in half-wave potentials between the two oxidations of (OETPP)FeCl (460 mV) or the two oxidations of (OETPP)Fe(C_6F_4H) (410 mV) are both much larger than the 200 mV separation in $E_{1/2}$ between the two ring-centered oxidations of (OETPP)In(C_6H_5). They are also larger than the 250 mV separation in $E_{1/2}$ between the latter two oxidations of (OETPP)Fe(C_6H_5). This might be due to the different axial ligands in the two series (i.e., Cl^- and C_6F_4H in one case and C_6H_5 in another).

It should also be noted that the half-wave potentials for the first oxidation of (OETPP)FeCl ($E_{1/2} = 0.66$ V) and (OETPP)InCl ($E_{1/2} = 0.88$ V)[49] in PhCN differ from each other by 220 mV, while the difference in half-wave potentials between the first oxidation of (OEP)FeCl and (OEP)InCl complexes is only 10 mV. Both complexes are oxidized at the porphyrin π ring system, and a similar assignment for the site of electron transfer can be given for (OETPP)InCl which contains an electroinactive metal center.

Spectral evidence for the different sites of electron transfer in the three types of σ-bonded compounds is given in Figure 3, which shows the spectral changes obtained upon controlled potential oxidation of (OETPP)Fe(C_6H_5), (OETPP)Fe(C_6F_4H), and (OETPP)In(C_6H_5) in PhCN, 0.2 M TBAP. The absorption spectrum of the stable Fe(IV) species, $[(OETPP)Fe^{IV}(C_6H_5)]^+$, has absorption maxima at 357, 426, and 538 nm, with the Soret band intensity of the oxidized species being almost equal to that of the neutral complex (see Figure 3a). This contrasts with singly oxidized $[(OETPP)In(C_6H_5)]^+$ (Figure 3c), which has Soret and visible bands that are much weaker than those of the neutral compound and is assigned as a porphyrin π cation radical on the basis of electrochemical data. Electrochemically-generated $[(OETPP)Fe(C_6F_4H)]^+$ (Figure 3b) has a spectrum which is similar to $[(OETPP)Fe^{IV}(C_6H_5)]^+$ in that it exhibits a blue-shifted Soret band with respect to the neutral compound. It differs however, in that the Soret band is broader and is of decreased intensity as compared to the neutral species, thus suggesting an involvement of the porphyrin π ring system in the singly oxidized C_6F_4H species.

Spectral data for the two-electron oxidized product, $[(OETPP)Fe(C_6F_4H)]^{2+}$, are also consistent with the above assignment in that the dication exhibits a broad absorption band at 360 nm (Figure 4a) and is typical of a porphyrin dicationic species.[48] An axial ligand migration of the phenyl ring can occur after the second one-electron oxidation of (OETPP)Fe(C_6H_5),[33] and the spectral changes associated with this process are depicted in Figure 4b. As the overall electrochemical/chemical reaction proceeds, the initial 426 nm band of the Fe^{IV} complex almost completely vanishes as new bands appear at 486 and 721 nm. The final spectrum in Figure 4b differs substantially from the spectrum of electrogenerated $[(OETPP)Fe(C_6F_4H)]^{2+}$ in Figure 4a and can be assigned to the migration product which has the phenyl axial ligand bound to one of the four nitrogens of the porphyrin ring.

It is important to note that both (OETPP)Fe(C_6H_5) and (OETPP)Fe(C_6F_4H) exist in a low-spin state which contrasts with the earlier studied (OEP)Fe(C_6F_5) and (OEP)Fe(C_6F_4H) derivatives both of which are high-spin. In fact, all previously investigated C_6F_4H derivatives contain high-spin iron(III),[30] and it was therefore proposed that the spin state of the iron(III) atom might actually govern the migration reaction since no migration was observed for the high-spin OEP and TPP σ-bonded compounds. The fact that (OETPP)Fe(C_6H_5) and (OETPP)Fe(C_6F_4H) are *both* low-spin and that no migration is observed for the latter compound thus clearly indicates that the spin state of the initial iron(III) is not the sole factor which governs the migration reaction of the axial ligand.

In summary, the results in the present study suggest that the site of electron transfer upon oxidation of (P)Fe(R) is affected by the type of axial ligand but not by the spin state of the initial iron(III) complex (see Scheme 1). Indeed, it seems quite clear that apparent differences in the site of oxidation between (OETPP)Fe(C_6H_5) and (OETPP)Fe(C_6F_4H) cannot be accounted by a simple difference in the iron(III) spin state since *both* compounds contain low-spin iron(III) as opposed to (OEP)Fe(C_6H_5) and (OEP)Fe(C_6F_4H), the first of which contains low-spin Fe(III) and the latter high-spin Fe(III).[30]

Our data also suggest that the site of electron transfer seems to be the same upon reduction for a given (P)FeCl and (P)Fe(R) complex when P = OEP, TPP, or OETPP. (OETPP)Fe(C_6H_5) and (OEP)Fe(C_6H_5) are both oxidized at the metal to give iron(IV) derivatives, but the stability of the electrogenerated iron(IV) differs when going from OEP to OETPP. Indeed, $[(OEP)Fe^{IV}(C_6H_5)]^+$ is unstable at room temperature and undergoes chemical reactions to give a migration product while $[(OETPP)Fe^{IV}(C_6H_5)]^+$ is very stable under similar experimental conditions. The facile oxidation of the OETPP derivatives with respect to their analogous OEP might be explained by considering the saddle shape of the macrocycle in these complexes since a distortion of the porphyrin macrocycle is expected to affect the HOMO more than the LUMO.[35,36]

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[49] (OETPP)InCl undergoes two reversible one-electron oxidations at $E_{1/2}$ = 0.88 and 0.97 V in PhCN, 0.1 M TBAP.