Electrochemistry of New σ-Bonded Metal(III) Complexes with Tetrapyrrole Ligands. Reactions of (EtioPc)M(C_6H_5) and (EtioPc)FeCl Where M = Fe or In and EtioPc Is the Dianion of 2,7,12,17-Tetraethyl-3,6,13,16-tetramethylporphycene

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The electrochemical reactivity of the first synthesized σ-bonded metalloporphycenes is reported. The investigated compounds are represented as (EtioPc)M(C_6H_5) where M = Fe or In and EtioPc = the dianion of 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene. Each compound was examined as to its redox properties in dichloromethane, benzonitrile, or pyridine, and the results of these studies are compared to data for (EtioPc)FeCl and (EtioPc)In(C_6H_5) under similar solution conditions. Both σ-bonded derivatives undergo two one-electron reductions at the conjugated π ring system. This was expected in the case of indium but not in the case of iron which is the first reported example where a monomeric iron(III) porphyrin-like molecule is reduced at the ring rather than at the metal center. (EtioPc)Fe(C_6H_5) also undergoes three one-electron oxidations, similar to what has been reported for (OETPP)Fe(C_6H_5) where OETPP is the dianion of octaethyltetraphenylporphyrin. The first oxidation of (EtioPc)Fe(C_6H_5) occurs at the iron center to give $[(\text{EtioPc})\text{Fe}^{IV}(C_6H_5)]^+$, which is characterized by UV–visible spectroscopy prior to migration of the phenyl group and demetalation to give (*N*-C_6H_5EtioPc)H as a final product. Assignments of the electron transfer sites for oxidation and reduction of (EtioPc)Fe(C_6H_5) are based both on spectroelectrochemical data for this compound and on comparison of its electrochemical behavior to that of (EtioPc)FeCl and (EtioPc)In(C_6H_5).

Introduction

σ-Bonded metalloporphyrins have long been used as model compounds in the study of biological redox reactions.[1–35] Numerous transition metal complexes have been investigated, including those of iron, which are of special interest because these compounds may exist in up to four different metal oxidation states depending upon the specific macrocyclic ring, the specific set of axial ligands, and the specific solvent or experimental conditions. In this regard, a large number of different iron porphyrins and related macrocycles have now been synthesized and characterized both as to their electrochemical

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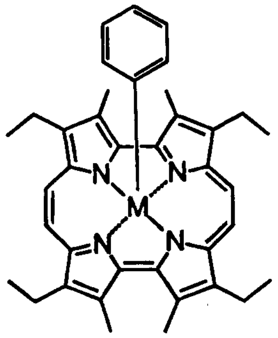
reactivity and as to their physicochemical properties in one or more metal oxidation states.

One experimentally interesting set of macrocycles have been the porphycenes, structural isomers of porphyrins, which were first synthesized by Vogel and co-workers.[36,37] Since then, a number of studies dealing with various theoretical and experimental aspects of metalloporphycenes have appeared in the literature, the majority of which have compared one or more properties of the metalloporphycenes to those of the related metalloporphyrins containing the same central metal ion.[38-43] These comparisons have been largely between monomeric complexes with metals in a +2 or +3 oxidation state, the latter of which have generally contained an anionic axial ligand. A comparison between iron(III) μ-oxo porphyrin and porphycene dimers has also been reported,[42] but virtually nothing at all is known about porphycene derivatives with other types of axial ligands. Especially conspicuous by their absence are the σ-bonded complexes, a class of compounds which have been very well characterized in the case of iron[15,16,32-35] and other[44,45] transition or main group metalloporphyrins.

All known phenyl σ-bonded iron(III) porphyrins can be reduced or oxidized at the metal center to give the Fe(II)[34] and Fe(IV) σ-bonded derivatives,[15,16,35,44,45] and it was of interest to know whether a similar reactivity would also be observed for the phenyl σ-bonded iron(III) porphycenes. This question is answered in the present paper which reports the first electrochemical data on iron and indium porphycenes containing a σ-bonded phenyl axial ligand. The investigated compounds, shown schematically as



M = Fe(III), In(III)

are the first σ-bonded porphycenes ever synthesized and are represented as (EtioPc)M(C_6H_5) where M = Fe or In and EtioPc = the dianion of 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene. Each compound was examined as to its redox properties in dichloromethane, benzonitrile, or pyridine, and the results of these studies were then compared to data for an iron porphycene derivative containing the same conjugated macrocycle and a chloride axial ligand, i.e., (EtioPc)FeCl.

Experimental Section

Chemicals. Benzonitrile (PhCN) was obtained from Aldrich Chemical Co. and distilled over P_2O_5 under vacuum prior to use. Pyridine (py) was distilled over CaH_2 under a nitrogen atmosphere prior to use. 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.

Synthesis. Syntheses were performed under an argon atmosphere. All common solvents were thoroughly dried in an appropriate manner and were distilled under argon prior to use. Schlenk techniques were used for all operations. Samples of (EtioPc)FeCl were prepared as described in the literature[42] and were obtained by metalation of (EtioPc)H_2[46] with $FeCl_2$.

Synthesis of (EtioPc)Fe(C_6H_5). (EtioPc)FeCl (100 mg, 0.18 mmol) was dissolved in 100 mL of freshly distilled benzene, after which a solution of phenylmagnesium bromide in benzene (1.8 mL of a 0.1 M solution) was added dropwise *via* a syringe. The reaction mixture was stirred for 5 min, and the reaction was quenched by addition of 5 mL of deaerated distilled water. The organic layer was then washed twice with water and dried over $MgSO_4$. After filtration, the solution was chromatographed on basic alumina using benzene as eluent. The solvent was removed under reduced pressure and the product recrystallized from a benzene/heptane mixture (yield 50%). UV–vis (CH_2Cl_2) (λ_{max} (nm), ϵ (mol^{-1} L cm^{-1} × 10^{-3})): 320, 40.5; 355, 66.9; 382, 65.0; 555 (sh), 17.5; 590, 44.4. ^{1}H NMR ($CDCl_3$, 294 K) (δ ppm)): 11.45 (12H, α-CH_3), 7.83 (4H, 2,7,12,17-α-CH_2, 4H meso), 6.69 (4H, 2,7,12,17-α′-CH_2), 3.49 (1H, p-$H_{axial\ ligand}$), 3.14 (4H, 9,10,19,20-H_{ligand}), 1.25 (12H, β-CH_3), −5.46 (4H, m-$H_{axial\ ligand}$ and o-$H_{axial\ ligand}$). ESR (toluene, 100 K): $g_x = 1.950$, $g_y = 2.260$, $g_z = 2.333$. Mass spectrum (DCI): $M^{\bullet+}$ *m/z* 609, 42%; (M − $C_6H_5)^{\bullet+}$ *m/z* 532, 100%. Anal. Calc: C, 74.87; H, 6.73; N, 9.19. Found: C, 73.25; H, 6.85; N, 8.84.

Synthesis of (EtioPc)In(C_6H_5). (EtioPc)InCl (70 mg, 0.11 mmol) was dissolved in 100 mL of freshly distilled benzene, and a solution of phenylmagnesium bromide in benzene (1.7 mL of a 0.1 M solution) was then added dropwise with a syringe. The reaction was quenched immediately by addition of deaerated distilled water (5 mL). The organic layer was washed once with water and dried over $MgSO_4$. After filtration, the solution was chromatographed on basic alumina (2 cm × 10 cm) using toluene as eluent. The title compound was recovered from the first eluted fraction after evaporation of the solvent under reduced pressure and recrystallization from toluene (yield 30%). UV–vis (toluene) (λ_{max} (nm), ϵ (mol^{-1} L cm^{-1} × 10^{-3})): 319, 23.8; 382 (sh), 34.2; 402, 148.0; 591, 20.3; 637, 92.5. ^{1}H NMR ($CDCl_3$, 294 K) (δ (ppm)): 9.79 (4H, s, 9,10,19,20-H), 5.83 (1H, t, p-$H_{axial\ ligand}$), 5.61 (2H, dd, m-$H_{axial\ ligand}$), 3.81 (8H, m, 2,7,12,17-CH_2), 3.67 (2H, d, o-$H_{axial\ ligand}$), 3.38 (12H, s, 3,6,13,16-CH_3), 1.67 (12H, t, 2,7,12,17-CH_3). Mass spectrum (CI): $M^{\bullet+}$ *m/z* 668.

Instrumentation. 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 an 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), the latter of which 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 using an EG&G Model 173 potentiostat and a thin-layer cell whose design has been

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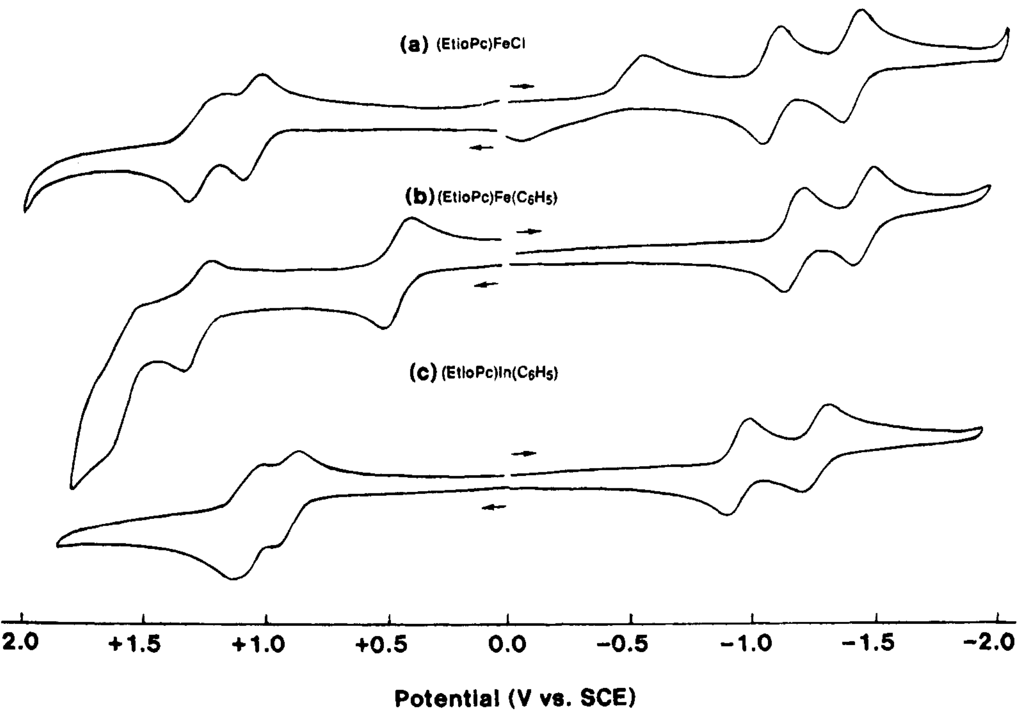

Figure 1. Cyclic voltammograms of (a) (EtioPc)FeCl, (b) (EtioPc)Fe(C_6H_5), and (c) (EtioPc)In(C_6H_5). The voltammograms in (a) and (c) were taken at room temperature in PhCN, 0.1 M TBAP at a scan rate of 0.1 V/s, while the one in (b) was taken at 225 K in CH_2Cl_2, 0.1 M TBAP at a scan rate of 0.3 V/s.

previously described.[47] Time-resolved UV−visible spectra were recorded with a Tracor Northern Model 6500 rapid-scan spectrophotometer/multichannel analyzer.

^{1}H NMR spectra were recorded at 400 MHz on a Bruker WM 400 spectrometer. ESR spectra were recorded on a Bruker ESP 300 spectrometer. The g values were measured with respect to diphenylpicrylhydrazyl (g = 2.0036 ± 0.0003). Electronic absorption spectra were recorded on a Varian Cary I or an IBM Model 9430 spectrophotometer.

Elemental analysis of (EtioPc)Fe(C_6H_5) was performed by the Service Central d'Analyse du CNRS, Vernaison, France.

Results and Discussion

Electrooxidation of (EtioPc)Fe(C_6H_5). (EtioPc)Fe(C_6H_5) undergoes three one-electron oxidations which occur at $E_{1/2}$ = 0.44, 1.27, and 1.54 V vs SCE at 225 K in CH_2Cl_2, 0.1 M TBAP. The first oxidation is well-defined in CH_2Cl_2, PhCN, or pyridine at room temperature, but the last two are only well-defined in CH_2Cl_2 at low temperature and at a scan rate higher than 0.3 V/s. A cyclic voltammogram under these conditions is shown in Figure 1b. For comparison are also shown the cyclic voltammograms of (EtioPc)In(C_6H_5) (Figure 1c) and (EtioPc)-FeCl (Figure 1a) at room temperature in PhCN, 0.1 M TBAP.

To date, there is only one example in the literature where a monomeric iron(III) porphyrin can be reversibly oxidized by three one-electron transfers.[35] The reported compound is (OETPP)Fe(C_6H_5), which is first converted to [(OETPP)Fe^{IV}-(C_6H_5)]$^+$ at relatively facile potentials, after which a second and a third one-electron oxidation lead to a stepwise generation of the Fe(IV) π cation radical and dication, both of which are moderately stable on the cyclic voltammetry time scale.[35] As seen in Figure 1b, (EtioPc)Fe(C_6H_5) also undergoes three reversible one-electron oxidations and this behavior contrasts with that of all previously characterized monomeric iron(III) porphycenes,[40,42] which show only a maximum of two reversible one-electron oxidations. The half-wave potentials for the first two reversible oxidations of (OETPP)Fe(C_6H_5) are separated in potential by 810 mV in PhCN[35] ($E_{1/2}$ = 0.27 and 1.06 V), a value similar to the 830 mV separation between the first two oxidations of (EtioPc)Fe(C_6H_5) ($E_{1/2}$ = 0.44 and 1.27 V) in CH_2Cl_2 (see Figure 1b). Both values of $\Delta E_{1/2}$ are significantly larger than the 100−250 mV separation generally observed between $E_{1/2}$ for formation of porphyrin[44,45] or porphycene[40−43] π cation radicals and dications, suggesting that a metal-centered reaction is involved in the first one-electron oxidation of (EtioPc)Fe(C_6H_5), as is the case for (OETPP)Fe(C_6H_5). Further evidence for the formation of Fe(IV) is also given by a comparison between the cyclic voltammograms of (EtioPc)Fe(C_6H_5) and (EtioPc)In(C_6H_5), the latter of which undergoes only macrocycle-centered redox reactions.

The σ-bonded iron porphycene is quite easy to oxidize with respect to the σ-bonded indium porphycene (see Figure 1b,c), and $E_{1/2}$ is negatively shifted by 420 mV with respect to the $E_{1/2}$ for the first reversible ring-centered oxidation of (EtioPc)-In(C_6H_5) in PhCN at room temperature (see Table 1). This difference in potentials cannot be accounted for by differences in inductive effects of the two metal ions, which have almost identical electronegativities. Furthermore, the 830 mV separation between the first two reversible one-electron oxidations of (EtioPc)Fe(C_6H_5) is much larger than the 150−250 mV separations observed between the two ring-centered one-electron oxidations of (EtioPc)In(C_6H_5) or (EtioPc)FeCl, thus strongly indicating that the first one-electron oxidation of (EtioPc)Fe(C_6H_5) must involve generation of an iron(IV) species.

However, the most conclusive evidence for assignment of a metal-centered oxidation in (EtioPc)Fe(C_6H_5) is given by spectroelectrochemical studies carried out in PhCN, 0.2 M TBAP. An example of the resulting data is shown in Figure 2, which illustrates the thin-layer UV−visible spectral changes that occur during controlled-potential oxidation of (EtioPc)Fe(C_6H_5) at 0.70 V, i.e., at a potential 260 mV more positive than $E_{1/2}$ for the first one-electron oxidation of this compound.

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Table 1. Half-Wave Potentials (V vs SCE) for Reduction and Oxidation of (EtioPc)FeCl, (EtioPc)Fe(C_6H_5), and (EtioPc)In(C_6H_5) in Nonaqueous Media Containing 0.1 M TBAP

		oxidn			redn			$\Delta E_{1/2}$(macrocycle)[d]	
compd	solvent	macrocycle		metal	metal	macrocycle		oxidn	redn
(EtioPc)FeCl	PhCN	+1.26	+1.05		−0.55[a]	−1.08	−1.42	0.21	0.34
(EtioPc)Fe(C_6H_5)	CH_2Cl_2[b]	+1.54	+1.27	+0.44		−1.13	−1.44	0.27	0.31
	PhCN	+1.60[c]	+1.34[c]	+0.48		−1.15	−1.47	0.26	0.32
	py	*e*	*e*	+0.51		−1.23	−1.59		0.36
(EtioPc)In(C_6H_5)	PhCN	+1.05	+0.90			−0.93	−1.25	0.15	0.32

[a] E_{pc} at 0.1 V/s. [b] At 225 K. [c] E_{pa} at 0.1 V/s. [d] $\Delta E_{1/2}$(macrocycle) is defined as the absolute potential difference (in volts) between the two one-electron ring-centered oxidations or two one-electron ring-centered reductions. [e] Electrode reactions cannot be observed due to solvent oxidation at ≈1.0 V vs SCE.

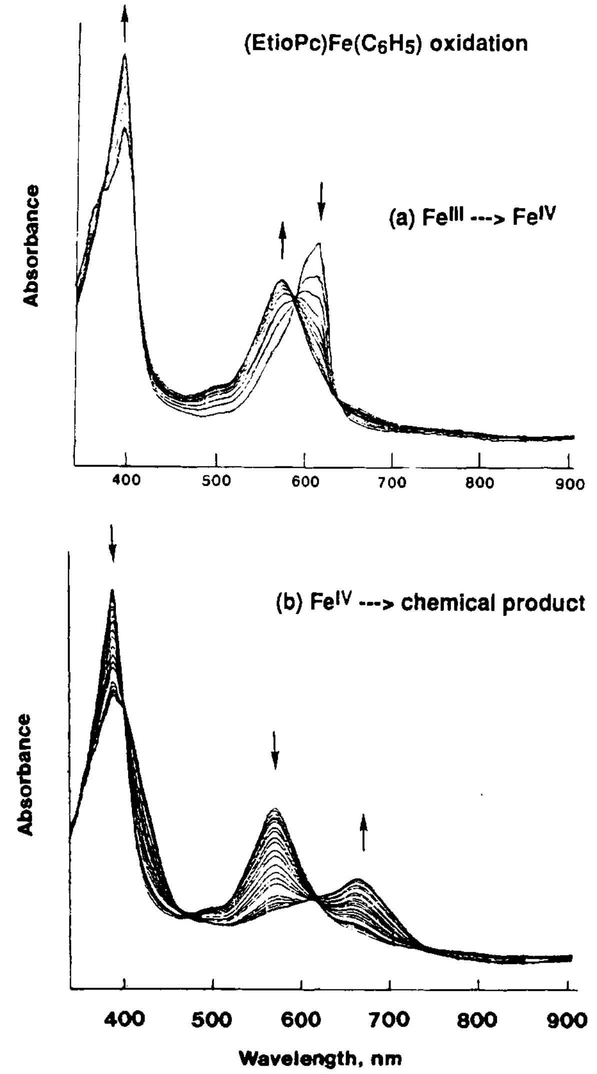

Figure 2. Time-resolved thin-layer UV−visible spectral changes obtained upon application of 0.70 V to (EtioPc)Fe(C_6H_5) in PhCN, 0.2 M TBAP (a) for 0−40 s and (b) between 1 and 15 min.

Singly oxidized metalloporphycenes containing an electroinactive central metal generally exhibit absorption bands between 700 and 900 nm, and this can serve as a strong diagnostic criterion to indicate formation of a porphycene π cation radical.[42,43] This band is not seen upon the first one-electron oxidation of (EtioPc)Fe(C_6H_5), nor are there any other spectral features of the singly-oxidized product that might suggest formation of a porphycene π cation radical such as is the case upon oxidation of other non-σ-bonded metal(III) porphycene derivatives.[43] On the other hand, the spectral changes are quite consistent with what might be expected for a metal-centered redox process. The formation of [(EtioPc)Fe(C_6H_5)]$^+$ results in a decrease in intensity of the 618 nm band of the neutral compound as a strong new band appears at 572 nm. At the same time, the near-UV (Soret) band increases in intensity, which would not be the case for formation of a porphycene π cation radical where a decreased intensity of the Soret band would be expected.[43] Isosbestic points are also observed at 409, 591, and 646 nm and, when combined with the above UV−visible spectral changes, indicate a well-defined Fe(III)/Fe(IV) transition with the lack of any spectral intermediates.

Further low-temperature electrooxidations of (EtioPc)Fe(C_6H_5) are located at $E_{1/2}$ = 1.27 and 1.54 V in CH_2Cl_2 at 225 K and lead to the stepwise formation of an Fe(IV) porphycene π cation radical and dication. The difference in potential between these two oxidations is 270 mV, and this value may be compared to a 240 mV separation between the last two oxidations of (OETPP)Fe(C_6H_5) under similar solution conditions.[35] The 270 mV separation for (EtioPc)Fe(C_6H_5) may also be compared to an average $\Delta E_{1/2}$ of 210 mV between the two ring-centered oxidations of (OEPc)M where M = Fe, Co, Ni, Cu, or Zn[43] and an average 270 mV between the two ring-centered oxidations of (TPrPc)M where M = Cu, Ni, Co, or Fe,[40] all of which have been assigned to the stepwise formation of porphycene π cation radicals and dications.

As is often the case, an electrochemical or chemical reversibility by cyclic voltammetry does not imply prolonged chemical stability of the electrogenerated product such that one can always isolate the electrooxidized or electroreduced species. The electrogenerated [(EtioPc)Fe^{IV}(C_6H_5)]$^+$ complex is stable in PhCN for up to 40 s of applied potential, but a chemical reaction occurs on longer time scales as indicated by the spectral changes shown in Figure 2b. Electrogenerated [(P)Fe(C_6H_5)]$^+$, where P = the dianion of tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP), undergoes a migration of the phenyl group from the Fe(IV) center to one of the four nitrogens of the porphyrin macrocycle,[15] and this leads to an *N*-phenyl iron(II) complex which is then oxidized to its Fe(III) form at the positive applied potential which is needed for an initial generation of the Fe(IV) compound. The same reaction sequence is proposed to occur for (EtioPc)Fe(C_6H_5), but in this case, the generated *N*-phenyl iron(II) porphycene is unstable at room temperature under these experimental conditions and a rapid demetalation occurs to give, as a final product, the free base *N*-phenylporphycene. This sequence of steps (eq 1) occurs upon the prolonged application of an applied potential and gives the spectral changes illustrated in Figure 2b.

$$\text{(EtioPc)Fe}^{III}(C_6H_5) \xrightleftharpoons{-e^-} [\text{(EtioPc)Fe}^{IV}(C_6H_5)]^+ \rightarrow [(N\text{-}C_6H_5\text{EtioPc})\text{Fe}^{II}]^+ \rightarrow (N\text{-}C_6H_5\text{EtioPc})\text{H} \quad (1)$$

The same above sequence of steps is proposed to occur during chemical oxidation using 1 equiv of phenoxathiinylium hexachlo-

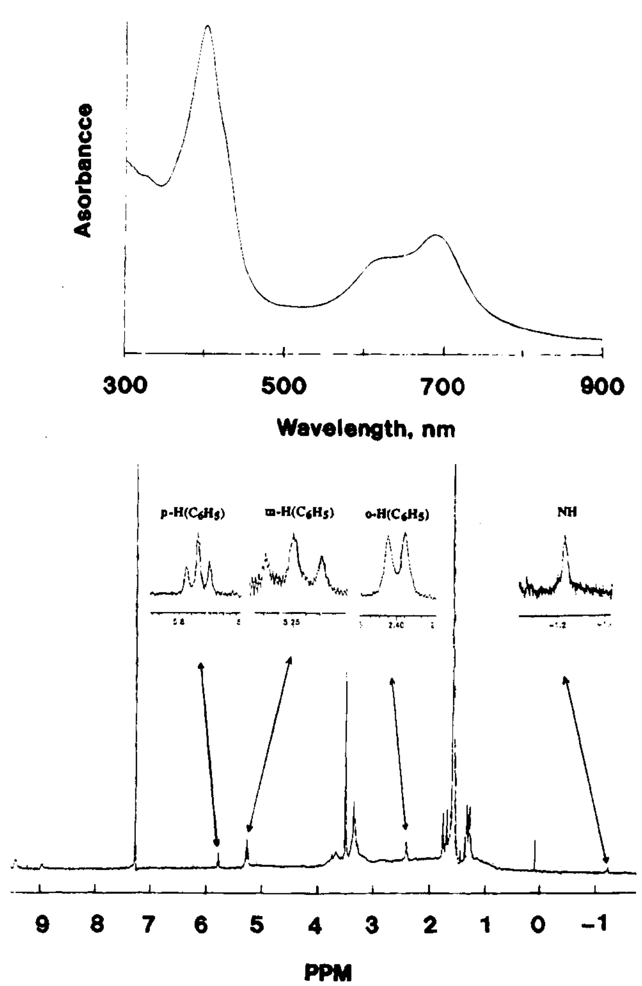

Figure 3. (Top) UV–visible (in CH_2Cl_2) and (bottom) ^1H NMR spectra of the demetalated (N-C_6H_5EtioPc)H product obtained from chemical oxidation of (EtioPc)Fe(C_6H_5) by 1 equiv of phenoxathiinylium hexachloroantimonate in $CDCl_3$.

roantimonate as oxidizing agent. The [(EtioPc)Fe^{IV}(C_6H_5)]$^+$ product could be stabilized for short periods of time by quickly freezing the solution, but upon warming, a rapid color change was observed and only the demetalated N-phenylporphycene product could be detected by mass spectrometry and UV–visible or ^1H NMR spectroscopy. The mass spectrum of the isolated product shows an $[M + H]^+$ peak at m/z 555, which corresponds exactly to the expected value for the free base N-phenylporphycene. The UV–visible spectrum of this species has absorption bands at 323, 400, 617, and 689 nm in CH_2Cl_2 (see Figure 3), while its room-temperature ^1H NMR spectrum (Figure 3) displays resonances for the N-phenyl group located at 2.43 (d, 2H, N-C_6H_5, o-H), 5.25 (dd, 2H, N-C_6H_5, m-H), 5.77 (t, 1H, N-C_6H_5, p-H), and −1.23 ppm (s, 1H, NH).

Electrochemistry in Pyridine or Mixed PhCN/py Solvents. The addition of pyridine to PhCN or CH_2Cl_2 solutions of (EtioPc)Fe(C_6H_5) leads to a stable hexacoordinated complex, (EtioPc)Fe(C_6H_5)(py). The binding constant, measured spectroscopically, for addition of pyridine to (EtioPc)Fe(C_6H_5) is 7.8×10^2 L mol^{-1} in PhCN, a value slightly larger than that for addition of pyridine to the corresponding OEP or TPP iron phenyl σ-bonded porphyrins under the same solution conditions.[16] Only the hexacoordinated species is present in neat pyridine, and its spectrum is characterized by absorption maxima at 368 and 608 nm. These absorptions are different from those of five-coordinate (EtioPc)Fe(C_6H_5) in CH_2Cl_2 (λ = 320 (sh), 364, 398, and 612 nm), and they also differ from the 385, 560, and 607 nm absorption bands of [(EtioPc)Fe$(py)_2$]$^+$,[49] which is therefore ruled out as a possible side product in the formation of (EtioPc)Fe(C_6H_5)(py) from (EtioPc)Fe(C_6H_5).

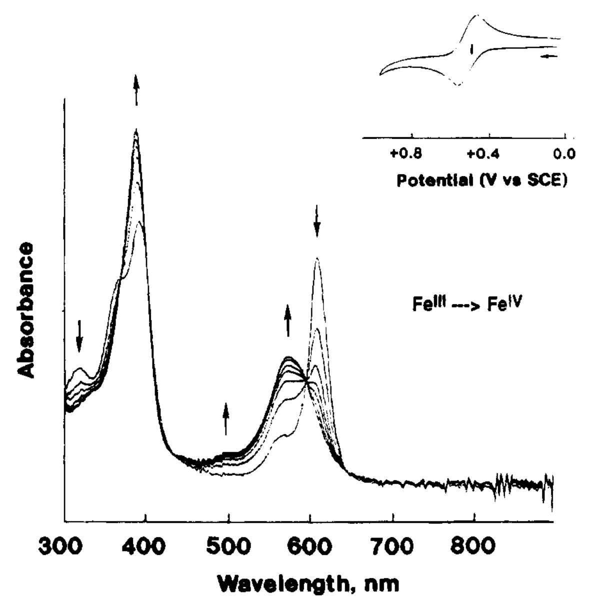

Figure 4. Time-resolved thin-layer UV–visible spectral changes recorded during the first one-electron oxidation of (EtioPc)Fe(C_6H_5) at +0.60 V in pyridine, 0.2 M TBAP. The final spectrum was obtained after 40 s of electrolysis, and no further changes were observed for times up to 15 min. The figure insert illustrates a cyclic voltammogram of the compound obtained under similar experimental conditions.

Figure 4 illustrates the thin-layer UV–visible spectral changes obtained upon controlled-potential electrooxidation of (EtioPc)Fe(C_6H_5)(py) in pyridine. The reaction is electrochemically reversible (see Figure 4 insert) and occurs at $E_{1/2}$ = 0.51 V, a value positively shifted by 30 mV from $E_{1/2}$ for the first one-electron oxidation of the same compound in PhCN. As the oxidation of (EtioPc)Fe(C_6H_5)(py) proceeds in the thin-layer cell, the Soret band of the neutral porphycene increases in intensity and its wavelength shifts from 390 to 386 nm. At the same time, the visible band at 609 nm collapses and a new band for the singly oxidized compound appears at 573 nm. The spectral changes are reversible, and the final spectrum is similar to the one obtained after the first one-electron oxidation of (EtioPc)Fe(C_6H_5) in PhCN (Figure 2a), thus confirming the occurrence of an initial Fe(III)/Fe(IV) transition in both solvents. However, unlike results in PhCN, no additional spectral changes are observed upon prolonged electrolysis in pyridine, thus indicating either that a migration of the phenyl group does not occur or that it occurs too slowly to be observed on the electrochemical time scale under these experimental conditions. Finally, it should be noted that because the UV–visible spectra of the singly oxidized species are almost identical in pyridine (Figure 4) and PhCN (Figure 2a), it is therefore difficult to tell whether the pyridine molecule of (EtioPc)Fe(C_6H_5)(py) remains complexed upon electrooxidation and conversion to the Fe(IV) form of the porphycene.

Electroreduction. Cyclic voltammograms illustrating the electroreduction of (EtioPc)FeCl, (EtioPc)Fe(C_6H_5), and (EtioPc)In(C_6H_5) are shown in Figure 1. The (EtioPc)FeCl derivative (Figure 1a) has electrochemical properties quite similar to those of (TPrPc)FeCl[40] and (OEPc)FeCl[42] in that all three porphycenes undergo three one-electron reductions at almost the same potentials. The first reduction of (EtioPc)FeCl is irreversible and leads to the formation of (EtioPc)Fe^{II}, similar to what has

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(49) [(EtioPc)Fe$(py)_2$]$^+$ was *in situ* generated by addition of pyridine to (EtioPc)FeCl in CH_2Cl_2.

been reported for a number of high-spin iron(III) porphyrins containing an anionic axial ligand other than ClO_4^-.[44,45] The second and third reductions of (EtioPc)FeCl are reversible and occur at $E_{1/2} = -1.08$ and -1.42 V vs SCE in PhCN. Both one-electron additions involve the conjugated π ring system, and a similar assignment has also been proposed for the two stepwise one-electron reductions of (TPrPc)Fe[40] in CH_2Cl_2 and (OEPc)Fe[42] in PhCN.

The separation in $E_{1/2}$ between the two ring-centered reactions of the chloroiron(III) derivatives is 360 mV for (EtioPc)FeCl or (OEPc)FeCl[42] and 370 mV for (TPrPc)FeCl,[40] all of which fall in the range of $\Delta E_{1/2}$ values measured for the ring-centered electroreductions of numerous other metalloporphycenes containing an electroinactive central metal ion.[40-43] The iron(III) and indium(III) σ-bonded porphycenes, (EtioPc)Fe(C_6H_5) and (EtioPc)In(C_6H_5), also show a similar 320 mV separation between the first two one-electron reductions (see Figure 1 and Table 1), suggesting the stepwise formation of a porphycene π anion radical and dianion in both investigated phenyl σ-bonded etioporphycenes. This assignment was expected for (EtioPc)In(C_6H_5), which has an electroinactive central metal ion, but not for (EtioPc)Fe(C_6H_5) since it is at variance with the behavior of all previously characterized phenyl σ-bonded iron(III) porphyrins where the first one-electron reduction occurs not at the conjugated π ring system but at the central metal ion.[34] A second one-electron reduction of these same σ-bonded iron(III) porphyrins either is not observed within the negative potential limit of the solvent or, if it occurs, is located at potentials shifted negatively from the first reduction by 930–1440 mV depending upon the specific porphyrin ring.[34]

As seen in Table 1, the $E_{1/2}$ values for the two reductions of (EtioPc)Fe(C_6H_5) are separated by only 320 mV in PhCN, a value quite comparable to the $\Delta E_{1/2}$ between the two ring-centered one-electron reductions of (EtioPc)FeCl and (EtioPc)In(C_6H_5). This similarity in $\Delta E_{1/2}$ further suggests the electrogeneration of an Fe(III) σ-bonded porphycene π anion radical and dianion at $E_{1/2} = -1.15$ and -1.47 V in PhCN. However, the most definitive evidence for assignment of two macrocycle-centered electrode reactions is given in Figure 5, which illustrates the thin-layer UV–visible spectral changes observed during the first and second one-electron reductions of (EtioPc)Fe(C_6H_5) in PhCN. As the first reduction proceeds (Figure 5a), the split Soret band at 380 and 400 nm disappears and is replaced by a single broad band at 380 nm while the visible band at 600 nm decreases in intensity and new absorption bands appear at 550, 650, and 800 nm. These latter three bands are almost identical to absorptions reported for both monomeric and dimeric metalloporphycene π anion radicals containing iron[42] or other[43,48] central metal ions and are probably the most definitive spectroscopic fingerprint for formation of these types of species in solution.

The UV–visible spectral changes shown in Figure 5b are also self-consistent with the data in Figure 5a in that the addition of a second electron to (EtioPc)Fe(C_6H_5) can be accounted for by formation of a porphycene dianion at $E_{1/2} = -1.47$ V. All of the UV–visible and near-IR bands collapse upon the controlled-potential addition of a second electron while a new broad absorption band emerges at around 330 nm (not shown in Figure 5b). Similar types of spectra have been reported for metalloporphycene π dianions[42,43] and provide further evidence for the generation of an Fe(III) porphycene π dianion as a doubly reduced product of (EtioPc)Fe(C_6H_5).

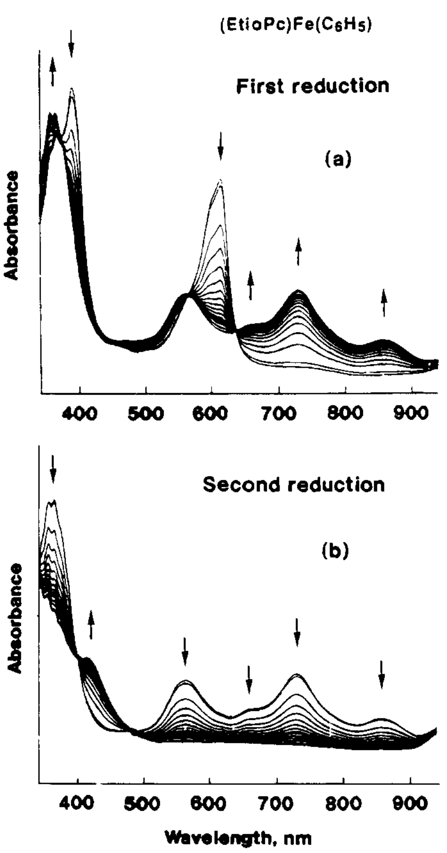

Figure 5. Thin-layer UV–visible spectral changes recorded during (a) the first and (b) the second one-electron reductions of (EtioPc)Fe(C_6H_5) in PhCN, 0.2 M TBAP to stepwise give the iron(III) porphycene π anion radical and dianion.

Summary. In summary, (EtioPc)Fe(C_6H_5) undergoes three one-electron oxidations, the first of which leads to an iron(IV) porphycene after which an iron(IV) π cation radical and dication are electrogenerated. The singly oxidized derivative is stable in PhCN for up to 40 s but undergoes a chemical reaction on longer time scales to ultimately give a transient *N*-phenyl iron(II) porphycene prior to demetalation of the iron and formation of the free base *N*-phenylporphycene derivative. However, the electrogenerated iron(IV) species seems to be more stable in the presence of a coordinating solvent such as pyridine, and this might be explained by the presence of a sixth axial ligand, which stabilizes the +4 oxidation state of the iron. (EtioPc)Fe(C_6H_5) also undergoes two reversible one-electron reductions in PhCN or pyridine, and the spectroelectrochemical data unambiguously prove that both reductions of this complex involve the porphycene π ring system rather than the metal center. Finally, (EtioPc)Fe(C_6H_5) is the first reported phenyl σ-bonded iron(III) tetrapyrrole complex to be reduced at the macrocycle rather than at the central metal.

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