($k_N^{C=O}(S^{-}\cdot) \sim k_N^{C=O}(PhN^{-}\cdot)$), However, they behave quite differently as nucleophiles in S_N2 displacement reactions at saturated carbon ($k_N^{sp^3}(S^{-}\cdot) > k_N^{sp^3}(PhN^{-}\cdot)$) with $S^{-}\cdot$ being the more potent. The two types of nucleophilic behavior manifest themselves when they are subject to potentially competitive processes within a given ion–molecule reaction,

Radical Group Fragmentation Order from the Tetrahedral Anion Radical Intermediates. From the data in Table I, the following radical group fragmentation order is established from the tetrahedral anion radical adducts formed in the reactions of $PhN^{-}\cdot$ with various carbonyl containing molecules; $CH_3CO > CO_2CH_3 > CH_3O > R\ (C_2H_5, (CH_3)_3C) > H$ and $CH_3 > CF_3$; exception, when R = CH_3, H > CH_3 was found by using CH_3CHO. From studies of the analogous reaction of $PhN^{-}\cdot$ with methyl vinyl ketone, the order $CH_3 > CH{=}CH_2$ was found.[1] Generally, the fragmentation orders reflect the bond dissociation energies of these groups to tertiary carbon[31] and the expected or known stabilities of the acyl anilide anion products. The major exception to this generalization was observed in the reaction of $PhN^{-}\cdot$ with CH_3CHO where the loss of H· was preferred (2:1) over loss of $\cdot CH_3$. Various considerations led us to speculate that this was due to a reduced $D°(C–H)$ in this tetrahedral anion radical intermediate, possibly the result of radical hyperconjugation.

It is the hope of the authors that the results of this gas-phase study and those of S_N2 displacement reactions will rekindle interest in understanding the various factors and their contribution to nucleophilic behavior in carbonyl addition and S_N2 displacement mechanisms. For example, are the factors involved in yielding similar $k_{rel}^{C=O}$ (for carbonyl additions) and $k_{CH_3}/k_{C_2H_5}$ (for S_N2 displacements) values in gas-phase and solution reactions the same in both circumstances or are they different? We believe that useful, transferable mechanistic information is obtained from related studies in both the gas and condensed phases. We must find out the degree to which this information can be transferred so that the special capabilities of each phase can be exploited.

Acknowledgment. We gratefully acknowledge support of this research from the U.S. Army Research Office and the National Science Foundation Foundation (equipment grant) and discussions with Professor D, W. Setser.

Registry No, $PhN^{-}\cdot$, 74586-02-0; CH_3Br, 74-83-9; CH_3Cl, 74-87-3; CH_3CHO, 75-07-0; C_2H_5CHO, 123-38-6; $(CH_3)_3CCHO$, 630-19-3; CH_3COCH_3, 67-64-1; $CH_3COC_2H_5$, 78-93-3; CF_3COCH_3, 421-50-1; CF_3COCF_3, 684-16-2; $CH_3COCOCH_3$, 431-03-8; c-$(H_2C)_3C{=}O$, 1191-95-3; c-$(H_2C)_4C{=}O$, 120-92-3; c-$(H_2C)_5C{=}O$, 108-94-1; c-$(H_2C)_6C{=}O$, 502-42-1; HCO_2CH_3, 107-31-3; $CH_3CO_2CH_3$, 79-20-9; $C_6H_5CO_2CH_3$, 93-58-3; $CF_3CO_2CH_3$, 431-47-0; $CF_3CO_2C_2H_5$, 383-63-1; $CF_3COSC_2H_5$, 383-64-2; CH_3COCl, 75-36-5; $CH_3COCO_2CH_3$, 600-22-6; CO_2, 124-38-9; COS, 463-58-1; CS_2, 75-15-0; O_2, 7782-44-7; $S^{-}\cdot$, 14337-03-2.

Reductive Electrochemistry of Iron–Carbene Porphyrins

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Abstract: The reductive electrochemistry of four types of iron–carbene porphyrins, vinylidene, thiocarbonyl, dichlorocarbene complexes, and the μ-carbido dimer, was investigated in aprotic solvents. The chemistry triggered by the successive injection of two electrons in the molecule essentially involves the carbene ligand. With the vinylidene and thiocarbonyl complexes, there is a 2e + H^+ reduction of the liganding carbon leading to the corresponding vinyl and thioformyl complexes. In the latter case, a remarkable reversibility is observed: electrochemical reoxidation of the thioformyl complex regenerates the thiocarbonyl complex. With the μ-carbido dimer the followup reaction mainly involves the cleavage of the carbon–iron bonds while with the dichlorocarbene complex, fast reductive dehalogenation finally yields the μ-carbido dimer. With the exception of the dichlorocarbene complex for which reduction is facilitated by the extreme unstability of the one-electron intermediate, the energies required to introduce successively two electrons in the molecules are remarkably similar for the various complexes. The acido-basic properties of the first and second electron intermediates are more sensitive to the nature of the carbene ligand and can be rationalized in terms of charge delocalization. Electronic cis effects are described and discussed in the case of the vinylidene and thiocarbonyl complexes.

The reductive chemistry of the carbon–iron bond in porphyrin complexes has received recent active attention. This has concerned the synthesis, under reducing conditions, of complexes involving iron–carbon bond as well as the oxidoreduction properties of such compounds. Two main types of complexes have been investigated in this connection: iron–carbene and iron–σ-alkyl porphyrins. It has been shown that the latter complexes can be generated electrochemically, both under their Fe(III) and Fe(II) oxidation states by reaction of iron(I) porphyrins with the corresponding alkyl halides.[2a] The main electrochemical and spectral characteristics of these σ-alkyl complexes have been described.[2a] The same sort of approach was recently extended to the case of σ-aryl- and σ-vinyliron–porphyrin complexes.[2b] The formation of σ-alkyl complexes has also been shown to occur by coupling of alkyl radicals with iron(II) deuteroporphyrin[3a,b] under pulse radiolytic conditions, and upon reduction of some halogenated compounds, such as p-nitrobenzyl chloride[3c] and halothane, $CF_3CHClBr$,[3d] by iron(II) tetraphenylporphyrin in the presence of a reducing agent in excess.

On the other hand, several iron–carbene–porphyrin complexes have been recently synthesized by reaction of polyhalogenated compounds with the iron(II) porphyrins in the presence of an excess of a reducing agent (iron powder or sodium dithionite). The carbenes, CCl_2,[4a,b] CBr_2, CF_2, CFCl, CFBr,[4c] CClCN,[4d]

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[2] (a) Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. (b) Lexa, D.; Savéant, J. M. *Ibid.* **1982**, *104*, 3503. (c) Lexa, D.; Momenteau, M.; Mispelter, J. *Biochim. Biophys. Acta* **1974**, *338*, **151**.

[3] (a) Brault, D.; Bizet, C.; Morlière, P.; Rougée, M.; Land, C. J.; Santus, R.; Swallow, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 1015. (b) Brault, D.; Neta, P. *Ibid.* **1981**, *103*, 2706. (c) Mansuy, D.; Fontecave, M.; Battioni, J. P. *J. Chem. Soc., Chem. Commun.* **1982**, 317. (d) Mansuy, D.; Battioni, J. P. *Ibid.* **1982**, 638.

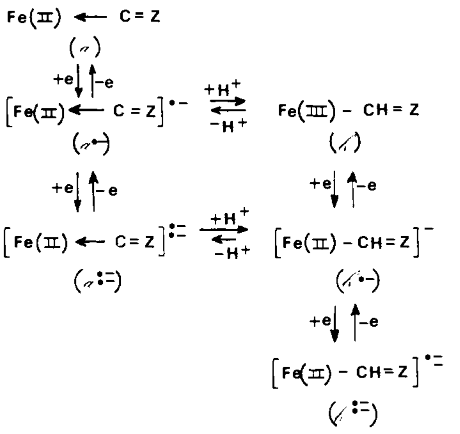
CClR,[4c] CClSR,[4f] the 1,3-benzodioxole-2-carbene,[4g] have thus been attached to the iron atom by reaction with CCl_4, CBr_4, CF_2Br_2, $CFCl_3$, $CFBr_3$, CCl_3CN, CCl_3R, CCl_3SR, and 2,2-dichloro-1,3-benzodioxole, respectively. Similarly, thiocarbonyl complexes were prepared by reaction of iron(II) porphyrins with thiophosgene.[4h,i] In the case of DDT, $CCl_3CH(p\text{-}ClC_6H_4)_2$, the reaction does not stop at the CClR complex; a further elimination of the HCl affords the vinylidene carbene complex $Fe^{II}(porphyrin)(C{=}C(p\text{-}ClC_6H_4)_2)$.[4j] A μ-carbido dimeric complex, [Fe(porphyrin)]$_2$C, is formed instead of the dihalocarbene complex upon reaction of carbon tetraiodide.[4k]

In the work reported hereafter, we describe the reductive electrochemistry of a series of iron–carbene and thioformyl porphyrin complexes as a contribution to the general knowledge of the oxido-reductive chemistry of the iron–carbon bond. The thermodynamic, mechanistic, and kinetic aspects of the problem will be considered. Besides its intrinsic interest involving the comparison with other transition metals[5] and its potential applications to the design of catalytic cycles,[9] such investigations of the redox chemistry of the iron–carbon bond in porphyrin complexes are relevant to the biochemistry of cytochrome P-450 by several aspects. Actually, cytochrome P-450–iron(II)–carbene complexes have been shown to be formed upon metabolic reduction of some polyhalogenated compounds such as CCl_4,[10a,b] and, very recently, preliminary results have been obtained showing the formation of σ-alkyliron(III)–cytochrome P-450 complexes upon metabolic reduction of halothane $CF_3CHClBr$[10c] and benzylic halides.[10d] Evidence has also been given for the formation of carbene complexes by oxidation of the methylene group of 1,3-benzodioxole derivatives by the active oxygen cytochrome P-450 complex.[4g,11] In the presence of NADPH, the natural cofactor of cytochrome P-450 dependent monooxygenases, a reduction of these iron–carbon bonds seems possible, and the present study should give interesting data in that respect. On the other hand, iron–carbene complexes are the carbon analogues of the oxene (or oxo) complexes assumed as active oxygen species in the catalytic cycles of various hemoproteins.[12]

Table I. Characteristic Standard Potentials (in V vs. SCE) of the Vinylidene, Thiocarbonyl, and μ-Carbido Complexes

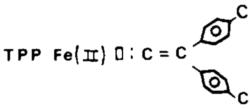
complex	couples $a/a^{-\cdot}$	$a^{-\cdot}/a^{2-\cdot}$	$b/b^{-\cdot}$	$b^{-}/b^{2-\cdot}$
1	−1,27	−1.65	−0.62	
1′	−1,31		−0,64	
2	−1,31	−1.69	−0.43	−1,79
3	−1.30	−1.70		

Scheme I



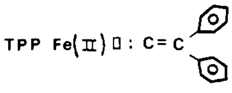
Z: $=C(p\text{-}C_6H_4Cl)_2$ (1); $=C(C_6H_5)_2$ (1′); $=S$ (2)

We describe hereafter the reductive electrochemistry of the following complexes in aprotic solvents:



$TPP\,Fe(II)\,□:C{=}C(p\text{-}C_6H_4Cl)_2$

: 1a



$TPP\,Fe(II)\,□:C{=}C(C_6H_5)_2$

: 1a′

TPP Fe(II) □ : C = S : 2a

TPP Fe(II) □ :C :□ Fe(II) TPP : 3a

TPP Fe(II) □ : C Cl_2 : 4a

This will be the occasion of observing, after similar initial steps, quite different fates of the reduction intermediates for the four selected types of complexes. All the investigations were carried out with tetraphenylporphyrin (TPP) complexes. However, some comparative experiments were made by using the corresponding octaethylporphyrin (OEP) complexes in the case of **1a** and **2a**. Most of the investigations were conducted with a platinum electrode. A few test experiments, carried out on glassy carbon, showed that the electrochemical

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(4) (a) Mansuy, D.; Lange, M.; Chottard, J. C.; Guērin, P.; Morlière, P.; Brault, D.; Rougée, M. *J. Chem. Soc., Chem. Commun.* **1977**, 648. (b) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.: Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781. (c) Mansuy D. *Pure Appl. Chem.* **1980**, *7*, 215. (d) Mansuy, D.; Guērin, P.; Chottard, J. C. *J. Organomet. Chem.* **1979**, *171*, 195. (e) Guērin, P.; Battioni, J. P.; Chottard, J. C.; Mansuy, D. *J. Organomet. Chem.* **1981**, *218*, 201. (f) Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056. (g) Mansuy, D.; Battioni, J. P.; Chottard, J. C.; Ullrick, V. *J. Am. Chem. Soc.* **1979**, *101*, 3971. (h) Mansuy, D.; Battioni, J. P.; Chottard, J. C. *Ibid.* **1978**, *100*, 4311. (i) Buckler, J. W.; Kolsisch, W.; Smith, P. D.; Tann, B. *Z. Naturforsch.* **1978**, *33B*, 1371. (j) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3213. (k) Mansuy, D.; Lecomte, J. P.; Chottard, J. C.; Bartoli, J. F. *Inorg. Chem.* **1981**, *20*, 3119.

(5) In this respect the comparison with cobalt tetraazamacrocyclic complexes shows both similarities and rather striking differences. The formation, under chemical or electrochemical reducing conditions, of σ-alkylcobalt complexes by reaction of Co(I) with alkyl halides is now a well-documented question.[6] The oxidoreduction characteristics of these complexes have been described in several instances.[6e,f,7] On the contrary, cobalt–carbene complexes appear unstable as noted for vitamin B12.[8a,b] In the case of Co(II) porphyrins, carbene show insertion in the metal–nitrogen bond rather than coordination to the metal.[8c,e]

(6) (a) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341. (b) Dolphin, D.; Johnson, A. N. *J. Chem. Soc., Chem. Commun.* **1965**, 494. (c) Pratt, J. M. "Inorganic Chemistry of Vitamin B12"; Academic Press: New York, 1972; pp 224–233 and references cited therein. (d) Momenteau, M.; Fournier, M.; Rougée, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1970**, *67*, 926. (e) Perret-Fauvet, M.; Gaudemer, A.; Boucly, P.; Devynck, J. *J. Organomet. Chem.* **1976**, *120*, 439. (f) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979**, *100*, 159.

(7) (a) Lexa, D.; Savēant, J. M. *J. Am. Chem Soc.* **1978**, *100*, 3220. (b) Finke, R. G.; Smith, B. L.; Droege, M. W.; Elliott, C. M.; Hershenhart, E. *J. Organomet. Chem.* **1980**, *202*, C25. (c) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558.

(8) (a) Zanette, D.; Nome, F. *J. Org. Chem.* **1974**, *44*, 2308. (b) Zanette, D.; Norme, F. *Can. J. Chem.* **1980**, *58*. (c) Batten, P.; Hamilton, A.; Johnson, A. W.; Shelton, G. Ward, D. *J. Chem. Soc., Chem. Commun.* **1974**, 550. (d) Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A.; Shelton, G.; Elson, C. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076. (e) Johnson, A. W.; Ward, D. *Ibid.* **1977**, 720. (f) Callot, H. F.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 307.

(9) Elliott, C. M.; Marrese, C. A. *J. Electroanal. Chem.* **1981**, *119*, 395.

(10) (a) Mansuy, D.; Nastainczyk, W.; Ullrich, V. *Naunyn-Schmiedeberg's Arch. Pharmakol.* **1974**, *285*, 315. (b) Wolf, C. R.; Mansuy, D.; Nastainczyk, N.; Deutschmann, G.; Ullrich, V. *Mol. Pharmacol.* **1977**, *13*, 698. (c) Arh, H. J.; King, L. J.; Nastainczyk, W.; Ullrich, V. *Biochem. Pharmacol.* **1982**, *31*, 383. (d) Mansuy, D.; Fontecave, M., unpublished results.

(11) (a) Ullrich, V. "Biological Reactive Intermediates"; Jollow, D. J., Kocsis, J. J., Saryder, R., Vaino, H., Eds.; Plenum Press: New York, **1977**; p 65 ff. (b) Mansuy, D.; Chottard, J. C.; Lange, M.; Battioni, J. P. *J. Mol. Catal.* **1980**, *7*, 215.

(12) (a) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437. (b) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J. C.; Mansuy, D. *Ibid.* **1981**, *103*, 2899. (c) Latos-Grazynski, L.; Cheng, R. J.; La Mar, G. N.; Balch, A. L. *J. Am. Soc.* **1981**, *103*, 4270.

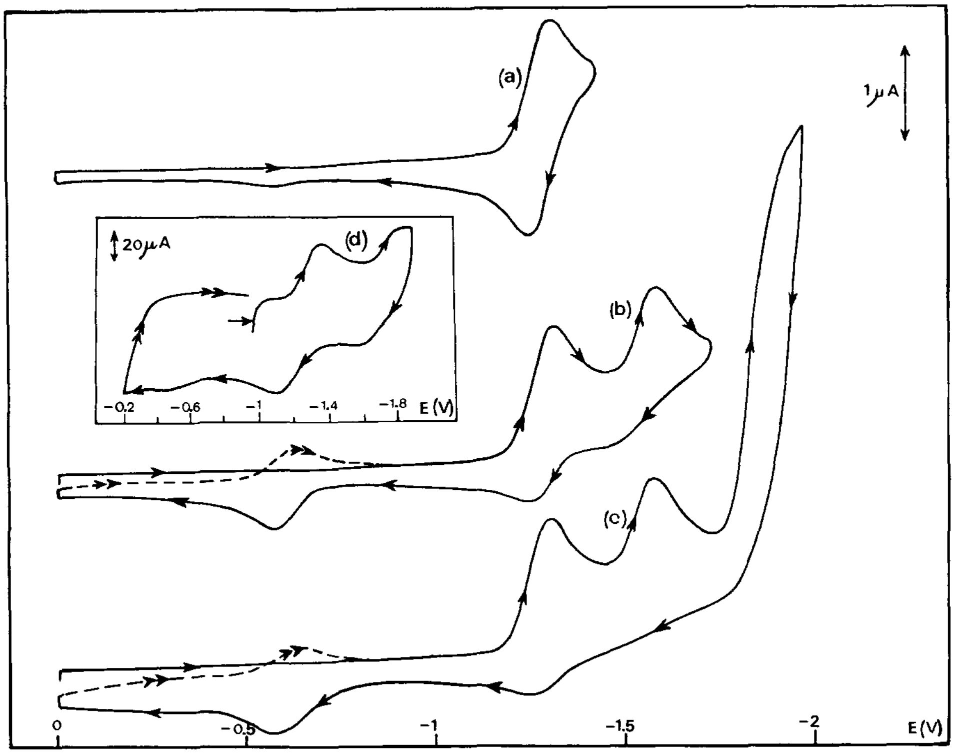

Figure 1. Cyclic voltammetry of **1a** (1.2 mM) in DMF (0.1–0.5% residual H_2O) + 0.1 M NBu_4BF_4 on a Pt electrode. Sweep rate: (a to c) 0.2 V s^{-1}; (d) : 200 V s^{-1}. Potential scanning: (a) 0 → −1.4 → 0 V; (b) 0 → −1.7 → 0 → −1 V; (c) 0 → −1.95 → 0 → −1 V; (d) −1 → −1.95 → −0.2 → −1 V.

behavior was very similar. This was also true for mercury although adsorption peaks were found in addition to the diffusion waves in some instances. DMF was mostly used as a solvent. Similar results were obtained in 50–50 acetonitrile–benzene mixtures, methylene chloride, and butyronitrile. The latter two solvents were especially used with **3a** and **4a**, respectively, for solubility reasons. All potentials are referred to the aqueous saturated calomel electrode.

A brief account of the electrochemical behavior of **1a**, **1a′**, and **2a** has been given in a preliminary communication.[13]

Results and Discussion

Vinyliden–Iron–Porphyrin Complexes (1a, 1a′). The cyclic voltammetry of **1a** in DMF at low sweep rate (Figure 1) shows the occurence of the following reactions. **1a** is first reduced into **1a**$^{-\cdot}$, giving rise to a reversible one-electron wave at 0.2 V s^{-1}. This shows that **1a**$^{-\cdot}$ is rather stable in the chemical sense under these conditions. Its halflife can be estimated as being larger than 10 s. At a more negative potential, **1a**$^{-\cdot}$ is itself reduced along a one-electron irreversible process (second wave), thus giving rise to a chemically unstable species **1a**$^{2-\cdot}$. This second wave tends to become reversible upon raising the sweep rate (Figure 1d). Its lifetime is about 5×10^{-4} s. The standard potentials for this two successive electron uptakes are given in Table I.

The product resulting from the decomposition of **1a**$^{2-\cdot}$ and **1b**$^{-\cdot}$ gives itself rise to a new system of waves: a very negative (peak potential ~ −1.92 V at 0.2 V s^{-1}) irreversible wave and a reversible one-electron wave at $E° = -0.62$ V. Such a cyclic voltammetric pattern is reminiscent of those found for σ-alkyl-, aryl-, or vinyliron–porphyrin.[2] It is thus suspected that **1b**$^{-\cdot}$ is the iron(II)-σ-vinyl porphyrin resulting from a 2e + H^+ reduction of the starting carbene complex as shown in Scheme I. **1b**, the stable reoxidation product obtained at −0.64 V, would thus be the corresponding iron(III)-σ-vinyl complex.

Further evidence of the nature of **1b**$^{-\cdot}$ is provided by the results of thin-cell spectroelectrochemical experiments (Figure 2). Reduction of **1a**, at −1.4 V, i.e., just after the first wave results in the transformation of the initial UV–vis spectrum into a spectrum very similar to those previously obtained for iron(II)-σ-alkyl TPP complexes.[2] It thus appears that in the context of spectroelectrochemistry, which has a time scale of several minutes, i.e., definitely larger than cyclic voltammetry even at low scan rates, the reduction product corresponding to the second wave, **1b**$^{-\cdot}$, is formed at the potential of the first wave. This is confirmed when looking carefully at Figure 1a: a small **1b**$^{-\cdot}$ → **1b** reoxidation wave is visible in low sweep rate cyclic voltammetry even when the potential scanning only encompasses the first wave. Coulometry, in a cell corresponding to a half-electrolysis time of 10–20 min, at −1.4 V, i.e., just beyond the first wave, shows the passage of two electrons per molecule. It is thus concluded that the same product, **1b**$^{-\cdot}$, is formed both at the first and at the second wave, much more slowly in the first case than in the second. The halflife of **1a**$^{-\cdot}$ is about 1 min as shown by spectroelectrochemistry at a fixed wavelength whereas that of **1a**$^{2-\cdot}$ is about 0.5 ms as already shown. The differences observed between cyclic voltammetry and spectroelectrochemistry or coulometry thus arise from differences in time scale.

A more rigorous proof that **1b**$^{-\cdot}$ is actually the iron(II)–σ-vinyl complex deriving from **1a** by a 2e + H^+ reduction was obtained by the following procedure. The experiments were carried out with **1a′** which has a cyclic voltammetric behavior almost identical with that of **1a**. An authentic sample of the corresponding iron(III)–σ-vinyl complex was prepared by reacting BrMgC=CPh_2 with $TPPFe^{III}ClO_4$ in THF[14] by analogy with already known procedures.[15] Upon reaction with HCl it leads quantitatively to $TPPFe^{III}Cl$ and 1,1-diphenylethylene. Its elemental analysis and

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(13) Lexa, D.; Savéant, J. M.; Battioni, J. P.; Lange, M.; Mansuy, D. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 578.

(14) Standard procedure: a solution of 0.5 mmol of (TPP)FeCl in THF was successively treated with 1 equiv of $AgClO_4$ and 3 equiv of $(C_6H_5)_2C$=CHMgBr (0.5 M in THF). The reaction mixture was filtered, the THF was removed, benzene was added, and the mixture was washed with degassed water; the benzene was partially removed. Upon addition of pentane, the complex (**1b′**) was obtained as a fine, purple powder. The crystals retain 1 mol of water, as shown by the elemental analysis.[16]

(15) (a) Clarke, D. A.; Dolphin, D.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* **1968**, 881. (b) Clarke, D. A.; Grigg, R.; Johnson, A. W. *Chem. Commun.* **1966**, *208*. (c) Ogoshi, H.; Sugimoto, H.; Yoshida, Z., IX International Conference on Organometallic Chemistry, Dijon, **1979**, France. (d) Cocolios, P.; Laviron, E.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C39.

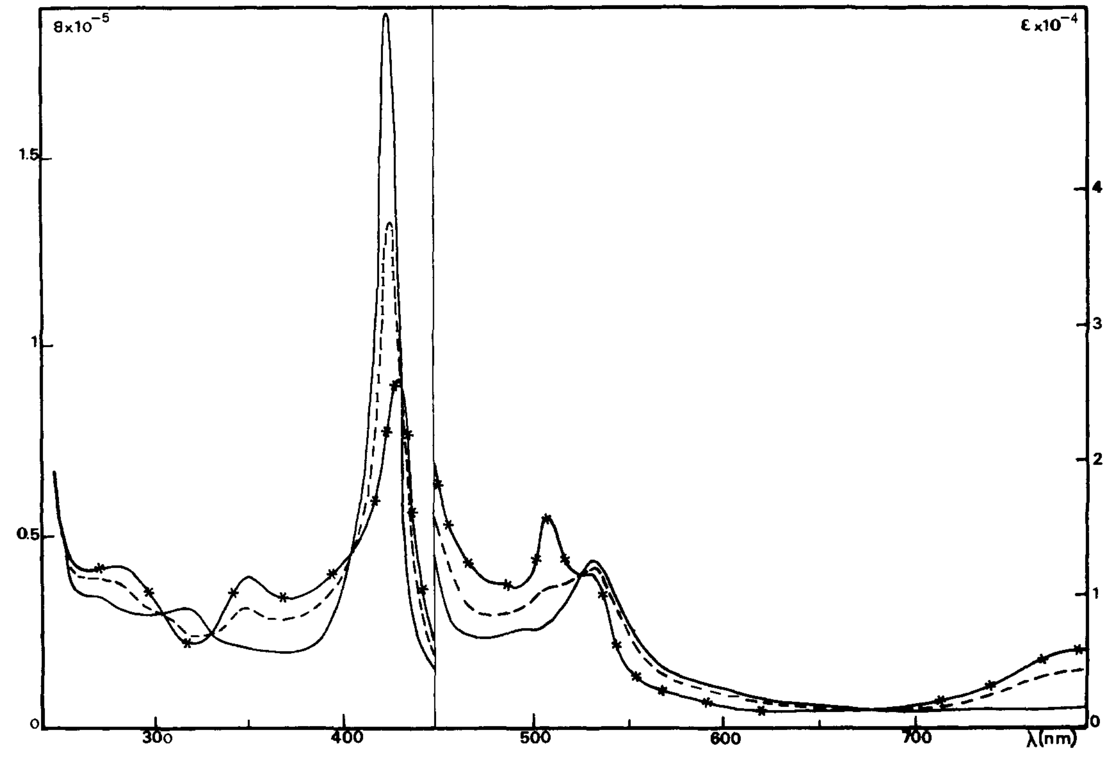


Figure 2. Thin-cell spectroelectrochemistry of **1a** in DMF + 0.2 M NBu_4BF_4 on a Pt grid electrode: electrode potential, −1.4 V; (—) initial spectrum; (*–*) final spectrum; (- - -) spectrum after 15 min electrolysis.

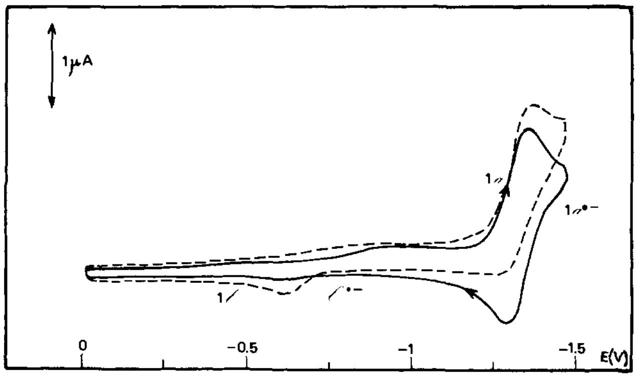


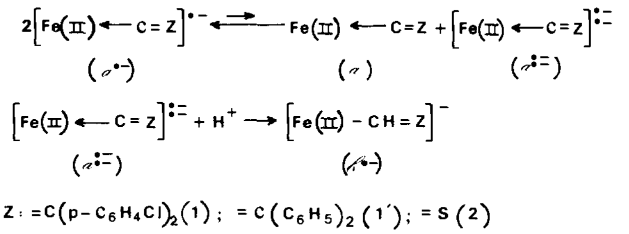
Figure 3. Effect of addition of water on the chemical stability of the one-electron reduction product of **1a** in DMF + 0.1 M NBu_4BF_4: (—) DMF with 0.1–0.5% residual water; (- - -) DMF with 5% added water.

mass and NMR spectra are in agreement with the suggested structure.[16] The cyclic voltammetry of this compound is exactly the same as that of **1b**, and the UV–visible spectrum obtained upon one electron reduction is exactly the same as that of **1b'**$^{-}$· (similar to the final spectrum in Figure 2). All this shows without ambiguity that the **1b'**/**1b'**$^{-}$· (and also the **1b**/**1b**$^{-}$·) couple are the σ-vinyl complexes represented on Scheme I.

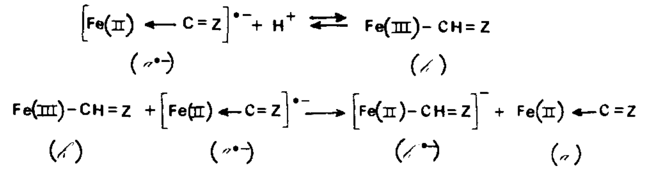
That residual water plays an important role in the protonation reaction leading to **1b**$^{-}$ is shown by the data given in Figure 3. Addition of 5% water to the DMF results in a loss of reversibility and an increase in height of the first reduction wave of **1a**. Concomitantly, the reoxidation wave of **1b**$^{-}$· into **1b** appearing upon scan reversal increases.

The reduction process thus involves, after the successive uptakes of two electrons, the protonation of the resulting product leading to the iron(II)-σ-vinyl complex which can itself be reoxidized electrochemically into the corresponding Fe(III) complex (Scheme I).[17]

Scheme II



Scheme III



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(16) UV–visible (in C_6H_6 at 27 °C) λ (nm), ε (mM^{-1} cm^{-1}) 411 (110), 552 (10.5), 549 (sh); ^1H NMR (in $DCCl_3$ at 20 °C) δ (ppm from Me_4Si) TPP, −14.00 (8 H, s), 6.44 (6H, m), 5.52 (12 H, m), 4.60 (2 H, m); CH=CPh_2 : 18.40 (2 H, s), 6.44 (2 H, s), 6.0 (2 H, s), −2.16 (1 H, s), −2.56 (1 H, s, −10.64 (2 H, s); mass spectrum (220 °C, 70 eV) 847 (M^+), 668. Elemental analysis for $Fe^{III}(TPP)(CH{=}CPh_2){\cdot}H_2O$: ($C_{58}H_{41}N_4FeO$) C, H, N calcd (80.46 − 4.73 − 6.47), measd (80.65 − 4.80 − 6.00).

(17) The following symbolism will be used throughout the paper for the various types of complexes. **a**'s are the starting carbene complexes. Then overall charge number is zero. They are conventionally represented as Fe(II) complexes. Successive addition of electrons leads to **a**$^{-}$· and **a**$^{2-}$· which shows how many electrons have been introduced and, separately, what is the charge number. They are still conventionally regarded as Fe(II) complexes which means that the relative weights of the various mesomeric form is not stated. Their chemical properties (protonation at the ligand carbon) indicates that the mesomeric form involving the localization of the charge on the carbene carbon atom has a significant weight. **b**'s are the σ-alkyl complexes deriving from the e + H^+ reduction of **a**. They are represented as Fe(III) complexes as conventional for all σ complexes. Successive addition of electrons leads to **b**$^{-}$· and **b**$^{2-}$· which shows how many electrons have been introduced into the Fe(III)-(σ-alkyl) complex and, separately, what is the charge number. **b**$^{-}$· is regarded as a Fe(II) complex according to the usual convention for σ complexes. **b**$^{2-}$· is represented conventionally still as an Fe(II) complex which means that the location of the additional electron is not specified.

This accounts for the generation of **1b**$^{-\cdot}$ at the level of the second cyclic voltammetric wave. For what regards the formation of the same product at the first wave, two types of mechanism are conceivable.

One (Scheme II) involves the prior disproportionation of two molecules of **1a**$^{-\cdot}$ leading to **1a** and **1a**$^{2-\cdot}$ which is rapidly protonated into **1b**$^{-\cdot}$ as occurs at the first wave.[18] A rough estimate of the halflife of **1a**$^{-\cdot}$ can be made in the context of this mechanism starting from the disproportionation equilibrium constant obtainable from the difference of the standard potentials of the two successive electron transfers (Table I). The halflife of **1a**$^{-\cdot}$ thus estimated, 23 min, is much larger than what was observed in spectroelectrochemistry ($\sim$1 min), showing that the disproportionation pathway can only play a minor role in the conversion of **1a**$^{-\cdot}$ into **1b**$^{-\cdot}$. It follows that direct protonation of **1a**$^{-\cdot}$ into **1b** followed by a one-electron reduction of the latter into **1b**$^{-\cdot}$ (Scheme III) is a more likely route.

In this context, the second electron transfer will occur in the solution, **1a**$^{-\cdot}$ being the electron source, rather than at the electrode surface. Since the protonation of **1a**$^{-\cdot}$ into **1b** is a very slow reaction, **1b** will indeed be formed far from the electrode surface and will therefore have not enough time to diffuse back before receiving one electron from **1a**$^{-\cdot}$ present in the solution.[19]

The OEP equivalent of **1a** exhibits an electrochemical behavior very similar to that of **1a** itself. Two points of difference are however worth notice. (i) All the waves are more negative by about 100 mV for OEP as compared to TPP. (ii) The chemical stability of the one-electron reduction product toward protonation is decreased by a factor of about 50–100.[20] These two phenomena reflect the larger electron-donating character of the porphyrin ring in the case of OEP as compared to TPP. The reductions are thus more difficult[21] and the species formed upon reduction more basic.

Thiocarbonyl–Iron–Porphyrin Complex (2a). Cyclic voltammetry at low sweep rate (Figure 4) reveals that the reduction of **2a** is rather similar to that of **1a**. We again observed first a reversible one-electron wave (**2a** → **2a**$^{-\cdot}$) and second a irreversible one-electron wave (**2a**$^{-\cdot}$ → **2a**$^{2-\cdot}$ → **2b**$^{-\cdot}$). These waves are located almost at the same potentials as for **1a**. However, the complex formed upon 2e + H$^+$ reduction of **2a**, **2b**$^{-\cdot}$ shows a rather different behavior, The reoxidation wave (**2b**$^{-\cdot}$ → **2b**) is now irreversible and more positive, while the reduction wave (**2b**$^{-\cdot}$ → **2b**$^{2-\cdot}$) is now reversible. Coulometry at the first wave indicates again the exchange of two electrons per molecule leading to the same 2e + H$^+$ product as at the second wave in cyclic voltammetry. This is confirmed by thin-cell spectroelectrochemical experiments at −1.4 V which show (Figure 5)[22] that the final product exhibits a UV–vis spectrum very similar to that obtained with **1a**, which was itsef very similar to those obtained with iron(II)–alkyl or iron(II)–aryl porphyrins.[2] This shows that the 2e + H$^+$ product obtained at the second wave in cyclic voltammetry and at the first wave with longer time range techniques such as coulometry or thin-cell speectroelectrochemistry is the thioformyl iron(II)–porphyrin σ complex.

It however appears that **2a**$^{-\cdot}$ and **2a**$^{2-\cdot}$ are significantly more stable than **1a**$^{-\cdot}$ and **1a**$^{2-\cdot}$ toward protonation. This is, for example,[23] apparent in spectroelectrochemical experiments carried out at the first wave. Isosbestic points as in the case of **1a** (Figure 2) are not longer observed.[22] The spectrum of **2a**$^{-\cdot}$, more or less overlapped by that of **2a** or **2b**$^{-\cdot}$, is visible in the intermediary time range. The halflife of **2a**$^{-\cdot}$ can then be estimated as about 10 min, i.e., significantly larger than that of **1a**$^{-\cdot}$. The spectrum of **2a**$^{-\cdot}$ can be extracted from these time-dependent recorded spectra. It has been given elsewhere in the context of a discussion of the similarities it exhibits with the spectrum of the corresponding thiolatoiron(II)–porphyrin as models of the ferrous cytochrome P-450 complexes,[24]

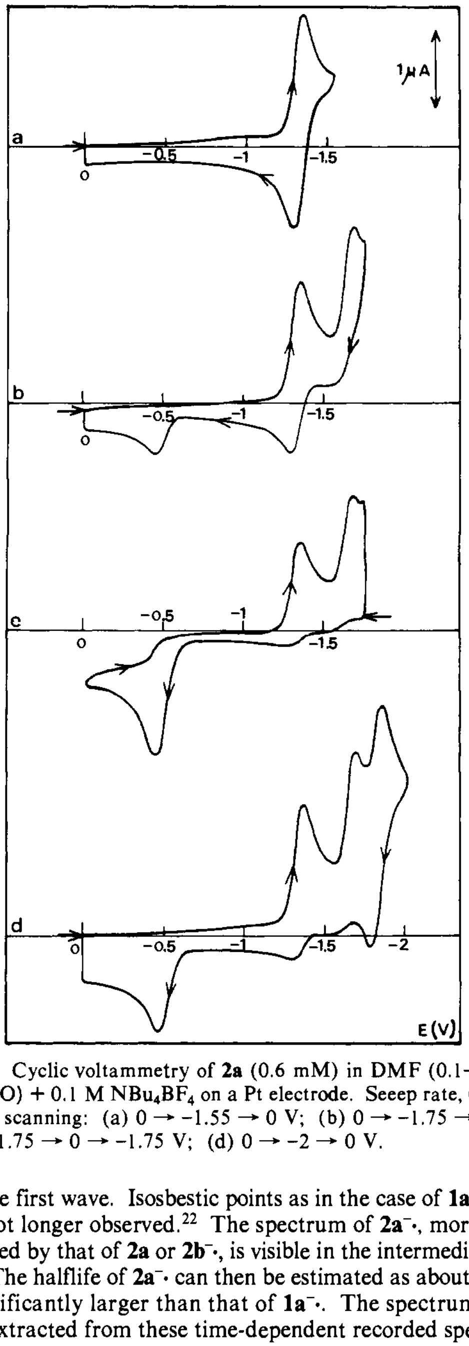

Figure 4. Cyclic voltammetry of **2a** (0.6 mM) in DMF (0.1–0.5% residual H$_2$O) + 0.1 M NBu$_4$BF$_4$ on a Pt electrode. Seeep rate, 0.2 V s^{-1}. Potential scanning: (a) 0 → −1.55 → 0 V; (b) 0 → −1.75 → 0 → −1 V; (c) −1.75 → 0 → −1.75 V; (d) 0 → −2 → 0 V.

As seen in Figure 6a, the second wave becomes more easily reversible upon raising the sweep rate in the case of **2a** than of **1a**. The halflife of **2a**$^{2-\cdot}$ is estimated as about 10^{-2} s instead of 5 × 10^{-4} s for **1a**$^{2-\cdot}$. The role of residual water is protonating **2a**$^{2-\cdot}$ is apparent in Figure 6 where it is seen that the addition of neutral alumina to the solution, removing the residual water,[25] results in a significant increase of the stability of **2a**$^{2-\cdot}$. The same degree of reversibility is obtained in the absence and presence of alumina for sweep rates that are approximately 20 times higher in the first

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[18] The disproportionation reaction is anticipated to act as a preequilibrium step with a rate-determining protonation reaction since the coproportionation reaction is expected to be much faster than the protonation reaction.

[19] (a) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27. (b) Amatore, C.; Savéant, J. M. *Ibid.* **1978**, *86*, 227. (c) Amatore, C.; Savéant, J. M. *Ibid.* **1979**, *102*, 21. (d) Amatore, C.; Savéant, J. M. *Ibid.* **1981**, *123*, 189. (e) Amatore, C.; Lexa, D.; Savéant, J. M. *Ibid.* **1980**, *111*, 81.

[20] Similar cyclic voltammetric patterns were found for the TPP complex at 0.2 V s^{-1} and the OEP complex at 10–20 V s^{-1}.

[21] Similar potential shifts were found for the waves of the simple iron–porphyrin complexes and for those of the σ-alkyl complexes.[2a]

[22] For sake of clarity the Soret region (400–480 nm) is omitted on Figure 5. The Soret maximum wavelengths of the three complexes **2a**, **2a**$^{-\cdot}$, **2b**$^{-\cdot}$ are very close to each other, not showing clearly the intermediacy of **2a**$^{-\cdot}$, which is much more apparent in the left-hand and right-hand side region of the spectrum. The characteristics of the Soret band of **2b**$^{-\cdot}$ are as follows: λ_{max} = 416 nm, ϵ 1.62 × 10^{-5} M^{-1} cm^{-1}.

[23] This also results from careful comparison of Figures 1a and 4a: showing the first wave for **1a** and **2a**, respectively, at the same sweep rate, 0.2 V s^{-1}; while a small **b**$^{-\cdot}$/**b** wave is observed upon scan reversal for **1a**, there is no trace of it in the case of **2a**.

[24] Lange, M.; Battioni, J. P.; Mansuy, D.; Lexa, D.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 888.

[25] Svenmark Jensen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

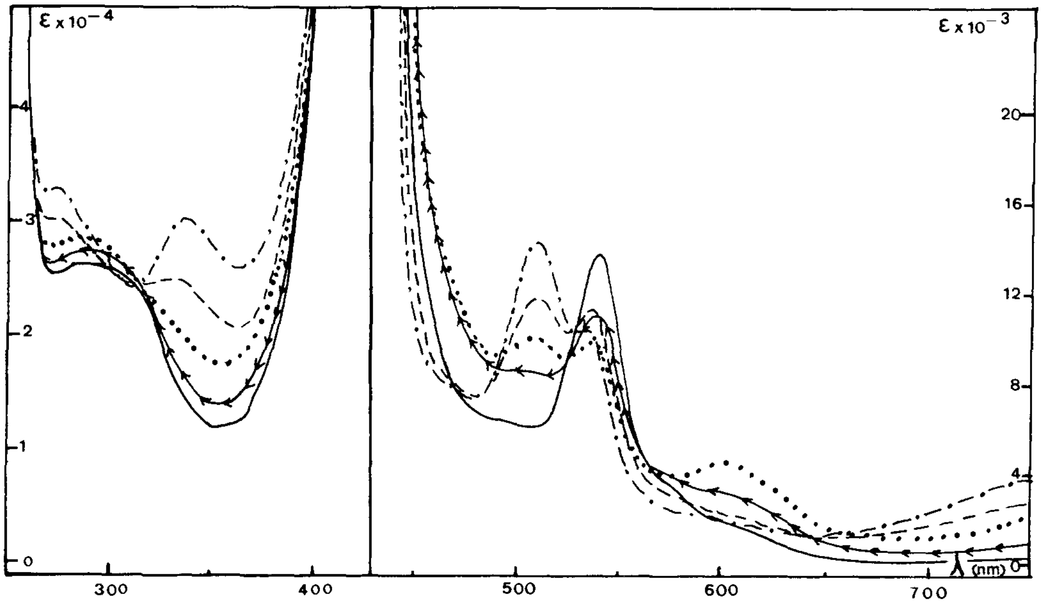

Figure 5. Spectroelectrochemistry of **2a** in DMF (0.1–0.5% residual water) +0.1 M NBu_4BF_4: (—) initial spectrum; (<<) and (•••) −1.4 V, appearance of **2**$^{-}$·; (- - -) and (··) −1.4 V, transformation into **2b**$^{-}$·.

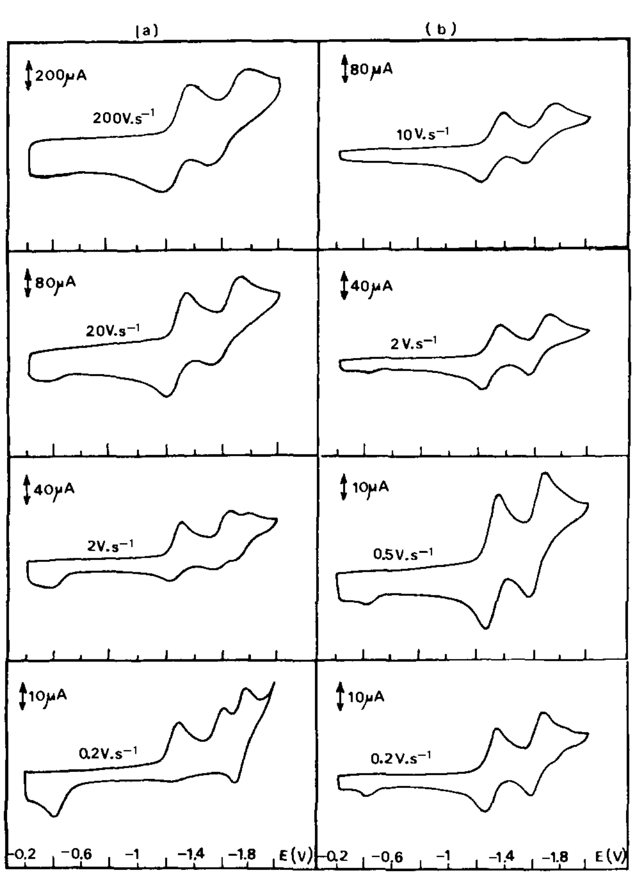

Figure 6. Cyclic voltammetry of **2a** in DMF + 0.1 M NBu_4BF_4 on a Pt electrode as a function of the sweep rate. Porphyrin concn. 1.8 mM; (a) 0.1–0.5% residual water; (b) in the presence of neutral alumina.

case than in the second. As in the case of the vinylidene complex, the formation of **2b**$^{-}$· at the first wave appears as following the direct protonation mechanism depicted in Scheme III rather than the disproportionation mechanism depicted in Scheme II. An estimate of the halflife of **2a**$^{-}$· in the context of the disproportionation mechanism from the rate of protonation of **2a**$^{2-}$· and the disproportionation equilibrium constant derived from the difference in standard potentials (Table I) indeed gives a value of 7–8 h instead of about 10 min as actually observed by thin-cell spectroelectrochemistry.

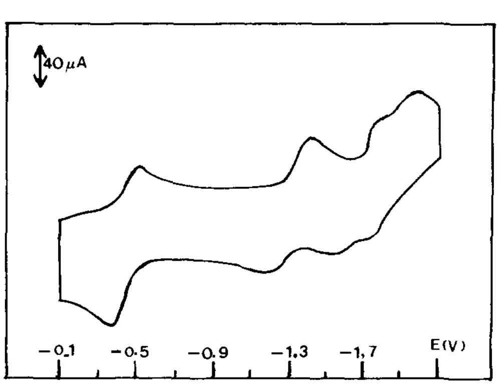

Figure 7. Repetitive stationary cyclic voltammogram of **2a** (0.6 mM) in DMF + 0.1 M NBu_4BF_4 on a Pt electrode at 100 V s^{-1} showing the four redox couples **2b**/**2b**$^{-}$·, **2a**/**2a**$^{-}$·, **2a**$^{-}$·/**2a**$^{2-}$·, **2b**$^{-}$·/**2b**$^{2-}$·, successively.

The irreversibility of the reoxidation wave of **2b**$^{-}$· into **2b** deserves further attention. First note that reversibility of the wave can be reached upon raising the sweep rate as seen in Figure 7 which shows a repetitive stationary voltammogram obtained at 100 V s^{-1} where chemical reversibility is visible for the four redox couples, **2b**/**2b**$^{-}$·, **2a**/**2a**$^{-}$·, **2a**$^{-}$·/**2a**$^{2-}$·, **2b**$^{-}$·/**2b**$^{2-}$·, taking into account the overlapping of the **2a**$^{-}$·/**2a**$^{2-}$· and **2b**$^{-}$·/**2b**$^{2-}$· couples, the corresponding standard potentials are given in Table I. On the other hand, after a preelectrolysis at −1.4 V yielding **2b**$^{-}$·, a solution of **2a** was electrolyzed at −0.4 V, i.e., positive to the **2b**$^{-}$· → **2b** wave. It was observed that the reaction gives back the starting complex **2a** as checked spectroscopically and by cyclic voltammetry.[26] The same succession of electrolyses carried out directly in a spectroelectrochemical thin cell also led to the regeneration of **2a**. It is thus concluded that the cause of the unstability of the iron(III)-σ-thioformyl complex is deprotonation leading back to the starting thiocarbonyliron(II) porphyrin as indicated in Scheme I. This reaction, which is not observed with the vinylidene complexes, is here rather rapid, the halflife of **1b** being about 10^{-2} s as derived from rapid scan repetitive cyclic voltammetric experiments of the type shown in Figure 7.

Replacement of the TPP cis ligand by OEP results in changes that are similar to those observed with the vinylidene complexes:

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[26] The reoxidation reaction was found to involve one electron per molecule instead of two as anticipated for the regeneration of **2a** and the production of one proton. The latter may well be reduced in this potential range at the platinum electrode. It was indeed observed that a millimolar solution of perchloric acid in DMF gives a reduction wave at −0.1 V.

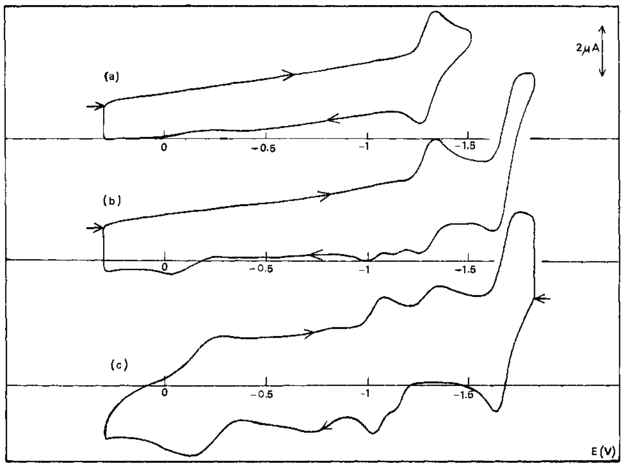

Figure 8. Cyclic voltammetry of **3a** (0.13 mM) in DMF + 0.1 M NBu_4BF_4 on a Pt electrode. Sweep rate; 0.2 V s^{-1}. Potential scanning: (a) 0.3 → −1.5 → 0.3 V; (b) 0.3 → −1.8 → 0.3 V; (c) −1.8 → 0.3 → −1.8 V.

all waves become more negative, by about 100 mV, and the $\mathbf{a}^{-\cdot}$ and $\mathbf{a}^{2-\cdot}$ complexes appear more reactive, by a factor of about 10–20, toward protonation in the case of OEP as compared to TPP.[27] Rationalization of these observations is along the same lines as for the vinylidene complexes involving the electron-donating character of the cis ring, larger for OEP than for TPP. This can also explain the additional observation that the reversibility of the $\mathbf{b}^{-\cdot}/\mathbf{b}$ wave is easier to reach upon raising the sweep rate with OEP than with TPP, showing that **b** is a weaker acid in the first case than in the second,

Comparing the thiocarbonyl and vinylidene complexes shows that they both follow essentially the same reduction mechanism involving the conversion of the initial carbene complex into a σ-alkyl type complex by a 2e + H^+ process as depicted by Schemes I and III. The two types of complexes were observed under three successive oxidation states in the investigated potential range. The most striking phenomenological difference between the thiocarbonyl and vinylidene complexes regards the reoxidation of the iron(II) σ-alkyl reduction product, It gives back the starting carbene complex in the first case, thus showing an overall reversibility of the 2e + H^+ oxido-reduction process, whereas this is not observed in the second case where the iron(III) σ-alkyl complex is chemically stable. The latter species is thus a weaker acid in the vinylidene case than in the thiocarbonyl case or equivalently the iron(II)–(σ-alkyl) as well as for the carbene complexes, $\mathbf{b}^{2-\cdot}$, $\mathbf{a}^{2-\cdot}$, $\mathbf{a}^{2-\cdot}$ are stronger bases for vinylidene than for thioformyl, This can be rationalized in terms of a better stabilization of the excess of negative charge by delocalization on the neighboring sulfur atom as compared to the delocalization on a neighboring carbon atom, The same effect also appears to influence the standard potentials in the σ-alkyl series— the $E°$'s of the $\mathbf{b}/\mathbf{b}^{-\cdot}$ and $\mathbf{b}^{-\cdot}/\mathbf{b}^{2-\cdot}$ are more negative in the vinylidene case as compared to the thiocarbonyl cases—while it does not seem to affect significantly the standard potentials in the carbene series which are approximately the same in both cases.

Carbido Dimer, 3a. The electrochemical behavior was found to be similar in DMF and CH_2Cl_2, Although solubility is poor in DMF, most of the following results concern this solvent for sake of comparison with the above described carbene complexes. The cyclic voltammetric results are shown in Figure 8. The first electron uptake is reversible, giving rise to a species $\mathbf{3a}^{-\cdot}$, chemically stable within the time scale of low sweep rate cyclic voltammetry. $\mathbf{3a}^{-\cdot}$ is stable even in longer time ranges as shown by spectroelectrochemistry: electrolysis at −1.4 V in the spectroelectrochemical cell gave rise to the spectrum shown in Figure 9 and reoxidation at −1 V gave back almost entirely the starting material with only modest (~10%) decomposition into Fe^{I}(TPP).[2c,28] This also suggests that the reduction going on at the first wave is a one-electron process.[29] This was further confirmed by comparing the height of the first wave to that of the μ-oxo dimer at the same concentration in the same solvent, CH_2Cl_2.[30] The two heights were found to be practically equal. Comparison with the first reduction wave of **2a** shows that it is about 20% higher than that of **3a** for the same concentration in the same solvent which is compatible with the expected difference in diffusion coefficients.

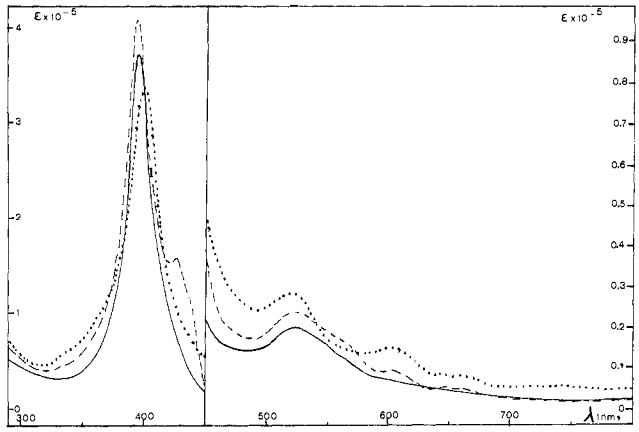

Figure 9. Spectroelectrochemistry of **3a** in DMF + 0.1 M NBu_4BF_4: (—) initial spectrum; (···) reduction at −1.4 V; (---) reoxidation at −1 V.

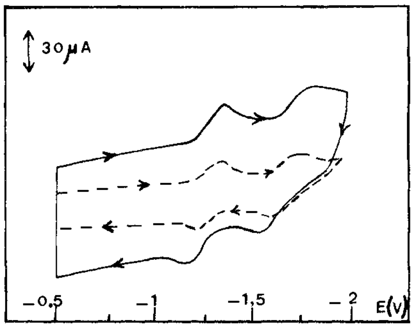

Figure 10. Cyclic voltammetry of **3a** (0.13 mM) in DMF + 0.1 M NBu_4BF_4 on a Pt electrode. Sweep rate: 20 V s^{-1} and 100 V s^{-1}. Potential scanning: −0.5 V → −2 V → −0.5 V.

The height of the second wave is between 2 and 3 times that of the first wave at low sweep rate (Figure 8b). It may look chemically reversible at first sight. This is actually a partial reversibility since upon raising the sweep rate the two waves become equal corresponding each to the exchange of one-electron per molecule (Figure 10). The $E°$ of $\mathbf{3a}^{-\cdot}/\mathbf{3a}^{2-\cdot}$ couple derived from the latter experiments is reported in Table I, The apparent reversibility at low sweep rate is partially due to the presence of the reoxidation wave of a decomposition product which is fortuitously falls in the same potential range as the reoxidation wave of $\mathbf{3a}^{2-\cdot}$. $\mathbf{3a}^{2-\cdot}$ is however not very unstable, its halflife being larger than 0.1 s, i.e., much more than for $\mathbf{1a}^{2-\cdot}$ and $\mathbf{2a}^{2-\cdot}$. Its decomposition products show a series of anodic and cathodic waves

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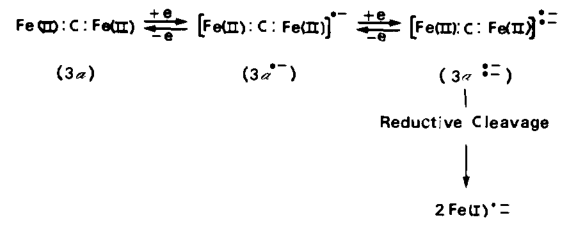
(27) The UV–visible spectrum for the $OEPFe^{II}—CH{=}S$ is found to have the following characteristics: λ (nm) (ε × 10^{-5} M^{-1} cm^{-1}): 395 (1.21), 538 (0.34), 500 (0.08), and those of the OEPFe(II)←C=S are found in ref 4i.

(28) The complex obtained upon 2e reduction of Fe^{III}TPP is designated here as a Fe(I) complex. We do not intend to dispute here about the actual Fe(I) nature of this complex as opposed to a Fe(II) anion-radical character. The electron is certainly delocalized over the whole complex structure. Note however that the fact that alkylation by alkyl halides occurs at the iron atom[2a] argues in favor of a significant weight of the Fe(I) mesomer. For more details on this question, see ref 2a,c and references cited therein. The next electron is however very unlikely to be mostly present on the iron atom. We thus noted the ensuing complex, $Fe(I)^{-\cdot}$, the anion radical of the "Fe(I) complex", the formation of which corresponds to the classical "ring wave" of iron porphyrins.

(29) Coulometry did not give reliable results due to poor solubility leading to a large and not easily controllable interference of the residual current.

(30) The reduction wave of the μ-oxo dimer in the −1 to −1.2 V region is indeed not reversible in DMF[32a] while it is reversible in CH_2Cl.[32b]

Scheme IV



(Figure 8b,c), The most abundant of these is the TPPFe porphyrin monomer which, is apparent through three of its redox waves, Fe(III)/Fe(II)/Fe(I)/Fe(I)$^{-}\cdot$, in cyclic voltammetry (Figure 8c) as checked by comparison with an authentic sample under the same conditions. Another small wave appears at −0.77 V, i.e., in a potential range where the Fe(III)/Fe(II) couple of the σ-alkyl complexes were found to be located.[2a] All these waves disappear upon raising the sweep rate as the **3a**$^{-}\cdot$/**3a**$^{2-}\cdot$ wave becomes reversible, This is confirmed by thin-cell spectroelectrochemistry where electrolysis at the second wave (−1.7 V) showed the appearance of the spectrum of the (TPP)Fe$^{1-}\cdot$ porphyrin (anion radical of the Fe(I) complex). A possible mechanism of the reaction sequence (Scheme IV) involves partial decomposition into the CH_2 carbene which could then react on the solvent and partial formation of a dimeric CH_2–σ-alkyl complex. Other modes of decomposition into the FeTPP complex and formation of other σ-alkyl complexes such as the CH_3 monomeric complex are however conceivable, the experimental data not allowing a clear-cut answer at present.

It is noted that the standard potentials (Table I) of the **3a**/**3a**$^{-}\cdot$ and **3a**$^{-}\cdot$/**3a**$^{2-}\cdot$ couples are remarkably close to those found for the vinylidene and thioformyl complexes, in spite of the large variations in electronic structure when passing from one of these three complexes to the other. The basicities of the reduction products again appear to be much more sensitive to these structural changes. The much larger stability of **3a**$^{-}\cdot$ and **3a**$^{2-}\cdot$ toward protonation as compared as **2a**$^{-}\cdot$, **2a**$^{2-}\cdot$ and **1a**$^{-}$, **1a**$^{2-}\cdot$ can be explained by delocalization of the charge on the two iron atoms and the two porphyrin rings.

It is noted that the two porphyrin moieties do not behave independently toward electron transfer:[31] the transfer of a first electron renders the transfer of the second more difficult by 0.4 eV. Comparison with "isoelectronic" μ-oxo and nitrido dimeric porphyrins previously described[32b–f] indicates that electron transfer to the carbido dimer $Fe^{IV}{=}C{=}Fe^{IV}$[33] is more difficult (~1.45 eV) than to the "isoelectronic" $[Fe^{IV}{=}N{-}Fe^{IV}]^+$ which is itself more difficult to reduce (by 0.94 eV) than the "isoelectronic" $[Fe^{IV}{-}O{-}Fe^{IV}]^{2+}$. The next reduction of the formally $[Fe^{III}{=}C{=}Fe^{IV}]^-$ carbido dimer is also more difficult (~0.59 eV) than the "isoelectronic" $[Fe^{III}{-}N{=}Fe^{IV}]$, itself more difficult (~2.05 eV) than the "isoelectronic" $[Fe^{III}{-}O{-}Fe^{IV}]^+$.[32d,f] In the latter series, the spectra of the isoelectronic carbido and oxo dimers are similar, being both different from that of the nitrido dimer. Isoelectronicity is obviously not a reliable basis for anticipating similar redox potentials as erroneously considered in earlier studies of the μ-nitrido and μ-oxo dimers,[2b] The latter conclusions were actually based on a wrong assignment of the oxidation and reduction waves of the nitrido dimer.[2b,d] The differences in charge clearly plays an important role in reducibility, and the electronic[32b,c,f,j] and even stereochemical[32g–i] properties of the bridging atom are obviously quite different from one case to the other.

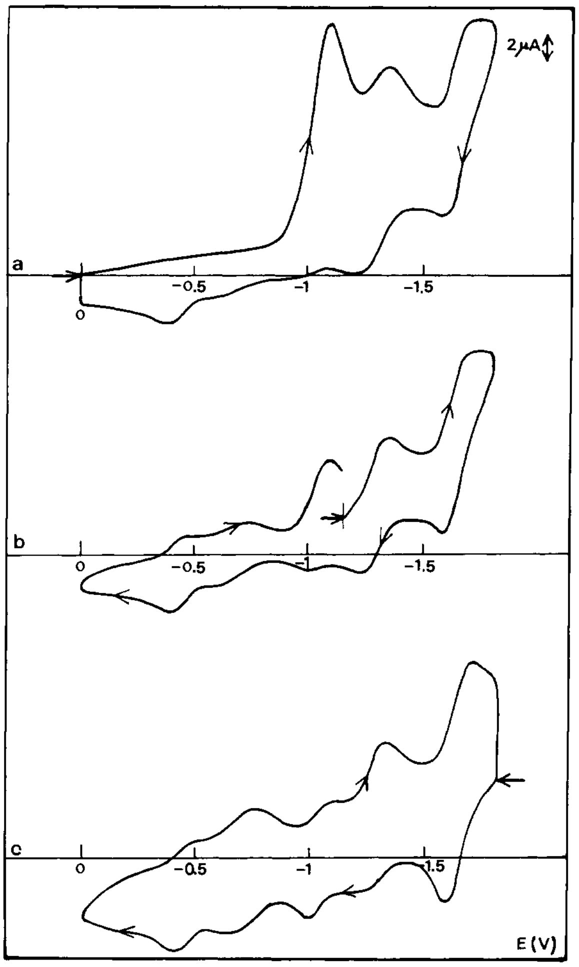


Figure 11. Cyclic voltammetry of **4a** (1 mM) in *n*-butanenitrile + 0.1 M NBu_4BF_4 on a Pt electrode. Sweep rate: 0.2 V s^{-1}. Potential scanning: (a) 0 → −1.8 → 0 V; (b) −1.15 → −1.8 → 0 V; (c) −1.8 → 0 → −1.8 V.

Scheme V

$$1^{st}\text{wave: } Fe(II) \leftarrow CCl_2 + 2e + 1H^+ \longrightarrow \tfrac{1}{2}\, Fe(II) \leftarrow C \rightarrow Fe(II) + \tfrac{1}{2}\, CH_2Cl_2{}^{34}$$

$$2^{nd}\text{wave: } \tfrac{1}{2}\, Fe(II) \leftarrow C \rightarrow Fe(II) + \tfrac{1}{2}\, e \longrightarrow \tfrac{1}{2}\left[Fe(II) \leftarrow C \rightarrow Fe(II)\right]^{\bullet -}$$

$$3^{rd}\text{wave: } \tfrac{1}{2}\left[Fe(II) \leftarrow C \rightarrow Fe(II)\right]^{\bullet -} + \tfrac{1}{2}\, e \longrightarrow \tfrac{1}{2}\left[Fe(II) \leftarrow C \rightarrow Fe(II)\right]^{\bullet =}$$

Dichlorocarbene Complex 4a. This compound is very sensitive to oxygen decomposing into the Fe^{III}(TPP)Cl or $[Fe^{III}(TPP)]_2O$ complexes. The rate of decomposition however depends upon the solvent. It was found much more stable in *n*-butanenitrile than in DMF. The former solvent was thus used for systematic investigation after checking that the behavior is very similar to that observed in DMF during a few test experiments involving partially decomposed solutions in the latter solvent. Cyclic voltammograms obtained at low sweep rate are represented in Figure 11. They show a first cathodic irreversible wave involving the exchange of two electrons per molecule as shown by comparison of its height with that of the reduction wave of Fe^{II}(TPP). The second reversible wave, corresponds to 0.5 electron per molecule while the third is higher and less reversible. The two latter waves exhibit the same characteristics as the reduction waves of the carbido dimer, **3a**, as described in the preceding section. The assignment of the carbido dimer as reaction product of the reduction of **4a** is further confirmed by the appearance of the same set of waves

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(31) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 115.

(32) (a) Kadish, K. M.; Larson, G.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975**, *97*, 282. (b) Kadish, K. H.; Cheng, J. S.; Cohen, I. A.; Summerville, D. *ACS Symp. Ser.* **1977**, *No. 38*, *65*. (c) Kadish, K. M.; Bottomley, L. A.; Brace, J. G.; Winograd, N. *J. Am. Chem. Soc.* **1980**, *102*, 4341. (d) Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3195. (e) Felton, R. H.; Owen, G. S.; Dolphin, D.; Fajer, J. *J. Am. Chem. Soc.* **1971**, *93*, 6332. (f) Phillip, M. A.; Goff, H. M. *Ibid.* **1979**, *101*, 7641. (g) Schick, G. A.; Bocian, D. F. *Ibid.* **1980**, *102*, 7984. (h) Tatsumi, K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1980**, 509. (i) Tatsumi, K.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328. (j) Bottomley, L. A.; Garrett, B. B. *Inorg. Chem.* **1982**, *21*, 1260.

(33) This is a formal and very artificial way of writing the iron oxidation states, concentrating 4 negative charges on the central carbon, for sake of comparison with the other two dimers.

upon the scan reversal. Also, electrolysis of **4a** at −1.1 V in the spectroelectrochemical thin cell resulted in the appearance of the UV–vis spectrum of **3a**.

When the sweep rate was raised, the two cathodic waves featuring the reduction of the carbido dimer gradually disappear while the first wave tends to decrease from 2e to 1e. Full reversibility of the first wave could not however be observed even at very high sweep rates (up to several thousand volts per second), showing that the complex resulting from the first electron uptake is extremely unstable.

These observations are compatible with the reaction sequence shown in Schem V involving the reductive elimination of two chloride ions and the reaction of the resulting species on the starting complex. The intimate mechanism of the dimerization process remains however unknown. The reductive electrochemical behavior of the dichlorocarbene complex is consistent with previously described synthesis of the carbido dimer, **3a**, by reaction of $Fe^{II}TPP$ with CI_4 under reducing conditions:[4k] as soon as the analogous diiodocarbene complex is formed by a reaction similar to that yielding the dichlorocarbene complex from CCl_4,[4a] it is immediately reduced with formation of the carbido dimer as observed electrochemically here for the CCl_2 complex. It is indeed anticipated that the diiodocarbene complex will be easier to reduce than its chloro analogue. It is noted in this connection, that the dichlorocarbene complex appears as significantly easier to reduce than the vinylidene, thiocarbonyl, and carbido dimer complexes for which the first electron transfer was occurring at very similar potentials. This is however partly a reflection of the extreme unstability of the first electron transfer product which pulls the reduction potential in the favorable direction.

Concluding Remarks

The main points emerging from the above description and comparison of the reductive electrochemical behaviors of vinylidene, thiocarbonyl, carbido dimer, and dichlorocarbene iron(II)–porphyrin complexes are as follows:

(i) The energy required for the first electron uptake is not very different from one of these complexes to the other with the exception of the dichlorocarbene complex which appears as easier to reduce than the three others. In the latter case, besides thermodynamic factors, the reduction is facilitated by the extreme unstability of the one-electron reduction intermediate. For the first three complexes, not only are the standard potentials for the first electron uptake close to one another but this is also the case of the second electron transfer.

(ii) The chemical fate of the first and second electron transfer intermediates varies significantly from one carbene complex to the other. The dichlorocarbene complex displays the most particular behavior. Electron transfer results in a very rapid dehalogenation giving rise finally to the formation of the μ-carbido dimer.

(iii) The vinylidene and thiocarbonyl complexes undergo essentially the same $2e + H^+$ reduction leading to the formation of the corresponding iron(II)–vinyl and –thioformyl complexes. It is noteworthy that the latter are the first reported thioformyl complexes of metalloporphyrins. This reduction occurs slowly after the first electron uptake and much more rapidly upon addition of a second electron. Residual water plays an imporant role in the protonation step. The basicities of the one- and two-electron intermediates are significantly larger in the vinylidene than in the thiocarbonyl case which can be rationalized in terms of favorable delocalization of the negative charge on the sulfur atom. There is an even more striking difference between the two kinds of complexes: reoxidation of the thioformyl complex gives back the thiocarbonyl complex whereas this is not observed in the σ-vinyl-vinylidene series. Again, favorable accomodation of the negative charge on the sulfur atom as compared to the carbon atom explains this difference. The replacement of TPP by OEP as cis ligand results in a general shift of the reduction potential toward negative values (by about 100 mV) and enhances the basicity of the first and second electron reduction intermediates. Both effects reflect the stronger electron-donating character of OEP as compared to TPP.

(iv) For the carbido dimer, while some protonation seems to still accompany the two-electron injection, the main decomposition pathway involves the cleavage of the carbon–iron bonds leading to the anion radical of $Fe^{I}(TPP)$. Stability of the first and second electron intermediates is significantly larger than for the vinylidene and thiocarbonyl complexes as can be anticipated from delocalization of the charge on the two iron atoms and the two porphyrin rings.

Experimental Section

Chemicals. The starting complexes were synthesized and characterized according to the previously published procedures: **1a**,[4l] **1a′**,[4i] **2a**,[4h] **3a**,[4k] **4a**.[4a]

The instrumentation, cells, electrodes, and procedures for cyclic voltammetry, thin-cell spectroelectrochemistry, and coulometry were the same as previously described.[2a,35]

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Registry No. **1a**, 72042-21-8; **1a**$^-$, 83928-13-6; **Ia**$^{2-}$, 83928-17-0; **Ia′**, 77745-20-1; **1a**$^{1-}$, 83928-14-7; **1b**, 83928-20-5; **1b**$^-$, 83928-21-6; **1b′**, 83219-57-2; **1b′**$^-$, 83928-23-8; **2a**, 67583-11-3; **2a**$^-$, 83928-15-8; **2a**$^{2-}$, 83928-18-1; **2b**, 83928-24-9; **2b**$^-$, 83928-25-0; **2b**$^{2-}$, 83928-26-1; **3a**, 75249-87-5; **3a**$^-$, 83928-16-9; **3a**$^{2-}$, 83928-19-2; **4a**, 65979-89-7.

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(34) Or any other set of compounds at the same carbon oxidation state.

(35) Lexa, D.; Savéant, J. M. Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786.