η^3-indenyl vs. η^3-cyclopentadienyl (Figure 4) strongly supports the contention that the dissociative loss of CO does not precede the η^3- to η^5-conversion. The bond dissociation energies for metal carbonyls varies widely,[25] but the (η^5-$C_5R'_5$)$Fe(CO)_2R$ complexes are typically robust complexes with respect to dissoctive loss of CO. Loss of one CO to form substituted complexes typically increases the back-bonding to the remaining CO, thereby increasing the metal–CO multiple-bond character and increasing the bond strength. Thus, it is very likely that a concerted η^3- to η^5-conversion/CO loss is the pathway by which the metallocenes are thermally formed from the monocarbonyls produced photochemically from I–III.

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Registry No. I, 12247-96-0; II, 33568-92-2; III, 101377-15-5; $Fe(\eta^5\text{-}C_5H_5)_2$, 102-54-5; $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$, 54845-16-8; $Fe(\eta^5\text{-}C_9H_7)_2$, 1272-49-7; $(C_5H_5)Fe(CO)_2{}^+BF_4{}^-$, 93757-32-5; $(\eta^5\text{-}C_9H_7)_2Fe_2(CO)_4$, 36632-68-5; $Fe(CO)_4I_2$, 14878-30-9; LiC_9H_7, 20669-47-0; $(\eta^5\text{-}C_9H_7)Fe(CO)_2I$, 36561-93-0; indene, 95-13-6.

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Electroreductive Alkylation of Iron Porphyrins. Iron(III), Iron(II), and Iron(I) Alkyl Complexes from the Reaction of Doubly Reduced Iron(II) Porphyrins with Alkyl Halides

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Electrochemical investigation of the reduction of four iron porphyrins (octaethylporphyrin, tetraphenylporphyrin, and two amide-linked basket-handle porphyrins) in the presence of alkyl halides shows that not only the singly reduced iron(II) complex, formally an iron(I) complex, undergoes alkylation at the iron atom but also this is the case for the doubly reduced iron(II) complex. No ring alkylation, as possible with a radical anion or a dianion structure, is observed. At low concentrations of alkyl halide, the one-electron reduction product of the iron(II) alkyl complex, formally an iron(I) alkyl complex, could be transiently observed. When the concentration is raised, catalytic reduction of the alkyl halide by the $Fe^{II}R^-/Fe^{I}R^{2-}$ couple occurs. It is found that the presence of the amide-linked chains exerts a pronounced influence on the electrochemical and chemical reactivity of the alkyl complexes, stabilizing the negatively charged species. Implications concerning the alkylation mechanism and the chemical catalysis of the electrochemical reduction of alkyl halides by metal complexes are discussed.

Three main ways of access to σ-alkyl–iron porphyrins have been demonstrated thus far: reaction of iron(III) porphyrins with a source of carbanions, usually a Grignard reagent[1] combination of an alkyl radical with an iron(II) porphyrin,[2] and reaction of iron(I) porphyrins with a source of carbocations, typically an alkyl halide.[3] In all three cases a (formal) $^+Fe^{III}R^-$ complex is first obtained. In the third case, however, owing to the fact that iron(I) is generated electrochemically, an $Fe^{II}R^-$ complex is actually obtained since the standard potential of the $Fe(II)/Fe(I)^-$ couple is negative with respect to that of the $^+Fe^{III}R/Fe^{II}R^-$ couple.[3] Electrochemically generated cobalt(I) in porphyrins or in vitamin B_{12} also reacts with alkyl halides yielding $Co^{III}R$ complexes.[4] In contrast with what happens with iron, however, the $Co^{III}R$ complex is electrochemically stable at the potential where Co(I) is generated. The $Co^{II}R^-$ complex can be obtained by reduction of $Co^{III}R$ at a more negative potential.

There has been thus far no report of the possibility of alkylating doubly reduced iron(II) porphyrins, formally iron("0") complexes, by alkyl halides. We discuss hereafter this problem starting from electrochemically generated iron("0") and using, for identification, the characteristics of the $Fe^{III}R$ and $Fe^{II}R^-$ complexes previously gathered by electrochemical generation of these species from Fe(I).[3]

The nature of singly and doubly reduced porphyrins, formally iron(I) and iron("0") complexes, has been the object of active investigation and discussion in recent years. Regarding the singly reduced complexes, there is strong evidence, based on ESR,[5] UV–vis,[5b,c,6,7] NMR,[6] and reso-

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nance Raman[5d] spectroscopies and X-ray crystal structure,[7] that they are best described as iron(I) complexes, i.e., that the unpaired electron density is mostly located in the d_{z^2} orbital of the iron atom, the contribution from an iron(II) porphyrin anion radical resonance form being minor. It is noteworthy that the reaction of singly reduced iron porphyrins with alkyl halides proceeds consistently with a dominant contribution from the iron(I) resonance form.[3] Alkylation occurs at the iron atom[3] and not at a ring carbon as expected for an aromatic anion radical.[8] Moreover, the activation vs. driving force free energy relationship exhibited by a series of iron porphyrins having different Fe(II)/Fe(I) standard potentials is clearly different from that observed in the reaction of the same alkyl halides with aromatic and heteroaromatic anion radicals.[3] The latter is known to involve, as rate-determining step, the transfer of one electron from the anion radical to the alkyl halides, followed by the coupling of the ensuing alkyl radical with the starting aromatic anion radical.[8] It was thus concluded[3] that alkylation at the iron(I) center proceeds along a S_N2 rather than an electron-transfer mechanism.[9]

The aim of the work reported herein was to investigate the alkylation of doubly reduced iron(II) porphyrins, iron("0") complexes, by alkyl halides, i.e., to answer the question: does alkylation occur at the iron atom or at the ring? The electronic structure of doubly reduced iron(II) porphyrins is less unequivocally defined than that of the singly reduced complex.[10] On the basis of spectroscopic and magnetic properties, it appears most likely that the iron(I) anion radical structure is the dominant resonance form.[10] Thus, besides its synthetic interest, part of the motivation of the work described below was to investigate the reactivity of iron in iron("0") porphyrins in relation to their electronic ground-state structure.

Another important motivation relates to the chemical catalysis of electrochemical reactions, the reduction of alkyl halides in the present case. The electrochemical reductive cleavage of alkyl halides is a very irreversible process: the rate-determining step $RX + e^- \rightarrow R^\bullet + X^-$ exhibits an overpotential of the order of 1.5 V.[8b,c] This is thus a typical case where catalysis of the electrochemical process appears particularly worthwhile. There are essentially two types of catalysis of electrochemical reactions by homogeneous systems. One, "redox catalysis", involves an homogeneous outer-sphere electron transfer between the active form of the catalyst and the substrate.[11a] Catalysis then results from physical rather than from chemical reasons: it is merely a consequence of the molecular three-dimensional arrangement of the electron-exchanging agent as opposed to the two-dimensional arrangement of the electrons (or holes) on the electrode surface. In contrast, "chemical catalysis" involves a deeper interaction between the catalyst and the substrate, a crucial step of the catalytic process being the formation of an adduct between catalyst and substrate.[11] In the case, for example, of the reduction of an electrophile, the first step of the catalytic process will be

$$M^n + e \rightleftarrows M^{n-1} \tag{1}$$

M^n = catalyst with the metal at the oxidation degree n

$$M^{n-1} + E^+ \rightleftarrows M^{n-1}E^+ \leftrightarrow M^nE^+ \leftrightarrow M^{n+1}E^- \tag{2}$$

E^+ = schematic representation of the electrophile

A second critical step is the decomposition of the resulting adduct upon further electron transfer:

$$M^{n+1}E^- + e \rightarrow M^nE^- \tag{3}$$

$$\begin{gathered} M^nE^- \rightarrow M^n + E^- \qquad E^- + E^+ \rightarrow \text{products} \\ M^nE^- + E^+ \rightarrow M^n + \text{products} \end{gathered} \tag{4}$$

The ensuing regeneration of the starting oxidation state, M^n, closes the loop which ensures the catalysis of the overall reduction:

$$E^+ + 2e \rightarrow E^-$$

It has already been shown that cobalt porphyrins and vitamin B_{12} derivatives[4] can be used as catalysts for the reduction of alkyl halides at the potential where the $Co^{III}R$ complex resulting from the alkylation of Co(I) is reduced into $Co^{II}R^-$. Although a detailed study of the mechanism was not attempted, the catalytic process presumably follows the reaction scheme depicted above.

It is, however, of importance to dispose of several catalyst couples for the same reaction in order to investigate the dependency of the catalytic efficiency upon the standard potential and the nature of the metal and of its ligands. This is now a well-documented question in the simple case of redox catalysis where the catalytic efficiency is a function of the rate constant of the outer-sphere electron transfer between the catalyst and the substrate, the magnitude of which can be related to the standard potentials in the framework of Marcus theory.[8c] Much less is known in the case of chemical catalysis, the efficiency of which depends jointly upon the rate constants of the two key-steps (2) and (4). Deeper insights into this question clearly require the finding of several examples of electrochemically well-characterized redox couples able to chemically catalyze the electrochemical reduction of alkyl halides. The possibilities offered by the $Fe(II)/Fe(I)^-$ and $Fe(I)^-/Fe(\text{"0"})^{2-}$ couples in this respect will be compared.

Another point which we have investigated is the electrochemical characteristics of the iron–alkyl complex obtained upon reaction of the alkyl halides either with the Fe(I) or the Fe("0") complex. It will be shown that the generation of the alkyl complex by the second of these routes allows one to observe a transient Fe^IR^{2-} complex. This is of particular interest in view of the fact that very few examples of axial coordination of iron(I) porphyrins

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(8) (a) Hebert, E.; Mazaleyrat, J. P.; Nadjo, L.; Savéant, J. M.; Welvart, Z. *Nouv. J. Chim.* **1985**, *9*, 75. (b) $E_p - E^\circ_{RX/R\cdot+X^-}$ = 1.63 V in dimethylformamide at 20 °C. E_p = cathodic peak potential at 0.1 V·s^{-1}.[8c] (c) Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638.

(9) (a) Another mechanism could be envisaged in which an electron would be transferred from the iron(I) complex to the alkyl halide which would immediately cleave,[9b] while the resulting alkyl radical would couple with iron(II) within the solvent cage:[9c]

$$Fe(I)^- + RX \xrightarrow[(a)]{} [Fe(II),R^\bullet,X^-] \xrightarrow[(b)]{} [Fe^{III}R,X^-] \xrightarrow[(c)]{} Fe^{III}R + X^-$$

However, this reaction sequence cannot be considered as the succession of a rate-determining outer-sphere electron transfer (reaction a) and of the coupling between the $R^\bullet$ radical and the Fe(II) complex. Otherwise, indeed, the activation–driving force relationship should be the same as for aromatic anion radicals which is not the case. It follows that the transfer of one electron (reaction a) and the coupling should be regarded as concerted, which amounts to a S_N2 mechanism when the coupling occurs within the time of a vibration. (b) There is good evidence that the reductive cleavage of aliphatic halide proceeds along a concerted electron-transfer bond-breaking mechanism.[8c] (c) Alkyl radicals have been shown to react with iron(II) porphyrins.[2]

(10) See ref 5 and the references cited therein.

(11) (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39.

(12) Simonet, J.; Michel, M. A.; Lund, H. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 489.

Table I. Characteristic Standard Potentials[a] of the Four Investigated Iron Porphyrins[b]

porphyrin	couple			
	$Fe(II)/Fe(I)^-$	$Fe(I)^-/Fe(\text{“O”})^{2-}$	Fe^{III}-*n*-Bu/Fe^{II} *n*-Bu^-	Fe^{II}-*n*-Bu^-/Fe^{I}-*n*-Bu^{2-}
a-$(C12)_2$-AC	−0.884 (106)[c]	−1.487 (150)	−0.585 (133)	−1.716 (270)
a-$(C12)_2$-CT	−0.895 (95)[c]	−1.527 (110)	−0.620 (98)	−1.800 (186)
TPP	−0.990[d]	−1.637	−0.718	−1.986
OEP	−1.195 (−205)[d]	−1.915 (−278)	−0.990 (−272)	−2.331 (−346)

[a] Supporting electrolyte is 0.1 M NBu_4ClO_4.[14d] All potentials are referred to the NaCl saturated calomel electrode. Temperature is 20 °C. [b] The numbers between parenthesis are the values of $E_{Porph} - E_{TPP}$ in mV for Porph = a-$(C12)_2$-AC, a-$(C12)_2$-CT, and OEP for each of the four redox reactions. [c] Corrected from the association of Fe(II) with Cl^-, 19 mV in the first case and 16 mV in the second.[14a,c] [d] Correction for the association of Fe(II) with Cl^- is negligible.

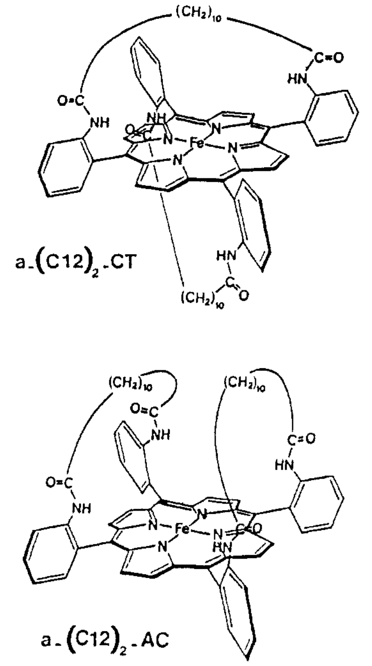
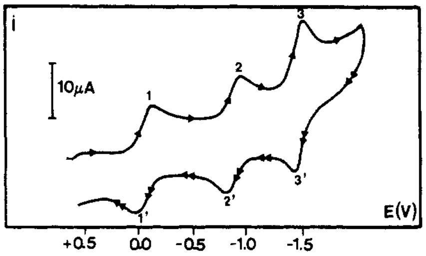


Figure 1. Cross-trans (a-$(C12)_2$-CT) and adjacent-cis (a-$(C12)_2$-AC) amide-linked basket-handle iron porphyrins.

have been described thus far.[5d,13]

The investigations were conducted with four porphyrins, the classical tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP) and also two basket-handle porphyrins bearing two 12-carbon chains attached to the ortho positions of the phenyl rings of TPP by secondary amide linkages in a cross-trans (a-$(C12)_2$-CT) and an adjacent-cis (a-$(C12)_2$-AC) configuration (see Figure 1). The presence of these amide-linked chains has been shown to strongly influence the redox and coordination chemistry of iron porphyrins resulting mainly in a stabilization of the negatively charged complexes.[14] We thus examined if such effects also influence the electrochemistry of the σ-alkyl–iron complexes at their various oxidation states.



$$Fe(III)^+ \underset{1'}{\overset{1}{\rightleftharpoons}} Fe(II) \underset{2'}{\overset{2}{\rightleftharpoons}} Fe(I)^- \underset{3'}{\overset{3}{\rightleftharpoons}} Fe(\text{“0”})^{2-}$$

Figure 2. Cyclic voltammetry of (a-$(C12)_2$-CT)$Fe^{III}Cl$ (1 mM) in DMF + 0.1 M NMe_4BF_4 (temperature = 20 °C; sweep rate = 0.1 V·s^{-1}).

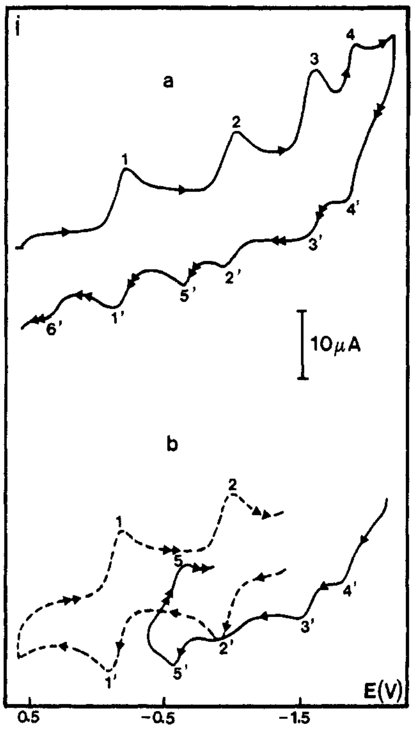


Figure 3. Cyclic voltammetry of (a-$(C12)_2$-CT)$Fe^{III}Cl$ (1 mM) in DMF + 0.1 M NMe_4BF_4 in the presence of 0.5 mM *n*-BuBr illustrating the formation of Fe^{II}-*n*-Bu^- from Fe(“0”) (temperature = 20 °C; sweep rate = 0.1 V·s^{-1}). Waves 1/1′, 2/2′, and 3/3′ are as shown in Figure 2. Waves 4/4′, 5/5′, and 6′: a, direct potential scanning; b, reverse potential scanning.

$$Fe(III) \underset{6'}{\longleftarrow} Fe^{III}\text{-}n\text{-}Bu \underset{5'}{\overset{5}{\rightleftharpoons}} Fe^{II}\text{-}n\text{-}Bu^- \underset{4'}{\overset{4}{\rightleftharpoons}} Fe^{I}\text{-}n\text{-}Bu^{2-}$$

Results

Alkylation of electrogenerated iron(I) porphyrins has been demonstrated to occur at the iron atom on the basis of NMR and ESR evidence, and the cyclic voltammetric and UV–vis spectrophotometric characteristics of the resulting $Fe^{II}R^-$ complexes have been described.[3] Since the iron(“0”) complex is expected to be more reactive than the

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(13) (a) Carbon monoxide has been shown recently to bind with iron(I) porphyrin provided that a nitrogen base serves as a second axial ligand and a superstructure holding secondary amide groups close to the porphyrin is present.[13b] However, the oxidation degree of iron in these formal Fe^{I}Co complexes is clearly larger than one due to extensive electron transfer to the CO moiety.[13b] (b) Croisy, A.; Lexa, D.; Momenteau, M.; Savéant, J. M. *Organometallics* **1985**, *9*, 1574.

(14) (a) Lexa, D.; Momenteau, M.; Rentien, P.; Rytz, G.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1983**, *106*, 4755. (b) Lexa, D; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1985**, *24*, 122. (c) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F., submitted for publication. (d) The $Fe(II)/Fe(I)^-$ and $Fe(I)^-/Fe(\text{“0”})^{2-}$ standard potentials depend to some extent upon the cation of the supporting electrolyte. They shift negatively when passing from Me_4N^+ to Et_4N^+ and Bu_4N^+, presumably due to ion-pair type interactions which tends to vanish as the size of the cation increases. The results obtained with Bu_4N^+ were similar to those obtained in the same solvent, DMF, with Li^+ as the supporting electrolyte[14a,c] which falls in line with the fact that Li^+ being strongly solvated by DMF behaves in fact as a large cation.

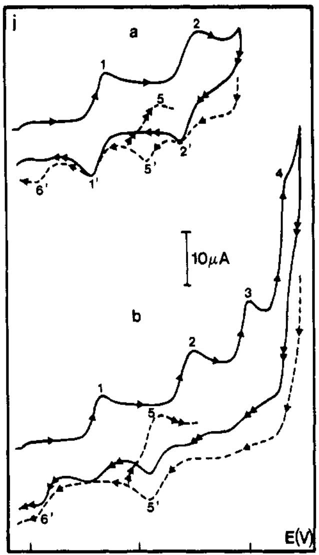

Figure 4. Cyclic voltammetry of (a-(C12)$_2$-CT)Fe^{III}Cl (1 mM) in the presence of 128 mM *n*-BuBr. Other conditions and numbering of the waves are the same as in Figures 2 and 3: a, potential scanning encompassing the formation of iron(I); b, potential scanning encompassing the formation of both iron(I) and iron("0").

corresponding iron(I) complex, our strategy was to investigate the alkylation of the former species by adding smaller amounts of an alkyl halide to characterize the resulting complex by its cyclic voltammetric and UV-vis spectrometric behavior.

Figures 2–4 summarize the cyclic voltammetric behavior observed in the case of the a-(C12)$_2$-CT porphyrin in dimethylformamide at 20 °C at a glassy carbon electrode upon addition of *n*-butyl bromide. In the absence of the latter, starting from the iron(III) chloride complex three reversible couples are seen (Figure 2) featuring the passage from Fe(III) to Fe(II) (1/1′), Fe(II) to Fe(I) (2/2′) and Fe(I) to Fe("0") (3/3′). The values of the standard potential for each couple are listed in Table I. Upon addition of small amounts of *n*-BuBr, in the millimolar range, to a millimolar solution of the iron porphyrin (Figure 3), the height of the anodic waves 3′ and 2′ decreases. That this indicates the consumption of the Fe("0") complex and not that of the Fe(I) complex by reaction with *n*-BuBr is demonstrated in Figure 3b where it is seen that no decrease of 2′ is observed when the potential scan encompasses only the 2/2′ wave and not the 3/3′ wave. Simultaneously, a new three-wave system, 4/4′, 5/5′, and 6′, intermingled with the original three-wave system shows up. Wave 5/5′ is reversible and wave 4/4′ quasi-reversible in the chemical sense whereas the anodic wave 6′ has no cathodic counterpart.[15] The same waves 5/5′ and 6′[15] are observed in an experiment where more *n*-BuBr (in the decimolar range) is added and the potential scan encompasses only the 2/2′ wave (Figure 4a). Thus, the complex obtained upon reaction of *n*-BuBr with Fe("0") has exactly the same electrochemical characteristics as that obtained upon reaction of *n*-BuBr with Fe(I).

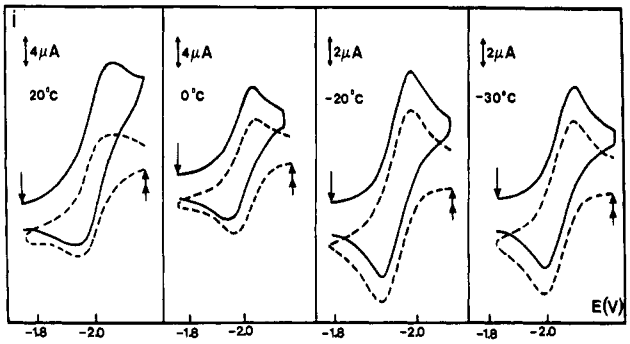

Figure 5. Cyclic voltammetry of (TPP)FeCl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$ in the presence of 2 mM *n*-BuBr as a function of temperature (sweep rate = 0.1 V·s^{-1}). Wave 4/4′ corresponding to the Fe^{II}R$^-$/Fe^{I}R^{2-} couple.

That the same complex is obtained in both cases is confirmed by thin-layer spectroelectrochemistry: the UV-vis spectrum obtained at the potential of the Fe(I)$^-$/Fe("0")$^{2-}$ couple in the presence of a small amount of *n*-BuBr is identical with that obtained at the potential of the Fe(II)/Fe(I)$^-$ couple in the presence of a large amount of *n*-BuBr.[3]

It is noteworthy that no other complex such as those resulting from the alkylation of the ring could be detected neither in cyclic voltammetry nor in UV-vis spectroelectrochemistry.

In the case of Fe(I), the σ-alkyl–iron complex is obtained first as an Fe^{III}R complex which is further reduced to the Fe^{II}R$^-$ complex by electron exchange with Fe(I)$^-$ at the potential where the reaction takes place:[14]

$$\mathrm{Fe(II)} + e^- \rightleftharpoons \mathrm{Fe(I)}^-$$

$$\mathrm{Fe(I)}^- + \mathrm{RX} \rightarrow \mathrm{Fe^{III}R} + \mathrm{X}^-$$

$$\mathrm{Fe^{III}R} + \mathrm{Fe(I)}^- \rightarrow \mathrm{Fe^{II}R}^- + \mathrm{Fe(II)}$$

In the case of Fe("0"), the reaction with *n*-BuBr yields directly the Fe^{II}R$^-$ complex:

$$\mathrm{Fe(``0")}^{2-} + \mathrm{RX} \rightarrow \mathrm{Fe^{II}R}^- + \mathrm{X}^-$$

We note that much less *n*-BuBr is required to obtain the σ-alkyl complex in the second case than in the first. The reactivity of Fe("0") toward alkyl halides is thus much larger than that of Fe(I) as expected from the higher electron density contained in the first species as compared to the second.

Quite similar qualitative results were obtained with the other three investigated porphyrins. However, the electrochemical and chemical reactivities vary in the series. The standard potentials of the Fe(II)/Fe(I)$^-$, Fe(I)$^-$/Fe("0")$^{2-}$, Fe^{III}R$^-$/Fe^{II}R$^-$, and Fe^{II}R$^-$/Fe^{I}R^{2-} are listed in Table I for each porphyrin. The reactivity of Fe("0") toward *n*-BuBr was found to vary in the order a-(C12)$_2$-AC $\lesssim$ a-(C12)$_2$-CT < TPP < OEP.

As noted previously, the reversibility of the Fe^{II}R$^-$/Fe^{I}R^{2-} (4/4′) wave is not complete at room temperature at 0.1 V·s^{-1}. The reversibility at a given temperature increases upon raising the sweep rate. Likewise, at a given sweep rate, reversibility increases upon lowering the temperature. Figure 5 illustrates the latter point in the case of TPP.

Similar results are obtained with *n*-butyl chloride and iodide. As seen in Figure 6 from the peak heights of the new system of waves (4/4′–5/5′–6′), the reactivity of the

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(15) (a) Wave 6 becomes reversible upon raising the sweep rate up to 50 V·s^{-1} as already described.[3] (b) The irreversibility of wave 6 observed at lower sweep rates indicates a cleavage of the carbon–iron bond. The ensuing fate of the R moiety—is it trapped by species present in the solution or by a porphyrin nitrogen[15c]—is not presently known. This wave was used here only for the purpose of fingerprinting the alkyl–iron complex by its whole cyclic voltammetric behavior. (c) Examples of alkyl, acyl, and aryl migration from the central metal to a porphyrin nitrogen upon oxidation have been described in the case of cobalt porphyrins.[15d,e] With iron porphyrins, only the migration of a phenyl group has been described thus far.[15f,g] In the case of an alkyl group there is thus far no evidence either against or in favor of such a reaction. (d) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348. (e) Callot, H. J.; Cromer, R.; Louati, A.; Gross, M. *Nouv. J. Chim.* **1984**, *8*, 765. (f) Lançon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472. (g) Lançon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *Organometallics* **1984**, *3*, 1164.

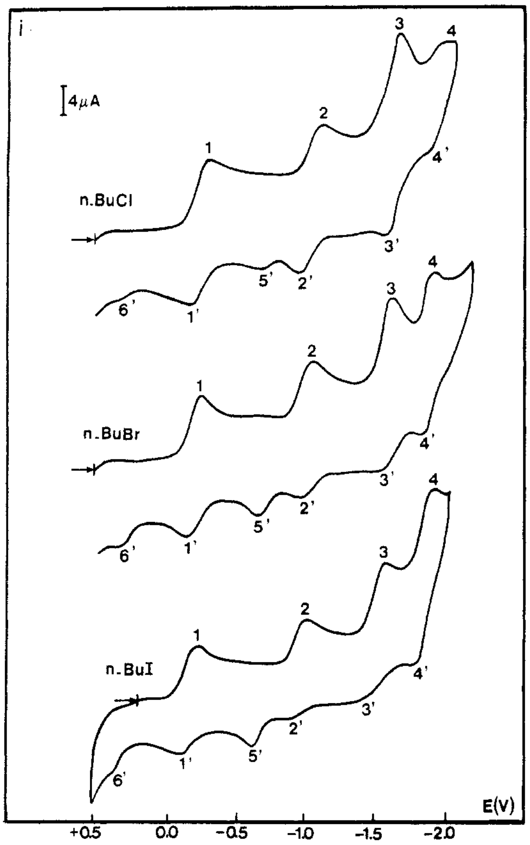


Figure 6. Cyclic voltammetry of (a-(C12)$_2$-CT)Fe^{III}Cl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$ in the presence of 0.5 mM n-BuCl, n-BuBr, or n-BuI (temperature = 20 °C; sweep rate = 0.1 V·s^{-1}). Numbering of the waves is the same as in Figures 2 and 3.

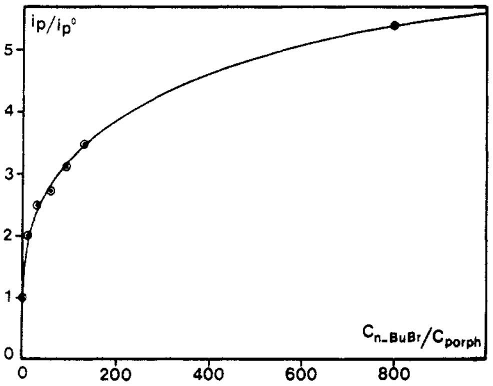
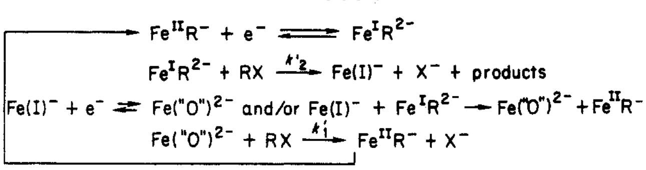


Figure 7. Cyclic voltammetry of (a-(C12)$_2$-CT)Fe^{III}Cl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$. Variations of the peak height of wave 4 (reduction of Fe^{II}-n-Bu$^-$) with the concentration of n-BuBr (i_p = observed peak current; i_p^0 = peak current corresponding to the reversible exchange of one electron per molecule).

Scheme I



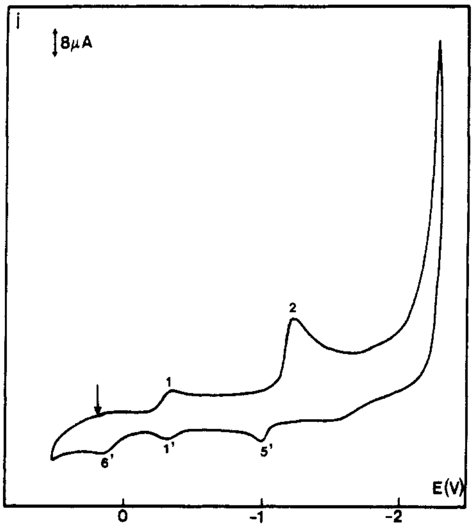


Figure 8. Cyclic voltammetry of (OEP)Fe^{III}Cl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$ in the presence of 100 mM n-BuBr (temperature = 20 °C; sweep rate = 0.1 V·s^{-1}).

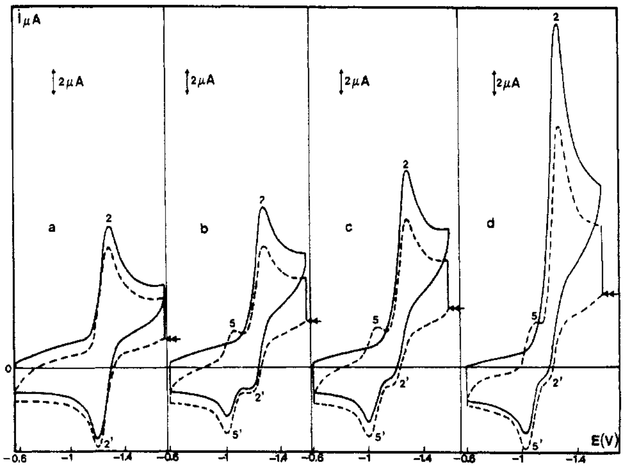


Figure 9. Cyclic voltammetry of (OEP)Fe^{III}Cl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$ in the presence of increasing amounts of n-BuBr. Variations of the Fe(II)/Fe(I)$^-$ (2/2′) and Fe^{III}R/Fe^{II}R$^-$ (5/5′) waves. Concentration of n-BuBr: a, 0; b, 20 mM; c, 80 mM; d, 900 mM (temperature = 5 °C; sweep rate = 0.1 V·s^{-1}). Direct (—) and reverse (- - -) potential scannings.

three halides on Fe("0") varies in the order Cl < Br < I.

Catalysis of the reduction of alkyl halides, for example, n-BuBr, can be obtained with both the electrogenerated Fe(I) and Fe("0") complexes.

In regard to Fe("0")$^{2-}$, this is seen in Figure 4b: addition of 0.1 M n-BuBr results in a large increase and a loss of reversibility of the Fe^{II}R$^-$/Fe^{I}R^{2-} wave 4/4′. As shown in Figure 7, the height of this wave increases regularly upon increasing the n-BuBr concentration, reaching values that are significantly above two electrons per molecule of porphyrins, thus clearly indicating the catalytic character of the wave. No complex other than the σ-alkyl–iron complex appears to be formed during this process. It is noticed that catalysis occurs not at the Fe(I)/Fe("0") reduction wave but rather at the Fe^{II}R$^-$/Fe^{I}R^{2-} wave, suggesting the mechanism shown in Scheme I, i.e., a typical bond-forming/bond-breaking chemical catalysis scheme as described in the introduction.

The (OEP)Fe("0")$^{2-}$ complex appears to give rise to a more efficient catalysis than the other three porphyrins. The 4/4′ wave is, however, so negative in this case that it merges with the current rise featuring the direct reduction of n-BuBr at the electrode (Figure 8). It is also noticed that, at about the same concentration of n-BuBr wave 3/3′ disappears in the case of OEP, whereas it is still present in the case of a-(C12)$_2$-CT (Figure 4b). This is due to the fact that the reactivity of Fe(I) toward n-BuBr is significantly larger in the first case than in the second.[3]

Catalysis of the n-BuBr reduction can also be obtained at the potential of the Fe(II)/Fe(I)$^-$ wave. It is, however, much less efficient than in the case of the Fe^{II}R$^-$/Fe^{I}R^{2-} wave. Quite large amounts of n-BuBr must be added in

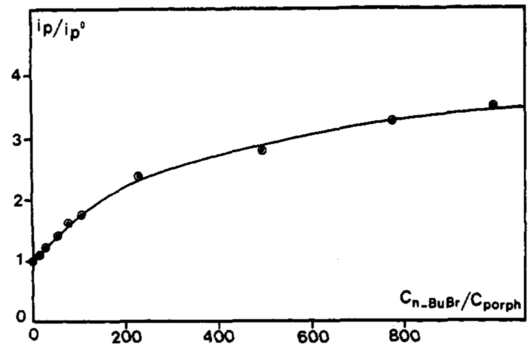
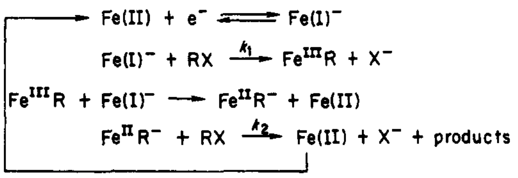


Figure 10. Cyclic voltammetry of (OEP)Fe^{III}Cl (1 mM) in DMF + 0.1 M NMe$_4$BF$_4$. Variations of the peak height of wave 2 (reduction of Fe(II)) with the concentration of n-BuBr (i_p = observed peak current; i_p^0 = peak current corresponding to the reversible exchange of one electron per molecule; temperature = 5 °C; sweep rate = 0.1 V·s^{-1}).

Scheme II



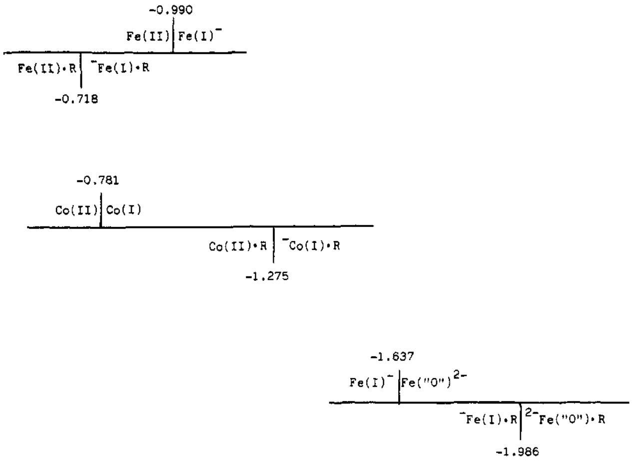
order to observe a significant increase of the wave for most of the four porphyrins. The OEP complex appears as significantly more reactive in this respect than the three others. Figure 9 shows the variations of the Fe(II)/Fe(I)$^-$ and Fe^{III}R/Fe^{II}R$^-$ waves upon addition of increasing amounts of n-BuBr. The peak height for the reduction of Fe(II) increases with the concentration of n-BuBr, reaching a value which corresponds to 3.2 electrons per molecule for a molar solution of n-BuBr (Figure 10). This demonstrates the catalytic character of the reaction. Upon addition of n-BuBr, wave 5/5′ which features the Fe^{III}R/Fe^{II}R$^-$ couple increases first and then decreases at high concentrations of n-BuBr. This falls in line with the chemical catalysis mechanism shown in Scheme II,[16] which is of the same type as with Fe("0") except that then the standard potential of the Fe^{III}R/Fe^{II}R$^-$ couple is positive with respect to that of the Fe(II)/Fe(I)$^-$ couple, whereas the Fe^{II}R$^-$/Fe^{I}R^{2-} couple is negative with respect to the Fe(I)$^-$/Fe("0")$^{2-}$ couple. This is the reason why catalysis can be obtained at the Fe(II)/Fe(I)$^-$ wave, whereas this was not possible at the Fe(I)$^-$/Fe("0")$^{2-}$ wave.

Discussion

One of the most important of the above described results is the observation that the reaction of the doubly reduced iron(II) complexes, iron("0"), with alkyl halides results in the formation of a σ-alkyl–iron complex without significant alkylation or protonation of the porphyrin ring as would be expected[17] if the iron(II) dianion resonance form of the iron("0") complex would be dominant. The alkylation of iron in the iron("0") complex is thus best rationalized in terms of an iron(I) anion radical and/or a true iron(0) resonance form. In both cases, one could envisage the occurrence of a direct S$_N$2 reaction or of an electron-transfer reaction followed by a rapid coupling of the ensuing alkyl radical and iron(I) complex:

$$[\mathrm{P(Fe^0)^{2-}} \leftrightarrow {}^{-\bullet}\mathrm{P(Fe^I)^-}] + \mathrm{RX} \rightarrow \mathrm{P(Fe^I)^-} + \mathrm{R^\bullet} + \mathrm{X^-} \rightarrow \mathrm{PFe^{II}R^-}$$

Chart I[a]



[a] The standard potentials are for the TPP complexes.

The σ-alkyl-iron complexes can be observed, by means of cyclic voltammetry under three successive oxidation states, formally as Fe^{III}R, Fe^{II}R$^-$, and Fe^{I}R^{2-}. It is remarkable that the latter complex is stable, at least within the time scale of cyclic voltammetry. This adds a new example to the short series of thus far observed axially coordinated iron(I) porphyrins.[5e,13a,18] The nature of the dominant resonance form of the σ-alkyl–iron(I) complex is open to question for the moment. In view of the large electron density introduced by the carbanion ligand, the dominant resonance form may well be the anion radical of the σ-alkyl–iron(II) complex.

The comparison between the potential location of the various oxidation states of the σ-alkyl complex and of those of the starting porphyrin shows an interesting phenomenon, while the Fe^{III}R/Fe^{II}R$^-$ couple is positive with respect to the Fe(II)/Fe(I)$^-$ couple, the Fe^{II}R$^-$/Fe^{I}R^{2-} couple is negative with respect to the Fe(I)$^-$/Fe("0")$^{2-}$ couple. In the second case, the order of the standard potentials is thus exactly the same as for the isoelectronic series of Co^{III}R/Co^{II}R$^-$ vs. Co(II)/Co(I)$^-$ porphyrins and vitamin B$_{12}$ derivatives.[4b] This is best rationalized in terms of mesomeric forms in which the alkyl ligand appears as a radical (Chart I). Since Fe(I) and Co(II) have a radical character whereas Fe(II), Co(I), and Fe("0") have not, association with R$^\bullet$ tends to stabilize Fe(I) vs. Fe(II), Co(II) vs. Co(III), and Fe(I) vs. Fe("0"), generating the observed shifts of potentials in each of the three cases.

The variations of the electrochemical and chemical reactivities with the structure of the porphyrin described above can be rationalized in the following way.

The comparison between OEP and TPP shows that all four characteristic standard potentials (Table I) are more negative in the first case than in the second. This results from the electron-donating effect of the eight ethyl groups in OEP as compared to TPP. It is observed that the electron-donating effect of the ethyl groups falls in the following order Fe(II)/Fe(I)$^-$ < Fe^{III}-n-Bu/Fe^{II}-n-Bu$^-$ <

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[16] (a) Since the reaction of n-BuBr on Fe(I)$^-$ is rather slow (25 M^{-1}·s^{-1}), the Fe^{III}R complex is formed far from the electrode surface and has therefore time, while diffusion back to the electrode, to be reduced by Fe(I)$^-$ molecules before reaching the electrode surface and being reduced there. For a quantitative discussion of this ECE–DISP problem see ref 16b and references cited therein. (b) Amatore, C.; Gareil, M.; Savéant, J. M. *J. Electroanal. Chem.* **1983**, *147*, 1.

[17] Lund, H.; Simonet, J. *J. Electroanal. Chem.* **1975**, *65*, 205.

[18] (a) The (formally) iron(I)–phenyl complex of a particular porphyrin, the tetracyanotetraphenylporphyrin, has recently been detected by cyclic voltammetry. No other characterization than an ill-defined UV–vis spectrum was reported.[18b] (b) Kadish, K. M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 2148.

$Fe(I)/Fe(“0”)^{2-} < Fe^{II}\text{-}n\text{-}Bu^-/Fe^{I}\text{-}n\text{-}Bu^{2-}$, indicating that the electron density on the electroactive part of the molecule is as expected: larger for $Fe(“0”)^{2-}$ and $Fe^{II}\text{-}n\text{-}Bu^-$ than for $Fe(I)^-$ and larger for $Fe^{I}\text{-}n\text{-}Bu^{2-}$ than for $Fe(“0”)^{2-}$. The fact that $Fe(“0”)^{2-}$, as observed here, as well as $Fe(I)^-$, as observed previously,[3] are more reactive toward alkyl halides in the case of OEP than in that of TPP derives from the same electronic inductive effect.

The presence of the amide-linked basket-handle chains anchored at the ortho position of the phenyl rings of TPP also exerts a strong influence on the reactivities. As observed before,[14a,c] the standard potentials of the $Fe(II)/Fe(I)^-$ and $Fe(I)^-/Fe(“0”)^{2-}$ couples become significantly more positive when passing from TPP to the two superstructured porphyrins. As discussed previously,[14a] this results from the strong dipole–charge interactions between the secondary amide groups and the single or double negative charge borne by the porphyrin. The effect is more pronounced for the AC than for the CT isomer (Figure 1) because additional stabilization of the negatively charged species by external solvation is more effective in the first case than in the second.[14a,c] The same is observed with the $Fe^{III}R/Fe^{II}R^-$ and the $Fe^{II}R^-/Fe^{I}R^{2-}$ couples which can be interpreted in the same manner. Stabilization is about the same for the $Fe^{III}R/Fe^{II}R^-$ and the $Fe(II)/Fe(I)^-$ couples, but it is significantly greater for $Fe^{II}R^-/Fe^{I}R^{2-}$ than for $Fe(I)^-/Fe(“0”)^{2-}$, thus indicating that more electron density is concentrated in the field created by the CONH groups in the case of $Fe^{I}R^{2-}$ than in that of $Fe(“0”)^{2-}$. A related effect has previously been shown to occur with the binding of carbon monoxide to iron(I) porphyrins.[13b]

The fact that iron(“0”) is alkylated at the iron atom without significant alkylation of the porphyrin ring provides a new system for chemically catalyzing the reduction of alkyl halides. This can be compared with the systems based on the electrochemical generation of iron(I) and cobalt(I) porphyrins. It appears that the iron(“0”) system is more efficient than the iron(I) system because both the bond-forming (eq 2) and the bond-breaking (eq 4) reactions are faster in the first case than in the second. It remains to measure precisely the rate constants of these two steps in each case which is currently in progress on the basis of a newly developed procedure for treating the cyclic voltammetric data in the context of bond-forming/bond-breaking chemical catalysis of the electrochemical reaction.[19] The product distribution in preparative scale electrolysis is also under current investigation with the aim of comparing the Fe(“0”), Fe(I), and Co(I) systems and the direct electrochemical reduction.

Experimental Section

Chemicals. $Fe^{III}(TPP)Cl$ and $Fe^{III}(OEP)Cl$ were from commercial origin and used as received. The two basket-handle porphyrins were synthesized and characterized as already described.[20] The DMF was vacuum distilled before use. Particular care must be exercised as to the purity of the tetraalkylammonium supporting electrolyte. Remaining traces of the alkyl halides used for their synthesis rapidly react with the Fe(“0”) porphyrins.[21] NMe_4BF_4 (Fluka) was found more satisfactory in this respect than a number of other tetraalkylammonium salts from commercial origin.

Instrumentation for cyclic voltammetry and thin-layer electrochemistry was the same as previously described.[13b,14] The working electrode was a glassy carbon disk and the reference electrode an aqueous saturated NaCl calomel electrode to which all potentials are referred throughout the paper.

Acknowledgment. Dr. M. Momenteau (Institut Curie, Orsay, France) is thanked for the gift of samples of the two basket-handle porphyrins. We thank Mrs. M. Jomain for her help with the UV–vis spectroscopy experiments.

Registry No. (OEP)FeCl, 28755-93-3; (TPP)FeCl, 16456-81-8; (a-$(C12)_2$-CT)FeCl, 90838-12-3; (a-$(C12)_2$-AC)FeCl, 90898-41-2.

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[19] Lexa, D.; Savéant, J. M.; Su, K. B.; Wang, D. L., in preparation.

[20] Momenteau, M.; Mispelter, J.; Look, B.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 221.

[21] The mysterious “form A” found in the electrochemical preparation of $Fe^{I}TPP^{4b}$ has the same UV–vis spectrum as a $Fe^{II}R^-$ complex. This is likely to be formed upon slow reaction of the Fe(I) complex with alkylating impurities in the supporting electrolyte.