prepared containing *p*-dichlorobenzene (22.0 mg, 0.150 mmol, 0.150 M) in dry $CDCl_3$, dry C_6D_6, or 0.15 M *p*-dichlorobenzene and acetic acid (63 μL, 66 mg, 1.1 mol, 1.1 M) in dry C_6D_6. The peroxide **6** was weighed into three 5-mm NMR tubes (40 mg, 0.40 mmol) and combined with 0.15 M *p*-dichlorobenzene in $CDCl_3$, 0.15 M *p*-dichlorobenzene in C_6D_6, or 0.15 M *p*-dichlorobenzene and 1.1 M acetic acid in C_6D_6 (0.40 mL). The solutions were mixed thoroughly, and the concentration of **6** relative to the internal standard, *p*-dichlorobenzene, was determined by ^1H NMR spectroscopy using the ratio of integrated areas of the peaks at δ 6.83 (C_6D_6) or 6.87 ($CDCl_3$) (s, 4 H) and δ 4.14 (C_6D_6) or 4.53 ($CDCl_3$) (s, 2 H) which corresponded to the internal standard and **6**, respectively.

The three NMR tubes were heated at 45.0 °C in a thermostated oil bath for 66 h. ^1H NMR spectra were recorded periodically and [**6**] relative to the internal standard was calculated for each time. Graphs were constructed from these data showing the decrease in [**6**] vs. time, and a value of $t_{1/2}$ (half-life) of [**6**] was determined from the graphs. Since thermolysis of **6** in nonpolar solvents is first order in [**6**],[21] the rate constant for disappearance (k) of **6** was calculated from the relation of $k = 0.693/t_{1/2}$.

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Registry No. 6, 279-35-6; **6**-d_6, 81477-78-3; **8**, 626-96-0; **9**, 26831-63-0; **10**, 930-30-3; hexadeuteriocyclopentadiene, 2102-16-1.

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Communications to the Editor

Arylation and Vinylation of Iron Porphyrins. Double Electrochemical Induction of a Nucleophilic Substitution

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There have been so far relatively few reports of the synthesis of σ-alkyl-, σ-aryl-, and σ-vinyliron porphyrins. A first route to these complexes is carbanion transfer from a Grignard reagent to the iron(III) porphyrin. Ethyl-[1a] phenyl- (or *p*-tolyl)-),[1] and 1,1'-diphenylethenyliron(III)[2] porphyrins have been prepared according to this reaction. Another possible way of generating the σ-alkyl complexes is by reacting an alkyl radical with an iron(II) porphyrin. Evidence has been provided for the formation along this route of σ-methyl- and mono-, di-, and trichloromethyliron porphyrins in pulse radiolysis studies.[3] More recently, several σ-alkyl iron porphyrins have been prepared in solution both under their Fe(III) and Fe(II) oxidation states by reacting aliphatic halides with electrogenerated iron(I) porphyrins.[4] The iron(I) complex there appears to function as the nucleophile in an S_N2-type nucleophilic substitution.

The extension of such a reaction to arylations and vinylations involving nonactivated aryl or vinyl halides seems a priori precluded by the inertness of these reagents toward nucleophilic substitution. It has, however, been shown that aromatic nucleophilic substitutions can be triggered electrochemically through reduction of the aryl halide.[5] The aryl radical thus generated is able to react with soft nucleophiles yielding the anion radical of the substitution product (SR_N1 substitution[6a]). Vinylic substitutions have also been carried out in the same context by using photostimulation.[6b] It is therefore conceivable that σ-aryl- and σ-vinyliron porphyrins could be formed by reacting the corresponding halides with electrogenerated iron(I) porphyrins under electrochemical stimulation of the substitution reaction. The electrochemical inducement would thus serve a double purpose: generate the nucleophile, i.e., the iron(I) porphyrin from the starting iron(III) complex and provide the electrons required for the stimulation of the aromatic (or vinylic) substitution. The preliminary results reported hereafter do show that σ-aryl- and σ-vinyliron porphyrins are formed upon electrolysis of a mixture of aryl or vinyl halides with an iron porphyrin provided the electrode potential is such that the aryl (or vinyl) radicals be generated in the presence of the iron(I) complex. To our knowledge, this is the first report of electrochemical induction of a nucleophilic substitution reaction in the field of organometallic chemistry.

A first example is shown on the Figure 1. The iron porphyrins display three chemically reversible waves corresponding to the successive formation of the species indicated on the figure. 4-Bromobenzonitrile shows one irreversible wave featuring the reductive cleavage into benzonitrile followed by the reversible one-electron wave of benzonitrile. The former is located slightly in front of the Fe(I)/Fe(I)$^{-\cdot}$ wave. When the potential scan is started in between the first and second 4-bromobenzonitrile wave and is swept anodically and then cathodically (Figure 1c), a new set of waves appears at the expense of that featuring the original porphyrin. This indicates the formation of a new complex. The location and characteristics of its waves (one reversible wave at $E° = -0.84$ V vs. SCE and one irreversible wave at $E_p = 0.2$ V for $v = 0.2$ V s^{-1}) are very close to those of the σ-alkyl complexes previously described.[4] Further evidence that a σ-aryliron complex is actually formed is provided by thin-cell spectroelectrochemistry. Electrolysis at −1.8 V, i.e., at the first 4-bromobenzonitrile wave, leads to the observation of a spectrum (λ_{max} = 348 nm (ϵ 4.50 × 10^4 M^{-1} cm^{-1}), 422 (1.76 × 10^5), 506 (1.76 × 10^4), 536 (1.61 × 10^4), 777 (0.56 × 10^4)) similar to those of the Fe^{III}R$^-$ complexes previously described.[4] Reoxidation at −0.7 V leads to a spectrum (λ_{max} = 422 (ϵ 1.49 × 10^5 M^{-1} cm^{-1}), 536 (1.27 × 10^4) similar to that of a FeIIIR$^-$ complex.[4] It is noted that no arylation occurs when the starting potential is set up just beyond the Fe(II)/Fe(I) wave (Figure 1d). This points to the necessity of generating aryl

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(7) C_{12}(TPP) designates a cross-trans-linked basket-handle porphyrin with two 12-carbon aliphatic chains bound through an ether linkage to the ortho positions of two opposite phenyl rings, one chain above the porphyrins ring, the other below.[8] This structure possesses the advantage of preventing μ-oxo dimer formation.

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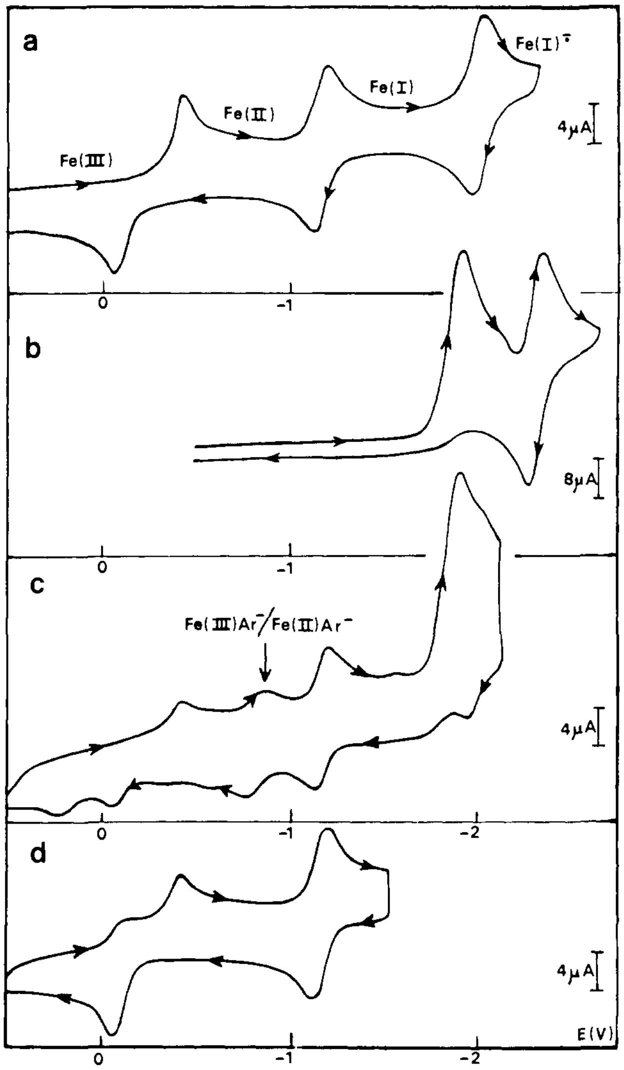

Figure 1. Cyclic voltammetry of $\mathrm{FeC_{12}(TPP)}$ in the presence of 4-bromobenzonitrile in DMF and 0.1 M $\mathrm{NBu_4BF_4}$ (working electrode, glassy carbon disc; reference electrode, aqueous SCE; sweep rate, 200 mV $\mathrm{s^{-1}}$): (a) $\mathrm{FeC_{12}(TPP)}$ (5×10^{-4} M) alone; (b) 4-bromobenzonitrile (7×10^{-4} M) alone; (c) $\mathrm{FeC_{12}(TPP)}$ (5×10^{-4} M) and 4-bromobenzonitrile (7×10^{-4} M) starting the potential scan at −2.1 V and scanning first anodically then cathodically; (d) $\mathrm{FeC_{12}(TPP)}$ (5×10^{-4} M) and 4-bromobenzonitrile (7×10^{-4} M) starting the potential scan at −1.5 V and scanning first anodically then cathodically.

radicals for the arylation of the iron porphyrin to occur. Arylation is, however, observed at this potential under spectroelectrochemical conditions that correspond to more efficient electrolysis than the cyclic voltammetric conditions. Aryl radicals can indeed be slowly generated at the Fe(II)/Fe(I) wave through redox catalysis of the reduction of 4-bromobenzonitrile.[9]

Similar behaviors were found with iodobenzene and 1-bromonaphthalene by using the same porphyrin. The spectra of the $\mathrm{Fe^{III}Ph^-}$ and $\mathrm{Fe^{II}Ph^-}$ complexes were found to be very similar to those of the 4-cyanophenyl and the alkyl complexes.[4] The spectrum found for $\mathrm{Fe^{III}Ph^-}$ was practically the same as that previously described for $\mathrm{(TPP)Fe^{III}Ph^-}$.[1c] Vinylation appears to occur in the same way. 1-Bromo-2,2-bis(4-chlorophenyl)ethylene gives rise to an irreversible wave located just behind the TPP $\mathrm{Fe(I)/Fe(I)^{-}\cdot}$ wave which then becomes irreversible, indicating that redox catalysis of the reduction of the vinylic chloride by the $\mathrm{Fe(I)/Fe(I)^{-}\cdot}$ couple is taking place. Starting the potential scan at the level of this wave or on the vinyl halide wave results in the formation of the σ-vinyliron porphyrin, which gives rise to a $\mathrm{(TPP)Fe^{III}Vi^-/Fe^{II}Vi^-}$ reversible wave at $E° = -0.63$ V and an irreversible oxidation wave at $E_p = +0.6$ V ($v = 0.2$ V $\mathrm{s^{-1}}$). The spectra of the $\mathrm{Fe^{III}Vi^-}$ and $\mathrm{Fe^{II}Vi^-}$ complexes were recorded under the same spectroelectrochemical conditions as above. The spectrum of the $\mathrm{(TPP)Fe^{II}Vi^-}$ complex was found to be exactly the same as for the same compound (λ_{max} = 355 nm (ε 2.66 10^4 $\mathrm{m^{-1}\,cm^{-1}}$), 428 (8.08×10^4), 510 (1.38×10^4), 800 (0.46×10^4)) obtained from electrochemical hydrogenation of the corresponding carbene complex: $\mathrm{Fe(II){\leftarrow}C{=}C(\textit{p}\text{-}ClC_6H_4)_2}$. The generation of $\mathrm{Fe^{II}Vi^-}$ at the Fe(II)/Fe(I) wave can also be observed as in the case of 4-bromobenzonitrile.

All these observations are compatible with a reaction mechanism involving the direct or indirect electrochemical generation of aryl (or vinyl) radical from the aryl (or vinyl) halide and its reaction with the electrochemically generated Fe(I) porphyrin yielding the Fe(II) σ-aryl (or -vinyl) porphyrins, which can then be reoxidized electrochemically into the Fe(III) σ-aryl (or -vinyl) complex. The possible interference of the Fe(II) and $\mathrm{Fe(I)^{-}\cdot}$ complexes in the reaction should, however, be more carefully investigated. This study is underway in an effort to assess more soundly the reaction mechanism through the study of the competition between the reaction of the aryl (or vinyl) radicals with the iron porphyrins and of side reactions such as reduction at the electrode or in the solution and H atom abstraction from the solvent.[5] The ESR and NMR characteristics of these complexes are currently under investigation.

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Registry No. $\mathrm{FeC_{12}(TPP)}$, 70196-65-5; 4-bromobenzonitrile, 623-00-7; iodobenzene, 591-50-4; 1-bromonaphthalene, 90-11-9; 1-bromo-2,2-bis-(4-chlorophenyl)ethylene, 23349-12-4.

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Chemiluminescence from a Phenoxide-Substituted 1,2-Dioxetane: A Model for Firefly Bioluminescence

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The chemiluminescent decomposition of 1,2-dioxetanes has been an active area of investigation.[1] Simple, isolable dioxetanes such as tetramethyl-1,2-dioxetane are relatively stable and afford predominantly triplet excited products upon thermolysis. These properties are, however, in sharp contrast to those of the key intermediate **2a**[2] in firefly bioluminescence.[3] The bioexcitation efficiency for the formation of singlet excited **3a** from **2a** is at

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