Electrochemical Characterization of Iron(II) and Iron(I) Phthalocyanine–Amine Derivatives

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Abstract: Electron transfer reactions and ligand binding properties of iron(II) and iron(I) phthalocyanine, PcFe and PcFe⁻, were investigated in Me_2SO by the techniques of cyclic voltammetry and polarography. Addition of substituted pyridines or imidazoles to PcFe in Me_2SO produced either a five-or six-coordinate amine complex depending on the ligand concentration in solution. Ten amine complexes were investigated. For five of these, reduction of $PcFe(B)_2$ involved a single electron to yield the five-coordinate iron(I) complex, $PcFe(B)^{-1}$. Two complexes could be reduced by a simultaneous two-electron transfer to yield a species identified as $PcFe(B)^{2-}$. Formation constants were calculated for each identified complex of iron(II) and iron(I) and three different electron transfer mechanisms were elucidated.

Recently, several studies have reported the effect of solvent, supporting electrolyte, and ring basicity on the reversible half-wave potentials of tetraphenylporphyrins.[2-4] It has been shown that appropriate attachment of electron-donating or electron-withdrawing groups to the porphyrin ring would produce a shift in potentials as defined by the Hammett linear free energy relationship and that this shift was not identical for each type of electrode reaction. Consequently, it should be theoretically possible to "tune" electron transfer reactions such that (a) a desired potential, (b) a desired number of electrons transferred (one or more), and/or (c) a desired electrode reaction type, i.e., metal or porphyrin ring, would preferentially occur for a given set of substituents. However, the relative potential shifts with changes in ring basicity were small, and only with complexes of nickel tetraphenylporphyrin could a significant change be observed.[5] In this example less than 100 mV initially separated the metal and ring oxidation, and these could, through proper substituent selection, either be isolated to yield two one-electron transfers or merged to give a single two-electron oxidation.

Similarly, changes in solvent, counterion, or axial ligand will produce shifts in redox potentials due to stabilization of either the oxidized or reduced form of the complex. However, changes in common polarographic solvents or counterions produced shifts mainly in the metal(III) ⇌ metal(II) equilibria[2,3] which for most metalloporphyrins and phthalocyanines (with the exception of nickel) are already separated from the radical reaction by up to 1200 mV.[6]

In this paper we report the first "tuning" of an iron phthalocyanine electrode reaction with the appropriate selection of axial coordination such that two reversible electrode reactions which are initially separated by over 400 mV have been merged to produce a single reversible two-electron transfer step.

Studies of phthalocyanines and its metal derivatives have been the subject of many spectroscopic investigations.[7] Most transition metals and many of the alkali earth metals form square planar complexes with phthalocyanines.[8] Octahedral complexes may also be formed by axial complexation of the metallophthalocyanine with donor ligands.[9] Investigations have focused on the reactions of iron phthalocyanine as a heme model system.[10] Specifically, the axial binding of nitrogenous bases,[11,12] CO,[13,14] NO,[15] and O_2[16] have been intensively studied and compared to the well-characterized iron porphyrin systems. PcFe complexes with organic bases have also been reported and characterized through Mossbauer, ESR, NMR, and magnetic properties.[5,6,15,17,19]

Figure 1 shows the structure of iron phthalocyanine, PcFe.

The iron is located at the center of four planar nitrogen atoms in the phthalocyanine ring and has an oxidation state of +2. The higher oxidation state (+3) of PcFe has been reported by Lever[17] while treatment with thionyl chloride or HCl[18] yields either a monohalide or dihalide complex with halide bound to iron on either side of the phthalocyanine ring.

Despite the recent interest in PcFe reactions, a systematic study of how thermodynamics of ligand addition to PcFe and PcFe⁻ affect the mechanisms and potentials for oxidation-reduction of these complexes has not been published. Therefore, we have undertaken[20] an in-depth investigation of the stability constants of iron phthalocyanine complexes in Me_2SO and have attempted to relate these results to the thermodynamics and kinetics associated with electron transfer reactions between phthalocyanine complexes of Fe(II), Fe(I), and the anion radical.

In this study we report the thermodynamic stability of $PcFeB_2$, PcFeB, and PcFeB⁻, where B is a substituted pyridine, I, or a substituted imidazole, II. Three different electron transfer mechanisms are proposed for the complexes of I and II with iron phthalocyanine.
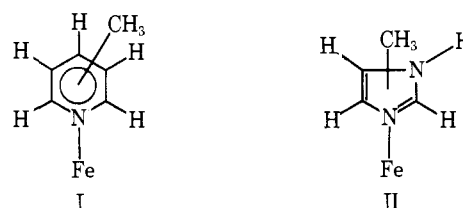
Experimental Section

Chemicals. Iron phthalocyanine, 3-picoline, and 4-picoline were purchased from Eastman Co. Pyridine was obtained from Fisher Scientific. Imidazole was purchased from Aldrich Chemical Co. Imidazole, 2-methylimidazole, and 1,2-dimethylimidazole were recrystallized from benzene prior to use. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP), products of Eastman Co., were dried at reduced pressure over P_4O_{10} at room temperature. These were used interchangeably as supporting electrolytes. Dimethyl sulfoxide (Me_2SO, Spectroquality, Eastman Co.) was shaken over activated molecular sieves and stored under nitrogen. Except where noted, all chemicals were used as obtained from their manufacturer.

Instrumentation. Polarographic measurements were made on a Princeton Applied Research (PAR) Model 174 polarographic analyzer utilizing a three-electrode system. A platinum wire served as the counter electrode and a commercial saturated calomel electrode (SCE) was utilized as the reference electrode. The SCE was separated
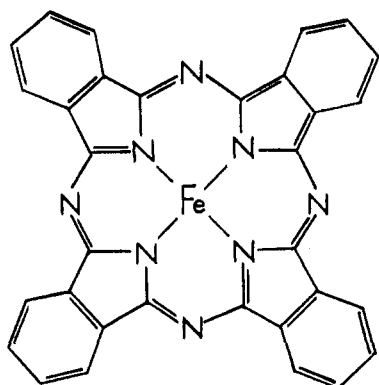
Figure 1. The structure of iron phthalocyanine, PcFe.

POTENTIAL (volts vs. SCE)

Figure 2. Cyclic voltammograms of 1.18 mM PcFe in Me₂SO/imidazole mixtures containing 0.1 M TEAP. Scan rate 0.100 V/s. Imidazole concentrations: (a) 0.00 M; (b) 0.01 M; (c) 0.95 M.

from the bulk of solution with a fritted-glass bridge filled with solvent and supporting electrolyte. Cyclic voltammetric measurements were made with a PAR Model 173 potentiostat/galvanostat driven by a PAR Model 175 universal programmer. Scans were recorded either on a Houston Omnigraphic 2000 XY recorder or on a Tektronix Model 5111 storage oscilloscope with camera attachment. A three-electrode system was utilized as above, but with the dropping mercury electrode (DME) being replaced by a platinum button. Current-voltage curves were collected at 0.02–10 V/s, while all titrations were recorded at 50 mV/s. At faster scan rates IR loss was held to a minimum by the use of a positive feedback device built into the Model 173 potentiostat. Spectroscopic measurements were taken on either a Cary 15 or a Beckman Model 26 spectrophotometer. Absorbances were taken only after equilibrium conditions were obtained. These conditions were determined spectroscopically for each ligand prior to performing optical titrations.

Measurement of Stability Constants. Changes in axial coordination upon electron transfer were determined by shifts in polarographic half-wave potentials as a function of the ligand concentration. Anodic or cathodic shifts in potential from the uncomplexed phthalocyanine depend on both the concentration of the free ligand in solution and the magnitude of the stability constant as shown in the equation

$$(E_{1/2})_c = (E_{1/2})_s - \frac{0.059}{n} \log \frac{K_{ox}}{K_{red}} - \frac{0.059}{n} \log (L)^{p-q} \quad (1)$$

at 25 °C. $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complexed and uncomplexed oxidized species, respectively; K_{ox} and K_{red} are the formation constants of the oxidized and reduced complexes; (L) is the free concentration of the complexing ligand; p and q are the number of ligands bound to the oxidized and reduced species, respectively; and n is the number of electrons transferred in the diffusion-controlled reaction.[21]

Half-wave potentials were measured for the uncomplexed iron phthalocyanine in Me₂SO and during electrochemical titrations with each nitrogenous base. The number of electrons transferred was determined by both polarographic wave analysis and cyclic voltammetry. Plots of $E_{1/2}$ vs. log (ligand) were constructed, and from the slope, the coordination number of the complex was determined using eq 1. Insertion of p and q into this equation yielded the ratio of the formation constants (K_{ox}/K_{red}) for PcFe(B)₂ or PcFe(B) and PcFe(B)⁻. Independent determination of K_1 (K_{red}) for PcFe(B)⁻ formation was accomplished by electrochemically monitoring the reduction of the iron(I) complex to the anion radical. For those complexes where the nitrogenous base did not bind the radical ($q = 0$) the formation constant (K_{red}) could be determined directly from the shift of $E_{1/2}$ with log (L). Insertion of K_{red} into K_{ox}/K_{red} enabled us to explicitly determine K_{ox}. For two complexes, formation constants were verified by plots of log $(A_i - A_0)/(A_c - A_i)$ vs. log of the ligand concentration.

All experiments were carried out in a controlled temperature room of 20 ± 1 °C. All solutions were 0.1 M in the supporting electrolyte. Deaeration was accomplished by bubbling pure nitrogen through the solution for at least 10 min prior to analysis. All potentials are reported vs. the SCE.
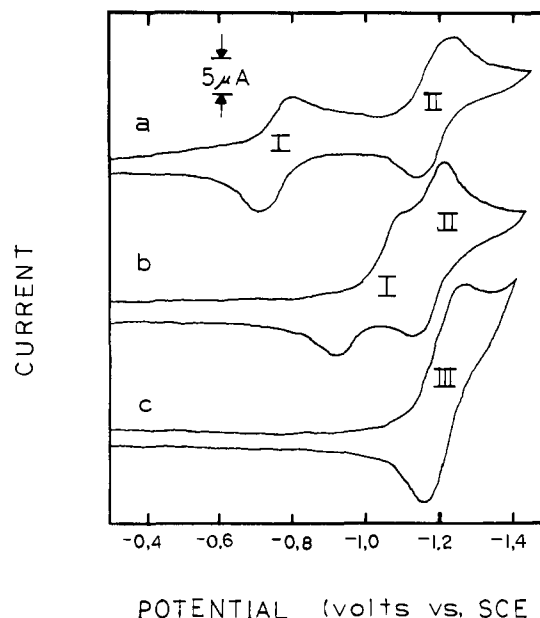
Results and Discussion

Electroreduction of iron phthalocyanine, PcFe, yields initially the iron(I) complex, PcFe⁻, and then a species assigned as a reduced iron(I) radical. The potentials of the first reduction are extremely dependent on the solvent and degree of axial coordination.[22] When dissolved in Me₂SO, iron phthalocyanine exists as the six-coordinate complex, PcFe(Me₂SO)₂, with two Me₂SO molecules bound to the metal center.[12] In this study we observed that PcFe(Me₂SO)₂ was reduced by two reversible one-electron transfer steps to yield PcFe(Me₂SO)⁻ at −0.74 V and the anion radical of iron(I) at −1.15 V. Assignment of a single Me₂SO molecule on PcFe(Me₂SO)⁻ is based on the results of an ESR study by Lever[23] which shows that five-coordinate complexes are formed from reduction of the stable Fe(II) complex.

A typical voltammogram of PcFe(Me₂SO)₂ is shown in Figure 2a and the reactions are labeled I and II, respectively. The two-electrode reactions were reversible and gave peak currents of approximately the same magnitude. Plots of $i_p/v^{1/2}$ were linear and $E_{1/2}$ was constant with scan rate, indicating a diffusion-controlled process and the absence of coupled chemical reactions.[24] Polarographic wave analysis also confirmed that a one-electron diffusion-controlled process was involved in each step. Half-wave potentials for these two reductions in Me₂SO containing ClO₄⁻ are within 30 mV of those reported by Lever.[22] It is interesting to note that almost identical potentials were obtained by Li and Chin[25] for reduction of the tetrasulfonate salt of PcFe in Me₂SO.

Mechanism I for PcFe(B)₂ Reduction. It is known from spectroscopic data[12] and was verified in our laboratory that PcFe(Im)₂ is the predominant complex in Me₂SO containing 10⁻¹ M imidazole. Spectrophotometric titrations in Me₂SO containing supporting electrolyte gave almost identical results as in neat Me₂SO. Before addition of imidazole, the well-characterized visible spectrum of PcFe(Me₂SO)₂ was obtained. Additions of 10⁻⁴–10⁻³ M imidazole produced a shift of the peaks at λ 660 and 595 nm and gave a spectrum identical with that reported for PcFe(Im)₂. Plots of log $(A_i - A_0)/(A_c - A_i)$ vs. log (imidazole) were constructed (Figure 3a). That PcFe(Im)₂ was formed is confirmed by the slope of 2.0. From
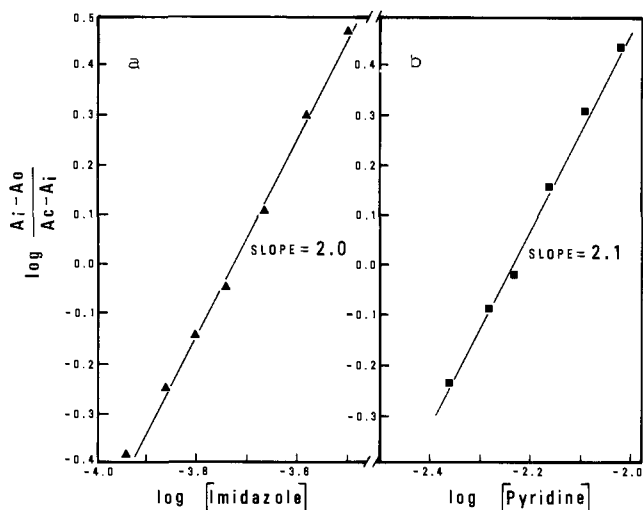
Figure 3. Plots of log $(A_i - A_0)/(A_c - A_i)$ vs. (a) log (imidazole); (b) log (pyridine) for PcFe in Me_2SO. Concentrations of PcFe were 1.58×10^{-5} and 7.04×10^{-5} M and wavelengths chosen were 660 and 415 nm for (a) and (b), respectively.
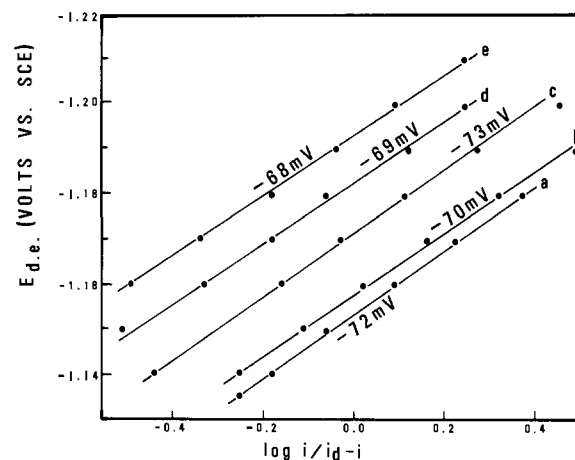

Figure 4. Wave analysis of PcFe reduction in Me_2SO/imidazole mixtures at imidazole concentrations: (a) 0.16 M; (b) 0.19 M; (c) 0.31 M; (d) 0.63 M; (e) 0.95 M.

the intercept, β_2 for $PcFe(Im)_2$ was calculated as 2.88×10^7 in Me_2SO, 0.1 M TEAP (Table II). This value compares, within experimental error, with the $\beta_2 = K_1K_2$ of 2.2×10^7 obtained by kinetic measurements in Me_2SO without supporting electrolyte.[12b]

Additions of imidazole or N-methylimidazole to $PcFe(Me_2SO)_2$ resulted in a dramatic cathodic shift of the iron(II) reduction potentials concomitant with complexation (see Figure 2). The direction of the potential shift for peak I is indicative of a loss of one or more ligands upon electroreduction.[21] At 10^{-2} M ligand, reduction peak I has shifted over 300 mV from an $E_{1/2} = -0.74$ V in neat Me_2SO and has become quasi-reversible ($E_{p,a} - E_{p,c} = 80$ mV). Polarographic wave analysis gave a 79-mV slope, confirming the quasi-reversible electron transfer process of peak I. No potential change occurred for formation of the radical anion (peak II). This peak remained diffusion controlled and independent of ligand concentration up to the point that overlap with peak I occurred.

It is significant to note the complete disappearance of a separate peak I at (imidazole) >0.1 M (Figure 2c). At these concentrations, peak I has shifted cathodically to overlap peak II and give a single peak, III. As shown in Figure 2c, the peak initially labeled as peak II has doubled in current and at the same time has shifted cathodically with increasing imidazole concentration. This increase in current was confirmed by polarographic wave analysis which gave a diffusion controlled $i_d(III) = 23.5 \times 0.9 \mu A$ at (imidazole) $= 0.95$ M, while in the absence of imidazole, an $i_d(II) = 11.3 \pm 1.2 \mu A$ was obtained. Based on this doubling of the diffusion currents and the potential dependence on imidazole concentration, peak III is therefore suggested to consist of an overall two-electron reduction step represented as follows:

$$PcFe(Im)_2 + 2e \rightleftharpoons PcFe(Im)^{2-} + Im \qquad (2)$$
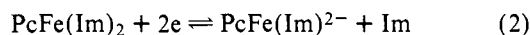
In order to determine whether reaction 2 involved a simultaneous two-electron transfer or two successive one-electron reductions, polarographic wave analysis was performed at several imidazole concentrations between 0.16 and 0.95 M. For the overall two-electron transfer process, peak III, wave analysis gave a quasi-reversible one-electron transfer slope of 70 ± 3 mV. This is shown in Figure 4. Based on the

already quasi-reversible one-electron transfer identified in peak I, it appears that reduction to iron(I) is still the rate-determining step in the overall two-electron transfer.

$$PcFe(Im)_2 + e \xrightarrow[\text{quasi-reversible}]{\text{rate controlling}} PcFe(Im)^- + Im \qquad (3)$$
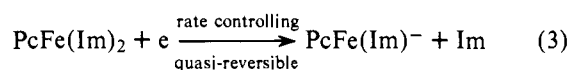
This reaction is further confirmed by plots of $E_{1/2}$ vs. log (imidazole) for peak I at imidazole <0.01 M, which gave a slope of -80 mV. This compares with a theoretical slope of -79 mV for a quasi-reversible one-electron transfer in which $\alpha n = 0.73$ and a single ligand is dissociated on reduction.[26] A second electron is added to $PcFe(Im)^-$ at -1.15 V when the concentration of ligand is less than 0.01 M. However, rapid addition of a second electron occurs immediately if (Im) >0.1 M and yields the overall two-electron transfer step shown in reaction 2. Analysis of the peak III cyclic voltammetric peak currents correspond to those found for two successive one-electron transfers at the same potential (an EE mechanism),[27] and not for a simultaneous two-electron transfer (where $i_p \propto n^{3/2}$).[24]

The five-coordinate complex, $PcFe(Im)^-$, is the proposed electroreduction product of $PcFe(Im)_2$ (reaction 2) in DMA and Me_2SO, and has been identified by Lever using ESR techniques.[23] Reduction of $PcFe(Im)^-$ to yield $PcFe(Im)^{-2}$ is suggested by the invariance of peak II potential with increasing imidazole concentration prior to overlap by peak I (see Figure 2a). Since it is the phthalocyanine ring and not the iron that is being reduced,[23] it is not surprising that an axial ligand would remain bound to the iron center after reduction to the radical anion.

Mechanism II for $PcFe(B)_2$ Reduction. In Me_2SO containing greater than 0.1 M pyridine, the reactant at the electrode surface is $PcFe(py)_2$. The identity of this species is derived from the spectrophotometric data[12c] which indicate that two pyridine molecules bind to Fe(II) according to the reaction

$$PcFe(Me_2SO)_2 + 2py \rightleftharpoons PcFe(py)_2 + 2Me_2SO \qquad (4)$$
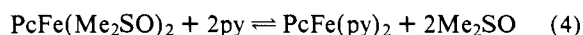
The wavelength of 415 nm was chosen for measuring absorbance changes during pyridine titrations. In solutions containing 0.1 M supporting electrolyte, addition of two pyridine molecules to $PcFe(Me_2SO)_2$ was confirmed by a slope of 2.1 from the plot of log $(A_i - A_0)/(A_c - A_i)$ vs. log (pyridine), shown in Figure 3b. In Me_2SO which was 0.1 M in TEAP, the for-

Table I. Half-Wave Potentials at Concentrations of 1.0 M in Ligand

| No.	Ligand	Peak I	Peak II	$\Delta E_{1/2}$ (I − II)	No. of electrons transferred/step
1	Imidazole	−1.21	−1.21	0.00	2
2	N-Methylimidazole	−1.17	−1.17	0.00	2
3	4-Picoline	−0.99	−1.23	0.24	1
4	2-Methylimidazole	−0.94	−1.20	0.26	1
5	Pyridine	−0.95	−1.22	0.27	1
6	3-Picoline	−0.93	−1.21	0.28	1
7	1,2-Dimethylimidazole	−0.87	−1.20	0.33	1
8	2,6-Lutidine	−0.82	−1.15	0.33	1
9	2,4-Lutidine	−0.80	−1.16	0.36	1
10	2,4,6-Collidine	−0.74	−1.14	0.40	1
	Neat Me₂SO	−0.74	−1.15	0.41	1

POTENTIAL VS. S.C.E.
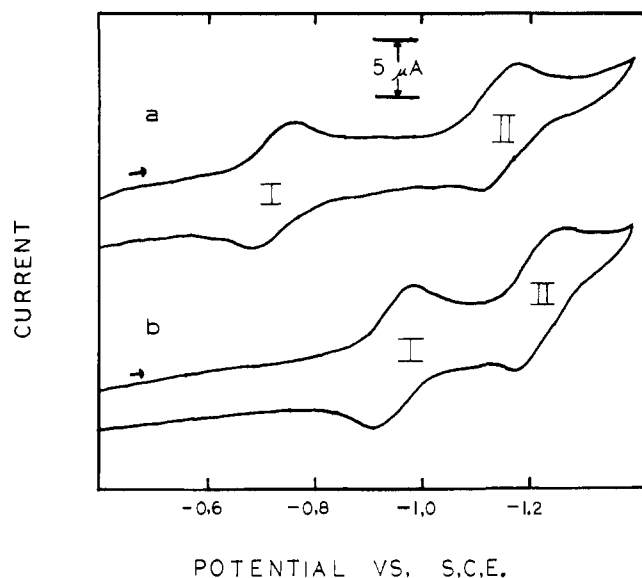
Figure 5. Cyclic voltammograms of 1.60 mM PcFe in Me₂SO/pyridine mixtures containing 0.1 M TBAP. Scan rate 0.050 V/s. Pyridine concentrations: (a) 0.00 M; (b) 1.0 M.
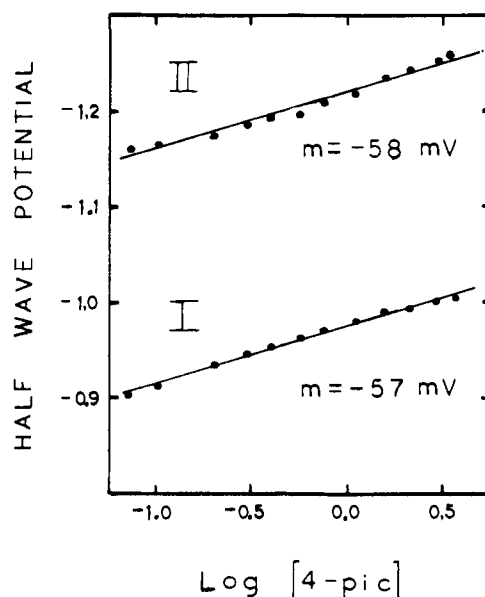

Log [4-pic]

Figure 6. Diagnostic plots of half-wave potential for PcFe(4-pic)₂ reduction as a function of 4-picoline concentration.

mation constant, $\beta_2 = K_1 K_2$, was calculated as 3.0 × 10⁴ from the intercept and is included in Table II for comparison with the electrochemically obtained formation constants.

Cyclic voltammograms of PcFe in Me₂SO and 1.0 M pyridine are shown in Figure 5. Similar cyclic voltammograms were obtained with Me₂SO solutions containing 3-picoline, 4-picoline, 2-methylimidazole, or 1,2-dimethylimidazole. Titrations of PcFe(Me₂SO)₂ with any of the above ligands yielded cathodic shifts of both peak I and peak II. At ligand concentrations less than 0.05 M, only peak I shifted, while at higher ligand concentrations both peaks shifted cathodically by approximately −59 mV/log (B). The net result was a decrease in the separation of the two peaks from 0.41 V in Me₂SO to 0.27 V in 1.0 M pyridine (see Figure 5 and Table I). The two peaks approached each other ($\Delta E_{1/2} \rightarrow 0$) but did not overlap in potential as was observed with imidazole and N-methylimidazole. An example of the potential dependence on $E_{1/2}$ between 0.07 and 3.2 M ligand is shown in Figure 6 for 4-picoline. Similar shifts of half-wave potential were observed with solutions containing pyridine, 3-picoline, 2-methylimidazole, and 1,2-dimethylimidazole. The $\Delta E_{1/2}/\Delta$ log (B) slope of −57 mV for peak I (Figure 6) is a clear indication that one less ligand is on the product than on the reactant, PcFe(B)₂.· A similar −58 mV slope for peak II also shows that a second ligand is released concomitant with the second electron

transfer. Thus, each electron transfer involves the simultaneous dissociation of a single ligand molecule.

$$PcFe(B)_2 + e \rightleftharpoons PcFe(B)^- + B \qquad (5)$$

$$PcFe(B)^- + e \rightleftharpoons PcFe^{2-} + B \qquad (6)$$
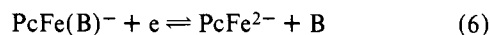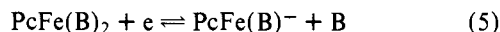
To investigate the reversibility of reaction 5 and 6 in pyridine, a dropping mercury electrode was used. The wave analysis slopes of −54 and −56 mV for these reactions and the measured $E_{3/4} - E_{1/4} = 55$ mV for the polarographic wave confirms that a one-electron diffusion-controlled process is involved in each case.[26] An $i_{p,a}/i_{p,c} = 1$ for the cyclic voltammogram and peak separation $|E_{p,a} - E_{p,c}| = 60$ mV also gave evidence of a reversible single-electron transfer reaction. Plots of $E_{1/2}$ and $i_p/v^{1/2}$ vs. scan rate were constant, again indicating a diffusion-controlled process and the absence of coupled chemical reactions.[24] Thus, the overall oxidation–reduction mechanism may be presented as in Scheme I, where B = pyridine, 3-picoline, 4-picoline, 2-methylimidazole, or 1,2-dimethylimidazole.

In all solutions, the potentials of the above reactions were a function of the ligand concentration. Values of n and $E_{1/2}$ for each phthalocyanine complex are listed in Table I for 1.0 M ligand. From the magnitude of the potential shifts, formation constants for mono and bis ligand addition to PcFe-

Table II. Formation Constants for Addition of Amines to Iron(II) Phthalocyanine in Me_2SO

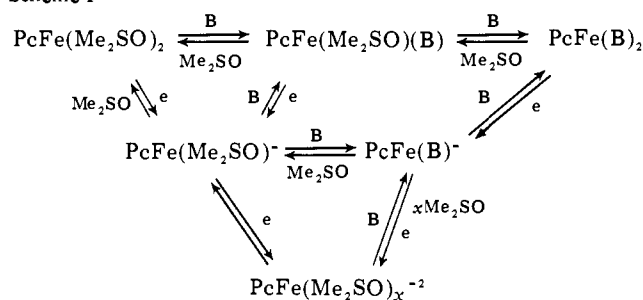| Ligand	pK_a	$\text{Log } K_1$	$\text{Log } K_2$	$\text{Log } \beta_2{}^f$
Pyridine	5.17[a]	3.10	1.88	4.98
Pyridine	5.17[a]			4.47[c]
Pyridine	5.17[a]	3.15[d]	1.55[d]	4.70[d]
3-Picoline	5.63[b]	3.08	1.56	4.64
2-Picoline	5.96[b]	1.35[d]	0.95[d]	2.30[d]
4-Picoline	6.03[b]	4.04	1.78	5.87
4-Picoline	6.03[b]	3.45[d]	1.95[d]	5.40[d]
2,6-Lutidine	6.60[b]	1.66	0.28	1.95
Imidazole	6.65[a]			7.46[c]
Imidazole	6.65[b]	3.45[e]	3.80[e]	7.34[e]
2,4-Lutidine	6.77[b]	1.43	0.26	1.70
N-Methylimidazole	7.33[a]			>7.5
2,4,6-Collidine	7.43[b]	0.24	NR	NR
2-Methylimidazole	7.56[a]	2.84	2.01	4.84
1,2-Dimethylimidazole	7.85[a]	2.38	1.05	3.43

[a] A. Albert, *Phys. Methods Heterocycl. Chem.*, **1**, 1 (1963). [b] Z. Rappoport, "Handbook of Tables for Organic Compound Identification", 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967. [c] Determined spectroscopically in 0.1 M TEAP. [d] Calculated from data in ref 12c. [e] Taken from ref 12b. [f] $\beta_2 = K_1 K_2$.

Table III. Formation Constants for Addition of Amines to Iron(I) Phthalocyanine in Me_2SO

Ligand	pK_a	$\text{Log } K_1$
Pyridine	5.17[a]	1.16
3-Picoline	5.63[b]	1.08
4-Picoline	6.03[b]	1.42
2-Methylimidazole	7.56[a]	1.08
1,2-Dimethylimidazole	7.85[a]	0.90

[a] A. Albert, *Phys. Methods Heterocycl. Chem.*, **1**, 1 (1963). [b] Z. Rappoport, "Handbook of Tables for Organic Compound Identification", 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

Scheme I

$$PcFe(Me_2SO)_2 \underset{Me_2SO}{\overset{B}{\rightleftharpoons}} PcFe(Me_2SO)(B) \underset{Me_2SO}{\overset{B}{\rightleftharpoons}} PcFe(B)_2$$

$$PcFe(Me_2SO)^- \underset{Me_2SO}{\overset{B}{\rightleftharpoons}} PcFe(B)^-$$

$$PcFe(Me_2SO)_x{}^{-2}$$

$(Me_2SO)_2$ and the mono ligand addition to $PcFe(Me_2SO)^-$ were calculated. These values are listed in Tables II and III, respectively. With no exceptions, the magnitude of the potential separation between peak I and peak II was monotonically related to the stability constants for addition of either one or two ligands to the Fe(II) complex of phthalocyanine. This is shown in Figure 7 where log β is plotted vs. $\Delta E_{1/2}$ (I − II). All of the formation constants refer to β_2 with the exception of 2,4,6-collidine (compound 10), which only adds one ligand. For this compound $\beta_1 = K_1$ is utilized in the plot.

Mechanism III for PcFe(B)$_2$ Reduction. In order to monitor the effect of steric hindrance on the axial ligand binding reactions of $PcFe(Me_2SO)_2$, titrations were performed with both sterically hindered imidazoles and pyridines. Addition of sterically hindered ligands to iron porphyrins results in substantially decreased stability constants for Fe(III) complexes for both mono and bis ligand adducts.[28] On the other hand,
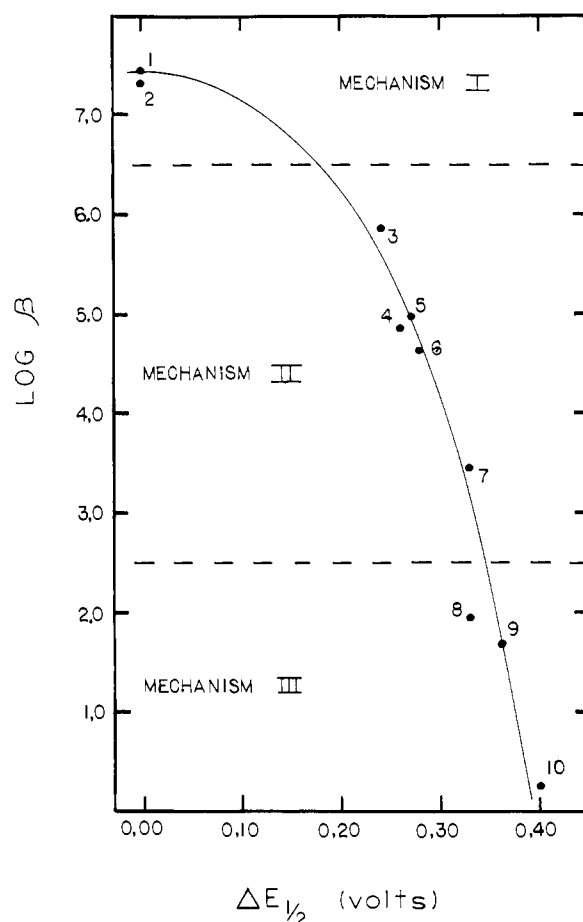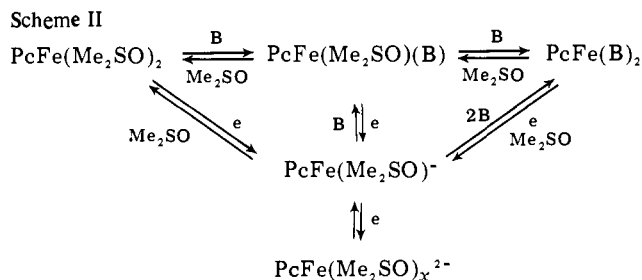

Figure 7. Plot of log β for PcFe complexation vs. the potential separation between peaks I and II at 1.0 M ligand concentration. The identity of the compounds has been given in Table I. For compound 10, β_1 is utilized, while for all others, β_2 has been selected.

large stability constants are obtained for iron(II) porphyrin complexes with sterically hindered ligands, but only a single mono ligand adduct is known to form.[29,30]

Titrations of the sterically hindered imidazoles, 2-methylimidazole and 1,2-dimethylimidazole, gave both mono and bis ligand adducts with PcFe as was described above. They were

also similar to the unhindered pyridines in that a complex with Fe(I) was formed in solution. Unlike results with imidazole and *N*-methylimidazole, a complete overlap of peaks I and II did not occur and the mechanism was as described is Scheme I.

Titrations of the hindered pyridines 2,4-lutidine, 2,6-lutidine, and 2,4,6-collidine with $PcFe(Me_2SO)_2$ resulted in the expected cathodic shifts of peak I with changes in log (B). Using eq 1 it was determined that either one or two ligands were bound to Fe(II) and none to Fe(I). Potentials for peak II did not shift as a function of ligand concentration, indicating the absence of ligand exchange upon electron transfer and confirming the lack of substituted pyridine coordination by $PcFe^-$. Thus, the mechanism of Scheme II is proposed.

Scheme II

$$PcFe(Me_2SO)_2 \underset{Me_2SO}{\overset{B}{\rightleftarrows}} PcFe(Me_2SO)(B) \underset{Me_2SO}{\overset{B}{\rightleftarrows}} PcFe(B)_2$$

$$PcFe(Me_2SO)^-$$

$$PcFe(Me_2SO)_x{}^{2-}$$

Values of K_1, K_2, and β_2 for each of the above mono and bis ligand complexes were calculated and are listed in Table II. As would be expected, reduced formation constants were obtained for both the five- and six-coordinate complexes as compared to the unhindered ligands. For 2,4,6-collidine, only a five-coordinate complex is formed, which is quite weak (K_1 = 1.7).

Effect of Base on Stability Constants and Mechanism Type. The data in Tables II and III can be broken into three categories, according to the electrode mechanism observed. When comparing the unhindered amines, there appears to be a good relationship between the basicity of the amine (as defined by the pK_a) and the value of the formation constant. In Table II, the β_2's for unhindered imidazole complexes are about 10^2-10^3 larger than β_2's for unhindered pyridine complexes. A similar 10^2-10^3 increase in β_2 is observed between complexes containing the sterically hindered imidazoles and pyridines. There does not appear to be a general trend between the pK_a and log β_2 among the unhindered pyridines as has been observed with the Fe(III) porphyrins.[28] However, it can be noted that the pK_as for the three unhindered pyridines in Table II span less than an order of magnitude.

The relationship between formation constants for Fe(II) binding and mechanism type is summarized in Figure 7. In this figure log β is plotted as a function of potential separation between peaks I and II. The general finding which emerges from this figure is that the potential separation between the $PcFe(B)_2$ reduction process (peak I) and $PcFe(B)^-$ or $PcFe(Me_2SO)^-$ reduction (peak II) is directly related to stabilization of the six-coordinate oxidized complex relative to the five-coordinate reduced species. Compounds 8–10 do not form complexes with $PcFe^-$ and only weakly with PcFe. These three compounds undergo mechanism III and $\Delta E_{1/2}$ is close to that obtained in the absence of amine (0.41 V). Compounds 3–7 have β_2's of 10^3-10^6 for $PcFe(B)_2$ and 10^1 for $PcFe(B)^-$ formation. This difference of 10^2-10^5 in stability constants for $PcFe(B)_2$ relative to $PcFe(B)^-$ produces a decrease in $\Delta E_{1/2}$ by up to 0.17 V from neat Me_2SO. These compounds undergo electrode mechanism II in Me_2SO.

The largest formation constants are found for *N*-methylimidazole and imidazole ($\beta_2 > 10^7$) and for these compounds $\Delta E_{1/2}$ = 0. Complete overlap of the peaks has been obtained and an overall two-electron transfer results. Of the ten com-

pounds investigated only these two undergo a simultaneous two-electron reduction. Both compounds give evidence of forming complexes with the Fe(I) radical and this appears to be the factor most influencing the changeover of electron transfer mechanism to mechanism I. None of the other investigated ligands are able to complex with the Fe(I) radical of phthalocyanine. As seen in Figure 6, half-wave potentials for $PcFe(B)_2$ and $PcFe(B)^-$ reduction shift cathodically by −58 mV per tenfold increase in ligand concentration. This cathodic shift of peak II is not observed for compounds undergoing mechanism I (see Figure 2). In these cases, $PcFe(B)^-$ reduction potentials do not shift as a function of the ligand concentration because the electrode reaction involves both a five-coordinate Fe(I) reactant and a five-coordinate Fe(I) product. Thus, the potentials for $PcFe(B)_2$ reduction are shifted cathodically with ligand concentration due ot stabilization of $PcFe(B)_2$ relative to $PcFe(B)^-$ and at the same time relative to $PcFe(B)^{2-}$. This results in a shifting of only one of the two reduction waves and causes an overlap of the peaks at high ligand concentrations. When $PcFe(B)^-$ dissociates on reduction to the radical, parallel shifts of both potentials occur (Figure 6) and two discrete processes are observed.

From Figure 7 it is predicted that overlap of peaks I and II and the generation of a two-electron reduction might be accomplished through strong complexation of PcFe, even when the radical does not complex with nitrogenous bases. Studies with iron phthalocyanine and other amines are presently underway in order to test this prediction.

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Alkyl Group Isomerization in the Oxidative Addition of Acyl Chlorides to Iridium(I) Complexes

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Abstract: Isomeric pairs of normal and α-branched acyl chlorides RCOCl [R = $(CH_2)_2CH_3$ or $CH(CH_3)_2$, $(CH_2)_3CH_3$ or $CH(CH_3)C_2H_5$, $(CH_2)_4CH_3$ or $CH(C_2H_5)_2$, and CH_2CH_2Ph or $CH(CH_3)Ph$] oxidatively add to $IrCl(PPh_3)_n$ (n = 2 or 3) to give the same n-alkyliridium(III) complexes $RIrCl_2(CO)(PPh_3)_2$ [R = $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, $(CH_2)_4CH_3$, and CH_2CH_2Ph respectively], which contain *trans*-triphenylphosphine ligands. The α-branched acyl chlorides give $IrCl(CO)(PPh_3)_2$ and $IrHCl_2(PPh_3)_3$ as by-products. It is suggested that an initially formed *sec*-alkyl complex undergoes rapid β-hydride migration to form an olefin hydride which can either re-form the sterically more favorable n-alkyl or can decompose irreversibly to $IrCl(CO)(PPh_3)_2$, olefin, and HCl. In agreement, n-butanoyl chloride and 2-methylpropanoyl chloride add to the sterically less crowded cyclooctene complex $[IrCl(CO)(C_8H_{14})_2]_2$ to give respectively dimeric n- and isopropyliridium(III) complexes $[RIrCl_2(CO)_2]_2$ [R = $(CH_2)_2CH_3$, $CH(CH_3)_2$] which interconvert in hot benzene to give an approximately 3:2 mixture of n and iso complexes. The equilibrium between the similarly prepared n- and *sec*-butyl complexes is established rapidly even at 34 °C and favors the n-butyl complex. The alkyl complexes $[RIrCl_2(CO)_2]_2$ are formed from $[IrCl(CO)(C_8H_{14})_2]_2$ via acyls $[RCOIrCl_2(CO)(C_8H_{14})]_2$ which can be isolated [R = CH_3, $CH(CH_3)_2$]. Owing to reversible β-elimination, the ethyl complexes obtained from 2-dideuteropropanoyl chloride, CH_3CD_2COCl, and $IrCl(PPh_3)_2$ or $[IrCl(CO)(C_8H_{14})_2]_2$ have their deuterium atoms scrambled between methyl and methylene carbon atoms to an extent which depends on the reaction time. The oxidative additions of acyl chlorides to $IrCl(PPh_3)_3$ and $RhCl(PPh_3)_3$ are compared, and the alkyl group isomerizations observed in other reactions promoted or catalyzed by transition metal complexes are briefly discussed. In the complexes $CH_3(CH_2)_nIrCl_2(CO)(PPh_3)_2$ ($n > 3$) the protons on the third and fourth carbon atoms from the metal are abnormally shielded, as also are the phenethyl aromatic protons in $PhCH_2CH_2IrCl_2(CO)(PPh_3)_2$. These protons probably lie in the shielding zone of the aromatic rings of the *trans*-triphenylphosphine ligands.

Decarbonylation of acyl halides catalyzed by planar d^8 metal complexes such as $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $IrCl(CO)(PPh_3)_2$ is a potentially useful process in organic synthesis.[1] It is based on a sequence of reactions at the metal atom involving oxidative addition of the acyl halide, alkyl or aryl migration from the acyl group, and reductive elimination of alkyl or aryl halide, or of olefin and hydrogen halide, as illustrated in Scheme I for $RhCl(PPh_3)_3$.[2-11] Although oxidative additions of acyl halides to iridium(I) complexes of the type $IrCl(CO)L_2$ (L = various tertiary phosphines or arsines) are well documented,[5,12-15] corresponding reactions with $IrCl(PPh_3)_3$ have received little attention. This complex oxidatively adds hydrogen,[16] thiols,[17] silanes,[18] and 1-alkynes[19] more readily than either $IrCl(CO)(PPh_3)_2$ or $RhCl(PPh_3)_3$ and, compared with the latter, is less prone to lose triphenylphosphine; its reaction with acyl halides is of obvious interest for comparative purposes. Kubota et al.[15,20,21] have reported on the reaction of the closely related dinitrogen complex $IrCl(N_2)(PPh_3)_2$ with various acyl halides and on the reaction of acetyl chloride with $IrCl(PPh_3)_3$, and in a preliminary communication[22] we noted that oxidative addition of isomeric straight- and α-branched-chain acyl chlorides to $IrCl(PPh_3)_3$ affords exclusively n-alkyliridium(III) complexes. Full details of this work are presented herein.

Results

Straight-chain acyl halides RCOCl react with $IrCl(PPh_3)_3$ in refluxing benzene to give colorless, crystalline, monomeric

Scheme I
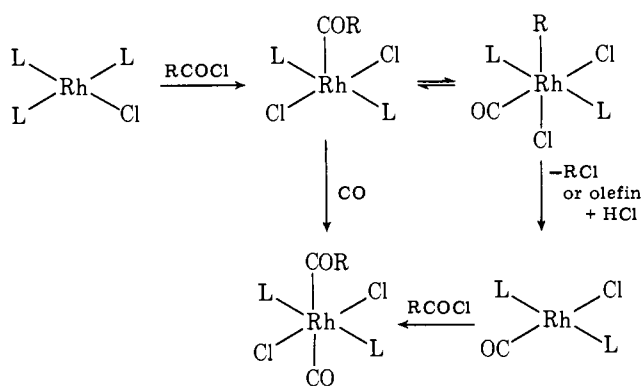
octahedrally coordinated iridium(III) alkyls $RIrCl_2(CO)(PPh_3)_2$ (R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_7H_{15}, and CH_2CH_2Ph) in 70–80% yield. In dichloromethane their IR spectra show one $\nu(CO)$ band in the range 2030–2040 cm^{-1}, and in Nujol mulls two such bands are occasionally observed, probably owing to solid state splitting (Table I). The far IR spectra show two strong $\nu(IrCl)$ bands at ca. 305 and 250 cm^{-1} assignable to Cl trans to CO and to σ-alkyl, respectively; these data are consistent with structure I. The ethyl complex obtained by this method is identical with that isolated from the reaction of $IrCl(N_2)(PPh_3)_2$ with propanoyl chloride.[15] The