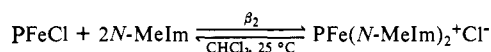


Electronic Effects in Transition-Metal Porphyrins. 6. The Effect of Unsymmetrical Phenyl Substitution on the Formation Constants of a Series of (Tetraphenylporphinato)iron(III)-Bis(*N*-methylimidazole) Complexes

Virginia L. Balke, F. Ann Walker,*¹ and Joyce T. West

Contribution from the Department of Chemistry, San Francisco State University, San Francisco, California 94132. Received June 1, 1984

Abstract: We have previously shown (*Inorg. Chim. Acta* 1984, 91, 95-102) that the formation constants of all zinc(II) tetraphenylporphyrins obey a common linear free energy relationship with the sum of the Hammett σ constants of the substituents, irrespective of whether the tetraphenylporphyrin is symmetrically or unsymmetrically substituted. In contrast, iron(III) tetraphenylporphyrins exhibit a more complex behavior. For the general reaction, tetra-para-substituted TPP complexes obey



one linear free energy relationship, with $\rho = -0.39$, while tetra-meta-substituted and unsymmetrically multiply para-substituted TPP complexes, $[(p\text{-X})_x(p\text{-Y})_{4-x}\text{TPP}]\text{FeCl}$, obey a different linear free energy relationship with $\rho = -0.18$. Monosubstituted TPP complexes, $[(m\text{- or } p\text{-X})_1\text{TPP}]\text{FeCl}$, are insensitive to the electronic effect of the substituent. These results have led to a reevaluation of the iron(III) porphyrin-axial ligand complex formation system, in which both mono- and tetra-para-substituted TPPs are now viewed as behaving anomalously. The reason for this "anomalous" behavior is believed to be nonadditivity of the substituent effects, leading eventually to the direct conjugation of the fourth phenyl ring in the product, $[(p\text{-X})_4\text{TPP}]\text{Fe}(N\text{-MeIm})_2^+\text{Cl}^-$, in order to remove the formal positive charge on Fe(III). The unsymmetrically multiply para-substituted TPP derivatives are also believed to engage in direct conjugation between phenyl and porphyrin ring, but by choosing to utilize the "least willing" substituent in this conjugation. The variation in energy of the Q_o electronic with the ratio of intensity of the Q_o and Q_v transitions for the bis(*N*-methylimidazole) adducts is in accord with an important role for direct conjugation in these low-spin complexes.

The degree and mode of transmission of electronic effects to and from various points on the porphyrin ring through the σ and π orbitals of the four porphyrin nitrogens to the central metal have long been an interest of those who have investigated the physical properties and chemical reactions of metalloporphyrins.²⁻³⁵

Because of the conjugated nature of the porphyrin ring system, electron-donating or -withdrawing substituents on the periphery of the molecule have been shown to affect the basicity of the porphyrin nitrogens,^{2,4} the rate of NH tautomerism in free base porphyrins,^{29,30} the chemical shifts of pyrrole and NH protons in tetraphenylporphyrins,^{28,31,32} rates of phenyl rotation³²⁻³⁴ and porphyrin inversion^{34,35} in metallotetraphenylporphyrins, visible

- (1) Recipient, NIH Research Career Development Award, 1976-1981.
- (2) Falk, J. E. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1964; pp 28, 42, 69, 93.
- (3) Caughey, W. S.; Deal, R. M.; McLees, B. D.; Alben, J. O. *J. Am. Chem. Soc.* 1962, 84, 1735-1736.
- (4) Caughey, W. S.; Fjuimoto, W. Y.; Johnson, B. P. *Biochemistry* 1966, 5, 3830-3843.
- (5) McLees, B. D.; Caughey, W. S. *Biochemistry* 1968, 7, 642-652.
- (6) Baker, E. W.; Storm, C. B.; McGrew, G. T.; Corwin, A. H. *Bioinorg. Chem.* 1973, 3, 49-60.
- (7) Higginbotham, E.; Hambright, P. *Inorg. Nucl. Chem. Lett.* 1972, 8, 747-750.
- (8) Worthington, P.; Hambright, P.; Williams, R. F. X.; Feldman, M. R.; Smith, K. M.; Langry, K. C. *Inorg. Nucl. Chem. Lett.* 1980, 46, 441-447.
- (9) Worthington, P.; Hambright, P.; Williams, R. F. X.; Reid, J.; Burnham, C.; Shamim, A.; Turay, J.; Bell, D. M.; Kirkland, R.; Little, R. G.; Datta-Gupta, N.; Eisner, U. *J. Inorg. Biochem.* 1980, 12, 281-291.
- (10) Williams, G. N.; Hambright, P. *Inorg. Chem.* 1978, 17, 2687-2688.
- (11) Kirksey, C. H.; Hambright, P.; Storm, C. B. *Inorg. Chem.* 1969, 8, 2141-2144.
- (12) Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* 1975, 97, 2390-2397.
- (13) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* 1976, 98, 3484-3489.
- (14) Walker, F. A.; Lo, M.-W.; Ree, M. T. *J. Am. Chem. Soc.* 1976, 98, 5552-5560.
- (15) Satterlee, J. D.; LaMar, G. N.; Frye, J. S. *J. Am. Chem. Soc.* 1976, 98, 7275-7282.
- (16) Vogel, G. C.; Beckmann, B. A. *Inorg. Chem.* 1976, 15, 483-484.
- (17) McDermott, G. A.; Walker, F. A. *Inorg. Chim. Acta* 1984, 91, 95-102.
- (18) Jones, R. D.; Summerville, D. A.; Basolo, F. J. *J. Am. Chem. Soc.* 1978, 100, 4416-4424.

- (19) Walker, F. A.; Barry, J. A.; Balke, V. L.; McDermott, G. A.; Wu, M. Z.; Linde, P. F. *Adv. Chem. Ser.* 1982, 201, 377-416.
- (20) Kadish, K. M.; Morrison, M. M. *Bioinorg. Chem.* 1977, 7, 107-115 and references therein.
- (21) Kadish, K. M.; Bottomley, L. A. *J. Am. Chem. Soc.* 1977, 99, 2380-2382.
- (22) Kadish, K. M.; Bottomley, L. A.; Beroiz, D. *Inorg. Chem.* 1978, 17, 1124-1129.
- (23) Rillema, D. P.; Nagle, K. J.; Barringer, L. F.; Meyer, T. J. *J. Am. Chem. Soc.* 1981, 103, 56-62.
- (24) Shears, B.; Shah, B.; Hambright, P. *J. Am. Chem. Soc.* 1971, 93, 776-778.
- (25) Reid, J. B.; Hambright, P. *Inorg. Chem.* 1977, 16, 968-969.
- (26) Meot-Ner, M.; Adler, A. D. *J. Am. Chem. Soc.* 1972, 94, 4763-4764.
- (27) Meot-Ner, M.; Adler, A. D. *J. Am. Chem. Soc.* 1975, 97, 5107-5111.
- (28) Walker, F. A.; Balke, V. L.; McDermott, G. A. *Inorg. Chem.* 1982, 21, 3342-3348.
- (29) Storm, C. B.; Teklu, Y. *J. Am. Chem. Soc.* 1972, 94, 1745-1747.
- (30) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* 1977, 99, 1601-1604.
- (31) Janson, T. R.; Katz, J. J. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 1-59 and references therein.
- (32) LaMar, G. N.; Walker, F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61-157 and references therein.
- (33) Eaton, S. S.; Fishwild, D. M.; Eaton, G. R. *Inorg. Chem.* 1978, 17, 1542-1545.
- (34) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* 1977, 99, 6594-6599 and references therein.
- (35) LaMar, G. N.; Satterlee, J. D.; Snyder, R. V. *J. Am. Chem. Soc.* 1974, 96, 7137-7138. Snyder, R. V.; LaMar, G. N. *Ibid.* 1976, 98, 4419-4424.

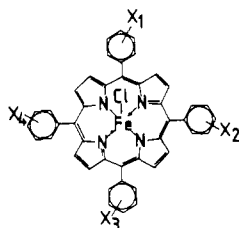


Figure 1. Structures of the tetraphenylporphyrins used in this study. X_1 – X_4 may be the same (symmetrical) or of two different types (unsymmetrical). In all cases X_1 – X_4 are present either on one meta position of each phenyl ring or on the para position of each ring. (No attempt was made to separate atropisomers of the meta-substituted TPPs.) If $X_1 = X_3 = p\text{-Cl}$ and $X_2 = X_4 = p\text{-NEt}_2$, the isomer is called trans, whereas if $X_1 = X_2 = p\text{-Cl}$ and $X_3 = X_4 = p\text{-NEt}_2$, the isomer is called cis.

absorption spectra,²⁷ rate,¹⁰ and equilibrium^{11–18} constants for axial ligation, redox potentials^{8,9,13,18–23} of both porphyrin ring and metal redox reactions, and metal incorporation rates.^{24–26} In almost all cases involving symmetrical tetraphenylporphyrins and their metal complexes (except for ref 26, 27, and 34) the above physical properties have been shown to correlate with the σ constants of the Hammett equation,^{36–38} where P_X is the observed physical

$$P_X - P_H = 4\sigma_X\rho \quad (1)$$

property of a compound having substituent X, σ_X is the Hammett substituent constant of X, and ρ describes the sensitivity of the property under study to the electron-withdrawing or -donating properties of X.

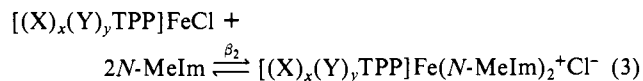
In the case of axial ligation to the metallotetraphenylporphyrins, where $P_X = \log K_{\text{eq}}$, linear free energy relationships with the Hammett σ constants have been shown to exist for the reactions of Lewis bases with V(IV),¹² Fe(II),²¹ Fe(III),^{14,15,21} Co(II),¹³ Ni(II),¹² and Zn(II)^{16,17} complexes of symmetrically substituted tetraphenylporphyrins. For addition of one ligand to V^{IV}, Co^{II}, and Zn^{II}(TPP)s, ρ values range from 0.113 to 0.188,^{12,13,16,17} whereas for addition of two ligands to Ni(II), $\rho = 0.331$,¹² and to Fe(III), where the product is an ion pair, $\rho = -0.39$ ¹⁴ to -0.41 .¹⁵ Thus electron-withdrawing substituents favor axial ligation to +2-charged metals by making the metal a better Lewis acid, while the same electron-withdrawing substituents disfavor bis-axial ligation to +3-charged metals because a positive charge must be localized on the metal ion product.¹⁴

Recently we have undertaken an investigation of the effects of unsymmetrical phenyl substitution on the physical properties and chemical reactivity of metal-free,²⁴ zinc(II),^{17,19,28} and iron(III)^{18,38} tetraphenylporphyrins. We have found that metal-free and Zn(II) derivatives of the series $\text{H}_2\text{TPP}(p\text{-Cl})_x(p\text{-NEt}_2)_y$ (Figure 1) behave according to eq 2, with respect to their

$$P_{(X,Y)} - P_H = (\sum \sigma_{X,Y})\rho \quad (2)$$

weighted-average pyrrole proton resonance position and also with respect to their individual pyrrole H positions, although with ρ of opposite sign.²⁸ (Definitions in eq 2 are as follows: $P_{(X,Y)}$ is the physical property of an unsymmetrically substituted tetraphenylporphyrin having various numbers of X and Y as its phenyl substituents, and $\sum \sigma_{X,Y}$ is the sum of the Hammett substituent constants for the number of X and Y present.) We have also shown that a large series of [(*m*- or *p*-X)(*m*- or *p*-Y)₃TPP]Zn^{II} complexes behave according to eq 2 with respect to electrochemical oxidation, but not reduction, of the porphyrin ring.¹⁹ In terms of iron TPPs, we have shown that the average pyrrole H isotropic shift of the slow-spin iron(III) bis(*N*-methylimidazole) complexes³⁹ as well as the average slopes and intercepts of the Curie plots,⁴⁰

Fe(III)/Fe(II) redox potentials,¹⁹ and g anisotropies^{19,41} of unsymmetrically substituted Fe^{III}(TPP)s behaves according to eq 2 but that the difference in isotropic shift to the individual types of pyrrole H in unsymmetrically substituted low-spin Fe^{III}(TPP)s varies with $\sigma_X - \sigma_Y$.³⁹ These results have been explained in terms of the electron-density distribution in the porphyrin π orbital(s) being probed in each of these studies.^{19,39,41} In the case of axial ligation reactions of metallotetraphenylporphyrins, we have recently shown¹⁷ that in the case of Zn(II), reacting with one 3-picoline molecule to form a 5-coordinate complex, the effects of unsymmetrical substitution on the periphery of the porphyrin molecule are averaged at the metal center, and $\log K_{\text{eq}}$ behaves according to eq 2. Our initial studies of unsymmetrically substituted iron(III) tetraphenylporphyrins, which react with *N*-methylimidazole according to eq 3, where X = *p*-Cl and Y =



p-NEt₂, showed that the mixed-substituent derivatives did not behave according to eq 2.¹⁹ In fact, the values of $\log \beta_2$ fell well below the linear free energy plot found earlier for tetra-*para*-substituted derivatives,^{14,15} suggesting some unique, nonadditive behavior for the linear free energy relationships for the formation constants of iron(III) tetraphenylporphyrins.¹⁹ In an attempt to elucidate the reasons for this nonadditive behavior, we have extended our initial studies¹⁹ to include more unsymmetrically substituted (TPP)Fe^{III} complexes as well as some new symmetrically (tetra-) substituted derivatives. The results of this study provide new insights into the importance of formal charge and resonance to the stabilization of bis(imidazole) complexes of iron(III) porphyrins.

Experimental Section

All solvents used in synthesis and chromatography were obtained from Spectrum Chemical Co. and were used as received. Benzaldehydes, pyrrole, and *N*-methylimidazole (Aldrich) were distilled before use. Spectroscopic grade chloroform was obtained from Aldrich (Gold Label) or Mallinckrodt (Spectr AR), and was used as received. Once opened, a bottle was used for no more than 2 days.

Preparation and characterization of the series of [(*p*-Cl)_{*x*}(*p*-NEt₂)_{*y*}TPP]H₂ isomers has been reported previously.²⁸ Other unsymmetrically substituted TPPH₂ derivatives were prepared similarly^{19,28,39} from a mixture of the two benzaldehydes according to the general procedure utilized for tetraphenylporphyrin synthesis.⁴² Separation of isomers was achieved by chromatography with silica gel (Baker, chromatographic grade) as stationary phase and benzene or benzene/petroleum ether (70/30) as moving phase. Identification of isomers was achieved by NMR spectroscopy, as outlined previously.²⁸ Tetra-*meta*-substituted TPPH₂ derivatives were prepared by literature methods⁴² and chromatographed as above to remove tar and chlorins.

Iron was inserted into the various TPP derivatives according to literature methods,⁴³ with the isolation of product modified as described previously.^{19,39} All iron porphyrins were chromatographed on silica gel with CH₂Cl₂ as moving phase to elute any free base porphyrin and then with CH₂Cl₂/CH₃OH (90/10) to elute the iron-containing fractions (PFeCl and PFeOFeP). Following removal of all solvent, including traces of water, the combined iron-containing fractions were redissolved in CH₂Cl₂, HCl gas was bubbled through, and the samples were reevaporated to dryness and dried at 100 °C for 1 h before use.

Spectrophotometric measurements were made on a Cary 17 or a Hewlett-Packard 8451A spectrophotometer, each equipped with a thermostated cell compartment and thermostated cuvette, attached to a circulating constant-temperature bath, which controlled the temperature within the cuvette at 25.0 ± 0.2 °C in the cell compartment. Equilibrium constants were measured from the absorbances of ca. 8 × 10⁻⁵ M solutions of the (TPP)Fe^{III} derivatives, to which aliquots of *N*-methyl-

(40) Walker, F. A.; Benson, M. *J. Phys. Chem.* **1982**, *86*, 3495–3499.

(41) Walker, F. A.; Reis, D.; Balke, V. L. *J. Am. Chem. Soc.* **1984**, *106*, 6888–6898.

(42) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. Datta-Gupta, N.; Bardos, T. *J. J. Heterocycl. Chem.* **1966**, *3*, 495–502.

(43) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. J. *Inorg. Nucl. Chem.* **1970**, *32*, 2443–2448.

(36) Hammett, L. P. *Trans. Faraday Soc.* **1938**, *34*, 156–165.

(37) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 172–173.

(38) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337.

(39) Walker, F. A.; Balke, V. L.; McDermott, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1569–1574.

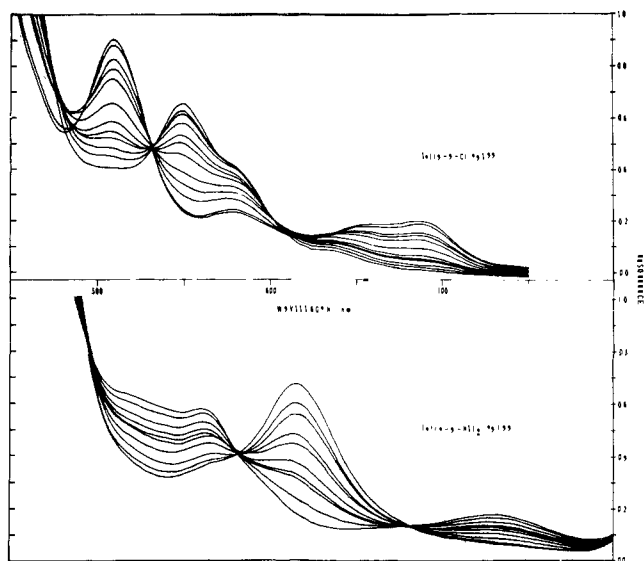


Figure 2. Spectral changes observed when *N*-methylimidazole is added to (A) [(*p*-Cl)₄TPP]FeCl and (B) [(*p*-NEt₂)₄TPP]FeCl in CHCl₃ at 25 °C.

imidazole stock solutions had been added. The data were analyzed as described previously.¹⁴

Results

In Figure 2 are shown two extreme examples of the spectral changes observed when *N*-methylimidazole is added to phenyl-substituted derivatives of (TPP)FeCl. The isosbestic points at ca. 530 and 620 nm for [(*p*-Cl)₄TPP]Fe^{III}, which shift to ca. 580 and 680 nm for [(*p*-NEt₂)₄TPP]Fe^{III}, are sharp for all compounds studied. However, the crossover point on the edge of the Soret band (480–500 nm) often showed evidence of two separate isosbestic points or complete lack of isosbesticity, suggesting the presence of three species in the solution at low [*N*-MeIm]. The third species is likely the mono(*N*-methylimidazole) complex, as suggested previously.¹⁴ Consistent with this, the low-*N*-methylimidazole-concentration samples typically fell above the line of slope 2 when $\log(A - A_0)/(A_c - A)$ was plotted against $\log[N\text{-MeIm}]$, as observed previously (Ref 14, Figure 2). Estimations, as made previously,¹⁴ of the stepwise K_1 ranged from 12 to 80 M⁻¹ among the complexes of this study, with the size of K_1 increasing as the electron-donating nature of the substituents increased. However, as pointed out previously,¹⁴ these estimations are based on the assumption that A_c , the absorbance of the fully formed complex, is the same for the mono *N*-MeIm complex as for the bis complex. This assumption is clearly not true, as evidenced by the nonisosbestic behavior of the visible spectrum in the 480–500-nm region. However, it seems unlikely that the absorbance difference $A_0 - A_c$ at the wavelength maximum of the high-spin (TPP)FeCl complex (510 and 565 nm in Fig. 2) can be more than a factor of 2 different from that observed on going from (TPP)FeCl to (TPP)Fe(*N*-MeIm)₂⁺Cl⁻, and thus the values of K_1 are probably within a factor of 2 of the estimated values, as suggested previously.¹⁴ For the parent complex, (TPP)FeCl, reacting with *N*-MeIm, smaller values of K_1 have been reported from electrochemical¹⁹ and kinetic⁴⁴ measurements. The products may be either the 6-coordinate Cl⁻ bound forms⁴⁴ or the 5-coordinate Cl⁻ dissociated forms.⁴⁵

One feature not displayed in Figure 2 is that in the case of *p*-(diethylamino)-substituted (TPP)FeCl derivatives the necessary treatment of the samples with HCl gas at the end of the synthetic procedure to destroy the μ -oxo dimer (see Experimental Section) had the effect of protonating the *p*-NEt₂ groups. Therefore, to record the spectrum of the 5-coordinate (TPP)FeCl derivative

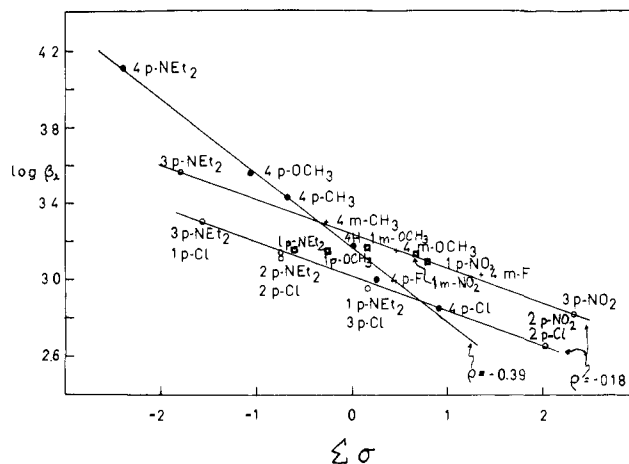


Figure 3. Plot of the values of $\log \beta_2$ for reaction 3 vs. the sum of the Hammett σ constants^{36,37} of the substituents present on the phenyl rings of the TPPFe^{III} derivative. The σ constant used for *p*-NEt₂ is -0.60 (see text). Circles = multiply para-substituted (solid = tetra, open = unsymmetrical) derivatives; crosses = tetra-meta-substituted; open squares = monosubstituted derivatives of (TPP)FeCl.

having deprotonated *p*-NEt₂ groups, a stoichiometric amount of base, taking into account the number of *p*-NEt₂ groups present, was added. The spectrum thus recorded was independent of whether the base used was triethylamine or *N*-methylimidazole. Thus *N*-methylimidazole was routinely used for convenience, and the concentrations of ligand available for binding to the axial positions of Fe(III) were corrected by the amount of *N*-methylimidazole used for deprotonation. Good isosbestic behavior in the 580- and 680-nm region was observed once the stoichiometric amount of *N*-methylimidazole had been added.

As indicated in Figure 2, large changes occur in the relative intensities and energies of the visible spectral bands of both the high-spin reactant and low-spin product forms of the Fe(III) complexes as the electronic nature of the substituents is varied. For the high-spin (TPP)FeCl derivatives, four visible bands having extinction coefficients of 10³ M⁻¹ cm⁻¹ or greater are typically observed. These are numbered I–IV in order of increasing energy, in conformance with the nomenclature of Gouterman.^{46,47} Bands III and IV correspond to the Q_0 and vibronically excited Q_v transitions from $a_{2u}(\pi) \rightarrow e_g(\pi^*)$, respectively,^{46,47} while bands I and II are the charge-transfer bands associated with the transitions $a_{2u}(\pi), b_{2u}(\pi) \rightarrow e_g(d_{xz}, d_{yz})$.⁴⁶ For the low-spin bis(*N*-methylimidazole) adducts, only two bands are typically observed, those corresponding to Q_0 and Q_v .^{46,47} Band III and IV correspond to the Q_0 and vibronically excited Q_v transitions from $a_{2u}(\pi) \rightarrow e_g(\pi^*)$, respectively,^{46,47} while bands I and II are the charge-transfer bands associated with the transitions $a_{2u}(\pi), b_{2u}(\pi) \rightarrow e_g(d_{xy}, d_{yz})$.⁴⁶ For the low-spin bis(*N*-methylimidazole) adducts, only two bands are typically observed, those corresponding to Q_0 and Q_v .^{46,47} The energies and extinction coefficients of these two bands and bands I–IV of the high-spin complexes are listed in Table I. It is evident that bands IV of the high-spin reactant and Q_v of the low-spin product vary very little in energy unless the complex contains at least three *p*-NEt₂ groups, while the other bands show more variation in both energy and intensity. Further discussion of the trends in energy and intensity of the visible absorption bands will be presented under Discussion.

Discussion

Equilibrium Constants for *N*-Methylimidazole Addition. The logarithms of the equilibrium constants β_2 for reaction 3 for the meta and para phenyl-substituted (TPP)Fe^{III} derivatives of this

(46) Zerner, M.; Gouterman, M.; Kobayashi, H. *Theor. Chim. Acta* **1966**, *6*, 363–

(47) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. III, pp 1–165.

(48) Bray, P. J.; Barnes, R. G. *J. Chem. Phys.* **1957**, *27*, 551–560.

(49) Price, C. C.; Belanger, W. J. *J. Am. Chem. Soc.* **1954**, *76*, 2682–2684.

(44) Burdige, D.; Sweigert, D. A. *Inorg. Chim. Acta* **1979**, *28*, L131. Fiske, W. W.; Sweigert, D. A. *Ibid.* **1979**, *36*, L429.

(45) Walker, F. A.; Buehler, J.; West, J. T.; Hinds, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 6923–6929.

Table I. Absorption Maxima and Extinction Coefficients of the Major Visible Spectral Bands of Symmetrically and Unsymmetrically Substituted Derivatives of (TPP)FeCl and Their Bis(*N*-methylimidazole) Complexes^a

| phenyl substituents | (TPP)FeCl | | | | (TPP)Fe(<i>N</i> -MeIm) ₂ ⁺ Cl ⁻ | |
|--|---|---|---|---|---|---|
| | 10 ³ ν _{IV} ^b (10 ³ ε _{IV}) ^c | 10 ³ ν _{III} ^b (10 ³ ε _{III}) ^c | 10 ³ ν _{II} ^b (10 ³ ε _{II}) ^c | 10 ³ ν _I ^b (10 ³ ε _I) ^c | 10 ³ ν _{Q_v} ^b (10 ³ ε _{Q_v}) ^c | 10 ³ ν _{Q_a} ^b (10 ³ ε _{Q_a}) ^c |
| (<i>m</i> -NO ₂) ₄ | 19.60 (10.9) | 17.33 (3.27) | 15.23 (2.75) | 14.80 (2.79) | 18.17 (8.35) | 17.39 (5.89) |
| (<i>p</i> -NO ₂) ₃ | 19.61 (10.7) | 17.33 (3.15) | 15.24 (2.72) | 14.77 (2.74) | 18.18 (8.24) | 17.39 (5.84) |
| <i>cis</i> - + <i>trans</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NO ₂) ₂ | 19.64 (11.2) | 17.33 (3.85) | 15.25 (2.80) | 14.71 (2.78) | 18.21 (8.70) | 17.39 (5.53) |
| (<i>m</i> -F) ₄ | 19.69 (11.8) | 17.33 (4.59) | 15.27 (2.86) | 14.66 (2.83) | 18.25 (9.07) | 17.39 (5.17) |
| <i>trans</i> -(<i>m</i> -NO ₂) ₂ (<i>m</i> -CH ₃) ₂ | 19.61 (9.51) | 17.30 (2.91) | 15.22 (2.42) | 14.64 (2.44) | 18.21 (9.29) | 17.30 (4.47) |
| <i>cis</i> -(<i>m</i> -NO ₂) ₂ (<i>m</i> -CH ₃) ₂ | 19.61 (9.72) | 17.27 (2.55) | 15.24 (2.21) | 14.62 (2.33) | 18.18 (7.08) | 17.30 (4.14) |
| (<i>p</i> -Cl) ₄ | 19.65 (12.8) | 17.30 (3.59) | 15.20 (2.97) | 14.56 (3.17) | 18.21 (9.36) | 17.30 (6.15) |
| (<i>p</i> -NO ₂) ₁ | 19.57 (9.33) | 17.42 (2.83) | 15.22 (2.10) | 14.60 (2.23) | 18.28 (6.94) | 17.36 (4.71) |
| (<i>m</i> -NO ₂) ₁ | 19.59 (9.57) | 17.29 (2.66) | 15.22 (2.08) | 14.49 (2.05) | 18.22 (7.24) | 17.36 (4.66) |
| (<i>m</i> -NO ₂) ₁ (<i>m</i> -CH ₃) ₃ | 19.57 (9.27) | 17.42 (2.50) | 15.22 (1.90) | 14.47 (2.28) | 18.18 (7.00) | 17.36 (4.98) |
| (<i>p</i> -F) ₄ | 19.65 (11.6) | 17.39 (4.14) | 15.29 (2.92) | 14.60 (2.95) | 18.25 (11.6) | 17.45 (6.31) |
| (<i>m</i> -OCH ₃) ₁ | 19.60 (9.57) | 17.25 (2.74) | 15.18 (2.36) | 14.49 (2.32) | 18.22 (7.34) | 17.37 (4.91) |
| (<i>m</i> -OCH ₃) ₄ | 19.61 (12.9) | 17.30 (3.63) | 15.13 (2.82) | 14.56 (2.88) | 18.25 (9.37) | 17.39 (5.94) |
| (<i>p</i> -Cl) ₃ (<i>p</i> -NEt ₂) | 19.53 (12.3) | 18.08 (6.99) | 15.46 (3.06) | 14.45 (3.05) | 18.05 (8.48) | 16.89 (7.73) |
| none | 19.61 (13.6) | 17.33 (4.08) | 15.15 (3.31) | 14.49 (3.60) | 18.25 (10.6) | 17.39 (7.27) |
| (<i>p</i> -OCH ₃) ₁ | 19.57 (12.5) | 17.39 (3.28) | 15.04 (2.57) | 14.45 (2.98) | 18.21 (8.98) | 17.36 (6.18) |
| (<i>m</i> -CH ₃) ₄ | 19.57 (12.9) | 17.30 (3.21) | 15.11 (2.56) | 14.43 (2.96) | 18.21 (9.18) | 17.39 (6.06) |
| (<i>p</i> -NEt ₂) ₁ | 19.54 (12.1) | 17.23 (5.51) | 15.76 (3.67) | 14.29 (3.23) | 18.18 (7.67) | 16.82 (6.76) |
| (<i>p</i> -CH ₃) ₄ | 19.57 (11.8) | 17.36 (2.80) | 14.95 (2.73) | 14.45 (2.93) | 18.18 (8.52) | 17.30 (6.06) |
| <i>trans</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NEt ₂) ₂ | 19.53 (11.2) | 18.11 (6.46) | 15.34 (3.01) | 14.41 (3.08) | 18.08 (7.62) | 16.89 (6.84) |
| <i>cis</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NEt ₂) ₂ | 19.49 (11.3) | 17.39 (4.20) | 15.31 (2.36) | 14.49 (2.55) | 18.12 (8.09) | 17.15 (6.33) |
| (<i>p</i> -OCH ₃) ₄ | 19.49 (13.2) | 17.45 (4.36) | 15.02 (2.80) | 14.35 (3.13) | 18.12 (9.35) | 17.15 (7.60) |
| (<i>p</i> -Cl) ₁ (<i>p</i> -NEt ₂) ₃ | 19.49 (10.7) | 18.05 (8.27) | 14.97 (2.21) | 13.99 (2.68) | 17.45 (7.72) | 16.37 (11.3) |
| (<i>p</i> -NEt ₂) ₃ | 19.46 (10.2) | 17.95 (8.35) | 14.95 (2.05) | 13.90 (2.62) | 17.44 (7.22) | 16.33 (10.8) |
| (<i>p</i> -NEt ₂) ₄ | 19.42 (9.48) | 17.83 (8.52) | 14.88 (1.72) | 13.76 (2.54) | 17.42 (6.62) | 16.23 (9.92) |

^a Measured in CHCl₃ at 25.0 ± 0.02 °C. ^b Frequency in cm⁻¹. ^c Extinction coefficient, in M⁻¹ cm⁻¹.

study are listed in Table II and are shown (except for those containing the *m*-NO₂ group) graphically in Figure 3, where log β₂ is plotted against the sum of the Hammett σ constants^{37,38} for the substituents present on the phenyl rings.⁵⁰ The σ constant for *p*-NEt₂ has been reported to be -0.90,⁴⁸ -0.70,⁴⁹ and -0.51.^{50,19,28,39,40} Previously we have used that reported for *p*-NMe₂ (-0.83)^{37,38} to describe the electron-donating nature of the *p*-NEt₂ group. However, in studies that correlate the properties of *p*-NEt₂-containing TPPs with those of a wide variety of other para-substituted TPP derivatives, the data for the *p*-NEt₂-containing complexes generally fell off the lines of best fit. (See, for example, ref 19, Figures 3 and 8.) Recently, we have looked back at those correlations and noticed that if the σ constant for *p*-NEt₂ was closer to -0.6, the redox potentials of *p*-NEt₂-containing (TPP)Fe(*N*-MeIm)₂⁺ complexes¹⁹ and the tetragonal and rhombic anisotropies of the same complexes¹⁹ would fit the linear correlations with Σσ much more closely. The choice of σ = -0.6 rather than one of the reported⁴⁸⁻⁵⁰ values is based in part upon the following reasoning: The σ constant for *p*-NHMe has been reported as -0.61,⁵¹ while that for *p*-NHMe is -0.84.⁵¹ Making the alkyl chain longer reduces the magnitude of the σ constant further (-0.51 for *p*-NHC₄H₉⁵¹), presumably due to the more bulky alkyl group interfering with the participation of the lone pair orbital of the amine nitrogen in direct conjugation with the phenyl ring. Adding a second alkyl group also appears to reduce the magnitude of σ (*p*-NHMe, -0.84;⁵¹ *p*-NMe₂, -0.83^{36-38,51}), probably for the same reason. Thus, it would appear that σ for *p*-NEt₂ should be slightly less negative than -0.61. In addition to these arguments, we have also found that the use of σ = -0.60 for the *p*-NEt₂ substituent provides better correlation of the logarithms of the equilibrium constants for complex formation of a series of substituted Zn^{II}(TPP) derivatives with 3-picoline¹⁷ with previously published data¹⁶ and, in the present case, of (TPP)Fe^{III} derivatives with *N*-methylimidazole, allows the [(*p*-NEt₂)₄TPP]Fe^{III} complex to lie on the line of slope *p* = -0.39 found previously^{14,15} for five other tetra-para-substituted derivatives of (TPP)Fe^{III} (see Figure 3). Thus we have used σ = -0.60 for

Table II. Equilibrium Constants for Addition of *N*-Methylimidazole to a Series of Symmetrically and Unsymmetrically Substituted Iron(III) Tetraphenylporphyrins^a

| phenyl substituents | Σσ | log β ₂ ^c | ref |
|--|---------------------|---------------------------------|----------|
| (<i>m</i> -NO ₂) ₄ | 2.840 | 3.32 (0.07) | <i>d</i> |
| (<i>p</i> -NO ₂) ₃ | 2.334 | 2.82 (0.10) | <i>d</i> |
| <i>cis</i> - + <i>trans</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NO ₂) ₂ | 2.010 | 2.65 (0.09) | <i>d</i> |
| (<i>m</i> -F) ₄ | 1.348 | 3.02 (0.06) | <i>d</i> |
| <i>trans</i> -(<i>m</i> -NO ₂) ₂ (<i>m</i> -CH ₃) ₂ | 1.282 | 3.28 (0.08) | <i>d</i> |
| <i>cis</i> -(<i>m</i> -NO ₂) ₂ (<i>m</i> -CH ₃) ₂ | 1.282 | 3.30 (0.06) | <i>d</i> |
| (<i>p</i> -Cl) ₄ | 0.908 | 2.85 (0.05) | 13 |
| <i>p</i> -NO ₂ | 0.778 | 3.09 (0.10) | <i>d</i> |
| <i>m</i> -NO ₂ | 0.710 | 3.16 (0.16) | <i>d</i> |
| <i>m</i> -NO ₂ (<i>m</i> -CH ₃) ₃ | 0.503 | 3.20 (0.06) | <i>d</i> |
| (<i>m</i> -OCH ₃) ₄ | 0.345 | 3.12 (0.06) | <i>d</i> |
| (<i>p</i> -F) ₄ | 0.248 | 3.00 (0.04) | 13 |
| <i>m</i> -OCH ₃ | 0.115 | 3.18 (0.14) | <i>d</i> |
| (<i>p</i> -Cl) ₃ (<i>p</i> -NEt ₂) | 0.081 ^e | 2.95 (0.10) | <i>d</i> |
| none | 0.000 | 3.18 (0.07) | 13 |
| <i>p</i> -OCH ₃ | -0.268 | 3.15 (0.06) | <i>d</i> |
| (<i>m</i> -CH ₃) ₄ | -0.276 | 3.35 (0.06) | <i>d</i> |
| <i>p</i> -NEt ₂ | -0.600 | 3.14 (0.10) | <i>d</i> |
| (<i>p</i> -CH ₃) ₄ | -0.680 | 3.43 (0.03) | 13 |
| <i>trans</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NEt ₂) ₂ | -0.746 ^e | 3.11 (0.04) | <i>d</i> |
| <i>cis</i> -(<i>p</i> -Cl) ₂ (<i>p</i> -NEt ₂) ₂ | -0.746 ^e | 3.12 (0.13) | <i>d</i> |
| (<i>p</i> -OCH ₃) ₄ | -1.072 | 3.56 (0.03) | 13 |
| (<i>p</i> -Cl)(<i>p</i> -NEt ₂) ₃ | -1.573 ^e | 3.32 (0.12) | <i>d</i> |
| (<i>p</i> -NEt ₂) ₃ | -1.800 ^e | 3.56 (0.11) | <i>d</i> |
| (<i>p</i> -NEt ₂) ₄ | -2.400 ^e | 4.11 (0.12) | <i>d</i> |

^a Solvent, CHCl₃; temperature = 25.0 ± 0.2 °C. ^b Taken from ref 35 and 36. ^c β₂ in units of M⁻²; error, in terms of log β₂, in parentheses. ^d This work. ^e The σ constant used for *p*-NEt₂ is -0.600 (see text).

the *p*-NEt₂ group in all of the data of Figure 3 and Table II.

Independent of the exact value of σ chosen for the *p*-NEt₂ group, there are two striking and unexpected features to the data of Table II and Figure 3 which were not observed for the study of complex formation of Zn^{II}(TPP)s with 3-picoline:¹⁶ (1) Unsymmetrically multiply substituted (TPP)Fe^{III} derivatives do not behave the same as tetra-para-substituted derivatives; (2) mono-phenyl-substituted (TPP)Fe^{III} derivatives are insensitive to the nature of the single substituted (TPP)Fe^{III} complexes; and (3) tetra-meta-substituted derivatives behave differently than tetra-para-substituted (TPP)Fe^{III} complexes. In fact, these three observations appear to be

(50) Pelizzetti, E.; Verdi, C. *J. Chem. Soc., Perkins Trans. 2* **1973**, 808-811.

(51) Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitani, D.; Lien, E. *J. Med. Chem.* **1973**, *16*, 1207-1216.

related, as will be discussed in more detail below.

To begin our discussion of these effects, let us consider reaction 3 for the six compounds $[(p\text{-Cl})_x(p\text{-NEt}_2)_{4-x}\text{TPP}]\text{FeCl}$, where $x = 0-4$. The values of $\log \beta_2$ for these six compounds have been reported previously,¹⁹ though the value reported at that time for $[(p\text{-Cl})_1(p\text{-NEt}_2)_3\text{TPP}]\text{FeCl}$ was erroneously that obtained for $[(p\text{-NEt}_2)_3\text{TPP}]\text{FeCl}$. With this limited set of data we were unable to explain satisfactorily why the mixed-substituent complexes did not behave according to eq 2 (i.e., why the values of $\log \beta_2$ did not lie on the line defined by the tetra-para-substituted derivatives studied previously.¹⁴ Once it was realized that five of the six complexes (excluding the $(p\text{-NEt}_2)_4$ derivative) obeyed a linear free energy relationship with slope approximately half that observed for the tetra-para-substituted derivatives, this hypothesis was tested by measuring the value of β_2 for the reaction of the mixture of isomers⁵² *cis*- and *trans*- $[(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPP}]\text{FeCl}$ with *N*-methylimidazole. Indeed, $\log \beta_2$ was found to fall on this line (Figure 3). From now on we will call this the "*p*-chloro-based line". We then noticed that the two tri-substituted complexes, $[(p\text{-NO}_2)_3\text{TPP}]\text{FeCl}$ and $[(p\text{-NEt}_2)_3\text{TPP}]\text{FeCl}$ had $\log \beta_2$ values that were not only on the tetra-meta-substituted (TPP)FeCl line, but that this line had a very similar slope to that of the *p*-chloro-based line. Thus we have confirmed the fact that unsymmetrically, multiply para-substituted (TPP)Fe^{III} derivatives are much less sensitive (by about a factor of 2) to the nature of the para substituents than are their symmetrical, tetra-para-substituted counterparts: The slope (ρ) of the tetra-para-substituted line is -0.39 , as reported previously,¹⁴ while those of the unsymmetrically multiply para-substituted complexes are $\rho = -0.18$ for both the *p*-chloro-based and "*para*-hydrogen-based and *meta*" lines (Figure 3).

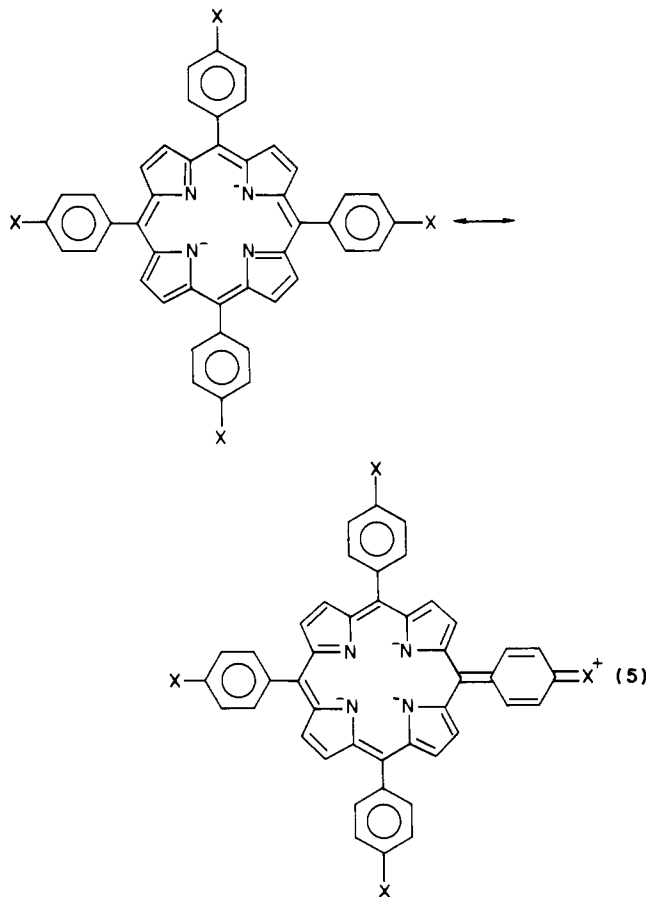
As mentioned above, we also found that all mono-substituted (TPP)FeCl derivatives (*p*-NEt₂, *p*-OCH₃, *m*-OCH₃, *m*-NO₂, and *p*-NO₂) had $\log \beta_2$ values well within experimental error of that of the parent compound, (TPP)FeCl (Table II, Figure 3). This immediately points out the fact that *substituent effects are not additive* in this system. Wells⁵³ has described the general case of the effect of two substituents, X and Y, on linear free energy relationships, with particular application to rate constants:

$$\log(k_{XY}/k_{00}) = (\sigma_X + \sigma_Y) + q\sigma_X\sigma_Y \quad (4)$$

He points out that the effects of X and Y will only be additive when $q = 0$, which in general may not be the case. In the present system, which includes multiply substituted TPP derivatives, the second term on the right-hand side of eq 4 will be of the form $q\sum\sigma_X\sigma_Y$. If q is finite, this term will equal zero only in the case of mono-substituted TPPs, since $\sigma_H = 0$. The fact that all mono-substituted (TPP)FeCl have, within experimental error, the same value of β_2 for *N*-methylimidazole addition suggests that the second term of eq 4 is fairly important, indeed, more important than the first. In addition, the $q\sum\sigma_X\sigma_Y$ term would be expected to have its largest contribution when $\sigma_X = \sigma_Y$ (tetra-para-substituted derivatives), since in most other cases the signs of the two σ constants are opposite, causing most of the contribution of the σ product to cancel. However, since in this system, we have a variable number of substituents, it is not possible to apply Wells' mathematical treatment quantitatively without doing a large number of additional measurements. Thus we will attempt to explain the behavior of multiply substituted (TPP)FeCl derivatives by initially assuming additivity of substituent effects (Figure 3, or eq 4 with $q = 0$) and then deal with the deviations from that additive behavior.

The fact that the three tetra-*meta*-substituted (TPP)FeCl derivatives obey the same linear free energy relationship as the two trisubstituted (TPP)Fe^{III} complexes helps to point us toward the

explanation of the unique behavior of multiply substituted iron(III) tetraphenylporphyrins: *Meta* phenyl substituents cannot engage in direct conjugation with the porphyrin ring, while *para* phenyl substituents can. If we consider the porphyrin dianion, conjugation with a *para* phenyl substituent can create a third negative charge at the porphyrin nitrogens:



Such creation of a third charge at the porphyrin nitrogens would neutralize the formal positive charge present at the iron center of (TPP)Fe(*N*-MeIm)₂⁺Cl⁻ complexes. This formal positive charge at the Fe(III) center of the product of reaction 3 has previously been suggested to be the explanation for the negative slope (ρ) for the linear free energy relationship for $\log \beta_2$ with $\sum\sigma$.¹⁴

We could say that the Hammett σ constants, which are appropriate for those systems in which there is not direct resonance between substituent and reaction center,³⁸ are simply not appropriate for the present system; if it were not for the fact that until the fourth identical substituent is added, *para* phenyl multiply substituted (TPP)Fe^{III} derivatives behave the same as the tetra *meta* phenyl (TPP)Fe^{III} complexes. (Compare the slope of the chloro-based line and that of the *meta* line.) In earlier studies of tetra *meta* and *para* phenyl substituted (TPP)Ni^{III} derivatives reacting with piperidine, the ρ values for *meta*- and *para*-substituted complexes were identical within experimental error, when the Hammett σ constants were used.¹² When a dual parameter treatment was tried using the Taft resonance and inductive parameters, σ_R and σ_1 ,⁵⁴ the contribution of resonance and inductive effects for the *para*-substituted derivatives was found to be nearly equal, which suggested π induction or weak π resonance rather than direct, strong π conjugation.¹² This finding of nearly equal contribution of resonance and inductive effects¹² was taken as evidence that the Hammett substituent constants were appropriate for describing the linear free energy relationships for stability constants for axial ligation to metalloporphyrins. Consistent with

(52) It was not possible to separate the *cis* and *trans* isomers of $(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPPH}_2$, but the similarity in values of β_2 for the two isomers of $[(p\text{-Cl})_2(p\text{-NEt}_2)_2\text{TPP}]\text{FeCl}$ and $[(m\text{-NO}_2)_2(m\text{-CH}_3)_2\text{TPP}]\text{FeCl}$ (Table II) indicates that the value of β_2 observed for *cis*- + *trans*- $[(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPP}]\text{FeCl}$ is representative of both isomers.

(53) Wells, P. R. "Linear Free Energy Relationships"; Academic Press: New York, 1968; p 33.

(54) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

this is the fact that $\log K$ for addition of 3-picoline to both meta- and para-substituted (TPP)Zn^{II} derivatives follows a common linear free energy relationship when the Hammett σ constants are used.¹⁷ However, for Fe^{III}(TPP) derivatives this is not the case. Use of various scales of σ_R ⁵⁵ or σ^+ ³⁸ for all para-substituted (TPP)Fe^{III} complexes, and ignoring the meta-substituted complexes, will not lead to a common linear free energy relationship for symmetrical and unsymmetrical derivatives, since, for example, the value of $\log \beta_2$ for [(*p*-NEt₂)₃TPP]FeCl is only halfway between those for [(*p*-NEt₂)₄TPP]FeCl and the parent (TPP)FeCl (Table II, Figure 3) and that for [(*p*-NEt₂)₁TPP]FeCl is identical with that of the parent. Thus we must conclude that both mono- and tetra-para-substituted (TPP)FeCl complexes are *anomalous* in their axial ligation reactions, while tetra-meta-substituted and unsymmetrically, multiply para-substituted (TPP)FeCl complexes exhibit *normal* behavior: When the first substituent is added to (TPP)FeCl, the system is able to ignore the presence of that substituent. Thereafter, as long as there is at least one "innocent" substituent present (i.e., one that cannot engage directly and strongly in electron donation through conjugation with the phenyl and porphyrin rings, as in eq 5, direct conjugation appears not to occur.

When the fourth identical para substituent is added, the system is forced to engage in direct conjugation. While this effect is most pronounced for strongly electron-donating substituents, it is clearly present for all para-substituted TPPs, thus giving rise to the *p*-chloro-based and para-hydrogen-based lines of Figure 3. Though this direct conjugation increases the sensitivity of $\log \beta_2$ to substituents ($\rho = -0.39$ vs. -0.18), it appears not to be a favorable process since it occurs only when the fourth identical substituent is added. This is not surprising, since it is generally agreed that because of steric interference between the β -pyrrole and ortho phenyl protons the phenyl rings are constrained to being out of the plane of the porphyrin most of the time and X-ray crystallographic structure determinations have confirmed this suggestion in numerous cases.⁵⁵ However, theoretical calculations of Wolberg⁵⁶ have suggested that in solution that phenyl rings can achieve positions nearly coplanar with the porphyrin and thereby allow significant resonance transfer of substituent effects. Certainly, the fact that the phenyl rings rotate, with activation energies of the order of 11–17 kcal/mol,^{32–34} indicates that they must be in the plane of the porphyrin ring for some fraction of the time. Traylor and co-workers⁵⁷ and Milgrom⁵⁸ have recently shown that tetrakis(*p*-hydroxyphenyl)porphyrins^{57,58} and their metal complexes⁵⁷ can be oxidized by two electrons to a di-quinone form which requires that direct conjugation occur between two of the phenyl rings and the porphyrin. Worthington et al.⁸ also found evidence for direct conjugation between a 4-(*N*-methylpyridyl) group of the series of H₂TPP derivatives having one to four phenyl groups replaced by 4-(*N*-methylpyridyl) groups: one 2-electron reduction wave was observed in these cases, rather than two 1-electron reduction waves, as for all other porphyrins investigated. The tetra-para-substituted (TPP)Fe^{III} system appears to be the third case in which direct conjugation can be demonstrated; however, in this case we believe that only one phenyl ring at a time is involved in this direct conjugation.

In line with this idea of direct conjugation from only one phenyl ring at a time, we have tried other LFE correlation schemes involving some sort of additivity of substituent effects, in the hope of finding one that would describe the behavior of all para-substituted (TPP)FeCl derivatives. The best correlation we have been able to find is that shown in Figure 4, where the values of $\log \beta_2$ are plotted against ($\sum \sigma_1 + \sigma_R^+$), where σ_1 and σ_R^+ are, respectively, the inductive and resonance substituent constants;⁵² values of σ_R^+ have been derived from systems in which there is strong,

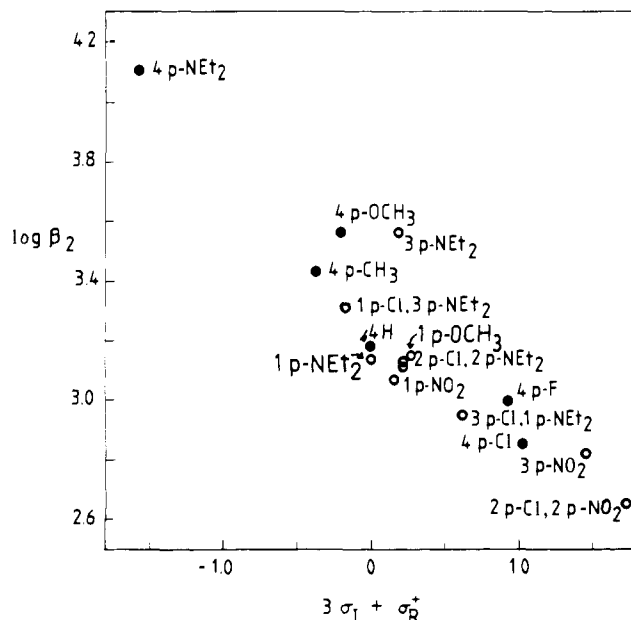


Figure 4. Plot of the values of $\log \beta_2$ for reaction 3 vs. the sum of the inductive substituent constants, σ_1 ,⁵⁴ for the three of the four substituents, plus the strongly conjugative substituent constant, σ_R^+ ,⁵⁴ for the fourth substituent, which in the case of the unsymmetrically substituted (TPP)FeCl derivatives is that substituent "least willing" to engage in direct conjugation. Only para-substituted derivatives are included. The values of σ_1 and σ_R^+ used for *p*-NEt₂ are those reported for *p*-NMe₂.⁵⁴

direct conjugation between substituent and reaction center.⁵⁴ The function ($\sum \sigma_1 + \sigma_R^+$) arises from the idea that only one substituent is involved in direct conjugation, that one being the "least willing" or, for unsymmetrically substituted complexes, the one that has the most positive Hammett σ constant. The other substituents present are thus accounted for in terms of their σ_1 values. As is apparent from Figure 4, the correlation is not perfect, but it does bring most symmetrical and unsymmetrical para-substituted (TPP)FeCl derivatives into an approximately common correspondence. There is one apparent inconsistency, however, between the presentation of data in Figures 3 and 4: The (*p*-NO₂)₃TPP of the hydrogen-based and meta line and the (*p*-Cl)₂(*p*-NO₂)₂TPP of the chloro-based line would, according to the interpretation of Figure 4, be involving one nitro group in direct resonance, rather than either the H or Cl as suggested by Figure 3. Also, it should be noted that the (*p*-NEt₂)₃ derivative does not fit this correlation well. Despite these weaknesses, however, the approximate correlation of Figure 4 is suggestive of an "unwilling" involvement of direct conjugation in the tetra-para-substituted TPP derivatives.

If we consider the potential relevance of these findings to the behavior of the heme proteins, we must consider the possible involvement of the vinyl groups of protoporphyrin IX in resonance with the porphyrin ring. The crystal structure of protoporphyrin IX dimethyl ester,⁵⁹ as well as that of hemoglobin⁶⁰ and cytochrome *b*₅,⁶¹ has shown that the vinyl groups are not in the same plane as the porphyrin ring. However, NMR evidence has suggested that in some cases, including aquomethemoglobin,⁶² there are protein residues near one or both vinyl groups which appear capable of restricting their oscillatory motion or even pressing them into the porphyrin plane. If this occurs, it is to be expected that the vinyl groups would become much more electron withdrawing than they are in their nonplanar configuration. This would create a tendency for electron flow which is opposite that proposed for the model compounds of the present study: The vinyl group is

(55) Meyer, E. F.; Cullen, D. L. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. III, pp 513–529 and references therein.

(56) Wolberg, A. *J. Mol. Struct.* **1974**, *21*, 61–66.

(57) Traylor, T. G.; Nolan, K. B.; Hildreth, R. *J. Am. Chem. Soc.* **1983**, *105*, 6149–6151.

(58) Milgrom, L. R. *Tetrahedron*, **1983**, *39*, 3895–3898.

(59) Caughey, W. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6639–6645.

(60) Takano, T. *J. Mol. Biol.* **1977**, *110*, 537–568.

(61) Mathews, F. S.; Czerwinski, E. W.; Argos, P. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. VII, pp 107–147.

(62) LaMar, G. N.; Budd, D. L.; Smith, K. M.; Langry, K. C. *J. Am. Chem. Soc.* **1980**, *102*, 1822–1827.

expected to interact by resonance (as well as induction) to withdraw electron density and charge from the porphyrin nitrogens.⁵⁶ Should this occur in a heme protein, we would expect that the Fe(III) state would be significantly destabilized with respect to Fe(II) when the vinyl groups are pressed into the plane of the porphyrin ring and thus that the Fe(III)/(II) redox potential would be more positive than would otherwise have been expected.

One substituent that proved to be anomalous, beyond our ability to explain, and was thus not included in the linear free energy correlation of Figure 3, is the *m*-NO₂ group: The series of complexes [(*m*-CH₃)₄TPP]FeCl, [(*m*-NO₂)₁(*m*-CH₃)₃TPP]Cl, the *cis* and *trans* isomers of [(*m*-NO₂)₂(*m*-CH₃)₂TPP]Cl, and [(*m*-NO₂)₄TPP]Cl were all prepared and the equilibrium constants for reaction 3 measured. The results for *m*-nitro-containing compounds are included in Table II but not in Figure 3. It is immediately apparent that all five of these values of log β₂ are within experimental error of each other, and whereas log β₂ for the (*m*-NO₂)₄ derivatives should have been 2.73 if it were to behave as do the other tetra-*meta*-substituted derivatives, the measured value is in fact 0.6 log units larger, or β₂ is a factor of 4 larger than expected. It thus appears that the system chooses not to acknowledge the presence of *m*-NO₂ groups. We could postulate that the *m*-NO₂ groups were reduced to some less electron-withdrawing group such as NHOH during iron insertion and purification were it not for the facts that (1) the pattern of pyrrole proton resonances observed for the (*N*-MeIm)₂ complexes of these compounds³⁹ are not anomalous when the Hammett σ constants³⁶⁻³⁸ for the *m*-CH₃ and *m*-NO₂ are utilized, (2) the redox potentials of the same complexes, assuming the presence of *m*-NO₂ groups, are not anomalous, and (3) the *p*-NO₂-containing unsymmetrically substituted complexes of this study do not behave anomalously (Table II, Figure 3). If NO₂ groups were sensitive to reduction, then both *m*- and *p*-NO₂ groups should behave similarly. However, the *p*-NO₂ group is not completely unambiguous, in that while we can make (TPP)FeCl derivatives having up to three *p*-NO₂ groups present, we have been unable to prepare the [(*p*-NO₂)₄TPP]FeCl complex. If we use highly purified (*p*-NO₂)₄TPPH₂ for the reaction with FeCl₂⁴³ (in order to avoid any possible confusion caused by the presence of tar in the crude (*p*-NO₂)₄TPPH₂), we observe similar color changes during metal insertion and similar behavior and colors during column chromatography. However, when dry HCl gas is bubbled through, the product immediately turns black and precipitates as an intractable tar. This suggests destruction of the porphyrin nucleus when four *p*-NO₂ groups are present on the periphery of (TPP)FeCl. This does not, however, explain the behavior of the *m*-NO₂-containing complexes, since their visible spectra are clearly those of otherwise typical (TPP)Fe^{III} derivatives (see below). We are unable to explain why *m*-NO₂ appear not to participate in determining the overall substituent effects in this system.

Visible Spectra of High- and Low-Spin (TPPE)Fe^{III} Derivatives.

The spectral bands I-IV for the high-spin (TPP)FeCl derivatives of this study listed in Table I are those that we previously called ν₅, ν_{5'}, ν₄, and ν₃.¹⁴ We have chosen to adopt the nomenclature of Gouterman^{46,47} in the present study. Each of these bands behaves somewhat differently as the electronic effects of substituents are varied; band IV, the Q_v a_{2u}(π) → e_g(π*) porphyrin transition,⁴⁵ is essentially insensitive to phenyl substitution, while band III, the Q₀ component of the same transition,⁴⁶ shifts slightly to higher energy as the electron-withdrawing nature of the substituents increases. Band III for unsymmetrically substituted (TPP)FeCl derivatives tends to shift less than for tetra-*meta*- and tetra-*para*-substituted derivatives, as shown in Figure 5.

Bands II and I have been identified as charge-transfer bands associated with the transitions a_{2u}(π), b_{2u}(π) → e_g(d_{xz}, d_{yz}).⁴⁶ It is believed that the e_g(d_{xz}, d_{yz}) orbitals contain 35-45% porphyrin π character in high-spin ferric porphyrin complexes.⁴⁶ Thus, the mixing of the iron e_g(d_{xz}, d_{yz}) orbitals with the lowest empty porphyrin e_g(π*) orbitals is expected to significantly intensify the charge-transfer bands.⁶³ This mixing is most directly affected

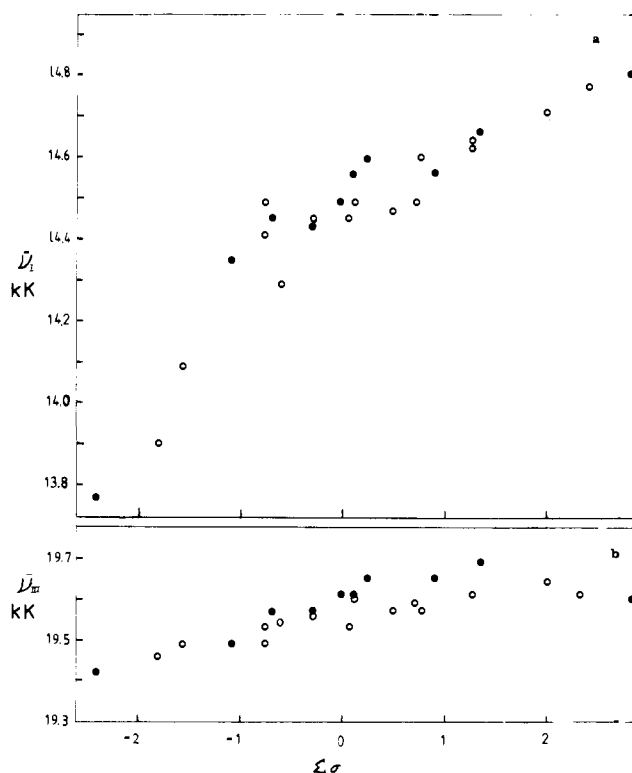


Figure 5. Plot of the energies of bands I (charge transfer) and III (Q₀ for high-spin TPPFeCl derivatives vs. the sum of the Hammett σ constants of the substituents. No such correlation is found for bands II and IV or the Q₀ and Q_v bands of the low-spin (TPP)Fe(*N*-MeIm)₂⁺Cl⁻ complexes.

by the strength of the axial ligand field.⁶³ However, it must be secondarily affected by the strength of the equatorial ligand field, since in our system the axial ligand remains constant, while band I shifts to higher energy as the electron-withdrawing nature of the substituents increases (Figure 5). Band II, which is often poorly defined, appears to show little systematic variation with phenyl substituents. The intensities of these two bands remain fairly similar (Table I), indicating a very similar degree of mixing of e_g(d_{xz}, d_{yz}) and e_g(π*) throughout the series.

For the low-spin derivatives of (TPP)Fe(*N*-MeIm)₂⁺Cl⁻, little systematic variation in the energies of either Q₀ or Q_v is apparent, except that both bands are shifted to lower energy when diethylamino groups are present (Table I). However, there are large changes in the relative intensities of the two bands.

Gouterman first suggested⁶⁴ and several other studies have since confirmed^{17,65} that the intensity of the Q₀ and Q_v bands should vary with their energies. In the present study we have found that such a relationship exists for the Q₀ band of low spin but not the corresponding band III of high-spin iron(III) porphyrins, as demonstrated in Figure 6a,b, where the log of the intensity ratio of the two bands is plotted against the energies of the respective bands. The respective Q_v and IV bands, however, do not show such a correlation. It is also interesting to note that only for bands Q₀ for low-spin and III for high-spin derivatives do the *cis* and *trans* isomers of [(*p*-Cl)₂(*p*-NEt₂)₂TPP]Fe^{III} differ significantly from each other (Table I). Yet, at least for the low-spin complexes, the differences in Q₀ band energies and the log of the intensity ratio of Q₀ to Q_v balance each other so as to maintain the linear relationship observed for other low-spin (TPP)Fe^{III} complexes. The *cis* and *trans* isomers are of different molecular symmetries (D_{2h} and C_{2v}, respectively). In fact, since the 3X, 1Y isomers are also of C_{2v} symmetry, though with a different principal axis than the *trans* isomer, it may be best to look at the *cis* isomer as the

(63) Eaton, W. A.; Hochstrasser, R. M. *J. Chem. Phys.* **1968**, *49*, 985-995.

(64) Gouterman, M. *J. Chem. Phys.* **1959**, *30*, 1139-1161.

(65) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075-5080.

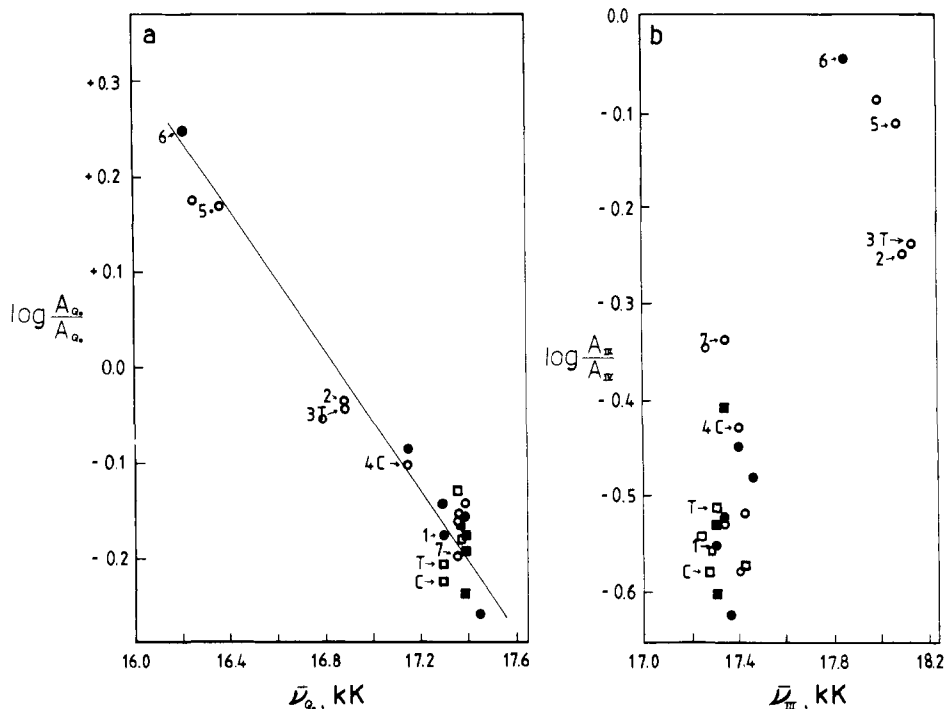


Figure 6. Dependence of the log of the ratio of intensities of the peaks corresponding to the transitions Q_0 and Q_v for (a) low-spin iron(III) porphyrins vs. the energy of the Q_0 band and (b) high-spin iron(III) porphyrins vs. the energy of band III. Solid circles, tetra-para-substituted; solid squares, tetra-meta-substituted; open circles and squares, unsymmetrically para- and meta-substituted derivatives. 1 = $[(p\text{-Cl})_4\text{TPP}]\text{Fe}^{\text{III}}$; 6 = $[(p\text{-NEt}_2)_4\text{TPP}]\text{Fe}^{\text{III}}$; 2-5 = mixed-substituent isomers in sequence; 7 = $[(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPP}]\text{Fe}^{\text{III}}$.

anomaly. This is borne out by the position of the *cis*-(*p*-Cl)₂, *p*-NEt₂)₂ isomer in Figure 6a.

The relationship between intensity ratio and energy, such as that shown in Figure 6a for low-spin (TPP)Fe^{III} derivatives, was described by Gouterman as an electronegativity effect.⁶⁴ In the present case we would reword Gouterman's explanation to say that, for low-spin (TPP)Fe^{III} derivatives, as more "electronegative" groups are placed on the periphery of the ring, more electron density will shift from the center of the ring toward the periphery. (We will allow the term electronegative to represent the complex balance of electron-withdrawing effects due to induction and resonance.) This shift, according to Gouterman,⁶ could raise the energy of both the $a_{2u}(\pi)$ and $e_g(\pi^*)$ orbitals involved in the electronic transition through σ inductive effects and, additionally, raise the energy of the filled $a_{2u}(\pi)$ orbital through π or conjugative effects. Each of these effects could change the oscillator strengths of the transitions Q_0 and its vibronically excited counterpart Q_v . The fact that the Q_0 transition of low-spin (TPP)Fe^{III} complexes is affected by changes in the electronic effects of substituents (Figure 6a) while band III of high-spin (TPP)Fe^{III} complexes is not (Figure 6b) is consistent with a major role for direct π conjugation in the low-spin but not the high-spin (TPP)Fe^{III} derivatives. Why the vibronically excited transition Q_v is not similarly affected is not clear, unless the displacement of atoms during the vibration is such as to destroy the possibility of direct resonance.

Summary

In the present study we have found that both mono- and tetra-para-substituted (TPP)FeCl derivatives are the exception to the rule in the stability of their bis(*N*-methylimidazole) complexes. The mono-substituted (TPP)FeCl derivatives are insensitive to the electronic effect of the single substituent, while the tetra-para-substituted derivatives show much greater sensitivity ($\rho = -0.39$) to the nature of the four identical substituents than do unsymmetrically, multiply para-substituted and symmetrically meta-substituted derivatives ($\rho = -0.18$). One way to look at these systems is to attribute the unique behavior of tetra-para-substituted

(TPP)FeCl derivatives to the involvement of one phenyl group and its para substituent in direct conjugation with the porphyrin ring, thus removing, or rather shifting, the formal positive charge from the Fe(III) center to the periphery of the molecule. Perhaps a better way to analyze the system, if much more data were available, would be to use a multisubstituent parameter approach. In any case, the present study indicates that the substituent effects in metalloporphyrins in which the metal carries a formal positive charge are considerably more complex than is apparent from a study of only symmetrically substituted compounds. The behavior of the visible band Q_0 is consistent with an important role for direct conjugation in the bis(*N*-methylimidazole) complexes, but not the high-spin chloroiron(III) starting materials.

Acknowledgment. The financial support of NIH RCDA (GM00227) and NIH research grant (AM31038) is gratefully acknowledged. This paper was written while F.A.W. was visiting professor in the Chemistry Department of the University of Queensland. She wishes to thank Professor Clifford J. Hawkins and his colleagues for their hospitality and helpful comments. Discussions with Professors Frederick R. Jensen and Peter F. Wells added significantly to the analysis and interpretation of this system.

Registry No. $[(m\text{-NO}_2)_4\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-29-8; $[(p\text{-NO}_2)_3\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-30-1; *cis*- $[(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-31-2; *trans*- $[(p\text{-Cl})_2(p\text{-NO}_2)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-32-3; $[(m\text{-F})_4\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-33-4; *trans*- $[(m\text{-NO}_2)_2(m\text{-CH}_3)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-34-5; *cis*- $[(m\text{-NO}_2)_2(m\text{-CH}_3)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-35-6; $[(p\text{-NO}_2)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-36-7; $[(m\text{-NO}_2)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-37-8; $[(m\text{-NO}_2)(m\text{-CH}_3)_3\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94569-36-5; $[(m\text{-OCH}_3)_4\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-38-9; $[(m\text{-OCH}_3)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94569-37-6; $[(p\text{-Cl})_3(p\text{-NEt}_2)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-39-0; $[(p\text{-OCH}_3)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94569-38-7; $[(m\text{-CH}_3)_4\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 61056-79-9; $[(p\text{-NEt}_2)\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-40-3; *trans*- $[(p\text{-Cl})_2(p\text{-NEt}_2)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-41-4; *cis*- $[(p\text{-Cl})_2(p\text{-NEt}_2)_2\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-42-5; $[(p\text{-Cl})(p\text{-NEt}_2)_3\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94569-39-8; $[(p\text{-NEt}_2)_3\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94569-40-1; $[(p\text{-NEt}_2)_4\text{TPP}]\text{Fe}(\text{N-MeIm})_2^+\text{Cl}^-$, 94537-43-6.