It is therefore of interest to compare the two systems PCl_5–$SnCl_4$ and PCl_5–$TiCl_4$. Both of these systems have been studied by vibrational spectroscopy[15,16,28] and X-ray analysis.[6,28] In the tin system three types of anions were verified to exist with the PCl_4^+ cation, in the following relative stabilities in which the dimer is more stable at higher temperatures:

$$\mathrm{SnCl_6^{2-}}\text{ (stable)};\quad \mathrm{Sn_2Cl_{10}^{2-}} \xleftarrow{\text{heat}} \mathrm{SnCl_5^-}$$

However, in the titanium system, no $TiCl_6^{2-}$ seems to exist with the PCl_4^+ cation[15] even with an excess of PCl_5. The relative thermodynamic stabilities are in the opposite direction, namely the monomer being more stable at higher temperatures:

$$\mathrm{TiCl_6^{2-}}\text{ (nonexistent)};\quad \mathrm{Ti_2Cl_{10}^{2-}} \xrightarrow{185\ ^\circ\mathrm{C}} \mathrm{TiCl_5^-}$$

We have no clear explanation for these differences, because the $TiCl_6^{2-}$ anion has been established in other salts with other cations. It is possible that these differences stem from steric effects or possibly from varying relative Lewis acidities and basicities.[15,16] Further work on the PCl_5–$TiCl_4$ system is in progress.

Registry No. **1**, 17731-85-0; **2**, 96211-86-8; **3**, 96211-87-9; **4**, 96211-88-0; PCl_5, 10026-13-8; $SnCl_4$, 7646-78-8; PCl_3, 7719-12-2; $SOCl_2$, 7719-09-7.

Supplementary Material Available: Tables of structure factors and thermal parameters for **2**, **3**, and **4** (24 pages). Ordering information is given on any current masthead page.

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(28) This work.

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Mechanism of Conversion of Iron(III) Tetratolylporphyrin Hydroxide to the Corresponding μ-Oxo-Bridged Dimer

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The rate of conversion of iron(III) tetra-*p*-tolylporphyrin hydroxide to the corresponding μ-oxo-bridged dimer was studied by ^1H NMR at room temperature in carbon tetrachloride solution. The dependence of the rate on the initial concentration of the iron porphyrin and on the concentration of hydroxide ion (OH and OD) was examined. The data are consistent with a two-step mechanism. The first step is dissociation of hydroxide from an iron porphyrin. In the second step that iron porphyrin reacts with a second iron porphyrin hydroxide to form the dimer. The deuterium isotope effect on the second step was about 5.

Introduction

The product that has been isolated after reaction of hydroxide with sterically unhindered iron(III) porphyrin chlorides (Fe(P)Cl[1]) in organic solvents is the μ-oxo-bridged dimer.[2] Recently it has been shown that sterically hindered porphyrins prevent dimer formation and permit isolation of Fe(P)OH.[3-11] It has also been reported that the visible spectrum of the product obtained by reaction of Fe(TPP)Cl with OH^- indicated that Fe(TPP)OH was formed.[3,12,13]

In our studies of metal–nitroxyl interactions in spin-labeled iron(III) porphyrins,[14] we observed that when a solution of Fe(P)Cl was shaken with aqueous OH^-, the initial product was Fe(P)OH and that complete conversion to the dimer required several hours. Similarly when Fe(TTP)Cl or Fe(TPP)Cl was shaken with OH^-, the product was Fe(P)OH which converted to $(Fe(P))_2O$ within several hours. These observations prompted us to examine the process by which Fe(TTP)OH was converted to $(Fe(TTP))_2O$. Fe(TTP)OH was selected for this study because the ^1H NMR spectra of the methyl groups provided a convenient method to follow the course of the reaction.

Experimental Section

Physical Measurements. Electronic spectra were obtained in toluene solution (ca. 0.05 mM) on a Beckman Acta V spectrometer in 1-mm cells for the region 300–470 nm and in 10-mm cells for the region 470–800 nm. Infrared spectra were obtained on benzene solutions (1 mM) in a 1-mm NaCl cell on a Digilab FTS-20B infrared spectrometer. The background spectrum of the cell and solvent was digitally subtracted from the spectrum of the solution of iron porphyrin. NMR spectra were obtained at 21–22 °C in carbon tetrachloride solution in 5-mm tubes on a Magnachem A200 FT NMR. For the kinetic studies 20 ppm spectra were obtained with 8*K* data points and sufficient delay between pulses to give accurate integration of the signals. In a sample containing tetramethylsilane (Me_4Si), the methyl signal in $(Fe(TTP))_2O$ was 2.81 ppm downfield of Me_4Si. In subsequent spectra of samples that did not contain Me_4Si, the shifts were assigned relative to the shift of this methyl signal.

Preparation of Iron Porphyrins. Pyrrole was distilled before use. Reagent grade and spectroscopic grade solvents were used without purification. H_2TPP[15,16] and H_2TTP[15,16] were purified by chromatography in chloroform solution on silica gel. Fe(TPP)Cl[17,18] and Fe(TTP)Cl[17]

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(1) Abbreviations: P = porphyrin dianion; TPP = dianion of 5,10,15,20-*meso*-tetraphenylporphyrin; TTP = dianion of 5,10,15,20-*meso*-tetra-*p*-tolylporphyrin.

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were purified by chromatography in chloroform solution on silica gel. The products were treated with base and rechromatographed on alumina to prepare $(Fe(TPP))_2O$ or $(Fe(TTP))_2O$, respectively.[18] Products were recrystallized from chloroform/heptane and dried in vacuo at 95 °C. The infrared, visible, and NMR spectra were in good agreement with spectra in the literature.

Preparation of Solutions of Fe(TTP)OH. A solution of $(Fe(TTP))_2O$ in 3–5 mL of toluene, benzene, or CCl_4 was stirred vigorously with 5 mL of 2 M HCl for about 10 min to form Fe(TTP)Cl. The color change of the organic phase from green to brown was complete within about 1 min. The organic phase was transferred to a flask containing 5 mL of 2 M NaOH and stirred vigorously for 5 min. The color change of the organic phase from brown back to green indicated that the conversion from Fe(TTP)Cl to Fe(TTP)OH was complete within a few minutes. The reaction proceeded more slowly for less concentrated NaOH solutions, so for all of the NMR studies the preparation of Fe(TTP)OH was done with 2 M NaOH. The aqueous phase was then diluted to the desired base concentration, and stirring was continued for an additional 5 min to equilibrate the concentration of base between the organic and aqueous phases. The phases were separated, and spectra were obtained on the organic phase. The starting time for the reaction was defined as the time when the solution turned green. This was usually about half-way through the 5 min of stirring with 2 M NaOH. Distilled H_2O was used to prepare the solutions of OH^-. NaOH was dissolved in distilled D_2O to prepare the solutions of OD^-. Distillation of the H_2O and D_2O was required to remove impurities that gave signals between 4.5 and 5.5 ppm in the NMR spectra.

Solutions of Fe(TPP)OH were prepared by a procedure similar to that used for Fe(TTP)OH except that longer reaction times or higher concentrations of base were required. The solution of Fe(TPP)Cl required about 5 min of vigorous agitation with 5 M NaOH to ensure complete conversion to Fe(TPP)OH.

Kinetic Studies. NMR spectra of the solutions of Fe(TTP)OH were recorded within 8–10 min after starting the reaction. Four to nine spectra were recorded during the course of the reaction, and the reaction was followed to about 90% completion. Five experiments were performed in which the initial concentration of Fe(TTP)OH was varied from 4 to 0.25 mM and the concentration of base in the aqueous phase was 2 M. A similar series of experiments was performed with Fe(TTP)OD. The initial concentration of Fe(TTP)OH or Fe(TTP)OD was then fixed at 1 mM while the concentration of OH^- or OD^- in the aqueous phase was varied from 2.5 to 0.005 M and from 3.0 to 0.1 M, respectively. A total of eight experiments were done with OH^- and eight with OD^-. The data acquisition time for each spectrum ranged from about 8 min for an initial Fe(TTP)OH concentration of 4 mM to about 60 min for 0.25 mM. The midpoint of the data collection was defined as the time for the measurement. The relative concentrations of Fe(TTP)OH and $(Fe(TTP))_2O$ were determined by integration of the corresponding methyl signals. The integrated areas of the pyrrole and phenyl protons in $(Fe(TTP))_2O$ and the meta protons on the phenyl rings in Fe(TTP)OH were consistent with the values of the integrals obtained from the methyl signals. The concentration of Fe(TTP)OH was plotted as a function of time. A plot of concentration as a function of time was generated by a computer program based on the rate law discussed below. For each set of experimental data there was a range of values of k_1 and k' that gave comparable agreement between the calculated and observed concentrations of Fe(TTP)OH. The apparent first-order rate constant for the experiments with high initial concentrations of porphyrin and low base concentration was used as the starting estimate of k_1. The value of k' was adjusted to match the observed dependence of the rate on the concentration of base. Different values of k' were required to fit the data for OH^- and OD^-. These values will be referred to as $k'(H)$ and $k'(D)$. The values of k_1 and $k'(H)$ were then adjusted iteratively to match all of the data obtained with OH^-. Similarly the values of k_1 and $k'(D)$ were adjusted iteratively to fit all of the data obtained with OD^-. The uncertainties given for the values are based on the range of values that gave acceptable fits to the data.

Results and Discussion

When a solution of Fe(TTP)Cl in an organic solvent was shaken with an aqueous solution of NaOH, the color of the organic phase changed from brown to green. The product was identified as Fe(TTP)OH on the basis of the following evidence. The visible spectrum in toluene solution had broad peaks at 418, 580, and 620 nm. It has been noted previously that the positions of the bands in the visible spectra of Fe(P)OH are similar to those for $(Fe(P))_2O$ although the peaks are broader for Fe(P)OH than for $(Fe(P))_2O$.[8] The spectrum of Fe(TTP)OH agreed well with spectra reported in the literature for Fe(P)OH.[19] The absence of a band at 866 cm^{-1} in the IR spectrum of freshly prepared Fe(TTP)OH in benzene solution indicated that the compound was not the μ-oxo dimer.[20] The ^1H NMR spectra of Fe(TTP)OH in CCl_4 solution had the pyrrole H at 80.5 ppm (~700-Hz line width), nonequivalent meta H at 10.85 and 10.10 ppm (90-Hz line widths), and the methyl H at 4.85 ppm (26-Hz line width). The shifts for the pyrrole and meta protons and the splitting of the signals for the meta protons are in good agreement with values in the literature for Fe(P)OH[8–10] and are characteristic of 5-coordinate high-spin Fe(III) porphyrins. The EPR spectra (Figure 1A) were similar to those reported for Fe(P)OH.[4,6–8] The g values were 6.37, 5.52, and 1.98. The rhombic splitting of the EPR spectra was not noted in the spectra of Fe(P)OH where P was sterically hindered. However, rhombic splitting was observed in the EPR spectra of Fe(TPP)OMe ($g_x = 5.55$, $g_y = 6.40$).[21] There may be a greater tendency toward rhombic splitting of the energy levels for sterically unhindered iron porphyrins than for sterically hindered iron porphyrins. This could reflect different orientations of the bent OH or OMe relative to the magnetic axes for sterically hindered and unhindered porphyrins.

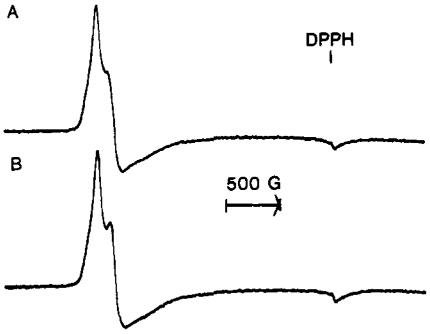

Figure 1. X-Band (9.105-GHz) EPR spectra in 2:1 toluene/chloroform glasses at −180 °C for (A) Fe(TTP)OH (0.87 mM) and (B) Fe(TPP)OH (0.89 mM). The spectra were 4000-G scans obtained with 50-mW power and 10-G modulation amplitude.

Similarly, when a toluene solution of Fe(TPP)Cl was shaken with an aqueous solution of NaOH, Fe(TPP)OH was formed. The visible spectra of a freshly prepared solution had peaks at 418, 575, and 620 nm, which is in good agreement with values recently reported in the literature.[3,12,13] The g values for the EPR spectrum (Figure 1B) were 6.29, 5.48, and 1.99. The peaks in the ^1H NMR spectra were as follows: pyrrole H, 80 ppm (~700-Hz line width); meta H, 10.95 and 10.10 ppm (90-Hz line widths). These spectra confirm the characterization of the product as Fe(TPP)OH.

At room temperature the spectral properties of the solution of Fe(TPP)OH changed gradually. After several hours, the visible spectrum was that of $(Fe(TTP))_2O$ and a peak at 866 cm^{-1} due to the Fe–O–Fe stretch in the dimer was observed in the IR. The EPR spectrum decreased in intensity over the course of several hours, which is consistent with the absence of an EPR signal for $(Fe(TTP))_2O$. The peaks in the NMR spectra for Fe(TTP)OH were gradually replaced with signals for $(Fe(TTP))_2O$: pyrrole, H, 13.3 ppm (65-Hz line width); meta H, 7.5 ppm (22-Hz line width); methyl H, 2.81 ppm (6-Hz line width).

The ^1H NMR spectra of Fe(TTP)OH included a broad peak near 0 ppm (Figure 2). Integration of the signal indicated that it corresponded to 16 mM protons, independent of the concentration of Fe(TTP)OH. The peak was absent from the solutions of Fe(TTP)OD and decreased in intensity when the solutions were dried over sodium sulfate or calcium hydride. The peak was

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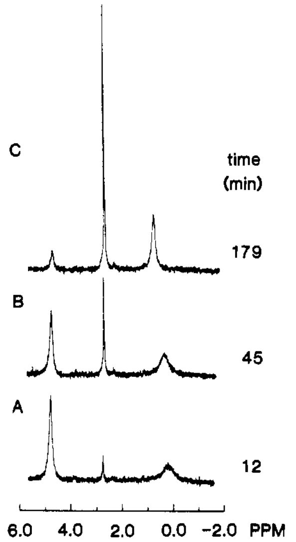

Figure 2. Portions of the 200-MHz ^1H NMR spectra of mixtures of Fe(TTP)OH and $(Fe(TTP))_2O$ as a function of time in CCl_4 solution. The initial concentration of Fe(TTP)OH was 1.61 mM. The solution was prepared by reaction with 1.8 M NaOH solution. The signals at 4.85 and 2.81 ppm are due to the CH_3 in Fe(TTP)OH and $(Fe(TTP))_2O$, respectively. The water signal shifted from 0.27 to 0.90 ppm as the reaction proceeded.

therefore assigned to H_2O. The position of the water signal varied from −1.0 ppm with a line width of about 200 Hz in a 4 mM solution of Fe(TTP)OH to 0.94 ppm with a line width of 18 Hz in a 0.24 mM solution of Fe(TTP)OH. As shown in Figure 2, the water peak moved downfield and the line width decreased in the course of the reaction, approaching a limiting value of 1.03 ppm and a line width of 6 Hz when all of the Fe(TTP)OH had been converted to $(Fe(TTP))_2O$. These observations are consistent with slow exchange between the observed H_2O signal and an undetected signal at higher field due to water that was interacting with the Fe(TTP)OH. In CCl_4 solutions of Fe(TTP)Cl that had been shaken with H_2O, the water signal was at 1.0 ppm and the line width varied from about 6 Hz for a 0.4 mM solution to 12 Hz for a 2 mM solution of Fe(TTP)Cl. It was assumed that the line width for the water signal in a solution of Fe(TTP)Cl was a reasonable approximation for the nonexchanging line width in a solution of Fe(TTP)OH at the same concentration. The rate of exchange of the free water was calculated from the increase in the line width of the water peak in the presence of Fe(TTP)OH.[22] If it is assumed that there was 1 mol of interacting water/mol of Fe(TTP)OH, the rate of exchange of interacting water was $1.1 \times 10^3\ s^{-1}$, independent of the concentration of Fe(TTP)OH.

There are two possible sites of interaction of the water with Fe(TTP)OH—weak coordination at the axial position or hydrogen bonding to the hydroxide. In ref 8 it was proposed that water was hydrogen bonded to the hydroxide in Fe(P)OH. The following arguments favor this interaction although the possibility of weak coordination cannot be unambiguously excluded. Electrochemical studies of Fe(TPP)Cl have suggested the possibility of solvent coordination to the sixth position.[23] Broadening of the water signal was observed in the presence of Fe(TTP)OH but not Fe(TTP)Cl. Both the rapid rate of water exchange and the similarity of the NMR spectra for Fe(TPP)OH and Fe(TTP)Cl rule out the possibility of strong coordination of water as a sixth ligand on Fe(TTP)OH. Since the tendency to form a six-coordinate complex would be expected to be similar for the two iron porphyrins, it is difficult to argue for even weak coordination of H_2O to Fe(TTP)OH, but not to Fe(TTP)Cl. Some support for a hydrogen-bonding interaction may be found by analogy. It has been proposed that there is hydrogen bonding between the hydroxide in Fe(P)OH and imidazole[10] and sterically hindered amines.[24] It has also been suggested that there is hydrogen bonding of methanol to the methoxide in Fe(TPP)OMe or that methanol is weakly coordinated.[21] Whichever mode of interaction is involved for Fe(TTP)OH, the on–off rate for the water was so much faster than the rates for the processes discussed below that the water was not included in the analysis of the kinetics.

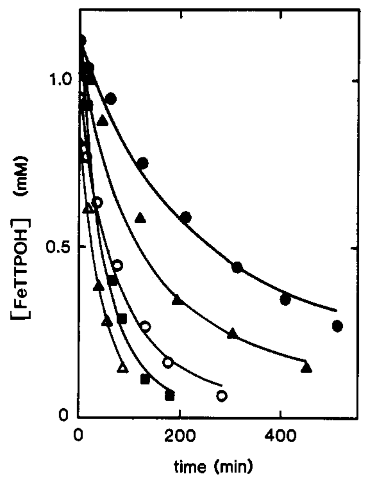

Figure 3. Changes in the concentration of Fe(TTP)OH as a function of time for solutions with 0.8–1.1 mM initial concentrations of Fe(TTP)OH. The solutions were prepared by stirring the CCl_4 solutions with (△) 0.005 M OH^-, (○) 2.2 M OH^-, (■) 0.1 M OD^-, (▲) 1.0 M OD^-, or (●) 3.0 M OD^-. The solid lines were calculated from the rate law in eq 3.

The change in the NMR spectra as a function of time is shown in Figure 2. The methyl signals were at 4.85 ppm (26-Hz line width) for Fe(TTP)OH and at 2.81 ppm (6-Hz line width) for $(Fe(TTP))_2O$. The methyl signal for Fe(TTP)Cl was at 6.24 ppm (16-Hz line width) so any impurity of Fe(TTP)Cl was readily detected. The greater line widths for the signals from Fe(P)OH than for Fe(P)Cl or $(Fe(P))_2O$ has been noted previously.[8] The changes in the integrated intensities of the methyl signals for Fe(TTP)OH and $(Fe(TTP))_2O$ as a function of time provided a convenient method to monitor the rate of the reaction. The rate of the reaction was determined for a range of initial concentrations of Fe(TTP)OH and Fe(TTP)OD. The solutions were equilibrated with aqueous solutions with a range of concentrations of OH^- or OD^-. The phases were then separated. Although the concentration of base in the organic layer was not known, it was assumed that the partition coefficient of hydroxide between the two phases was a constant. The apparent reaction order varied from approximately second order in Fe(TTP)OH at low porphyrin and high base concentrations to nearly first order in Fe(TTP)OH at high porphyrin and low base concentrations. Typical plots of the concentration of Fe(TTP)OH as a function of time are shown in Figure 3 for a series of reactions with similar initial concentrations of Fe(TTP)OH. At low concentrations of base the rates were similar for OH^- and OD^-, but at high base concentrations there was a large deuterium isotope effect on the rate. A decrease in the concentration of base caused a much larger increase in the rate of reaction for OD^- than for OH^-. These observations suggested the following two-step mechanism:

$$\mathrm{Fe(TTP)OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(TTP)^+ + OH^-} \quad (1)$$

$$\mathrm{Fe(TTP)^+ + Fe(TTP)OH} \xrightarrow{k_2} \mathrm{(Fe(TTP))_2O + H^+} \quad (2)$$

Using the steady-state approximation this mechanism gives the rate law

$$-\frac{\Delta[\mathrm{Fe(TTP)OH}]}{\Delta t} = \frac{2k_1[\mathrm{Fe(TTP)OH}]^2}{k'[\mathrm{OH^-}] + [\mathrm{Fe(TTP)OH}]} \quad (3)$$

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where $k' = k_{-1}/k_2$ times the partition coefficient for the distribution of OH^- or OD^- between water and CCl_4. Axial ligand dissociation of I^- from Fe(TTP)I occurs to a sufficient extent in chloroform solution at room temperature that it provides a mechanism for inversion at the iron on the NMR time scale.[25] Although OH^- would be expected to bind more strongly than I^-, some dissociation is likely to occur as indicated in eq 1. Although one of the products of eq 2 is written as H^+, it is undoubtedly hydrated, so if there is 1 mol of water hydrogen bonded to the hydroxide of Fe(TTP)OH, formation of H_3O^+ would only require proton transfer from OH to water.

The concentration of Fe(TTP)OH as a function of time was calculated from the rate law as shown in Figure 3. The data for OH^- were fit with $k_1 = (1.4 \pm 0.2) \times 10^{-4}\ s^{-1}$ and $k'(H) = (0.2 \pm 0.15) \times 10^{-3}$. The data for OD^- were fit with $k_1 = (1.7 \pm 0.3) \times 10^{-4}\ s^{-1}$ and $k'(D) = (1.0 \pm 0.3) \times 10^{-3}$. Within experimental uncertainty the values of k_1 were the same for the data obtained with OH^- and OD^-. The secondary deuterium isotope effect on the dissociation of OH^- or OD^- would be expected to be less than the uncertainty in the data.[26] Therefore, the absence of a large deuterium isotope effect on k_1 is consistent with the proposal that k_1 is the rate of axial ligand dissociation. The values of k' were substantially different for OH^- and OD^-. The most likely source of an isotope effect on k' is the proton dissociation step described by k_2. If it is assumed that the isotope effect on k' was due entirely to changes in k_2, then $k_2(H)/k_2(D) = k'(D)/k'(H) = 5$. Since deuterium isotope effects between 4 and 9 have been reported for proton transfer from oxyacids to bases,[26] the magnitude of the observed isotope effect is consistent with the proposal that the second step of the reaction involves transfer of a proton from a bridging OH(D) to H_2O or D_2O.

Comparison with Dimerization of Other Iron Porphyrins

The equilibria between monomeric and dimeric iron(III) porphyrins have been studied extensively in aqueous solution. However, much less information has been obtained concerning the mechanism of dimerization. In an early report on the characterization of $(Fe(P))_2O$, Caughey and co-workers proposed that dimerization might occur by reaction of $Fe(P)^+$ and Fe(P)OH (pathway 1) or by reaction of 2 mol of Fe(P)OH to form a dihydroxy-bridged intermediate (pathway 2).[27] Both of these possibilities were found to occur in studies of the iron(III) complex of ethylenediamine-*N,N,N',N'*-tetraacetate (EDTA = L). It was shown that dimerization occurred about 100 times faster for $FeL(H_2O)$ + FeL(OH) (pathway 1) than for reaction of 2 mol of FeL(OH) (pathway 2).[28] It was proposed that the rate of reaction by pathway 1 might be controlled by the rate of water exchange. It would then be equivalent to Caughey's proposal of $Fe(P)^+$ + Fe(P)OH. On the basis of temperature-jump kinetics it was proposed that dimerization of the iron(III) complex of tetrasulfonated tetraphenylporphyrin proceeded by a dihydroxy-bridged intermediate (pathway 2) and there was no evidence of a contribution from pathway 1 in the pH range 6.1–7.5.[29] Temperature-jump studies of the dimerization of the iron(III) complex of deuterioporphyrin were only possible over a limited pH range. The data were consistent with pathway 1.[30] Thus, either pathway 1 or pathway 2 may be appropriate for iron porphyrins in aqueous solution. The preferred pathway is probably a function both of the porphyrin and of the pH of the solution. Our results clearly indicate that dimerization of Fe(TTP)OH in CCl_4 proceeds by pathway 1.

The rates of these reactions suggested that it might be possible to isolate Fe(TTP)OH. The solvent was rapidly (2–3 min) removed from a 2 mM solution of Fe(TTP)OH in CCl_4. The solid was dried overnight and redissolved in CCl_4. The NMR spectra indicated that the porphyrin was about 10% Fe(TTP)OH and 90% $(Fe(TTP))_2O$. The conversion of Fe(TTP)OH to $(Fe(TTP))_2O$ is slower in the presence of OH^- than in the absence of OH^-. Therefore, another sample was dissolved in CCl_4 that had previously been shaken with 2 M NaOH. This sample contained about 30% Fe(TTP)OH and 70% $(Fe(TTP))_2O$. For both of the solutions the extent of conversion of Fe(TTP)OH to $(Fe(TTP))_2O$ was greater (for the short time that the Fe(TTP)OH was in solution) than can be explained by the rates obtained for pathway 1. Thus, other mechanisms of reaction to form $(Fe(TTP))_2O$ must occur during precipitation or in the solid state.

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Notes

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Synthesis and Study of (Dimethylamino)benzyl and (Diphenylphosphino)benzyl Compounds of Early-Transition-Metal Metallocenes and Their M(III) Derivatives

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Monoalkylated derivatives of dicyclopentadienyl group 4[20] metal dichlorides $Cp_2M(Cl)R'$, where M = Ti, Zr and R′ is a group attached through an alkyl linkage, have attracted attention as intermediates in CO insertion reactions[1-4] and other organic syntheses.[5-8] Furthermore, their compounds with alkyl-bound benzyl ligands containing tertiary nitrogen and phosphorus functionalities offer a number of interesting possibilities, such as the formation of heterobimetallic species through the bifunctional ligand, the stabilization of lower oxidation states of the metal through chelation by the alkyl and N (or P) functionalities, and the stabilization of reduced heterobimetallic species. For the

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