J. Org. Chem. 1985, 50, 5342–5351

N-Alkenylporphyrins from the Reaction of DDT with Chloroiron(III) Tetraphenylporphine and Iron Powder

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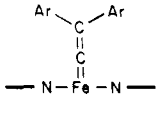
Received November 29, 1984

The reaction of DDT with chloroiron(III) tetraphenylporphine and a large excess of iron powder in 9:1 methylene chloride–methanol produces a mixture of porphyrin products. Demetalation of the product solution under argon yields DDD, tetraphenylporphine, *N*-[2,2-bis(*p*-chlorophenyl)ethenyl]tetraphenylporphyrin ("*N*-vinyl"), and the monocation of N_{21},N_{22}-[2,2-bis(*p*-chlorophenyl)ethenylidene]tetraphenylporphine ("Rhodo"). The alleged "vinylidene carbene" of DDT reported to be generated in this reaction and its reversibly obtained one-electron oxidation product are shown by several means including demetalation and synthesis to be iron(II) and iron(III) complexes of *N*-vinylporphyrin. The diamagnetic nature of the iron(II) porphyrin and, in part, its unusual stability to air are explained by back (π) bonding of the metal to the adjacent olefinic linkage. The iron(III) complex of *N*-vinyl is converted to the bridged Rhodo porphyrin by Lewis acids and reagents capable of polarizing the nitrogen-bound olefin.

Introduction

The reaction of iron(III) porphyrins with polyhalomethanes in the presence of a large excess of reductant has been reported to produce a variety of unusual porphyrin–iron bonded carbene species.[1] The principal and central example of this class of structures is the "vinylidene carbene" complex of the insecticide DDT with iron tetraphenylporphine (**1**, Ar = *p*-chlorophenyl, porphyrin drawn end on). This substance is the most stable of these entities, and consequently its structure and general chemistry[1d,l] are best characterized. Its properties and that of the "oxidized carbene" **2**,[1j,k] reversibly obtained from it by one electron redox reagents, have been the basis for extensive biochemical speculation[1-3] about the modes of catalase and cytochrome P-450 reaction and the nature of oxygen binding in these enzymes. Structures akin to **1** have been employed to explain the synergistic action of insecticides.[1g] Moreover, the unique bonding in such structures has attracted serious attention by theoreticians.[4,5] The original impetus for these endeavors was the postulate by Ullrich and associates[1b] that the anesthetic halothane reacted with cytochrome P-450 to produce a porphyrin–iron carbene (Porp Fe=CH—CF$_3$). More recently this formulation, based primarily upon visible spectra, has been reconsidered with P-450[6] and with an iron–porphyrin model system.[7]



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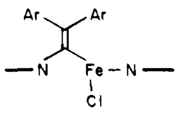

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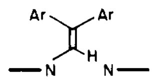

3

While the possibility of generating carbenes or carbenoids by the reaction of polyhalomethanes with low-valent transition-metal ions has been apparent[8,9] for some time, we have found no evidence for this occurrence with iron(II) porphyrins[10] or heme proteins[11] in homogenous solution. A specific study of the enzyme cytochrome P-450 cam with a series of polyhalomethanes[12] demonstrates a remarkable consistency in the chemistry of the heme whether it is in solution, ensconced in the enzyme, or a part of its native cell. In all cases quantitative hydrogenolysis ensues (eq 1, P = porphyrin or P-450 in vitro or in vivo). Carbenes are not produced.

$$RCX_3 + 2PFe^{II} \xrightarrow[\text{solv-H}]{H^+ \text{ or}} RCHX_2 + 2PFe^{III} \qquad (1)$$

This enzyme is actually inert toward oxidation by DDT. Presumably the substrate is too large to penetrate the active site. However, DDT will readily oxidize hemes[10] and other heme proteins.[13] The reaction proceeds quantitatively according to eq 1 in a kinetically clean process.

The uniformity of the chemistry displayed by hemes and heme proteins in their oxidation by polyhalomethanes suggests that the massive excess of reductant and/or the heterogenous nature of the conditions employed by Mansuy and colleagues alters the normal course of these reactions.

In an effort to plumb the reactivity of porphyrin complexes that contain an iron–carbon single or double bond we have sought to prepare these substances by reported pathways. In this work we focus upon the air-stable "carbene" **1** and the iron–carbon single-bonded "oxidized carbene" derived from it, **2**. Our major finding is that neither substance contains an iron–carbon σ bond. Both

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1 and **2** are best formulated as iron(II) and iron(III) complexes of *N*-vinylporphyrin **3**.

Results

The reaction of chloroiron(III) tetraphenylporphine with DDT and iron powder in 9:1 methylene chloride–methanol was conducted under high-purity argon. A variety of reaction and workup procedures were employed to determine the nature of the reactants and products. Salient observations and reaction characteristics are summarized below.

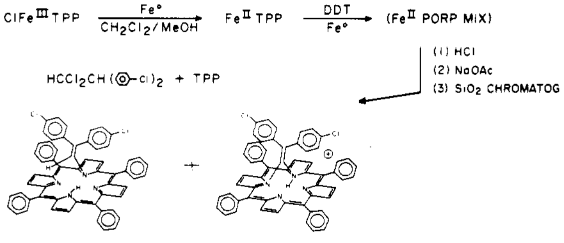
The Iron Powder Activation. Carefully washed iron powder is essential for reaction. Throughout we have employed acetic acid washed and thoroughly methanol-rinsed Matheson electrolytically prepared reagent grade iron powder as reductant.

The Heme. The generation of iron(II) porphyrin is essential. However, the reaction also requires a massive excess of iron powder. Thus, generation of iron(II) TPP via the iron powder reduction followed by removal of excess reductant and addition of DDT, i.e., a homogenous reaction, results in the production of iron(III) TPP and DDD quantitatively (eq 2) as it does with other porphyrins and heme proteins (vide infra).

$$2\mathrm{Fe^{II}TPP} + \mathrm{Ar_2CHCCl_3} \xrightarrow{\mathrm{CH_2Cl_2{-}MeOH}} 2\mathrm{Fe^{III}TPP} + \mathrm{Ar_2CHCHCl_2} \quad (2)$$

Vigorous Stirring. Initial reactions, with magnetic stirring and a small excess of iron powder, yielded only DDD (eq 2). The "carbene" was not generated. However the use of a creased flask and vigorous mechanical stirring, along with a massive excess of Fe^0, did alter the course of reaction 2. In our hands DDD was always a product. It was however, not a reactant, DDD, when substituted for DDT, was recovered unchanged.

The spectrum of the iron(II)–porphyrin reaction mixture in 9:1 methylene chloride–methanol (solid line) and the spectrum of the product solution after reaction with DDT (dashed line) are shown in Figure 1. The same shift in the iron(II)–porphyrin spectrum was (observed whether the DDT was added slowly or was a part of the initial) charge. Workup consisted of demetalation of the iron(II) product solution and chromatography or chromatography of the iron–porphyrin concentrate. In general, the neutralized concentrated demetalated mixtures yielded three major porphyrin fractions upon chromatography: 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD; 50%) and recovered tetraphenylporphine (50%); *N*-[2,2-bis(*p*-chlorophenyl)ethylenyl]tetraphenylporphine (40%; "*N*-vinyl", **3**); and the monocation of N_{21},N_{22}-[2,2-bis(*p*-chlorophenyl)ethenylidene]tetraphenylporphine (10%; **4**, "Rhodo"). The reaction is generally formulated in eq 3. Thus, the reaction product spectrum (Figure 1) is a composite of at least three porphyrins.



3 **4**

(3)

Workup without demetalation proceeded in similar fashion to yield the corresponding metal complexes. Generally upon chromatography, the first orange fraction contained "the carbene" (λ_{max} *417*, 521, 543 (sh) nm) and DDD. This was followed by the μ-oxo dimer of TPP, the olive drab "oxidized carbene" (λ_{max} 425, 669 nm), "N-vinyl" porphyrin, and the cation of "Rhodo".[14a] Essentially, the product composition of nondemetalated chromatographed reaction mixture paralleled that indicated above except that TPP was replaced by its iron(III) μ-oxo dimer and the *N*-vinylporphyrin was replaced by a composite of "carbene", "oxidized carbene", and *N*-vinylporphyrin. The minor porphyrin product, the "Rhodo" H^+ (**4**) was never obtained as a metal complex. Purified fractions of the "carbene" and "oxidized carbene" were subjected to further scrutiny. In accord with results reported by Mansuy,[1] reduction of the "oxidized carbene" under argon with Fe^0 in methylene chloride–methanol yielded the orange-red air-stable iron(II) "carbene". This substance can be reconverted to the oxidized carbene with ferric chloride. Direct demetalation of the "oxidized carbene" in methylene chloride with trifluoroacetic acid under argon proceeded gradually to a green dication. Neutralization with aqueous sodium acetate afforded *N*-vinylporphyrin **3**. This result is in keeping with that recently reported.[1k] However, demetalation of the corresponding "carbene" under argon (Figure 2) and neutralization yields *the same N-vinylporphyrin.* Second-order rate constants for the demetalation (rate = k (FePorp)(TFAH)) are 0.17 and 3.0 L/mol/s, respectively, for the "carbene" and "oxidized carbene".

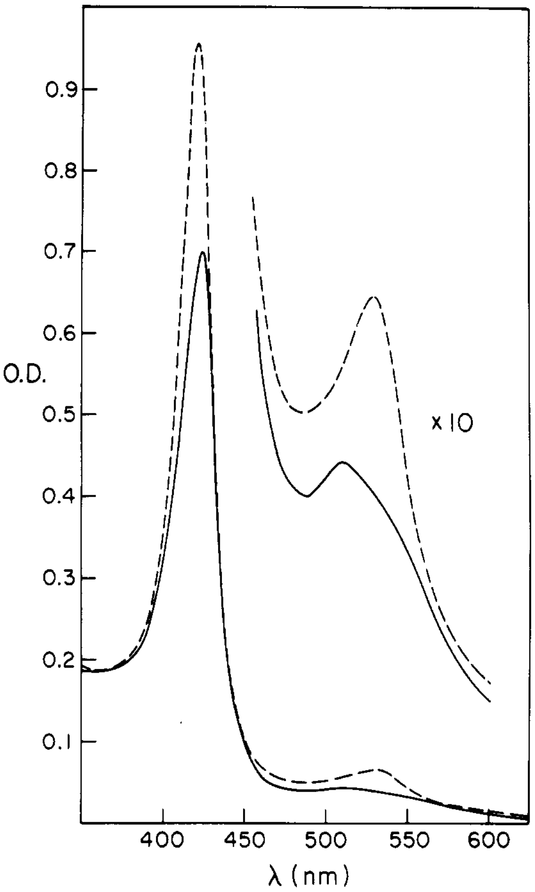


Figure 1. Visible spectrum of the $Fe^{II}TPP$ reaction mixture before (—) and after (--) reaction with DDT (0.005-cm cell; $(FePorp)_0 = 1.0 \times 10^{-3}$ M).

The NMR spectrum of *N*-vinylporphyrin and the coupling assignments established by irradiation are shown in Figure 3. It is important to note that the vinyl proton at δ −1.8 is not coupled to any of the other protons nor does it exchange with CH_3OD or CF_3CO_2D through the dication of the porphyrin is obtained in the latter case.

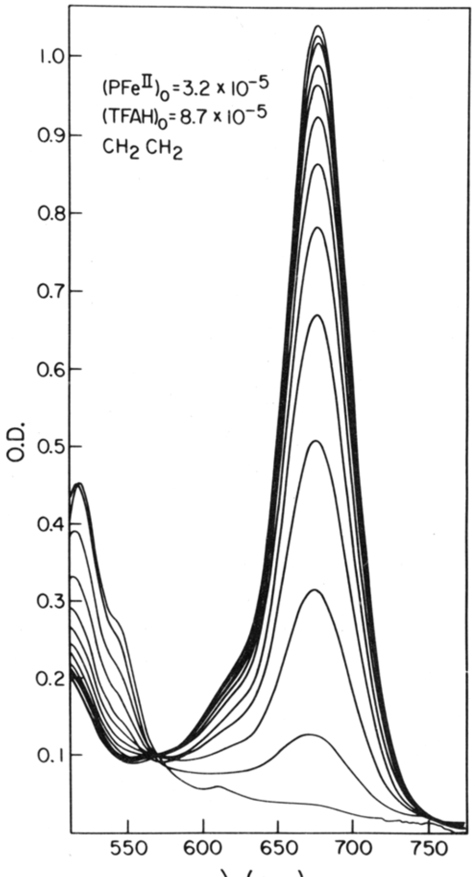


Figure 2. Demetalation of the "carbene" to *N*-vinylporp (**3**) dication in CH_2Cl_2. Repeat scans are at 1- and 4-min intervals thereafter.

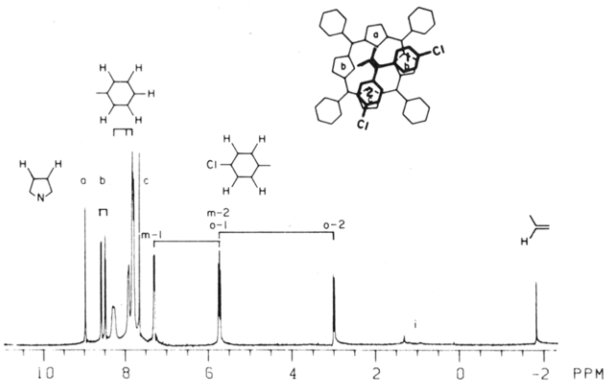
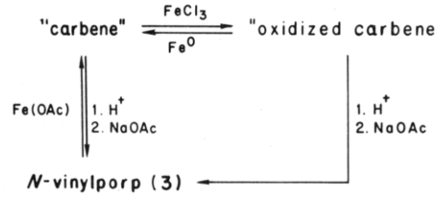


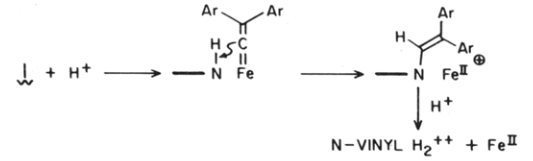
Figure 3. 300-MHz NMR spectra of *N*-vinylporphyrin in $CDCl_3$.

Insertion of iron(II) into *N*-vinylporphyrin (Fe$(OAc)_2$–CH_2Cl_2–MeOH) yields an iron(II) complex that is identical with the "carbene" (UV–vis, NMR). These results are formulated in eq 4. The sequence of reactions



(4)

presented in eq 4 would ordinarily by themselves constitute a proof by synthesis that the "carbene" is the iron(II) complex of *N*-vinylporphyrin. The results would also establish that the "oxidized carbene" is simply the corresponding iron(III) complex. However an alternate explanation of these findings can be envisioned. The "carbene" could rearrange by inserting into the N–H bond formed during demetalation (eq 5). A formal reversible process can be written (eq 6).[14b] Alternatively direct protonation



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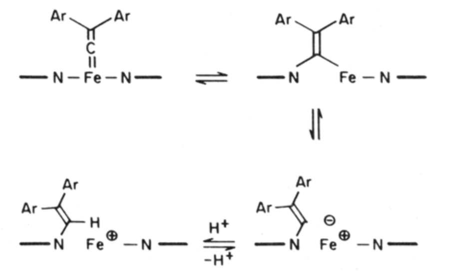
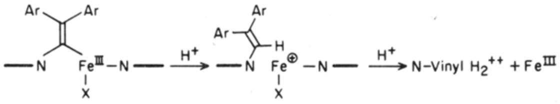


(6)

at the carbenic carbon would produce an iron complex of a vinyl cation (cf. below). Whatever actual path may be theoretically possible though, the demetalation of **1** by acid to **3** demands that a proton be incorporated at the vinyl carbon. A similar strict constraint is placed upon the demetalation of the "oxidized carbene" **2** (eq 7). These



(7)

systems are particularly well suited to deuterium labeling and NMR analysis. Accordingly the "carbene" and "oxidized carbene" were demetalated under argon with trifluoroacetic acid-*d* (99.5% D assessed by NMR) in dry methylene chloride. The ^{1}H NMR of the *N*-vinylporphyrin obtained quantitatively from each after neutralization with aqueous sodium acetate was *identical* with the spectrum shown in Figure 3. In particular the vinyl proton was undiminished in intensity and integrated as one proton. Usually, though not always, the porphyrin was chromatographed in CH_2Cl_2 on silica before NMR analysis. There was no substantial difference in the NMR spectrum before or after chromatography, but the chromatographed substance was cleaner. As a more rigorous check on the possibility of exchange on the mildly acidic silica column, a sample of *N*-vinylporphyrin was exposed to high concentrations of CF_3CO_2D for 3 days and neutralized. No deuterium was incorporated (eq 8).

$$N\text{-vinyl} \underset{\text{aqueous NaOAc}}{\overset{\substack{\text{3 DAYS} \\ 1:1\ CF_3CO_2D\text{–}CH_2Cl_2}}{\rightleftarrows}} N\text{-vinyl}\ H_2^{2+} \qquad (8)$$

Samples of the iron complexes demetalated with TFAD were also analyzed for deuterium incorporation by ^{2}H NMR. The ^{2}H NMR of *N*-vinyl obtained by demetalation of the same sample of the "carbene" with TFAH and TFAD are compared in Figure 4. While only the upfield vinyl-*d* region is shown, no deuterium could be detected anywhere in the spectrum. Deuterium detection was sensitive to at least 5 mol %. The same results were obtained with the iron(III) complex. Thus, demetalation with CF_3CO_2D *does not* introduce deuterium into the vinyl carbon of **3**. Hence the *N*-vinyl moiety must be intact in *both* iron complexes.

The lack of deuterium incorporation into *N*-vinylporphyrin described above prompted an investigation of the source of the vinyl proton. A series of additional labeling experiments were undertaken to selectively pinpoint

Table I. A Summary of D-Labeling Experiments

				products[b,c]		
				DDD		*N*-vinylporp (vinyl C)
run	solv	Fe^0 (wash)[a]	DDT (C$_\beta$)	C$_\beta$Ar$_2$	C$_\alpha$Cl$_2$	
1	$CH_3OH-CH_2Cl_2$	HOAC	H			H
2	$CH_3OD-CH_2Cl_2$	HOAC	H			H
3	$CH_3OD-CH_2Cl_2$	DOAC	H			H
4	$CD_3OD-CD_2Cl_2$	HOAC	H			H
5	$CD_3OD-CD_2Cl_2$	DOAC	H	H	D	H
6	$CH_3OH-CH_2Cl_2$	HOAC	D	D	H	H
7	$CD_3OD-CD_2Cl_2$	DOAC	D	D	D	H

[a] Iron powder was activated with the indicated acid. For runs 1 and 6 this was followed by wash with ^{1}H MeOH and solvent. For runs 2, 3, 4, 5, and 7, the acetic acid wash was followed by MeOD rinses and solvent. [b] In runs 1–4, only the *N*-vinylporphyrin was analyzed for D content. [c] In all cases demetalation with TFAH or TFAD produced the same results. In runs 1–4 isolated samples of the "carbene" and "oxcarbene" were demetalated. In runs 1, 5, 6, and 7 the entire reaction mixture was demetalated.

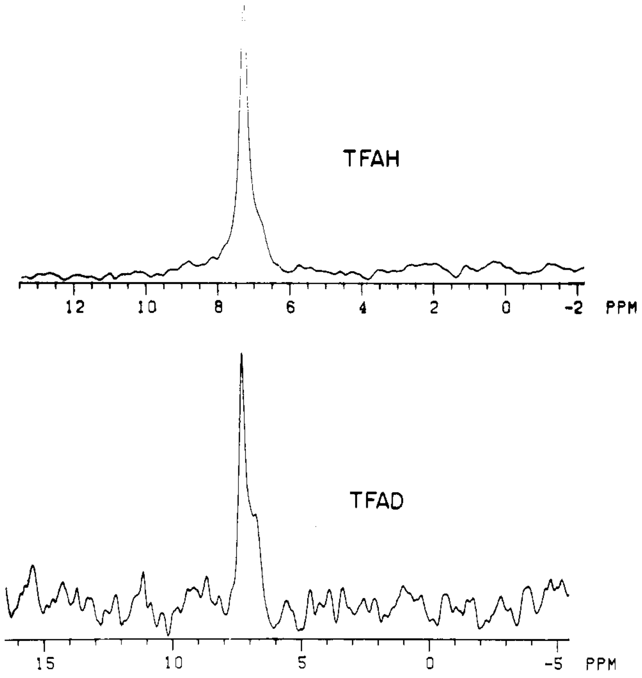


Figure 4. ^{2}H NMR spectra of *N*-vinylporphyrin from TFAH and TFAD demetalation of the "carbene" ($CDCl_3$ reference; eight times the concentration of porphyrin).

this source. They are presented in short form in Table I. While a variety of D labels and workup conditions were employed, this work did not delineate the source of the vinyl proton. In no case was *N*-vinylporphyrin labeled with deuterium either as the isolated substance or as part of the product composite.

In run 5 the entire reaction mixture was demetalated with TFAD only. In all other cases demetalation was accomplished with both TFAH and TFAD. This had *no* effect upon the results. The conditions for run 1 are the general ones described above. The reaction was conducted many times and in a variety of ways but usually at 10^{-3} M ClFe^{III}TPP. In all cases the ratio of Fe^0/DDT/Fe^{III}TPP was 125/1.4/1. Run 6 was conducted at both 10^{-3} M and 2.2×10^{-3} M iron TPP. This change in concentration had no effect upon the results. To conserve deuterated solvents, runs with these were conducted only at the higher concentration of reactants. In runs 1–4 purified samples of the "carbene" and "oxidized carbene" were demetalated separately in dry CH_2Cl_2. The resulting *N*-vinylporphyrin was subjected to ^{1}H and ^{2}H NMR analysis. In runs 5–7, however, the entire reaction mixture was demetalated as is (run 5) or in dry CH_2Cl_2 or CD_2Cl_2 (runs 6 and 7). Visible spectra obtained before the demetalation showed the presence of both the "carbene" and "oxcarbene". The demetalation of the mixtures enabled the acquisition of both ^{1}H and a ^{2}H NMR of the complete product composite before chromatographic separation and purification. In addition half of each of these demetalated mixtures was chromatographed. Purified samples of *N*-vinylporphyrin, TPP, and DDD obtained from each were analyzed by NMR for ^{1}H and ^{2}H. Neither of the porphyrins exhibited deuterium incorporation as part of the product composite or as pure substances. On the other hand, the DDD was labeled on the α- (CCl_2) carbon. The ^{1}H and ^{2}H 300-MHz NMR spectra of the product mixtures for runs 5, 6, and 7 are shown in Figure 5. All of the spectra are from samples demetalated with TFAD, though identical spectra were obtained (runs 6 and 7) upon TFAH demetalation. The NMR of isolated DDD is shown as the inset.

The assignment of the *d* signals at δ ~6 and/or ~5 in the product composite to the α- and β-carbon hydrogens of DDD was confirmed by spiking the product mixtures with the purified DDD isolated from each reaction. (Though shown only for run 5, $CDCl_3$ was also added to the samples as a standard.) In each case single but enhanced *d* signals were obtained. The deuterium signals in the reaction mixtures were shifted somewhat from those obtained for the isolated DDDs in CCl_4. The DDD-*d* assignments were also confirmed by comparing the spectra with the NMR of the C$_\beta$-*d* isomer ($Ar_2CDCHCl_2$) obtained by independent synthesis.

A special feature of the product mixture analysis is that the DDD deuterium atom provides an internal standard of intensity approximately equal to that of 1.2 deuterons (the yield of DDD and *N*-vinylporphyrin are about the same). Clearly then in run 5 deuterium is incorporated in the CCl_2 carbon of DDD but not in *N*-vinylporphyrin. Moreover, in run 6, the deuterium in starting DDT (at C$_\beta$) remains on the β-CAr_2 carbon. Again *N*-vinylporphyrin is not labeled. Finally when both the solvent and DDT (C$_\beta$-*d*) are deuterated, both the α- and β-carbons of DDD are labeled and *N*-vinyl is not.

The vinyl proton at δ ~−2 in run 7 did appear to be somewhat diminished in both the TFAH- and TFAD-demetalated mixtures. However, the presence of deuterium could not be confirmed by ^{2}H NMR of the mixture or ^{1}H or ^{2}H NMR of the isolated porphyrin.

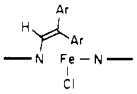
An additional run not shown in the figure or table was conducted with ClFe^{III}TPP (β-pyrrole-d_8) and nonlabeled solvent or DDT. The NMR of the *N*-vinylporphyrin (TFAH or TFAD demetalation) and product composite showed the pyrrole protons (Figure 3) to be labeled (broad D signal at δ ~8.9) but the vinyl carbon was not.

Our results do not agree with the facile deuteration of the vinyl carbon upon demetalation of the "oxidized carbene" with TFAD reported recently by Balch and associates.[14f]

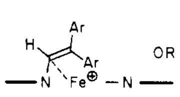
The infrared spectrum of *N*-vinyl and its iron complexes are remarkably similar except for those absorptions characteristic of the presence or absence of metal ligation.[15a] In particular, there are no unique bands in the far-infrared region of the iron(II) or iron(III) complexes that might be ascribed to an iron–carbon double or single bond. A weak absorption is present in the iron(III) adduct at 522 cm^{-1}, but it is also observed in the free base. The strong porphyrin vibrational mode at 966 cm^{-1} in *N*-vinyl and TPP[15a] is shifted to the 1000 cm^{-1} region in the iron complexes. While TPP, Rhodo, *N*-vinyl, and its iron complexes all show a strong band at 800 cm^{-1} characteristic of β-pyrrole-H, the *N*-vinyl derivatives also show a distinct additional medium intensity band at 831 ± 1 cm^{-1} that is absent from TPP or Rhodo. This could be attributed to the vinylic C–H, or it may be an additional β-pyrrole-H deformation mode due to the common asymmetry in these structures.

Taken together these results establish that the structural framework of the iron porphyrins depicted as **1** and **2** consists in part of iron bonded to *N*-vinylporphyrin **3**. Moreover, the redox interconversion between the species (eq 4) would seem to proceed without rearrangement of the iron–*N*-vinyl skeleton.[15b] By themselves these data do not explain the low-spin character of the iron(II) adduct or the unusual stability of this particular iron(II) porphyrin in air. Nor do they specify the entire structure of each complex.

Fast atom bombardment mass spectroscopy did not discern parent ions for these complexes. However, masses corresponding to TPPFe–Cl (loss of vinyl) were apparent in some runs. In general though, high mass peaks corresponded to FeTPP. The results indicate an axial ligation of chloride anion though acetate may also be present. Elemental analyses of purified samples of the iron(II) complex obtained in the usual workup (AnOAc wash) were in fact consistent with a mixture of chloro and acetato species. Reaction product solutions washed with aqueous NaCl rather than NaOAc did yield the chloro adduct **5**.[15c] This was verified by demetalation of the iron(II) complex and a direct gravimetric determination of chloride as AgCl. The yield of chloride correlated well with the yield of *N*-vinylporphyrin. The magnetic properties of both iron complexes are known.[1,3] The iron(II) adduct is diamagnetic and the iron(III) complex is of intermediate spin ($^3/_2$). While a stability to O_2 seems to be characteristic of (*N*-alkylTPP)Fe^{II} complexes, (*N*-methylTPP)Fe^{II}Cl is of high spin.[16] The magnetic properties of these porphyrins can be understood with the realization that an iron complex like **5** is well suited for a metal (π) bond to the adjacent olefinic link (**6**). A structure similar to **5** but with an unspecified "x" on the vinyl carbon had been considered to be compatible with the NMR of the "oxidized carbene"[17] before the iron–nitrogen bridged structure **2** was considered firm.

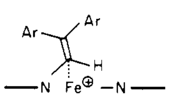


5



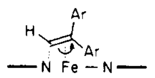
6

OR

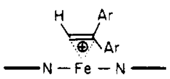


6'

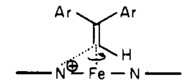
While the asymmetry of **6** is compatible with the NMR findings[3] for the iron(III) adduct, it is not consistent with the apparent C_{4v} symmetry manifest in the spectrum of the iron(II) complex. Given the propinquity of olefin and iron and the extensive delocalization of metal electrons to the olefin required to render the iron(II) adduct diamagnetic, a fluxional binding at carbon to porphyrin-nitrogen is not unreasonable **7**. The structure **7'**, essentially an iron(II) complex of delocalized vinyl cation, is identical with a protonated (at carbon) form of carbene **1**. Accordingly, variable-temperature NMR studies of the iron(II) adduct were undertaken to possibly "freeze out" a fixed structure, **7**. While some minor sharpening in the NMR spectrum was apparent at −60 °C (Figure 6), the spectrum was essentially unchanged from that at 22 °C. Nevertheless, a freely rotating vinyl moiety π-bonded to iron will accommodate the NMR as well as the general chemistry of the complex recorded herein.



7

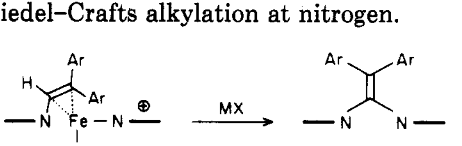


7'



7''

The iron(III)-*N*-vinyl complex will itself undergo a transformation that emphasizes the ease of pyrrole nitrogen–vinyl carbon interaction. Treatment of iron(III) *N*-vinyl with Lewis acids in dry CH_2Cl_2 results in the production of Rhodo porphyrin **4** (eq 9) (MX = $AlCl_3$, $FeCl_3$, $AgNO_3$, $ZnCl_2$). The reaction is essentially an internal Friedel–Crafts alkylation at nitrogen.



(9)

Gold and colleagues[18] have recently characterized by NMR an N_{21},N_{22}-bridged porphyrin analogous to **4** that

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(14) (a) Reaction mixtures allowed to stand days before chromatography contained a higher amount of *N*-vinyl and the "oxidized carbene" and a lesser amount of the "carbene". Best yields of the "carbene" were obtained by slow additions of DDT and immediate workup and chromatography. Fractions of the "oxidized carbene" that contained significant amounts of "*N*-vinyl" approach a λ_{max} of 428 nm. (b) Recent examples of iron to nitrogen migration of aryl, alkyl, and alkenyl substituents have been reported to occur upon chemical or electrochemical oxidation: (c) Ortiz de Montellano, P. R.; Kunze, K. J.; Auguste, A. *J. Am. Chem. Soc.* **1983**, *104*, 3546. (d) Mansuy, D.; Battioni, J. P.; Dupre, D.; Sartoni, E.; Chottard, G. *J. Am. Chem. Soc.* **1982**, *104*, 6159. (e) Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472. The process is described as reversible upon reductions. The pathway (eq 6) is unique, however, in that it requires no oxidant or reductant theoretically or experimentally. (f) Balch, A. L.; Chan, Y.-W.; Lamar, G. N.; Latos-Granzynski, L.; Renner, M. W. *Inorg. Chem.* **1985**, *24*, 1437.

(15) (a) Alben, J. O.; Choi, S. S.; Adler, A. D.; Caughey, W. S. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 278. Alben, J. O. In "The Porphyrins"; Dolphin, D., Academic Press: New York, 1978; Vol. III, Chapter 7. (b) A possible iron–vinyl structure for **1** is equally inconsistent with the IR spectra. Moreover, an iron(III)–vinyl compound would not be diamagnetic nor would it contain the chloro or acetato ligand found here. In this regard it is interesting that a reported[14d] iron(III)–vinyl structure, produced by treatment of an *N*-vinyl compound with Fe^{II} and dithionite possesses a visible spectrum very similar to that of the "carbene". (c) Note the simple 2D drawings **5**–**7** are not intended to portray the exact stereochemistry of the vinyl moiety. Thus, in the "bent over" conformation the aryl groups would lie in a plane angled up from the plane of the porphyrin (cf. the upper view of *N*-vinyl in Figure 3 and the model in Figure 5.

(16) Anderson, O. P.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1980**, *19*, 2197.

(17) Goff, H.; Phillippi, M. A. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 2339–2342.

(18) Wisnieff, T. J.; Gold, A.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5616.

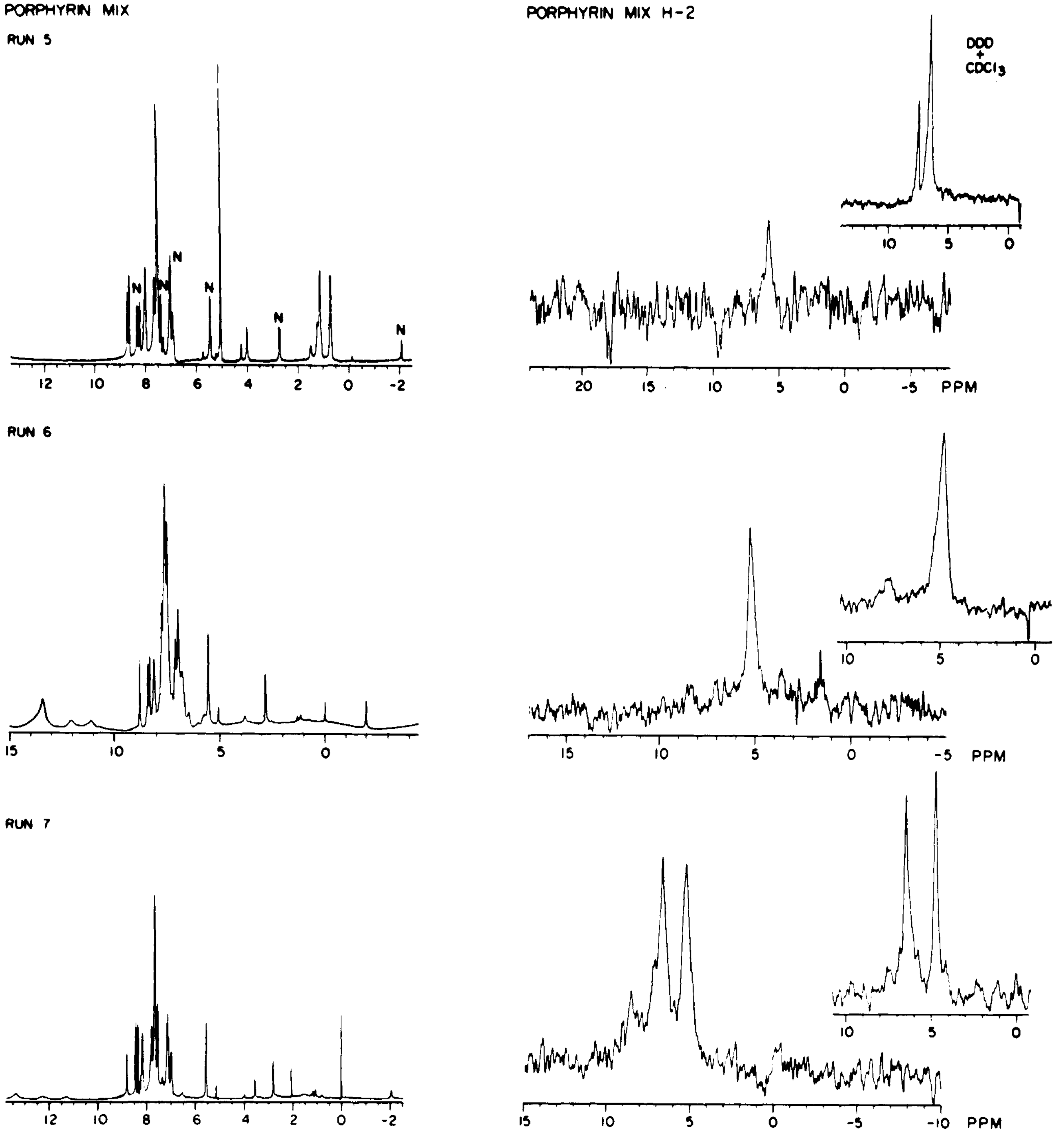

Figure 5. ^1H and ^2H NMR spectra of the reaction composite from runs 5–7 (Table I). ^2H NMR spectra of isolated DDD as inset (N = *N*-vinylporp).

resulted from a reaction under Mansuy conditions of DDT with iron tetraanisylporphyrin followed by treatment with $FeCl_3$. The visible spectrum reported for their Rhodo porphyrin indicate it is most likely the corresponding monocation. The oxidative rearrangement proposed (the carbene to a presumably unstable iron complex like **4**) was reasonable on the basis of the evidence at hand. In light of the present work the actual transformation though was the conversion noted in eq 9. This conversion could be a means of generating **4** in the original reaction mixture though a high concentration of $FeCl_3$ sems unlikely under the vigorous reducing conditions. Either the metal complex of **4** is not produced in the reaction or it demetalated upon chromatography. We have not successfully inserted iron into this porphyrin. Presumably, the extra ridgidity and distortion of the structure and its basicity render the porphyrin a difficult ligand for iron(II).[19] The reaction of **4** with $Fe(CO)_5$, however, has been reported to produce the carbene **1**.[20]

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(19) The ease of demetalation of N-substituted porphyrins has been noted by Callot and Tschamber: Callot, H. J.; Tschamber, T. *Bull. Soc. Chem. Fr.* **1973**, *11*, 3192. The difficulty of metal insertion into an N_{21},N_{22}-bridged porphyrin was emphasized by Johnson and colleagues: Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. I.; Shelton, G.; Elson, C. M. *J. Chem. Soc. Perkin Trans. 1* **1975**, 2076. Formation of Hg^{2+} and Pd^{2+} complexes with two N atoms of bridge porphyrins has been observed.[22]

(20) Chan, Y. W.; Ranner, M. V.; Balch, A. L. *Organometallic* **1983**, *2*, 1888. However, metals incapable of bonding to the olefin produce the metal-*N*-vinyl structure in the same reaction. It is reasonable that a related structure, like **6**, applies to the iron complex as well.

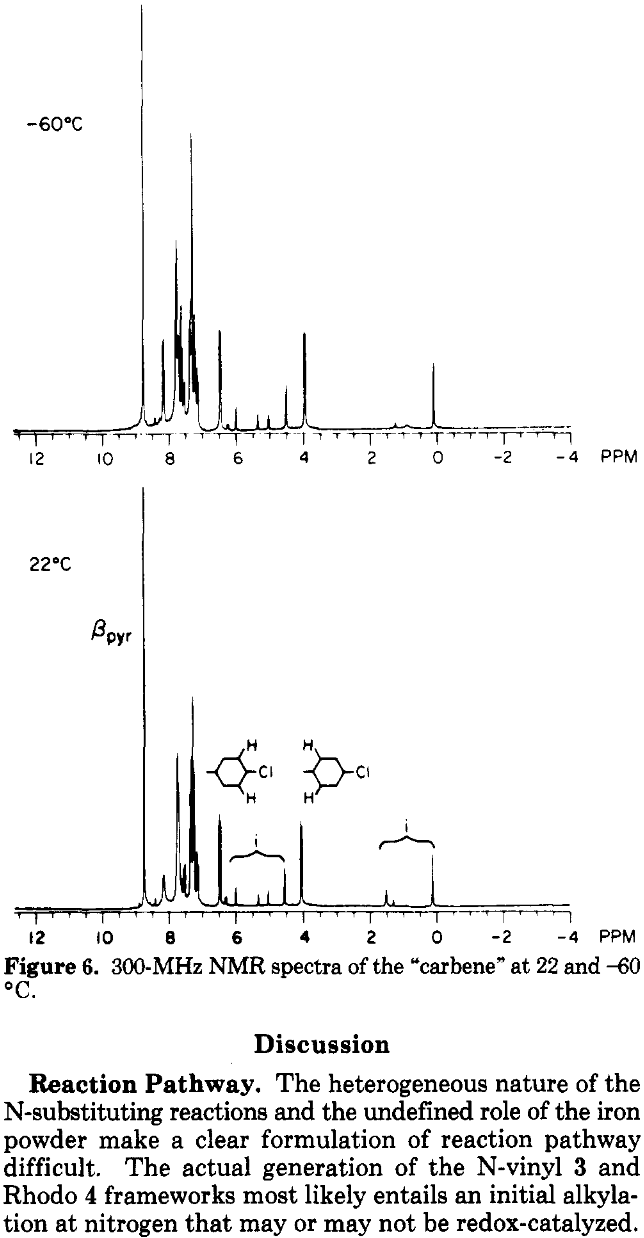
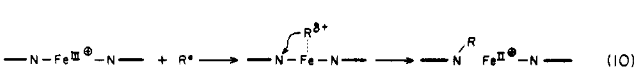


Figure 6. 300-MHz NMR spectra of the "carbene" at 22 and -60 °C.

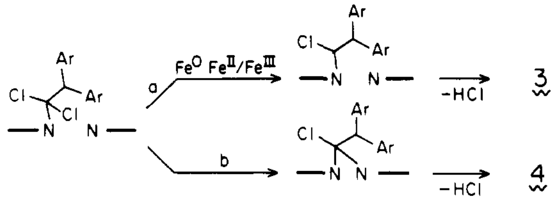
Discussion

Reaction Pathway. The heterogeneous nature of the N-substituting reactions and the undefined role of the iron powder make a clear formulation of reaction pathway difficult. The actual generation of the N-vinyl 3 and Rhodo 4 frameworks most likely entails an initial alkylation at nitrogen that may or may not be redox-catalyzed. Attack of an initially generated dichloromethanyl radical[10] upon iron(III) porphyrin could result in electron transfer[21] to yield iron(II) porphyrin and the corresponding cation which may then attack pyrrole nitrogen to yield 8 (eq 10).



$$\text{—N–Fe}^{\text{III}\oplus}\text{–N—} + \text{R}\cdot \longrightarrow \text{—}\overset{\text{R}^{\delta+}}{\text{N}}\text{–Fe–N—} \longrightarrow \text{—}\overset{\text{R}}{\text{N}}\ \ \text{Fe}^{\text{II}\oplus}\text{–N—} \qquad (10)$$

Alternatively a direct alkylation of porphyrins with $CHCl_3$ under phase-transfer conditions is known and will yield N_{21},N_{22}-bridged structures.[22] We find the hydrogenolysis product DDD (from the homogeneous reaction 2) is recovered unchanged from reaction mixtures when it is employed as a starting halide in place of DDT. Thus, DDD cannot be the precursor for *N*-vinyl. Moreover Rhodo is not converted to *N*-vinyl under reaction conditions. Nor is *N*-vinyl converted to Rhodo. Neither is *N*-vinyl oxidized to Rhodo by $FeCl_3$. Consequently, we believe *N*-[1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethyl]tetraphenylporphine (8) or its iron complex may be the common precursor for 3 and 4 (eq 11). Thus, internal or external reduction by iron(II) porphyrin would result in the *N*-α-monochloroethyl derivative, and elimination of HCl would yield "*N*-vinyl" (path 11a). Competitive internal second alkylation followed by HCl elimination would yield "Rhodo". The relative amounts of these substances may well be a function of the state of the iron powder, the vigor of stirring, and the acidity of the preparation. We have not isolated any of the *N*-(chloromethano)porphyrins in eq 11, but given the basicity of N-alkylated derivatives, the ease of internal alkylation and elimination, and the presence of such a massive amount of iron powder, this is not surprising.



Barring enormous isotope effects, the exchange experiments (Table I) eliminate a potential *N*-α-chloromethanyl radical in the first step of (11a). Thus, a 1,2-hydrogen shift from the CAr_2 carbon (runs 6, 7), hydrogen abstraction from solvent (runs 4, 7), DDT, or DDD (runs 6, 7), or reduction of the radical and protonation (runs 2, 3, 4, 5, 7) should have incorporated deuterium at the vinyl carbon.

We have not examined the nature of related porphyrin–iron carbene structures.[1,2] However, it is possible that they are nitrogen rather than iron-bonded entities. For example, the properties of the CCl_2 adducts[1] including a low-resolution X-ray structure[1f] could as well be explained by the N_{21},N_{22}-bridged structures of the Rhodo class or perhaps by simple *N*-dihalomethyl derivatives. Both N_{21},N_{22}-bridged structures[23] and N-alkylated[24] porphyrins in the TPP series are known to be thermally unstable. The corresponding bridged ethoxymethenyl derivative reverts to TPP in warm solvents.[23] Thus, such structures could well be a dihalocarbene source.[25]

It would seem the chemistry ascribed to 1 and 2 is more reasonably explained by the known properties of *N*-alkylporphyrins cited above. The easy demetalation of the complexes upon standing or chromatography is characteristic of N-substituted porphyrins. We also call attention to the transformation of "the oxidized carbene" to rhodo porphyrin. The chemistry embodied in eq 9 is far more reasonable than the oxidative rearrangement of 2 to 4. Especially since the reaction will occur with Lewis acids that are not oxidants.

A possible conflicting point for structure 7 rather than 1 is the reaction with amine bases to produce low-spin iron(II)–bis(amine) adducts.[1] It has recently been shown, however, that nucleophilic displacement at carbon bonded to porphyrin nitrogen is facile.[26] That is, *N*-alkylporphyrins are handily dealkylated by amines. Displacement by anions (Grignard regents) has been known for some time.[27]

X-ray structures for 2 (tetra-*p*-tolylporphyrin) have recently appeared.[28a] We do not believe the iron(III)-*N*-

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[21] Castro, C. E.; Roberts, C.; Davis, H. *Biorg. Chem.* **1974**, *3*, 343.

[22] Callot, H. J.; Fisher, J.; Weiss, R.; *J. Am. Chem. Soc.* **1982**, *104*, 1271.

[23] Johnson, A. W.; Ward, S. *J. Chem. Soc., Prekin Trans. 1* **1977**, 720.

[24] Callot, H. J.; *Bull. Soc. Chim. Fr.* **1972**, *11*, 4357.

[25] Indeed, Bruice and colleagues have reported the transfr of CCl_2 to cyclohexene (cf. Bruice, T. C.; Furter, P. G.; Ball, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 4578, footnote 10) and amines.

[26] Kuila, D.; Lavallee, D. K. *Inorg. Chem.* **1983**, *22*, 1095.

[27] Ellingson, R. C.; Corwin, A. H.; *J. Am. Chem. Soc.* **1956**, *68*, 1112.

[28] (a) Olmstead, M. M.; Cheng, R.-J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143. (b) Chisholm, M. H.; Folting, K.; Hottun, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.

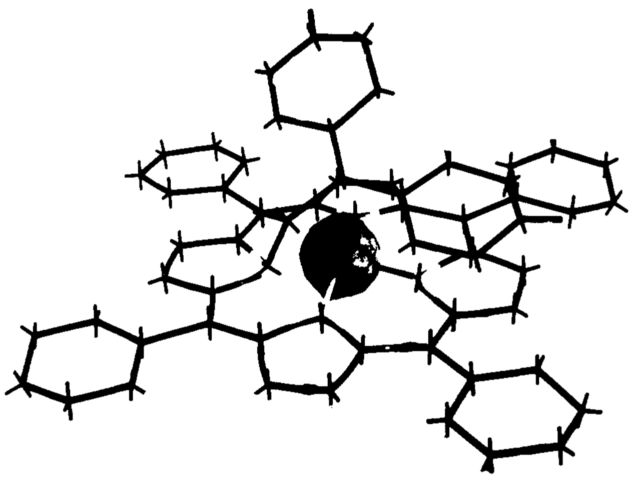

Figure 7. Partial model of Fe^{II}(*N*-vinylporphyrin).

vinyl structure is in conflict with the X-ray findings. Models of either the "upright" **6′** or "bent over" **6** (and Figure 7) conformations for the *N*-vinyl structure suggest an extremely close approach of vinyl carbon to iron. Simply, a π rather than a σ bond to iron can as well explain the data, and there is adequate space for the vinyl proton in the structure. For comparative purposes, the structures **6** or **7** can be taken to resemble the "flyover" complexes described by Chisholm.[28b] In this analogy the Fe–C "bond" of a "flyover complex" would be replaced by the pyrrole N–C bond. For FeC$_4$–π-Fe systems,[28,29] bond distances for Fe–C (2.06–2.19 Å) and Fe–C$_\sigma$ (1.94–1.98 Å) are both longer than the 1.92 Å found for the Fe–C bond of the porphyrin–iron(III) complex. This shorter distance though would not seem to exclude a π rather than σ bond to iron. Our results do not challenge the close approach of iron to carbon in either the iron(II) or iron(III) complex. On the basis of the X-ray work, solution structures for the iron(III) complex are best formulated with the vinyl group in the "upright" conformation perpendicular to the porphyrin plane, **6′**. The "upright" conformer **7″** could also accommodate the properties of the iron(II) complex. The actual conformation of the vinyl moiety is moot in this case.

In sum, the structures **1** and **2** are not consistent with the chemistry observed herein. On the other hand the structures **6** and **7** do accommodate these findings and allow a more rational interpretation of the literature. It has recently been noted that electrochemical reduction of presumed **1** via cyclic voltammetry[30] results in a σ-bonded iron–vinyl derivative, though evidence for the structure rests only on visible spectra. In light of the fact that **1** is actually **7** the probable conversion was to an *N*-alkyl derivative of an iron(I) species. The assignment of other porphyrin–iron alkyls prepared by physical[31a] and chemical[14d] means and characterized by solution spectra may be open to question.[31b,c]

Reactions run with iron porphyrins in the presence of massive amounts of reductant are not good models for cytochrome P-450. On the other hand, the N-substituted porphyrins like those generated in these reactions, could be involved in the inactivation of P-450 and other heme proteins.[32] The results are in harmony with the suggestion originally made by Bonnet[33] that *N*-hydroxyporphyrins or their iron-bridged counterparts may be a part of P-450-catalyzed reactions.

Finally, we note that while no porphyrin–iron olefin complexes have been previously reported, kinetic evidence for the affilliation of both quinones[34] and nitroaromatics[35] with heme iron has been ascertained. Moreover, hemes are well-known to bond with oxygen and carbon monoxide. In this sense, the porphyrin **3** represents a novel pentacoordinate porphyrin with a π-bonding site.

Experimental Section

Tetraphenylporphine was prepared and purified essentially by the procedure of Adler[36] as summarized by Fuhrhop and Smith.[37] Iron insertion was accomplished by transferring, under argon, a suspension of freshly prepared Fe(OAc)$_2$ in acetic acid into a refluxing solution of the porphyrin in acetic acid and allowing the iron(II) complex to oxidize in the presence of HCl.[38]

Chloroiron(III) Tetraphenylporphine-β-*pyrrole*-d_8. The corresponding TPP-d_8 was prepared by condensation of pyrrole with benzaldehyde in propionic acid-*d*[39] and purified by treatment with dichlorodicyanobenzoquinine.[37] Iron insertion was accomplished by addition of the porphyrin to a refluxing suspension of ferrous acetate in DOAC containing excess NaCl.

Acetic acid-*d*, bp 118–119 °C, was obtained from the reaction of acetic anhydride with D$_2$O. NMR analysis indicated a minimum of 99% deuteration.

Methanol-*d*, tetradeuteriomethanol, and dichloromethane-d_2 were Aldrich minimum 99.5% atom D reagents. The trifluoroacetic acid-*d* was minimum 99% atom D Aldrich Gold Label.

DDT-*d* and DDD-*d* were prepared by condensation of appropriately labeled di- and trichloroacetaldehyde with chlorobenzene and sulfuric acid.[40] The starting material was 1,1-dideuterio-1-hydroxyethane.

1,1-Dideuterioethanol, bp 75–76 °C, was prepared by the LiAlD$_4$ reduction of acetic anhydride in triethyleneglycol dimethyl ether:[41] NMR δ 0.88 (s, CH$_3$).

2,2-Dichloroacetaldehyde-d_1 Hydrate-d_2. Following a patent procedure[42] for the trichloro compound, 25.0 mL of α,α-dideuterioethanol (0.41 mol) was chlorinated in 4.0 g (0.20 mol) of D$_2$O. Chlorine was bubbled through the solution for 4.5 h while the bath temperature was increased from 60 to 85 °C. The crude yellow liquid (29.0 g) showed a major high mass multiplet at δ 113 for dichloroacetaldehyde-d_1.

1,1-Dichloro-2,2-bis(*p*-chlorophenyl)-2-deuterioethane (DDD-*d*). With vigorous stirring, 5.5 g of the above crude dichloroacetaldehyde hydrate was condensed with 6.8 g of chlorobenzene in 60 mL of D$_2$SO$_4$ at 93 °C.[43] The three-time 95% ethanol recrystallized substance (1.51 g): mp 110.5 °C; NMR δ 6.9 (s, 8 H, *p*-ClPh), 5.9 (s, 1 H, CH).

2,2,2-Trichloroacetaldehyde-d_1 Hydrate-d_2. A mixture of 6.9 g of 1,1-dideuterioethanol, 1.4 g of D$_2$O, and 0.9 g of anhydrous cupric chloride was gassed with chlorine for 18 h at 65 °C followed by 11 h at 100 °C. Upon cooling the material partially crystallized. The whole was distilled through a small vigreaux column under

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(29) Hock, A. A.; Mills, D. S. *Acta Crystallogr.* **1961**, *14*, 139. Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5069.

(30) Lexa, D.; Saveant, J. M.; Battoni, J. P.; Lange, M.; Mansuy, D. *Angew. Chem., Int. Engl. Ed.* **1981**, *20*, 578.

(31) Lexa, D.; Mispelter, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705. (b) Castro, C. E.; Koshore, D. *J. Organomet. Chem.* **1985**, *287*, C27. (c) Wade, R. S.; Castro, C. E. *Inorg. Chem.* **1985**, *24*, 2862.

(32) Kunze, K. L.; Ortiz de Montellano, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 4225. Ortiz de Montellano, P. R.; Kunze, K. L. *Biochemistry* **1981**, *20*, 7266 and references therein.

(33) Bonnet, R.; Ridge, R. J.; Appleman, E. H. *J. Chem. Soc., Chem. Commun.* **1978**, 310.

(34) Castro, C. E.; Hathaway, G. M.; Havlin, R. *J. Am. Chem. Soc.* **1977**, *99*, 8032.

(35) Ong, J. H.; Castro, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 6740.

(36) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Kursakott, L. *J. Org. Chem.* **1967**, *32*, 476.

(37) Fuhrhop, J. H.; Smith, K. M. In "Porphyrins and Metalloporphyrins"; Elseiver: New York, 1975; pp 769–770.

(38) Warburg, O.; Nejelein, E. *Biochemistry* **1932**, *7*, 244.

(39) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581. Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dophin, D. *Ann. N.Y. Acad. Sci.*, **1973**, *206*, 350.

(40) Bailes, E. L. *J. Chem. Educ.* **1945**, *22*, 122.

(41) Shiner, V. J. *J. Am. Chem. Soc.* **1952**, *75*, 2929.

(42) Ohse, W. *Chem. Abstr.* **1944**, 3621.

(43) It was found H$_2$SO$_4$ could be employed, cf. below.

argon, bp 97–100 °C. VPC analysis, 2.5-ft Poropak P, still indicated the presence of dichloroacetaldehyde (~5%). To the distilled material (~7 mL) were added 0.5 g of $CuCl_2$ and 1 mL of D_2O. The mixture was rechlorinated at 135 °C for 4 h and then distilled under Cl_2, bp 99–100 °C. The receiver crystallized.

1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)-2-deuterioethane (DDT-*d*). In the manner described above 6.2 g of the above deuterated chloral hydrate was condensed with 7.9 g of chlorobenzene in 70 mL of H_2SO_4. The flask was warmed from 50 to 93 °C over a 9-h period. After being cooled, the mixture was poured onto ice and extracted with methylene chloride. The CH_2Cl_2 extracts were washed with aqueous $(NH_4)SO_4$ and NaOAc and dried over Na_2SO_4. The dry methylene chloride solution was concentrated and chromatographed on a 40 × 2 cm column of Grace silica gel in CH_2Cl_2. The first 100 mL of eluate following the front contained the DDT. The fraction crystallized upon concentration. The material was recrystallized three times from hot hexane. Crystals from the final filtrate: mp 99 °C; weight 0.75 g; ^{1}H NMR δ 7.68 (q); ^{2}H NMR δ 4.98 (s).

Iron Powder Varied in Its Reactivity. Consistent results were obtained with Matheson electrolytically generated reagent grade material. In a small Erlermeyer flask, 3.5 g of iron powder was stirred with 30 mL of glacial acetic acid on a magnetic stirrer (without the stirring bar). Stirring in air was continued until the supernatant solution was visibly brownish ($Fe(OAc)_3$) and hydrogen was being evolved. (More refractory grades of iron powder required gentle heating.) At this point a magnet was held to the bottom of the flask and the acetic acid was decanted. Quickly in similar fashion the Fe^0 was stirred five successive times with methanol and finally suspended in reaction solvent before adding to the reaction mixture.

Aldrich gold label DDT and an authenic sample of DDD, mp 111 °C, were used without purification. Reagent grade MeOH and CH_2Cl_2 were distilled prior to use.

The reactor consisted of a 1-L creased flask fitted with a mechanical stirrer, addition funnel, argon inlet, outlet stopcock, and a serum-capped stopcock for sample removal. The argon outlet was connected to a mercury trap. A run consisted of the reaction of 0.252 g of DDT (7.1×10^{-4} mol) with the iron(II)–porphyrin solution generated from vigorous stirring of 0.352 g of $ClFe^{III}TPP$ (5.0×10^{-4} mol) with 3.5 g of Fe^0 (6.3×10^{-2} mol) in 0.5 L of 9:1 CH_2Cl_2–MeOH. The reaction was monitored spectrally by direct transfer into 0.05-mm length optical cells under argon. First, the $ClFe^{III}TPP$ in 430 mL of 9:1 CH_2Cl_2–MeOH was vigorously stirred and purged with argon for 0.5 h. Under an argon flush, the iron powder was added in suspension in 20 mL of reaction solvent. Vigorous stirring was recommenced, and the reaction was conducted under a slight positive pressure of argon. Samples for spectophotometric analysis were pressured out via no. 18 hypodermic tubing into an argon-purged curvette. Usually the red iron(II) complex was obtained in between 15 min and 1 h (Figure 1).[44] The DDT in 50 mL of reaction solvent was added dropwise with continued vigorous stirring over a period of 2 h. The final reaction product spectrum could also be obtained by mixing all reactants from the start and stirring vigorously. Demetalation was accomplished by addition of 5 mL of concentrated HCl to the entire reaction mixture under argon or more efficiently by addition of dry HCl-saturated CH_2Cl_2 to the filtered, concentrated, and redissolved (CH_2Cl_2) heme mixture under argon. Green porphyrin dication solutions were opened to air and washed successively with water and sodium acetate, and dried over sodium acetate. The concentrate was chromatographed on Grace silica gel. Workup without demetalation was analogous, but the addition of acid was omitted. In general, demetalated mixtures yielded three major porphyrin fractions upon chromatography: a reddish brown fraction (CH_2Cl_2) contained 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD 50%) and recovered tetraphenylporphine (153 mg, 2.5×10^{-4} mol) followed by a red porphyrin with a greenish fluorescence (95:5 CH_2Cl_2–methanol) and identified as *N*-[2,2-bis(*p*-chlorophenyl)ethenyl]tetraphenylporphine (172 mg, 2×10^{-4} mol, 40%; "*N*-vinyl", **3**); and a final raspberry red porphyrin with a greenish fluorescence (50% methanol–CH_2Cl_2 or 94:5:1 CH_2Cl_2–methanol–acetic acid) identified as the monocation of N_{21},N_{22}-[2,2-bis(*p*-chlorophenyl)ethenylidene]tetraphenylporphine (42 mg, 5×10^{-5} mol, 10%; **4**, "Rhodo"). The yield of DDD was determined by gas chromatography on a 1-ft Poropak P column. A mixed-melting point of the trapped substance with authentic DDD was undepressed. Analytical samples of "*N*-vinyl" and "Rhodo" were obtained by rechromatography of each porphyrin on silica. Runs 1–4 in Table I were conducted in this fashion but were demetalated with trifluoroacetic acid.

***N*-[2,2-Bis(*p*-chlorophenyl)ethenyl]tetraphenylporphine.** "*N*-vinyl": λ_{max} (CH_2Cl_2) *436*, 530, 572, 622, 682 nm; NMR (90 MHz) δ 2.9 (d, 2 H), 5.6 (d, 4 H), 7.2 (d, 2 H, *p*-ClPh), 2.0 (s, 1 H, vinyl-H), 1.3 (s, 1 H, N-H), 7.7, 8.2 (m, 20 H, meso-Ph), 7.6 (d, 2 H), 8.5 (q, 4 H), 8.95 (s, 2 H, β-pyrrole) (see Figure 3); MS, *m/e* P, P + 1 (860–865) 860–865, P/2 (430) 430–431, (*p*-ClPhCCH (247), 246–250. Anal. Calcd for $C_{58}H_{38}N_4Cl_2 \cdot H_2O$: C, 79.17;f H, 4.61; N, 6.36. Found: C, 78.86; H, 4.99; N, 6.37.

N_{21},N_{22}-[2,2-Bis(*p*-chlorophenyl)ethenylidene]tetraphenylporphine. "Rhodo": λ_{max} (CH_2Cl_2) *432*, 508, 549, 587, 632 nm; NMR δ 2.7, 6.1 (d, 4 H, *p*-ClPh), 8.2 (m, 4 H), 7.8 (m, 16 H, meso-Ph), 8.5, 9.4 (d, 2 H), 9.1 (m, 4 H, β-pyrrole); *mS*, *m/e* P + 2, P + 3 (860–865) 860–865, P + 2/2 (430–431) 430, 431, (*p*-ClPhCC) (246–250) 246–250. Anal. Calcd for $C_{58}H_{36}H_4Cl_2 \cdot HCl \cdot 2H_2O$: C, 74.70; H, 4.43; N, 6.00. Found: C, 70.51, 74.50; H, 4.93; N, 5.67. The basicity of "Rhodo" and its monocationic nature was established by the fact that its spectrum is unchanged in acetic acid. It can be converted to the dication (λ_{max} *441*, 578, 628 nm) with trifluoroacetic acid or the free base (λ_{max} 357, *439*, 532, 620 nm) upon treatment with *tert*-butylamine. Concentration of *tert*-butylamine solutions however yields the mono cation.

Attempted Synthesis of *N*-Vinyl and Rhodo. Reactions of TPP, K_2TPP, Ag_2TPP, or MgTPP with DDT or DDE failed to produce either the *N*-vinyl or Rhodo framework. Reactions with DDE in the presence of $AlCl_3$ also failed. Similarly the reaction of DDD with $Fe^{II}TPP$ under the exact conditions employed above yielded only recovered DDD and no condensation products.

Chromatography of the product concentrate without demetalation afforded four major porphyrin fractions from the silica gel column. The red-orange band I (CH_2Cl_2) contained the "carbene" and the DDD. This was followed in turn by the μ-oxo dimer of TPP (95:5 CH_2Cl_2–MeOH), the "oxidized carbene", *N*-vinyl, and "Rhodo", (10% MeOH–CH_2Cl_2). Heart cuts of each fraction were rechromatograhed to purity. Rechromatography of the orange-red "carbene" in CH_2Cl_2 on mildly acidic SiO_2 columns always produced some *N*-vinylporphyrin that was easily separated and removed from the top of the column. Similarily rechromatography of the oxidized carbene (5% MeOH) always generated some *N*-vinylporphyrin. As noted in the Results yields generally paralleled those noted for the demetalated porphyrin. The combined yield of "carbene", "oxocarbene", and *N*-vinylporphyrin averaged about 50%. The Rhodo porphyrin yield was of the order of 5–10%.

In an attempt to obtain the iron(II) adduct solely as the chloro complex a reaction like the one above was worked up without demetalation, but aqueous NaCl rather than NaOAc was used to wash the CH_2Cl_2 product solution. In the subsequent CH_2Cl_2 chromatography the products were the same except that iron TPP chromatographed primarily as the chloro adduct. A three-time rechromatographed heart cut of the iron(II) complex was demetalated in a small volume of CH_2Cl_2 with TFAH and washed with water. The H_2O phase was treated with $AgNO_3$. A precipitate of AgCl formed immediately, and Cl^- was determined gravimetrically after being dried. The yield of AgCl (1.2 mg) corresponded to 75% of the *N*-vinylporphyrin determined spectroscopically after neutralization. Blank CH_2Cl_2 treated similarly did not produce AgCl.

"The Carbene"—Iron(II) *N*-[2,2-Bis(*p*-chlorophenyl)ethenyl]tetraphenylporphine Chloride (Acetate). The UV–vis, NMR, and MS matched literature spectra.[1d] Essential facets of the IR are in the text. Elemental analyses varied widely on the same sample. Anal. Calcd for $C_{58}H_{38}N_4Cl_2FeCl_{1/2}(CH_3CO_2)_{1/2}$: C, 73.60; H, 4.04; N, 5.84; Cl, 9.24; Fe, 5.80. Found: C, 73.50; H, 4.55; N, 5.91; Cl, 9.34; Fe, 5.78. The substance is more fragile than indicated and easily demetalates in solution to *N*-vinylporphyrin. For example CH_2Cl_2 solutions dried over Na_2SO_4 demetalated overnight. Rechromatography on Grace SiO_2 in CH_2Cl_2 (even after

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[44] Very slow reductions can be hastened by adding 0.5 mL of HOAc without altering the reaction course.

being dried over NaOAc) invariably resulted in some demetalation. Solutions in CCl_4 oxidized to the iron(III) complex.

The variable-temperature NMR studies with a twice chromatographed sample exhibited a single broad proton at δ 0.9 (−60 °C) (Figure 6). Upon warming, this proton gradually shifted downfield and sharpened. It appeared as a sharp singlet at δ 1.5 (22 °C) and integrated exactly as one proton. This signal diminished substantially, however, upon chromatography of the substance once again. We presume the observation reflects some solvation near the porphyrin core.

The "Oxidized Carbene"—Chloroiron(III) *N*-[2,2-Bis(*p*-chlorophenyl)ethenyl]tetraphenylporphine Hydroxide. The physical properties of this substance match those in the literature. Salient information is in the text. The UV-vis was slightly different than reported. In CH_2Cl_2 we find λ_{max} = 427 and 669 nm. Only fractions that contained a significant amount of *N*-vinyl approach the λ_{max} of 428 nm reported. On standing the pure substance gradually demetalates to *N*-vinyl and also is converted to Rhodo porphyrin. Presumably the Fe^{III} from demetalation is responsible for the conversion to "Rhodo". Anal. Calcd for $ClFeC_{58}H_{37}N_4Cl_2(OH)$: C, 72.20; H, 3.86; N, 5.82; Cl, 11.00; Fe, 5.76. Found: C, 72.62; H, 4.25; N, 5.59; Cl, 11.27; Fe, 5.48.

Insertion of Iron into *N*-Vinyl A solution of 10 mg of *N*-vinylporphyrin in 20 mL of 1:1 CH_2Cl_2–MeOH was stirred under argon and treated with 4 mL of a thick suspension of $Fe(OAc)_2$ in HOAc and a trace of Fe^0 (to keep the mixture reduced). The mixture was warmed for 4 h. The solution gradually changed from a green to orange-brown. After being cooled, the mixture was washed with sodium acetate and chromatographed as above. The Fe^{II}–*N*-vinyl complex eluted as the first band in CH_2Cl_2. This was followed by unreacted *N*-vinylporphyrin. The distribution of *N*-vinyl and the iron(II) complex actually isolated are very much a function of workup. For example, a reaction mixture composed of 8:1 Fe^{II} complex–porphyrin (visible spectrum for sorets) yielded after chromatography 20% of the iron(II) complex and 80% of recovered *N*-vinyl.

Conversion of Iron(III) *N*-Vinyl to Rhodo. This reaction could be cleanly effected at very low concentrations. Ten milliliters of a 5 × 10^{-5} M solution of iron(III) *N*-vinyl in 9:1 CH_2Cl_2–MeOH was shaken with 1 mg of solid $AlCl_3$. The solution changed color immediately. Reaction was complete in 1 min. Neutralization with aqueous NaOAc yielded Rhodo porphyrin. Both $FeCl_3$ and $AgNO_3$ reacted in similar fashion but the reaction was slower (~3 and 10 h, respectively). The conversion with $ZnCl_2$ was much slower and required 4 days for completion. the iron(II) complex, in air, underwent the same transformation. Reaction proceeded through the iron(III) adduct.

Noninterconversion of *N*-Vinyl $\rightleftarrows$ Rhodo. Each porphyrin was subjected to the original reaction conditions and recovered without change.

Demetalation of Purified "Carbene" and "Oxidized Carbene". An argon-purged solution of the iron porphyrin in 20 mL of CH_2Cl_2 was treated with 1 mL of trifluoroacetic acid (H or D) under argon. The green dication color began to develop immediately. The reaction mixture was allowed to stand 10 min. It was opened to air, washed twice with aqueous sodium acetate, and dried over anhydrous sodium acetate. The dried solution was concentrated to dryness on a rotary evaporator at 40 °C, redissolved in 0.5–1 mL of CH_2Cl_2, and chromatographed on a silica column as described above. In the case of the iron(II) complex a very small fraction of the nondemetalated porphyrin (0–5%) ran with the CH_2Cl_2 front. The *N*-vinylporphyrin was eluted cleanly in 5% MeOH–CH_2Cl_2 and was obtained in 95–100% yield. No other porphyrin was produced. For NMR analysis the solution was filtered, concentrated to dryness, and redissolved in $CDCl_3$ or CCl_4. The demetalations as shown in Figure 2 were conducted at the concentrations indicated.

Runs 1–4 (Table I). These were conducted in the manner described above.

Run 5 (Table I). With use of a 500-mL creased three-neck flask, 0.352 g of $ClFe^{III}TPP$ in 197 mL of 9:1 CD_2Cl_2–CD_3OD was reduced under argon by vigorous stirring with 3.5 g of iron powder. The iron powder was activated by gentle warming in 10 mL of acetic acid-*d* until hydrogen evolution commenced and then stirred magnetically for 1 min. The reddish brown supernatant ($Fe^{III}OAC$) was poured off the magnetically held Fe^0, and the metal was rinsed three times with methanol-*d* and once with 9:1 CD_2Cl_2–CD_3OD before transferring to the reaction flask. After vigorous argon purging for 10 min, stirring was commenced. The argon flow rate was adjusted to a slow rate after 2 min. After 1 h the mixture had the red color of the iron(II) TPP. A solution of DDT in 22.3 mL of 9:1 CD_2Cl_2–CD_3OD was added slowly over a 4-h period. After 1 h of additional stirring, 6 mL of trifluoroacetic acid-*d* were added. The mixture was stirred an additional 2 min and allowed to stand for 20 min. The mixture did not demetalate well, presumably because of the presence of $Fe^{II}OAC$ and CD_3OD. Water, 150 mL, was added with stirring. The CD_2Cl_2 phase was more redish orange than green (porphyrin dication). It was separated, filtered, and washed again with 150 mL of H_2O and dried over Na_2SO_4. The UV–vis of the $CDCl_2$ solution showed the presence of the carbene and oxcarbene (λ_{max} 417, 519, 545 (sh), 655). To 150 mL of the dry filtered CD_2Cl_2 solution was added 1.5 mL of TFAD under argon. The color began to change to green immediately. After 10 min the visible spectrum was that of the green porphyrin dication (λ_{max} 438, 658 nm). The CD_2Cl_2 dication solution was washed with aqueous sodium acetate to pH 5 and dried over NOAc. The visible spectra of the product mixture indicated the presence of predominately *N*-vinylporphyrin and TPP (λ_{max} 436, 520, 575, 622, 645, 685 nm). The solution was filtered, and the CD_2Cl_2 was removed with a rotary evaporator. The solid purple mass was taken up in 20 mL of CH_2Cl_2. Ten milliliters of this solution was stripped to dryness of the rotary evaporator and chromatographed on a 2 × 40 CH_2Cl_2/SiO_2 column. The remaining 10 mL was treated as the product mixture (cf. below). Elution was begun with CH_2Cl_2. The first pink band of TPP, containing DDD, moved with the front. Following removal of this fraction, elution was commenced with 5% MeOH in CH_2Cl_2. *N*-vinylporphyrin was brought off the column cleanly with this solvent. The trace of "Rhodo" remained near the top of the column. The visible spectra of the phorphyrin fraction represented by bands I and II corresponded exactly to TPP and *N*-vinylporphyrin. Both were filtered and concentrated to dryness on the rotovap. The TPP fraction was rechromatographed on a hexane/SiO_2 column like the one above.

This fraction was placed atop the column in CH_2Cl_2, but elution was commenced with hexane. After elution with 375 mL of hexane, elution with CH_2Cl_2 was begun to bring the TPP off the column. The fraction of CH_2Cl_2 eluate just preceding the TPP band was collected. The third and TPP fraction was eluted with CH_2Cl_2. Both the first two colorless (hexane and methylene chloride) DDD fractions crystallized upon concentration.

Samples of porphyrin or product mixture, *N*-vinylporphyrin, TPP, and DDD, were then prepared for ^1H and ^2H NMR analysis. Corresponding solutions were filtrated and concentrated to dryness on the rotary evaporator. Each sample was then evacuated at 0.05 mm for at least 3 h. Dried samples were then treated with ~$^3/_4$ mL of freshly distilled CCl_4 or $CDCl_3$. About $^1/_2$ mL of each of these solutions were transferred to NMR tubes.

Run 7. Reaction was conducted in the manner described for run 5 above except that DDT-*d* was a reactant. Workup was slightly different. Following reaction, the solution was washed twice with 100 mL of water and dried over Na_2SO_4. The dried filtered CD_2Cl_2 solution was divided into two 50-mL portions. One was demetalated under argon with 0.5 mL of TFAD and the other with 0.5 mL of TFAH. The porphyrins or product mixture was handled and analyzed as described above. Chromatography of products was accomplished by beginning with a hexane/SiO_2 column and eluting with hexane. This removed most of the DDD, but the colorless CH_2Cl_2 eluate just preceding the TPP fraction was combined with the hexane fraction. As befoe, eluting with 5% MeOH–CH_2Cl_2 brought off the *N*-vinylporphyrin but this was preceded by a fraction of the μ-oxo dimer of TPP. Pure *N*-vinyl was separated from the latter by rechromatography on a CH_2Cl_2 column and eluting with 5% MeOH–CH_2Cl_2.

Run 6 (Table I). This run was conducted like runs 1–4 and like run 7 above.

Acknowledgment. This work was supported in part by NIH Grants ES00158 and AM28271. We are grateful for this support.