J. Org. Chem. 1986, 51, 4651–4656

naphthalene, 91-20-3.

Supplementary Material Available: ^{1}H NMR spectra (full-scale aromatic region and expanded-scale individual multiplets), ^{13}C NMR spectra (full-scale aromatic region), IR, MS (70-eV electron impact (with proposed schematic of fragmentation), positive and negative chemical ionization), fluorescence spectra (emission and excitation), and MNDO-MO calculated molecular geometry for **2c** (15 pages). Ordering information is given on any current masthead page.

[*N*-(2,2-Bis(*p*-chlorophenyl)vinyl)tetraphenylporphyrinato]iron(II) Chloride, Its Structure and Comparison with Other Products Obtained through the Reaction of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) and Iron Porphyrins

Alan L. Balch,* Yee Wai Chan, Marilyn M. Olmstead, and Mark W. Renner

Department of Chemistry, University of California, Davis, California 95616

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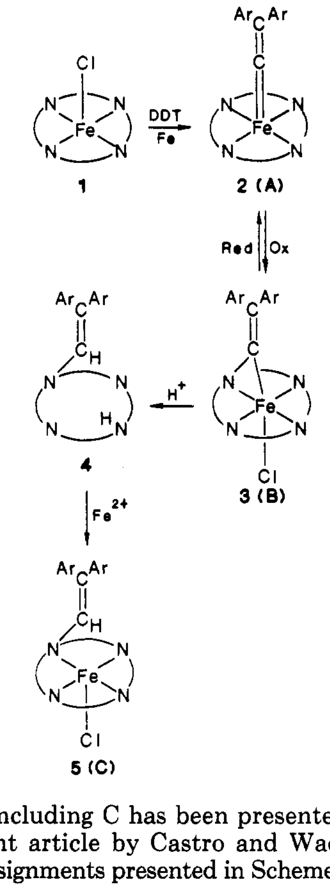
The X-ray crystal structure of green [*N*-(2,2-bis(*p*-chlorophenyl)vinyl)tetraphenylporphyrinato]iron(II) chloride has been determined by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 12.133$ (8) Å, $b = 26.520$ (9) Å, $c = 15.190$ (6) Å, and $\beta = 107.86$ (5)° and was refined to $R = 0.069$. The structure shows the iron to be in a distorted square-pyrimidal environment with the chloride ligand at the unique apex and the four nitrogens in the basal plane with one very long Fe–N distance. There is no evidence for bonding of the iron to the vinyl group as suggested by Castro and Wade (*J. Org. Chem.* **1986**, *50*, 5342). Structural and spectroscopic data indicate that this material is distinct from the red brown iron carbene complex obtained from the reaction of tetraphenylporphyriniron(III) chloride, iron powder, and DDT.

Introduction

Products resulting from the reactions between iron porphyrins and halocarbons are important since carbon–halogen bonds are present in a variety of substances introduced by man into the environment as insecticides, anesthetics, and drugs. In animals these substances can come in contact with the various heme proteins, particularly cytochrome P450 which is responsible for metabolism of many foreign substances.

Treatment of the porphyrin iron(III) chloride 1 with the insecticide DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) and a reducing agent (iron powder) yields the diamagnetic complex A which has been assigned structure 2 shown in Scheme I.[1] Upon oxidation this species undergoes migration of the axial ligand into an Fe–N bond to form the green iron(III) complex B which has been assigned structure 3.[2-4] This reaction is reversible; treatment of B with aqueous sodium dithionite yields A. The structure of paramagnetic ($S = {}^3/_2$) B as 3 has been established through two independent X-ray studies[3-5] and extensive spectroscopic studies.[6,7] Treatment of purified B with acid results in demetalation to give the *N*-vinylporphyrin 4.[8] Insertion of iron(II) into this N-substituted porphyrin yields the paramagnetic ($S = 2$) iron(II) complex C assigned structure 5.[9] An extensive analysis of the ^{1}H NMR spectra of N-substituted porphyrin iron(II) halide complexes including C has been presented.[10]

Scheme I. Interconversions among Porphyrin Complexes. The Correlation between Structures 2, 3, and 5 and Substances A, B, and C Is That Described in Paragraph 2 of the Introduction



In a recent article by Castro and Wade (CW),[11] the structural assignments presented in Scheme I are disputed. In essence, CW claim that the diamagnetic material A

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[1] Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3212.

[2] Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437.

[3] Chevrier, B.; Weiss, R.; Lange, M.; Mansuy, D.; Chottard, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2899.

[4] Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270.

[5] Olmstead, M. M.; Cheng, R.-J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143.

[6] Mansuy, D.; Morgenstern-Badaraus, I.; Lange, M.; Gans, P. *Inorg. Chem.* **1982**, *20*, 4348.

[7] Balch, A. L.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L. *Inorg. Chem.* **1985**, *24*, 2651.

[8] Lange, M.; Mansuy, D. *Tetrahedron Lett.* **1981**, *22*, 2561.

[9] Mansuy, D.; Battioni, J.-P.; Dupré, D.; Sartori, E. *J. Am. Chem. Soc.* **1982**, *104*, 6159.

[10] Balch, A. L.; Chen, Y.-W.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *Inorg. Chem.* **1985**, *24*, 1437.

[11] Castro, C. E.; Wade, R. S. *J. Org. Chem.* **1985**, *50*, 5342.

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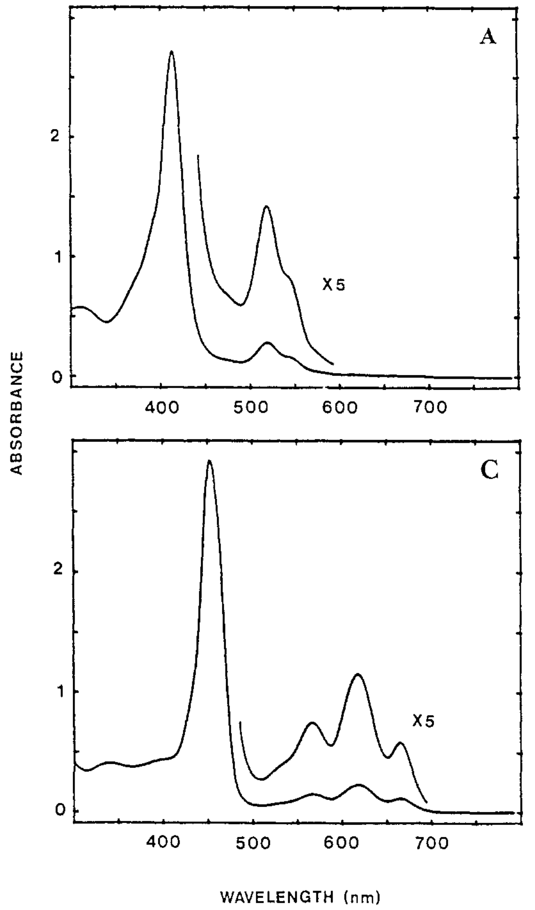

Figure 1. Electronic spectra of benzene solutions of (A) substance A (**2**) (3.3×10^{-5} M) and (C) substance C (**5**) (2.7×10^{-5} M) with 1.0-mm path-length cells.

obtained from the reaction of **1**, iron powder, and DDT is an iron(II) complex of *N*-vinylporphyrin and that the oxidation product B is an iron(III) *N*-vinylporphyrin complex.[12] In order to account for the fourfold symmetry observed in the ^{1}H NMR spectrum of the diamagnetic substance A, CW propose extensive π-bonding between iron and the *N*-vinyl substituent.

In order to clarify this matter we have undertaken the studies reported here. Since we were aware of an X-ray diffraction study on A (i.e., **2**),[13] we focused our attention on C (the iron(II) complex of the *N*-vinylporphyrin **4**) which we show to have structure **5**. This structure is compared to that of the corresponding *N*-methylporphyrin iron(II) chloride complex[14] and to that of B (i.e., **3**).[5] These data allow us to access the nature of any interaction between the vinyl group and iron in these complexes and to reinforce the original conclusion that B contains an iron–carbon σ bond. Finally we reemphasize differences between substances A and C.

Results

Electronic Spectra. The electronic spectra of substances A and C are compared in Figure 1. The spectra shown here agree with the numerical data presented previously by Mansuy and co-workers.[1,9] Clearly two different substances are involved. The difference is easily discerned visually in solution. A is red brown; C is green as are other N-substituted porphyrin complexes of iron(II).[14]

Table I. Atomic Positional Parameters ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	*U*
Fe	1883 (2)	1666 (1)	6621 (2)	10 (1)[a]
Cl(1)	218 (3)	1923 (2)	5547 (3)	19 (2)[a]
Cl(2)	6943 (4)	293 (2)	10805 (4)	50 (2)[a]
Cl(3)	−956 (4)	1222 (2)	11430 (3)	37 (2)[a]
N(1)	3222 (9)	1287 (4)	6306 (7)	6 (3)
N(2)	1396 (9)	965 (4)	7050 (7)	6 (3)
N(3)	1315 (10)	1954 (4)	7996 (8)	15 (3)
N(4)	3049 (9)	2284 (4)	7041 (7)	9 (3)
C(1)	3997 (11)	1520 (5)	5943 (9)	3 (4)
C(2)	4429 (12)	1159 (5)	5414 (10)	17 (4)
C(3)	3970 (11)	718 (5)	5501 (10)	11 (4)
C(4)	3187 (13)	782 (6)	6073 (11)	22 (5)
C(5)	2581 (12)	409 (5)	6371 (10)	17 (4)
C(6)	1796 (12)	492 (5)	6867 (10)	11 (4)
C(7)	1177 (12)	111 (6)	7192 (10)	17 (4)
C(8)	412 (12)	338 (5)	7550 (10)	16 (4)
C(9)	538 (12)	879 (5)	7452 (10)	14 (4)
C(10)	−105 (12)	1260 (5)	7713 (10)	11 (4)
C(11)	167 (11)	1757 (5)	7850 (9)	9 (4)
C(12)	−585 (12)	2185 (5)	7778 (9)	10 (4)
C(13)	54 (11)	2615 (5)	7854 (9)	12 (4)
C(14)	1225 (12)	2485 (5)	7961 (10)	16 (4)
C(15)	2094 (12)	2825 (5)	7947 (10)	9 (4)
C(16)	3053 (11)	2692 (5)	7601 (9)	9 (4)
C(17)	4078 (11)	2997 (5)	7705 (9)	12 (4)
C(18)	4639 (12)	2784 (5)	7172 (10)	17 (4)
C(19)	4017 (12)	2350 (5)	6751 (9)	10 (4)
C(20)	4376 (11)	2027 (5)	6174 (9)	10 (4)
C(21)	5262 (12)	2238 (6)	5747 (10)	16 (4)
C(22)	6377 (12)	2029 (6)	6011 (10)	24 (5)
C(23)	7203 (13)	2237 (6)	5589 (10)	24 (5)
C(24)	6887 (14)	2623 (6)	4975 (11)	29 (5)
C(25)	5771 (13)	2816 (6)	4697 (11)	27 (5)
C(26)	4970 (13)	2614 (5)	5113 (10)	22 (4)
C(27)	2848 (13)	−122 (6)	6178 (11)	23 (5)
C(28)	3946 (13)	−306 (6)	6529 (10)	21 (4)
C(29)	4213 (14)	−812 (6)	6403 (11)	35 (5)
C(30)	3340 (13)	−1126 (7)	5913 (10)	33 (5)
C(31)	2256 (14)	−964 (6)	5552 (11)	29 (5)
C(32)	1964 (13)	−458 (5)	5683 (10)	19 (4)
C(33)	−1291 (11)	1106 (5)	7721 (10)	12 (4)
C(34)	−1990 (12)	804 (5)	6984 (10)	18 (4)
C(35)	−3109 (12)	674 (5)	6937 (10)	12 (4)
C(36)	−3555 (13)	829 (5)	7624 (10)	21 (4)
C(37)	−2883 (12)	1124 (6)	8350 (11)	27 (5)
C(38)	−1751 (12)	1250 (5)	8436 (10)	17 (4)
C(39)	1994 (11)	3359 (6)	8206 (9)	12 (4)
C(40)	2233 (12)	3762 (5)	7684 (11)	20 (4)
C(41)	2030 (12)	4258 (6)	7894 (10)	19 (4)
C(42)	1575 (11)	4358 (5)	8613 (9)	13 (4)
C(43)	1300 (11)	3966 (5)	9122 (10)	12 (4)
C(44)	1544 (11)	3465 (5)	8918 (9)	7 (4)
C(45)	2339 (11)	1705 (5)	8564 (9)	14 (4)
C(46)	2436 (12)	1425 (5)	9292 (10)	9 (4)
C(47)	1576 (12)	1387 (6)	9828 (10)	14 (4)
C(48)	1116 (12)	1811 (5)	10123 (9)	18 (4)
C(49)	337 (12)	1763 (6)	10602 (10)	24 (5)
C(50)	17 (13)	1275 (6)	10779 (11)	21 (4)
C(51)	442 (12)	852 (6)	10507 (10)	16 (4)
C(52)	1244 (11)	900 (5)	10002 (9)	13 (4)
C(53)	3574 (12)	1133 (5)	9686 (10)	17 (4)
C(54)	4112 (12)	1102 (6)	10645 (10)	22 (4)
C(55)	5157 (13)	862 (6)	10966 (11)	27 (5)
C(56)	5639 (13)	620 (5)	10374 (11)	19 (4)
C(57)	5118 (14)	635 (6)	9407 (11)	31 (5)
C(58)	4083 (13)	892 (5)	9083 (11)	25 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Structural Study. A perspective drawing of **5** is shown in Figure 2, which gives the atom numbering scheme used here. A stereoscopic view of the molecule is

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[12] A significant factor in the arguments of Wade and Castro concerning these structures was their report that treatment of B (**3**) with deuterated trifluoroacetic acid did not result in deuteration of the *N*-vinylporphyrin **4**.[11]. However, in our hands the reaction between B (**3**) and deuterated trifluoroacetic acid yields **4** with 95% deuteration of the unique vinyl proton.[10]

[13] Weiss, R., personal communication.

[14] Anderson, O. A.; Kopelove, A. B.; Lavallee, D, K. *Inorg. Chem.* **1980**, *19*, 2101.

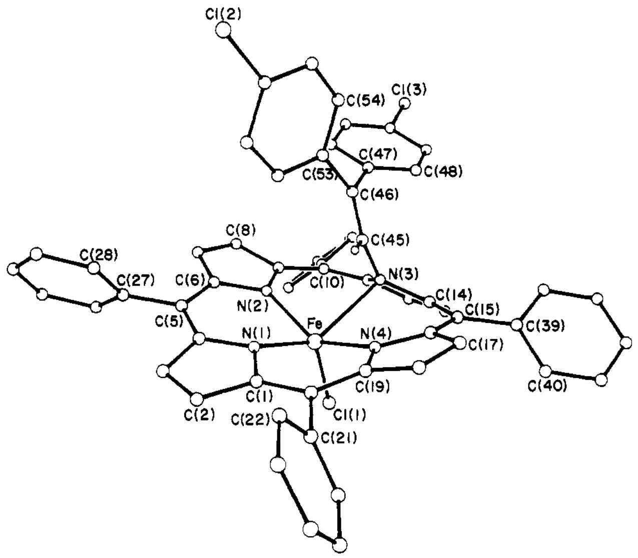


Figure 2. Perspective drawing of C (**5**) showing the atomic labeling scheme.

Table II. Comparison of Structural Parameters of Compounds

	5	**6**[a]	**3**[b]
	Bond Length		
Fe–N(1)	2.087 (12)	2.082 (2)	2.002 (4)
Fe–N(2)	2.113 (11)	2.118 (2)	1.991 (4)
Fe–N(4)	2.131 (11)	2.116 (2)	1.985 (4)
Fe–N(3)	2.510 (11)	2.329 (2)	2.529 (4)[c]
Fe–Cl(1)	2.277 (4)	2.244 (1)	2.299 (1)
Fe···C(45)	2.834 (12)[c]		1.921 (5)
	Bond Angles		
N(1)–Fe–Cl(1)	124.2 (3)	114.38 (7)	111.7 (1)
N(1)–Fe–N(3)	140.3 (4)	142.13 (8)	127.8 (2)[c]
N(1)–Fe–N(4)	86.9 (4)	86.64 (8)	91.4 (2)
N(1)–Fe–N(2)	87.6 (5)	87.12 (8)	92.2 (2)
N(2)–Fe–Cl(1)	102.3 (3)	105.36 (7)	97.0 (1)
N(2)–Fe–N(4)	143.8 (4)	145.60 (9)	164.5 (2)
N(2)–Fe–N(3)	80.6 (4)	82.18 (8)	82.8 (2)[d]
N(3)–Fe–Cl(1)	95.5 (3)	103.48 (6)	120.5 (1)[d]
N(3)–Fe–N(4)	81.0 (4)	82.25 (8)	83.1 (2)[d]
N(4)–Fe–Cl(1)	110.2 (3)	108.03 (7)	95.6 (1)

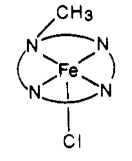
[a] From ref 13, renumbered to conform with Figure 2. [b] From ref 5, renumbered to conform with Figure 2, the porphyrin is tetra(*p*-tolyl)porphyrin. [c] Nonbonded separation. [d] Here C(45) replaced N(3).

shown in Figure 3. Final atomic coordinates and thermal parameters are given in Table I. Some structural parameters are given in Table II.

Crystals of C consist of discrete neutral molecules possessing structure **5**. No chemically significant intermolecular interactions are present within the solid.

The iron coordination can be viewed as a highly distorted square pyramid with the chloride at the unique apex. In this view the iron is bound by four nitrogen atoms in the basal plane but the distance to one of these, N(3), is exceeding long, 2.510 (11) Å, and all of the Fe–N distances are longer than the Fe–N distances in comparable, five-coordinate iron(II) complexes of normal porphyrins: Fe(TPP)(2-MeIm), 2.086 (9) Å;[15] Fe(TPivPP)(2-MeIm) 2.072 (6) Å;[16] Fe(TPP)SC_2H_5, 2.096 (4) Å[17] [with TPP, tetraphenylporphyrin dianion; TPivPP, tetrakis(*o*-pivalamidophenyl)porphyrin dianion; 2-MeIm, 2-methylimidazole].

Overall, the iron environment is quite similar to that of the *N*-methyl analogue, (*N*-methyltetraphenylporphyrinato)iron(II) chloride (**6**).[14] A comparison of some of the bonding parameters is given in Table II. In both cases the shortest Fe–N distance involves the nitrogen that is trans to the substituted pyrrole and the three normal Fe–N distances are all of comparable length. Likewise, the two Fe–Cl distances are similar. However the Fe–N(3) distance in **5** is much greater (by 0.18 Å) than the corresponding distance in **6**. Likewise, the angular distribution of ligands about iron is similar in both cases. The largest differences involve the N(1)–Fe–Cl(1) and N(3)–Fe–Cl(1) angles which differ by 10° and 8°; other differences are all less than 5°. In both structures the Fe–Cl group lies on the opposite side of the porphyrin plane from the porphyrin N-bound methyl or vinyl substituents.



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The shapes of the porphyrin ligand in **5** and **6** are also similar. The N-substituent causes the affected pyrrole ring to be tilted out of the plane of the remainder of the porphyrin. Nevertheless, each of the pyrrole rings in **5** has retained its planarity. The degree of tilting of the substituted pyrrole is greater in **5** than in **6**. This can be appreciated by turning to Figure 4, which shows the deviation of the atoms in the porphyrin skeleton from a least-squares plane calculated on the basis of the three normal pyrrole rings. The dihedral angle between the plane containing the reacted pyrrole and the plane of the rest of the porphyrin is 44° in **5**. In **6** that dihedral angle is 30°.

The presence of an N-substituent has previously been noted to cause important differences in the N–C and C–C distances within the affected pyrrole as compared to the nonsubstituted pyrrole rings.[14] This reflects the change in hybridization at the affected nitrogen. Similar alterations are found in **5**. Thus the N(3)–C(11) and N(3)–C(14) distances, 1.44 (2) and 1.41 (2) Å, are longer than the other $N–C_a$ distances (average, 1.38 Å). The C(11)–C(12) and C(14)–C(15) distances, 1.44 (2) and 1.39 (2) Å, are shorter than the average, 1.45 Å, of the other $C_a–C_b$ distances in the unreacted pyrrole rings. Finally the C(12)–C(13) distance is, 1.36 (2) Å, greater than the $C_b–C_b$ distances (average, 1.33 Å) in the normal pyrrole rings. Such differences have been previously ascribed[14] to the change to sp^3 hybridization at N(3) which lengthens the $N(3)–C_a$ bonds. The shortening of the $C_a–C_b$ bonds and lengthening of the $C_b–C_b$ bonds in the affected pyrrole occurs because of less effective delocalization into the modified pyrrole. Tilting of the pyrrole also inhibits delocalization through that ring.

The structure of **5** can also be compared to that of **3**.[7] The iron geometry of **3** is best described as trigonal bipyramidal with two of the porphyrin nitrogens in the axial position and chloride, carbon, and porphyrin nitrogen (the one trans to the modified pyrrole) in the equatorial plane. In this case the nitrogen of the modified pyrrole does not

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(15) Collman, J. P.; Kim, N.; Hoard, J. L.; Lang, G.; Radonovich, L. J.; Reed, C. A. *Abstract of Papers*, 167th National Meeting of the American Chemical Society, Los Angeles, CA, April 1974; American Chemical Society: Washington, D.C., 1974; INOR 29.

(16) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; and Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 6769–6770; **1980**, *102*, 3224–3237.

(17) Caron, C.; Mitschler, A.; Riviere, G.; Ricard, L.; Schappacher, M.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7401–7402.

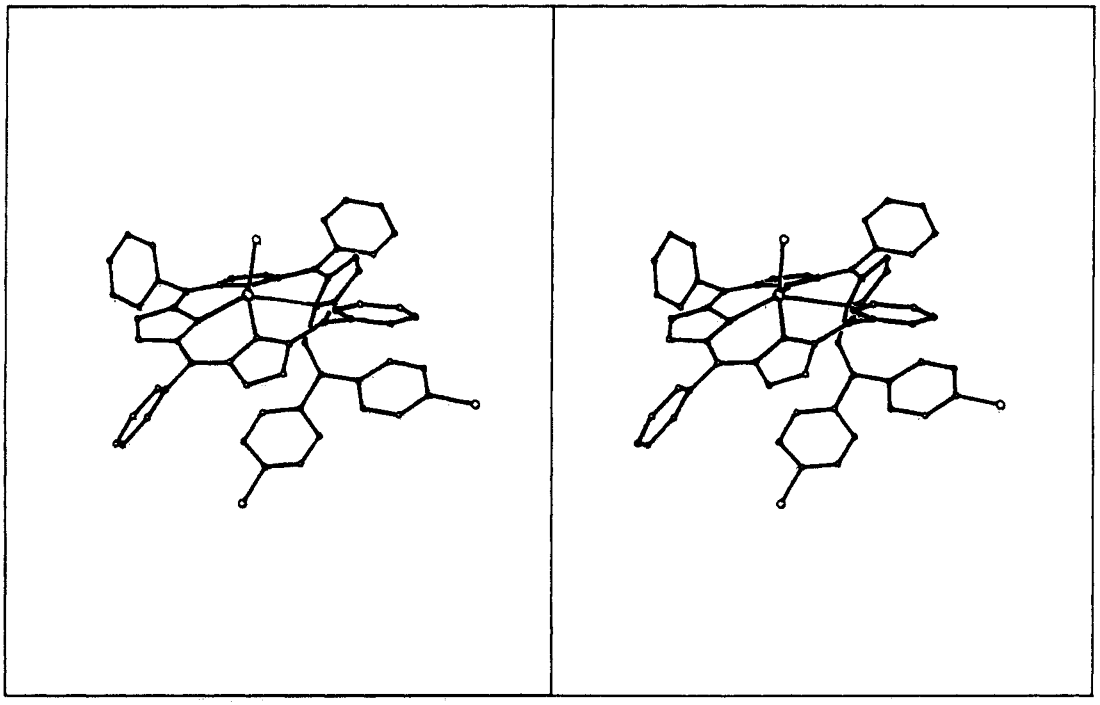
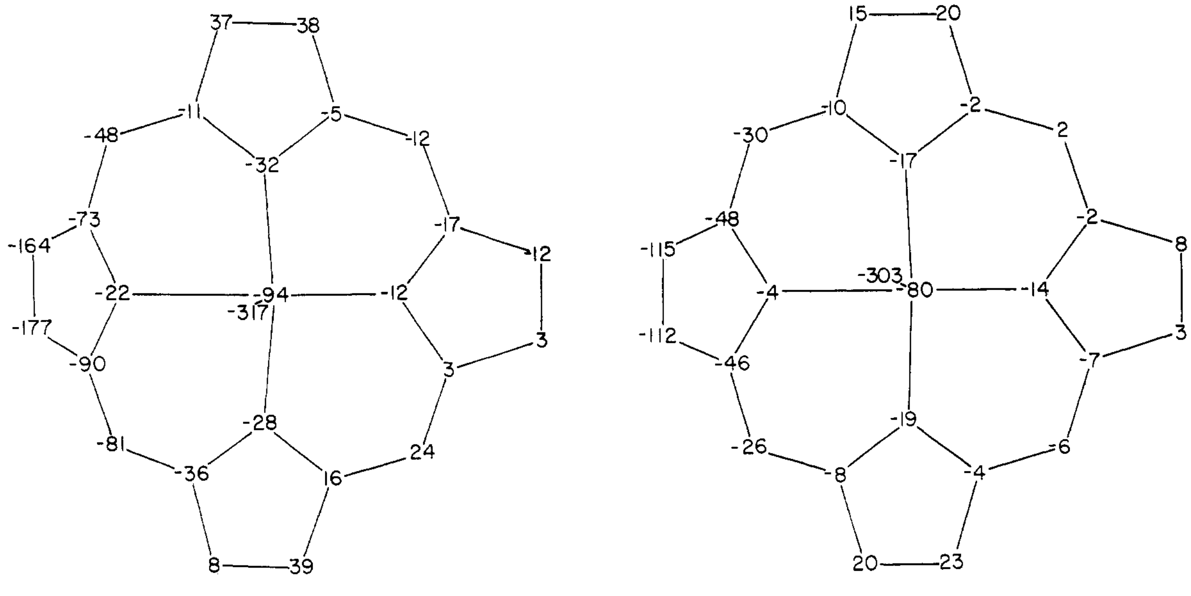


Figure 3. stereoscopic drawing of C (5).



5 **6**

Figure 4. Diagram of the porphyrin cores of C (5) (left) and 6[13] (right). Each atom symbol has been replaced by a number representing the perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphyrin. This plane is based on the location of the three unreacted pyrrole rings and the meso carbon atoms connecting them. The N-substituted pyrrole ring is on the left in each diagram.

appear to be bound to iron. Detailed comparison of some of the bond distances and angles involved in these structures are presented in Table IV (supplementary material).

Analysis of Vinyl-Iron Bonding in 3 and Its Absence in 5. Comparison of the structures of 3 and 5 allows definitive conclusions to be reached regarding the suggestions of CW. In 5 the vinyl group is positioned on the opposite side of the porphyrin from the iron. The orientation of the iron in 5 with regard to the vinyl group and some dimensions within that group are shown on the right side of Figure 5. Notice that the structural parameters of the vinyl group are all close to the ideal for sp^2 hybridization of the olefinic carbons. The hydrogen atom on the vinyl carbon was clearly located in the X-ray diffraction study. Figure 5 shows that the iron atom is indeed remote from the vinyl group. The Fe–C(45) distance is 2.833 (13) Å and the Fe–C(46) distance is 3.955 (14) Å. In contrast, iron–olefin π-bonding requires much closer approach of the iron and the carbon atoms. From the compilation by Kruger, Barnett, and Brauer on 42 compounds containing η^2-coordinated olefins and acetylenes, the range of Fe–C distances is 1.94 to 2.304 Å.[18] Moreover, in these η^2-bonded compounds, the iron resides near the midpoint of the C–C double bond and above the plane of the olefin itself. In 5, however, the iron atom lies well off to the side of the olefin and the overlap required for π-bonding is

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[18] Kruger, C.; Barnett, B. L.; Brauer, D. In *The Organic Chemistry of Iron*; Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I. Eds.; Academic Press: New York, 1978; Vol. 1, p 1.

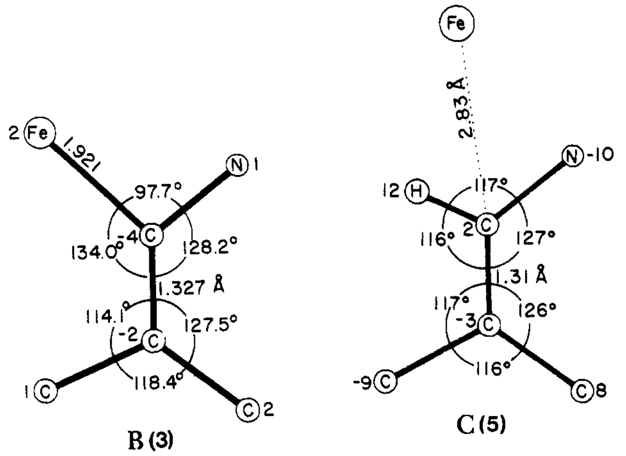


Figure 5. Some dimensions of the vinyl group in (B(3)) substance B (**3**) and (C(5)) substance C (**5**). The numbers to the right or left of the atom circles give the vertical deviation in 0.01 Å of that atom from the least-squares plane of the vinyl group.

negligible. Consequently, there is no evidence for an iron–olefin interaction in **5**.

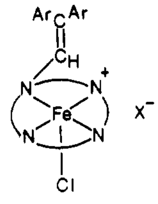
The left side of Figure 5 shows the corresponding arrangement for **3**.[5] Here, the iron is bound to one of the vinyl carbons. The Fe–C distance, 1.921 (5) Å, is consistent with the presence of a σ bond from iron to an sp^2-hybridized carbon. For comparison, the Fe–C distance in TPPFe^{III}C$_6$H$_5$ is 1.955 (3) Å,[19] and the compilation of Kruger et al. gives the range of Fe–C(sp^2) distances as 1.87 to 2.000 Å.[18] The angular arrangement of substituents about the two internal sp^2 carbon atoms of the vinyl group are consistent with a normal olefinic unit. The angles are close to the ideal 120°. The major deviation involves the N–C–Fe angle, which is considerably compressed. That compression results from the constraints imposed by the porphyrin macrocycle. To open that angle would require elongation of the N···Fe distance and opening of the central core of the porphyrin. Because of the cyclic nature of the porphyrin, that opening cannot occur. The iron atom resides within the plane of the vinyl group. The out-of-plane deviation from the least-squares plane defined by the C$_4$NFe unit is only 0.02. Consequently, the iron atom lies in the nodal plane of the π bond of the vinyl group. Thus, the iron–carbon bond is a σ bond, not the π bond proposed by CW.

Discussion

Comparison of Properties of the Carbene Complex A and the *N*-Vinyl Complex C. Complexes A and C are distinctly different substances. Their electronic absorption spectra are shown in Figure 1. The ^{1}H NMR spectrum of an impure sample of A is shown in Figure 6 of ref 11. Similar spectroscopic properties have been reported by Mansuy and co-workers in their original description of this compound,[1] and we have also obtained similar spectra.[20] These spectra indicate the A is a diamagnetic complex with full fourfold symmetry. The spectra are wholly in accord with the structure 2. The ^{1}H NMR spectrum of C is reproduced in Figure 3 of ref 10. The spectrum is that of a paramagnetic complex and is distinctly different from that of A. The spectrum shows that the symmetry of the porphyrin has been lowered to C_s. As a consequence there are four pyrrole resonances, and the pattern of these, as well as all other resonances, is consistent with observations made on the corresponding *N*-methylporphyriniron(II) chloride complex.[10] The ^{1}H NMR spectrum of C is in accord with the solid-state structure. Although the solid-state structure has no crystallographic symmetry, normal molecular motion involving free rotation about single bonds is enough to introduce an effective mirror plane which would contain the atoms N(1), Fe, Cl(1), N(3), C(45), and C(46). Rotation about the C(46)–C(53) and C(46)–C(47) single bonds is also required in order to account for the presence of only four *p*-chlorophenyl resonances into the ^{1}H NMR spectrum of **5**.

Comments on the Structural Proposals of CW. The structural work described here establishes that there is no interaction between the vinyl group of **5** with the iron center in the solid state, and there is no spectroscopic information to suggest that that situation is altered in solution. All of the properties of **5**, its paramagnetism, electronic spectrum, solid-solid structure, and ^{1}H NMR spectrum, are typical of N-substituted prophyrin complexes of iron(II) in general.[10,14] Moreover, **5** is not the iron carbene complex A for which structure 2 accounts for all of the available data.

CW propose that B is the iron(III) complex of an *N*-vinylporphyrin. That requires that it be the salt **7**.



7

Compounds of this type have been prepared with *N*-methylporphyrins.[21,22] The ^{1}H NMR spectra of these are clearly different from the ^{1}H NMR spectrum of B which is shown in Figure 2 of ref 7. For example, the pattern of pyrrole resonances is reversed. [*N*-MethylTPPFe(III)Cl]$^+$, which would be a model for **7**, has three pyrrole resonances shifted far downfield (at +28, 92, and 79 ppm) and one upfield at 2.4 ppm (at −60 °C)[22] while B has three pyrrole resonances shifted upfield (at −38, −43, and −60 ppm) and one downfield at 17 ppm (at −60 °C).[7]

The X-ray structural data on B are also inconsistent with the proposed structure **7** for C of CW. No anion is present. Moreover, the iron-vinyl relationship found for **5** would be expected to be maintained in **7**. However, inspection of Figure 5 shows that the relationship of these units in **3** and **5** is different and, as discussed above, an iron–carbon σ bond is present in **3**. There is no evidence for a hydrogen atom on either of the vinyl carbon atoms and there are other groups bound where CW would have to place this hydrogen atom.

Experimental Section

Preparation of Compound. Samples of A (2),[7] 4,[8] and C (5)[10] were prepared by established routes described previously.

X-ray Data Collection, Solution, and Refinement. Thin, dark green parallelepipeds of FeCl$_3$N$_4$C$_{58}$H$_{37}$, M_r 952.18, crystallize in the monoclinic space group $P2_1/c$ (No. 14) with cell dimensions (at 130 K) of a = 12.133 (8) Å, b = 26.520 (9) Å, c = 15.190 (6) Å, and β = 107.86 (5)°. For Z = 4, D_c = 1.36 g cm^{-3}. Data were collected at 130 K using Mo Kα radiation (λ = 0.71069 Å) on a Syntex P2$_1$ diffractometer to a 2θ max of 45°. A total of 6608 reflections were collected, of which 6091 were unique. Of these,

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1833 with $I > 3\sigma(I)$ were retained for solution and refinement of the structure. The large number of unmeasured reflections stems from the small crystal size of 0.020 × 0.175 × 0.325 mm. The structure was solved by direct methods and refined to a final R value of 0.069. In the final refinement Fe and Cl atoms were assigned anisotropic thermal parameters and hydrogen atoms were included at calculated positions using a riding model and U(H) = 1.2U(bonded C). The largest feature in a final difference map was 0.5, the size of a hydrogen and of no possible chemical significance. H(45) is the largest peak on a difference map computed with it omitted. Tables of anisotropic thermal parameters, hydrogen atom coordinates, and complete tables of bond distances and angles are available as supplementary material.

Acknowledgment. We thank the National Institutes of Health (GM 26226) for support, Professor C. Castro for a preprint of ref 11, and Professor R. Weiss for informing us of his results.

Registry No. 5, 83219-58-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, H atom positional parameters and isotropic thermal parameters, bond lengths and bond angles (5 pages). Ordering information is given on any current masthead page.

Selective Thermolysis Reactions of Bromo-1-nitro-1*H*-pyrazoles. Formation of 3-Nitro-1*H*- vs. 4-Nitro-1*H*-pyrazoles[1]

J. P. H. Juffermans[†] and Clarisse L. Habraken*

Department of Organic Chemistry, Gorlaeus Laboratories, University Leiden, 2300 RA Leiden, The Netherlands

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Refluxing 3,4,5,-tribromo-1-nitro-1*H*-pyrazole (**1a**) in benzene results in the evolution of bromine and NO_2 and gives the 4-nitro-1*H*-pyrazole **2** and the 1-phenyl-1*H*-pyrazoles **4** and **5**, while heating **1a** in toluene gives **2** and benzyl bromide. Thermolysis of **1a** in refluxing acetonitrile affords both **2** and the isomeric 5-nitro-1*H*-pyrazole **6a**. Refluxing **1a** mixed with the electron-rich 3,5-dimethyl-1*H*-pyrazole (**7**) in all three solvents gives **6a** and 4-bromo-3,5-dimethyl-1*H*-pyrazole (**8**), whereas refluxing **1a** mixed with anisole in benzene solution gives **2** and bromoanisoles. 3,5-Dibromo-1-nitro-1*H*-pyrazole (**1b**) in refluxing acetonitrile gives mainly 3,4-dibromo-5-nitro-1*H*-pyrazole (**6a**) and 3,5-dibromo-1*H*-pyrazole (**3b**), but refluxing **1b** mixed with **7** affords 3-bromo-5-nitro-1*H*-pyrazole (**6b**). Possible mechanisms are discussed involving intramolecular rearrangements to intermediates 3-bromo-3-nitro-3*H*-pyrazoles **9a,b** and 4-bromo-4-nitro-4*H*-pyrazole **10** responsible both for the loss of bromine and NO_2 as well as for the electrophilic bromination of **7** and anisole.

Thermal intramolecular rearrangements involving a migration of a nitro group from a nitrogen to a carbon atom in the five-membered ring is a characteristic property of 1-nitro-1*H*-azoles.[2-6]

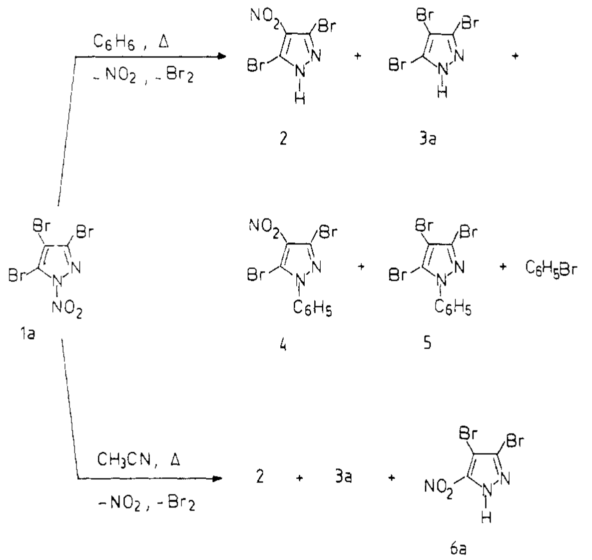
Recently[4] we reported on the thermolysis of 3-bromo-1-nitro-1*H*-indazoles. Thermolysis in refluxing benzene results in the evolution of bromine and NO_2 affording 3-bromo-1-phenyl-1*H*- and 3-nitro-1-phenyl-1*H*-indazoles in addition to 3-bromo- and 3-nitro-1*H*-indazoles. Only the latter two compounds are formed besides benzyl bromide on refluxing in toluene solution. These products, we argued, strongly suggest a radical process. Because simple N–N bond cleavage does not explain the formation of the 3-nitro-1*H*-indazoles we supposed an initial intramolecular rearrangement to a 3-bromo-3-nitro-3*H*-indazole followed by a homolytic cleavage to give either NO_2 or a bromine atom and the corresponding indazolyl radicals. In benzene subsequent homolytic substitution of a benzene molecule then affords the 1-phenyl-1*H*-indazoles.

Here we report the results of our studies of the thermolysis of 3,4,5-tribromo-1-nitro-1*H*-pyrazole (**1a**) and 3,5-dibromo-1-nitro-1*H*-pyrazole (**1b**).

Results and Discussion

Thermolysis of **1a** in refluxing benzene solution is accompanied by evolution of NO_2 and bromine, and after 3 h no **1a** is found to be present. The products obtained from the thermolysis mixture are 3,5-dibromo-4-nitro-1*H*-pyrazole (**2**), 3,4,5-tribromo-1*H*-pyrazole (**3a**), the 1-phenyl-1*H*-pyrazoles **4** and **5**, and a substantial amount of bromobenzene (see Scheme I). Refluxing **1a** in toluene for 1 h gives benzyl bromide in addition to **2** and **3a** and

Scheme I



[†] Current address: Centraal Laboratorium, Sikkens B.V., Rijksstraatweg 31, 2171 AJ Sassenheim, The Netherlands.

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