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Electronic Structure of Low-Spin Ferric Chlorins: Characterization of Bis(dimethylphenylphosphine)(*meso*-tetraphenylchlorinato)iron(III) Triflate

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Introduction

There is currently a large interest in determining what factors affect the electronic structure of low-spin hemoproteins. Thus an attractive attempt regarding the structure−function relationship is to substitute oxygen by various exogen ligands.[1] Several small nonphysiological ligands have been examined by various spectroscopic methods in hope of gaining information about structural and reactivity perturbations of the heme environment. Examples using iron porphyrin models include mainly carbon monoxide, cyanide, isocyanides, and to a less extent phosphines.[2] So far, experimental investigations have mostly focused on the electronic structure of low-spin iron(III) porphyrins.[3] Studies of the electronic structures with simple iron chlorins which might serve as models for naturally occurring iron chlorin proteins have been more limited.[4−13] This is related to the synthetic difficulty of preparing pure compounds due to the oxygen sensitivity of reduced macrocycle.

Nature utilizes iron chlorins such as heme d, found in a terminal oxidase complex,[14] or a catalase, hydroxyperoxidase II,[15] all from *Escherichia coli*, to perform diverse biological reactions. A chlorin is a hydroporphyrin with one reduced pyrrole double bond. There is currently limited data available of the physical properties of iron chlorins to explain their biological properties. In contrast, much more information is available with iron porphyrins. Thus it has been accepted that most of the low-spin iron(III) have a $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ ground state. However, we reported that when two molecules of *tert*-butylisocyanide are bound to ferric tetraphenylporphyrin, the ^{1}H NMR spectrum is indicative of a low spin complex which shows the chemical shifts of the pyrrole protons in the diamagnetic area.[16,17] The hyperfine shifts were separated into their dipolar and contact contributions. The separated components reflect the very low magnetic anisotropy of the iron, and the unusual orientation of the unpaired spin density when the nitrogen axial ligands are exchanged for isocyanide ligands leads to complete reverse localization. Subsequently, it was recognized that the unusual ^{1}H NMR behavior results from the formation of an unusual $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ ground state.[18,19] It should be underlined that a similar $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ situation was also reported with low-basicity cyanopyridine complexation to ferriporphyrins. The change in ground state of low-spin iron(III) from $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ to $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ electron configuration occurs progressively through the series of pyridine complexes of both Fe(III)TPP and Fe(III)TMP complexes, the low-basicity pyridines stabilizing the unusual $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ state.[3,20] The axial EPR spectra, with $g_\perp > g_{||}$ are also indicative of a $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ state. With the TPP compound, the X-ray structure shows that the two axial ligands have relative perpendicular orientations along with an extensively S_4-ruffled porphyrin core which is related to electronic factors rather than steric factors. This electronic contribution may be due to the partial delocalization of the $(d_{xy})^1$ unpaired electron into the $3a_{2u}(\pi)$ orbital of the porphyrin ring, which is made possible by the twisting of the nitrogen p_z orbitals of the nitrogen out of the plane of the porphyrin ring, as suggested recently.[3,20] The Mössbauer spectrum shows also an unusually small positive to large negative quadrupole splitting in the ferric tetraphenylporphyrinato complexes.[3]

To find out the general conditions for the formation of low-spin ferric chlorin complexes with the $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ or $(d_{xz},d_{yz})^4$ $(d_{xy})^1$ ground state, we have decided to examine a large series of low-spin iron(III) chlorin complexes bearing various different axial ligands by means of ^{1}H NMR and EPR spectrocopies and X-ray crystallography. We previously observed an unusual electronic structure for [(TPC)Fe(*t*-BuNC)$_2$]CF$_3$SO$_3$ by ^{1}H NMR.[21] We have now further extended our studies to the preparation and complete spectral characterization (NMR and EPR) of [(TPC)Fe(PPh(Me)$_2$)$_2$]CF$_3$SO$_3$. Its X-ray

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structure has also been determined which is one of few stucture determinations of a low-spin ferric chlorin complex.(13) A comparison with [(TPP)Fe (PPh(Me)$_2$)$_2$]ClO$_4$ shows a small distortion of the chlorin ring in the former complex.[22]

Experimental Section

General Information. As a precaution against the formation of the μ-oxo dimer [Fe(TPC)]$_2$O,[7,23] all reactions were carried out in dried solvents in Schlenk tubes under an Ar atmosphere. Solvents were distilled from appropriate drying agents and stored under argon. ^{1}H NMR spectra were recorded on a Bruker AC 300P spectrometer in CD$_2$Cl$_2$ or CDCl$_3$ at 300 MHz. Tetramethylsilane was used as the internal reference. The temperatures are given within 1 K. EPR spectra were recorded in CH$_2$Cl$_2$ on a Bruker EMX 8/2,7 spectrometer operating at X-band frequencies. Samples were cooled to 4.2 K in a stream of helium gas in frozen CH$_2$Cl$_2$, the temperature of which was controlled by an Oxford Instruments ESR 900 cryostat. Visible spectra were measured on a Uvikon 941 spectrometer in CH$_2$Cl$_2$.

Reagents. The following iron chlorins were prepared by literature methods: (TPC)FeCl[24] and (TPC)FeCF$_3$SO$_3$.[21] P(Me)$_2$Ph is commercially available.

Synthesis. (TPC)Fe[P(Me)$_2$Ph]$_2$ 1. A solution of (TPC)FeCl (0.1 g, 0.14 mmol) in dichloromethane was reduced under argon by Zn−Hg amalgam. The solution was then filtered and 8 equiv of dimethylphenylphosphine added by a syringe to in situ (TPC)Fe species. Hexane addition (30 cm^3) was added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration. Yield: 0.094 g (70%). UV−vis (toluene): λ_{max}/nm 370 (ϵ 13.7 dm^3 mmol^{-1} cm^{-1}), 444 (ϵ 62.4) 569 (ϵ 7.9), 609 (ϵ 17.1), 654 (ϵ 4.3). ^{1}H NMR (δ, CDCl$_3$, ppm, 273 K): 8.2 (2H, H$_{pyrr}$), 7.8 (4H, H$_o$), 7.6 (m, 20 H, H$_{pyrr,}$ H$_{o,m,p}$), 4.35 (4H, pyrrolidine). Ligand: 6.9 (H$_p$), 6.7 (H$_m$), 4.9 (H$_o$) and −2.35 (Me). FAB MS (m/z): [M]$^+$ 946.3, [M − P(Me)$_2$Ph]$^+$ 808.3, [M − 2P(Me)$_2$Ph] 670.3.

[(TPC)Fe(PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ 2. To a solution of 0.1 g (0.12 mmol) of (TPC)FeCF$_3$SO$_3$ in 2.5 mL of dichloroethane was added 2.5 equiv (43.5 μL) of P(Me)$_2$Ph by a syringe under stirring at room temperature. After being stirred for 15 mn, the solution became green. Then 5 mL of pentane was added and the solution was set aside overnight for crystallization at 0 °C. Purple crystals of Fe(TPC)[P(Me)$_2$Ph]$_2$CF$_3$SO$_3$ were collected by filtration and washed with hexane. Yield: 0.097 g (73%). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm 371 (ϵ 33.7 dm^3 mmol^{-1} cm^{-1}), 437 (ϵ 65.6), 605 (ϵ 13.5).

Single-Crystal Structure Determination on Fe(TPC)[P(Me)$_2$Ph]$_2$CF$_3$SO$_3$ 2. The X-ray study was carried out on a NONIUS Kappa CCD diffractometer using graphite monochromatized Mo Kα radiation. The cell parameters were obtained with Denzo and Scalepack[25] with 10 frames (Φ rotation: 1° per frame). Crystallographic data are presented in Table 1. Crystals of the compound were obtained as reported above. The data collection ($2\theta_{max} = 60°$, 91 frames via 2.0° ϕ rotation and 60 s per frame, 46 frames via 2.0° ω rotation and 60 s per frame, range hkl: h, 0.18; k, −16.18; l, −20.21, gave 14 211 reflections. The data reduction leads to 13 322 independent reflections from which 8606 reflections satisfied $I > 2.0\sigma(I)$. The structure was solved with SIR-97, which reveals the non-hydrogen atoms of the two conformationally different cations and the two disordered anions.[26] The two resulting complexes are designated **2A** and **2B**. After anisotropic refinement, some peaks were found and assigned to the nonstoichiometric pentane (30%). The whole structure was refined by the full-matrix least-squares techniques[27] (use of F magnitude; x, y, z, $\beta_{i,j}$ for Fe, N, P, and C atoms; x, y, z for triflate anions and riding mode for hydrogen atoms; 1320 variables and 8606 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o)^2 + (0.125P)^2 + 2.06P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.071$, $R_w = 0.187$ and $S_w = 1.029$ (residual $\Delta\rho < 0.76$ eA^{-3}). Atomic scattering factors were from the International Tables for X-ray crystallography.[28] ORTEP views were realized with PLATON98.[29]

Table 1. Crystallographic Data for Fe(TPC)[P(Me)$_2$Ph]$_2$CF$_3$SO$_3$ **2**

	2 (C_5H_{12})		
empirical formula	2($C_{61}H_{52}FeF_3N_4P_2O_3S$)	V, Å^3	2796.2(2)
fw	2263.83	Z	1
crystal system	triclinic	ρ calcd g.cm^{-3}	1.345
space group	$P1$	μ cm^{-1}	4.36
a, Å	14.1570 (4)	T (K)	294
b, Å	14.1860 (6)	R_w	0.187
c, Å	16.1270 (8)	final R	0.071
α, deg	75.202(3)		
β, deg	77.913(2)		
γ, deg	63.979(2)		

Results and Discussion

Preparation of Compounds 1 and 2. The synthesis of the symmetric bis-phosphine species (TPC)Fe(PMe$_2$Ph)$_2$ **1** is a variation of our method, previously reported for the synthesis of (TPP)Fe(PMe$_2$Ph)$_2$,[30] and the reduction of Fe(III) to Fe(II) was carried out with Zn−Hg amalgam. The compound is obtained as a crystalline solid with 70% yield and characterized by ^{1}H NMR (see above).

Two major difficulties may be encountered in preparing phosphine ferric complexes of chlorins. First, oxidation of the chlorin ring to the porphyrin ring may occur, as was previously reported with imidazole ligands.[12] Second, a possible autoreduction of the ferric state may occur. This situation was previously encountered with ferric porphyrins.[22,31]Using triflate, a weak axial ligand, as an intermediate, allowed us to solve this problem. Thus, a similar strategy was used to prepare low-spin ferric tetraphenylchlorins. Starting from (TPC)Fe(CF$_3$SO$_3$) in dichloroethane solution, [(TPC)Fe(PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ **2** was readily obtained from P(Me)$_2$Ph addition in 70% yield. **2** exhibited two Soret bands, one at 437 nm and the second in the near-ultraviolet region (371 nm). It is interesting to note that hyperporphyrin spectra were reported for bis(phosphine) iron(III) porphyrin complexes, the highest wavelength being red-shifted (442 nm).[22] Suitable crystals were obtained by diffusion of hexane in the dichloroethane solution of **2** in a thin tube.

Structure Determination. The crystal structure of **2** is comprised of two independent ion pairs in the asymmetric unit of structure. The iron chlorines differ in the orientation of the phenyl rings of the axial ligands with respect to the porphyrin plane. Compound **2A** has its phosphine ligands with the aromatic

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(21) Starting from Fe(TPC)Cl[24] in tetrahydrofuran solution, Fe(TPC)CF$_3$SO$_3$ **3** was readily obtained from AgCF$_3$SO$_3$ addition in 70% yield. The [Fe(TPC)]CF$_3$SO$_3$ complex exhibited UV−vis spectra with a Soret band at 402 nm ($\epsilon = 66$ dm^3 mmol^{-1} cm^{-1}) and a characteristic chlorin second band at 649 nm ($\epsilon = 9$ dm^3 mmol^{-1} cm^{-1}). ^{1}H NMR δ, CDCl$_3$, ppm, 273 K: 114 (br, 2H, H$_{pyrr}$), 88 (br, 2H, H$_{pyrr}$), 58 (br, 2H, H$_{pyrr}$), 25.5 (br, 4H, pyrrolidine), 12.35 (br, 8H, H$_o$); 11 (br, 4H, H$_m$) and 10.3 (br, 4H, H$_m$); 9.6 (br, 2H, H$_p$); 9.2 (br, 2H, H$_p$). EPR: $g = 5.87$ and 1.99. Simonneaux, G.; Kobeissi, M. *J. Chem. Soc., Dalton Trans.*, in press.

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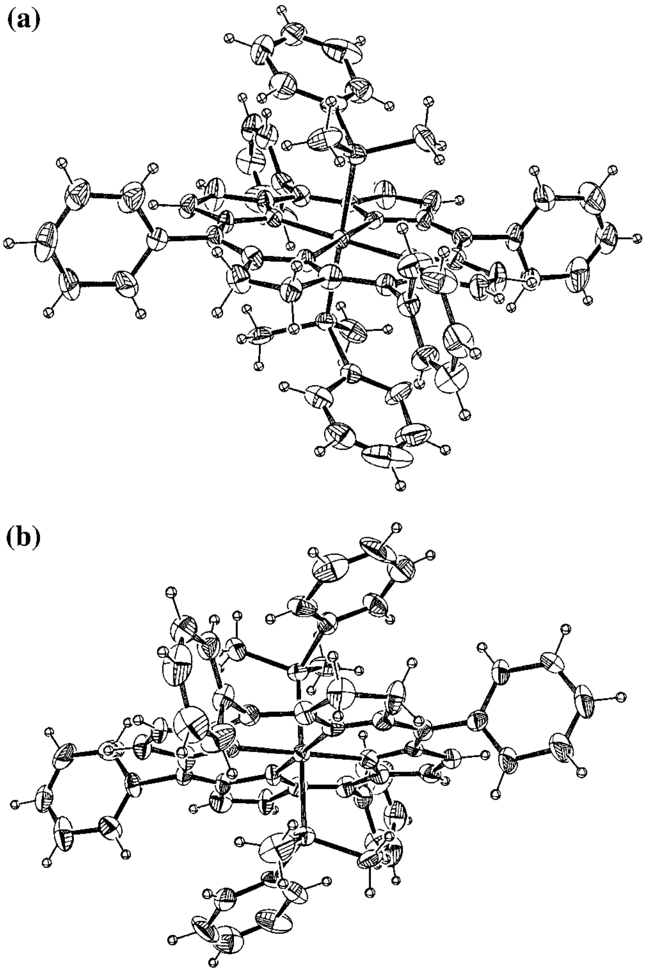

Figure 1. Perspective view for the cations (a) **2A** and (b) **2B** in crystal **2**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Fe(TPC)[P(Me)$_2$Ph]$_2$CF$_3$SO$_3$ **2**

Molecule A				Molecule B			
Fe(1)	P(1)		2.350(3)	Fe(61)	P(61)		2.356(4)
Fe(1)	P(2)		2.348(3)	Fe(61)	P(62)		2.358(4)
Fe(1)	N(1)		2.0009(8)	Fe(61)	N(61)		2.046(9)
Fe(1)	N(2)		1.971(9)	Fe(61)	N(62)		1.974(9)
Fe(1)	N(3)		2.022(10)	Fe(61)	N(63)		2.012(10)
Fe(1)	N(4)		1.992(9)	Fe(61)	N(64)		1.997(9)
C(2)	C(3)		1.446(16)	C(62)	C(63)		1.479(16)
C(7)	C(8)		1.368(19)	C(67)	C(68)		1.327(13)
C(12)	C(13)		1.373(18)	C(72)	C(73)		1.385(13)
C(17)	C(18)		1.362(16)	C(77)	C(78)		1.353(14)
P(1)	Fe(1)	P(2)	179.4(2)	P(61)	Fe(61)	P(62)	179.5(2)
N(1)	Fe(1)	P(1)	89.9(3)	N(61)	Fe(61)	P(61)	90.7(3)
N(2)	Fe(1)	P(1)	91.5(3)	N(62)	Fe(61)	P(61)	89.2(3)
N(3)	Fe(1)	(P1)	89.6(3)	N(63)	Fe(61)	P(61)	87.5(3)
N(4)	Fe(1)	P(1)	89.1(3)	N(64)	Fe(61)	P(61)	91.2(3)

groups parrallel to two trans pyrrole rings; **2B** has its phosphine ligands with the aromatic groups parallel to two phenyls of TPC. Thus the orientation of the ligands with respect to the N(1)−Fe−N(3) axis is not equivalent for the two independent molecules. The angle, defined as the angle between the N−Fe−N axis and the projection of the ligand normal onto the porphyrin plane, is 53.4(2)° for molecule A and 172.8(1)° for molecule B. The structures of **2A** and **2B** are shown in Figure 1. Individual values of bond distances and angles for **2A** and **2B** are given in Table 2.

The metal−nitrogen distance to the reduced pyrrole, N(1), 2.009 (8) Å, is longer than the remaining three nitrogens: N(2), N(3), and N(4) (average Fe−N distance: 1.995(9) Å) in **A**. Similar situation was found in **B**: Fe−N(61) = 2.046(9) Å and average Fe−N distance: 1.994(9) Å. In [(TPP)Fe(P(Me)$_2$Ph)$_2$]-ClO$_4$,[32] the two different Fe−N distances, 1.992(2) Å and 1.988(2) Å, average 1.990(2) Å in agreement with other low-spin iron(III) porphyrin structures (range: 1.970(14)−2.000(6) Å.[33] Thus there is a core-hole expansion of the macrocycle due to the reduced pyrrole. Such a situation has been previously reported for high spin iron(III) quinoxalinotetraphenylporphyrin[13] and iron(III)dioxoisobacterio chlorin,[34] and discussed with molecular mechanics calculations.[35,36]

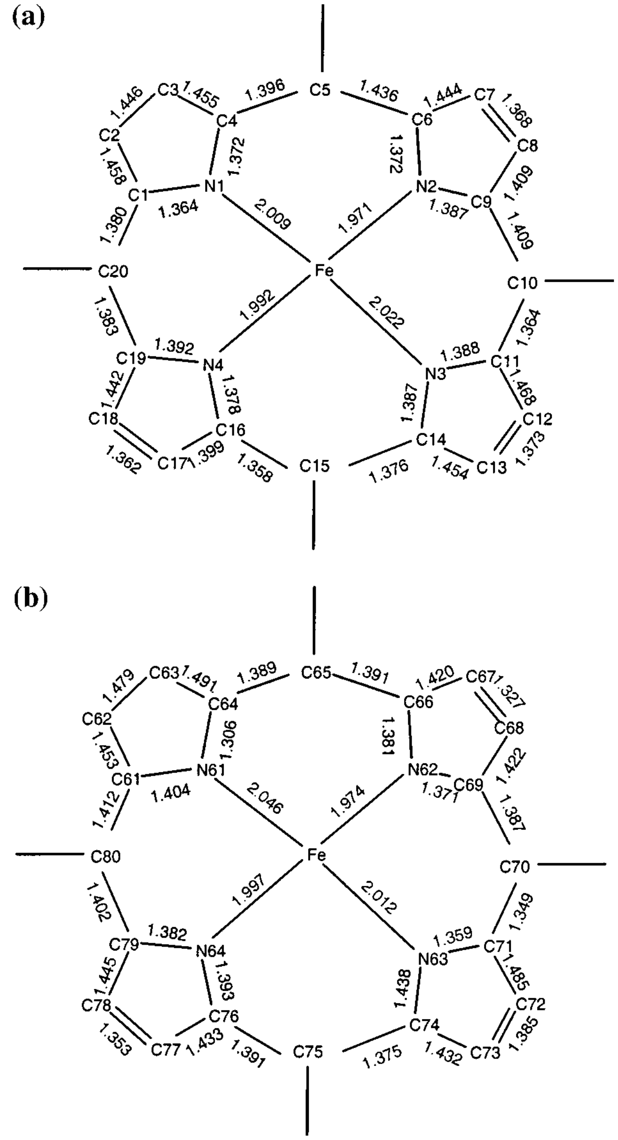

Figure 2. Atom labels and formal diagrams of the chlorinato core showing the distances for the cations (a) **2A** and (b) **2B**.

The C(2)−C(3) (**2A**: 1.446(16) Å, **2B**: 1.479(16) Å) distance in the pyrroline ring is longer than the usual values of the three remaining pyrroles (average value of 1.367(18) Å) and reflects the sp^3 hybridization of the corresponding pyrroline atoms. Such

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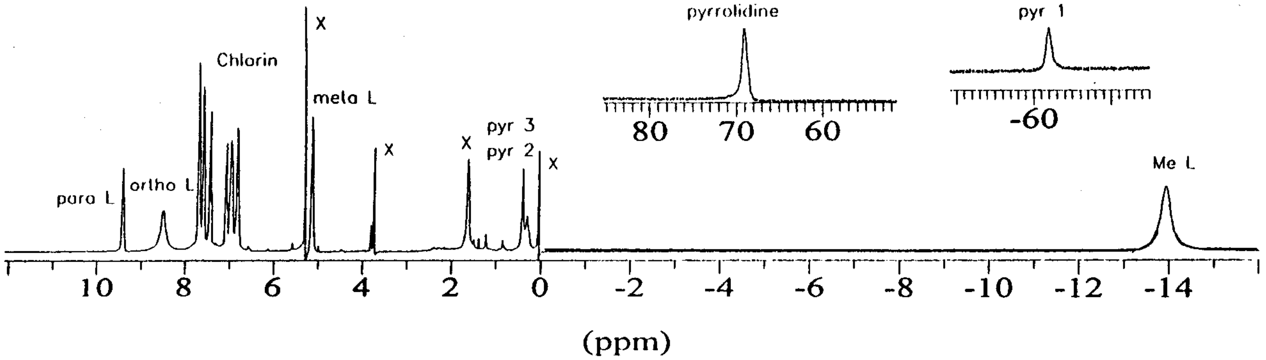

Figure 3. ^{1}H NMR spectrum of [(TPC)Fe (PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ **2** recorded at 283 K in CD$_2$Cl$_2$.

Table 3. Observed and Isotropic Shifts of [Fe(TPC)(PMe$_2$Ph)$_2$]CF$_3$SO$_3$ **2** (δ, CD$_2$Cl$_2$, ppm)

proton chlorin	H*o*	H*o*′	H*m*	H*m*′	H*p*	H*p*′	Hpyrro	Hpyr	Hpyr	Hpyr
$(\Delta H/H)^a$	6.85	6.98	7.62	7.71	7.10	7.44	64.6	0.66	0.66	−57.86
$(\Delta H/H)^b$	7.6	7.8	7.6	7.6	7.6	7.6	4.35	7.6	7.6	8.2
$(\Delta H/H)_{iso}{}^c$	−0.75	−0.82	0.02	0.11	−0.5	−0.16	60.25	−7.14	−7.14	−65.66

proton ligand	H*o*	H*m*	H*p*	Me
$(\Delta H/H)^a$	8.3	5.28	9.32	−13.2
$(\Delta H/H)^b$	4.9	6.7	6.9	−2.35
$(\Delta H/H)_{iso}{}^c$	3.4	−1.42	2.42	−10.85

[a] Chemical shift of [(TPC)Fe(PMe$_2$Ph)$_2$]CF$_3$SO$_3$ at 298 K with TMS as internal reference. Abbreviations used: H*o* and H*o*′ = *ortho*-protons; H*m* and H*m*′ = *meta*-protons; H*p* and H*p*′ = *para*-protons. [b] Chemical shift of (TPC)Fe(PMe$_2$Ph)$_2$ at 298 K with TMS as internal reference. [c] Isotropic shift of **2** with diamagnetic complex (TPC)Fe(PMe$_2$Ph)$_2$ as reference. We used a medium value of 7.8 ppm for the chemical shifts of the diamagnetic pyrroles since the relative assignment was not possible at this stage.

a situation was previously observed with two iron chlorins: the ferrous octaethylchlorin (OEC)Fe (C−C distance: 1.508(7) Å)[5] and with the μ-oxo complex [(TPC)Fe]$_2$O (C−C distance: 1.419(9) Å).[7]

The pyrrole and pyrroline rings are only slighly displaced above and below the mean plane of the chlorin (maximum displacement: 0.12(2) Å for **2A** and 0.15(2) Å for **2B**). Thus the conformation of the chlorin macrocycle can be described as weakly distorted. Figure 2 gives out of plane distances for the atoms in the chlorin core from the mean chlorin plane.

The axial Fe−P distances are very similar to those in the iron(III) complex of tetraphenylporphyrin containing the same axial ligand (2.350(1) Å).[32] but are longer than in the iron(II) complex of TPP containing the same ligand (2.284(1) Å).[30]

^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of [(TPC)-Fe(PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ **2** at 297 K is shown in Figure 3. The peaks for the phenyl protons of the porphyrin ring are assigned completely by 2D COSY spectra (Supporting Information). For the phosphine ligands and the pyrroles, the relative intensities and 2D COSY determine the assignment. The shifts of the phosphine ligands are independent of the presence of excess ligand, and hence axial ligand dissociation does not appear to be significant at ambient temperature. Magnetic measurements using the method of Evans[37,38] were made for 0.03 M CD$_2$Cl$_2$ solutions of **2** at 297 K, employing Me$_4$Si as the reference. The solution magnetic moment $m = 1.87\mu_B$) is compatible with a low-spin state, $S = {}^1/_2$.

The spectrum of [(TPC)Fe (PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ **2** shows the pyrrole proton signals at 0.66 (4H) and −57.8 (2H) ppm (293 K). This is quite different from the pyrrole proton signals of another low-spin Fe(III) chlorinates at ambient temperature [Fe-(QTPP)(Im)]$^+$ (−12.2, −15.6 and −21.7 ppm, 293 K)[13] but close to the pyrrole proton signals of [(TMC)Fe(Im)$_2$]Cl (−2.4, −12.3, and −47.1 ppm, 203 K).[12] The hyperfine shifts, obtained by referencing the observed shift to that of the corresponding diamagnetic complex (TPC)Fe(PPh(Me)$_2$)$_2$ are summarized in Table 3. The hyperfine shifts for symmetrical low-spin ferric porphyrins are known to consist of large contact shifts and smaller upfield dipolar shifts due to the magnetic anisotropy. In chlorin, the symmetry is lost but La Mar and co-workers have suggested that such a situation is also highly probable with low-spin ferric chlorins.[10] Thus they have noted that the HOMO in ferric chlorins (a$_{1u}$) is symmetry and energitically situated for interactions with the iron dπ orbitals.[39]

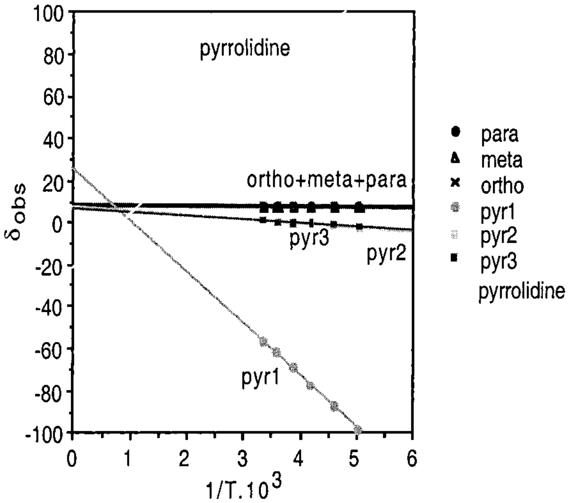

Figure 4. Curie plot of the chemical shifts vs reciprocal temperature of [(TPC)Fe (PPh(Me)$_2$)$_2$]CF$_3$SO$_3$ **2** in CD$_2$Cl$_2$.

For the saturated pyrroline ring, the protons are expected to exhibit low-field π contact shifts.[10] The observed large low-

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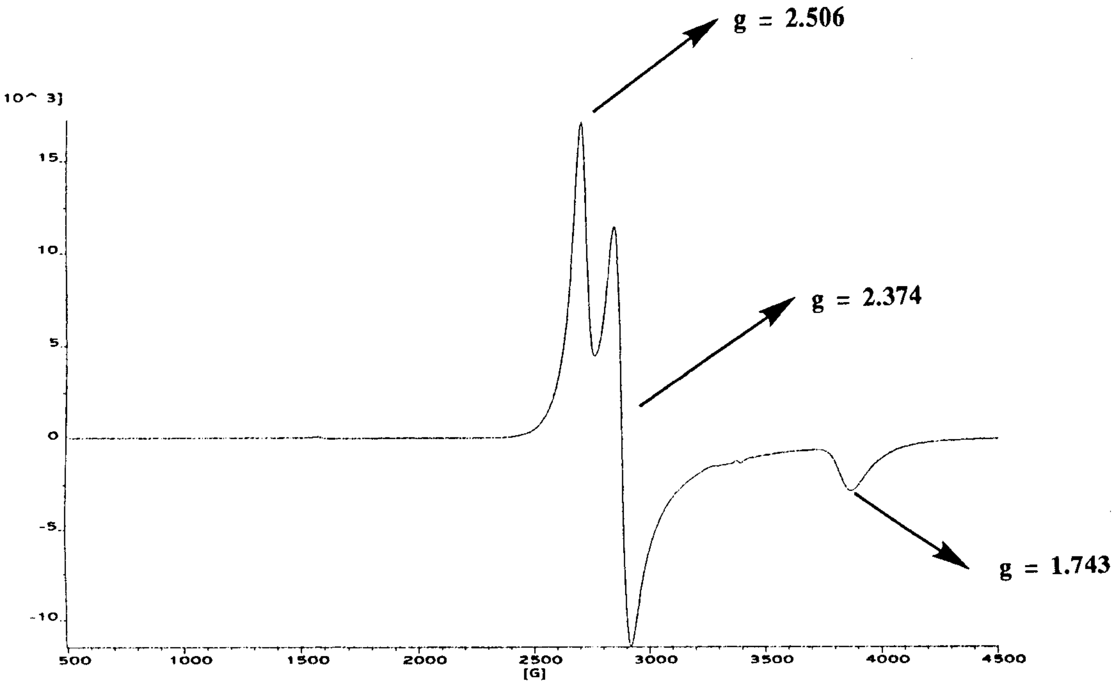

Figure 5. EPR spectrum of $[(TPC)Fe(PPh(Me)_2)_2]CF_3SO_3$ **2** in a CH_2Cl_2 glass, recorded at 4 K.

field shift ($\delta = 69$ ppm) agrees with an important π metal bonding involving a molecular orbital of the chlorin derived from the a_{1u} of a porphyrin. Nevertheless, this contact shift is much higher than those of the corresponding $[(TMC)Fe(Im)_2]$-Cl ($\delta = 38.3$ ppm)[12] and pyropheophorbide a methylester iron(III) ($\delta = 24$ and 28 ppm).[10] Since the contact shift has been shown to arise predominantly from spin delocalization into the bonding dxz and dyz orbitals,[10] this result agrees with a $(dxy)^2$-$(dxz,dyz)^3$ electronic structure in this aryl phosphine derivatives (see below).

The isotropic shift obtained for the phosphine methyl groups of PMe_2Ph in $[(TPP)Fe[P(Me)_2Ph]_2]ClO_4$ is slightly upfield (-2.5 ppm).[22] A dramatic change is observed for $[TPC)Fe(P(Me)_2Ph)_2]CF_3SO_3$. In comparison with the porphyrin, the signal is at a stronger field ($\delta = -14$ ppm), implying that contact shift dominates. This large upfield methyl proton contact shifts agree with unpaired spin density on the methyl group occurring from occupied π-symmetry d_{xz} and d_{yz} orbitals of the metal. This results also confirms the $(d_{xy})^2$ $(d_{xz}, d_{yz})^3$ ground state, both in porphyrin and chlorin complexes

Analysis of the curve in the Curie plot was made for the $[TPC)Fe(P(Me)_2Ph)_2]CF_3SO_3$ complex. The temperature dependences of the chemical shifts of the protons in CD_2Cl_2 are shown in Figure 4. A magnetically simple molecule is expected to follow Curie-law behavior in that a plot of the chemical shifts vs $1/T$ is linear with an intercept equal to the resonance in the diamagnetic complex. Plots of ortho, meta, and para signals of meso-aryl protons of the chlorin ring are reasonably linear which intercept respectively at 8.03, 7.4, and 7.34 ppm. However these protons show only small temperature dependence, consistent with a weak spin density on the *meso* position. For the pyrrole resonances, the chemical shifts vary linearly with $1/T$, but the extrapoled lines do not pass through the diamagnetic value at $1/T = 0$.

EPR Spectroscopy. It has been recognized that the EPR g values of low-spin ferriporphyrins provide valuable information about the orbital of the unpaired electron.[3,40] EPR properties of $[(TPP)Fe(Imidazole)_2]^+$ and other low-spin complexes formed from tetraphenylchlorin derivatives have been reported.[40-42] The apparent extent of rhombicity is smaller for hydroporphyrin than for porphyrin complexes with the same set of axial ligands but all of the hydroporphyrin complexes evidence rhombic spectra. In contrast, the EPR spectrum of $[(TPP)Fe(P(Me)_3)_2]ClO_4$ is axial in frozen solution with $g = 3.5$ at 4 K.[43] This g_{max} signal is consistent with near degeneracy of the d_{xz} and d_{yz} as expected for low-spin ferric complexes with axial ligands that have effective cylindrical symmetry. It should also be underlined that previous NMR results showed that the ferrous hydroporphyrin complex FeTPC is magnetically different from FeTPP despite their common $S = 1$ ground state: it is rhombic instead of axial.[6]

Compound **2** shows the principal g values $g_1 = 2.506$, $g_2 = 2.374$, and $g_3 = 1.743$. As expected, the reduction of the porphyrin to a chlorin-type ring removes the degeneracy of the d_π orbitals. These values are also quite similar to those of the bis-imidazole complex of iron(III) tetraphenylchlorin which shows the principal g values at $g_1 = 2.49$, $g_2 = 2.39$, and $g_3 = 1.75$.[40,41,44] Since Walker and co-workers in a recent ENDOR and ESEEM study demonstrate that the bis(imidazole) complexes of iron(III) tetraphenylchlorin and tetraphenylporphyrin have the same order of g-values and the same electronic ground state,[44] it seems reasonable to propose also a $(d_{xy})^2$ $(d_{xz}d_{yz})^3$ ground state for $[TPC)Fe(P(Me)_2Ph)_2]CF_3SO_3$, in agreement with the ^1H NMR study.

In conclusion, these spectroscopic observations are indicative of a metal-based electron in the d_π orbitals for $[TPC)Fe(P(Me)_2Ph)_2]CF_3SO_3$ complex at any temperature. Thus the change in ground state of low-spin Fe(III) from the usual $(d_{xy})^2$ $(d_{xz},d_{yz})^3$ to the unusual $(d_{xz},d_{yz})^4$ $(d_{xy})^1$ electron configuration

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which was previously suggested to occur from porphyrin to chlorin macrocycles[41] is not observed with phosphine ligands.

Supporting Information Available: Tables of parameters, positional and thermal parameters for all atoms, anisotropic displacement parameters for non-hydrogen atoms, and bond distances and bond angles; plots of chemical shifts versus 1/*T* and 2D COSY spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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