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Iron Porphyrin–Nitrene Complexes: Preparation from 1,1-Dialkylhydrazines. Electronic Structure from NMR, Mössbauer, and Magnetic Susceptibility Studies and Crystal Structure of the [Tetrakis(*p*-chlorophenyl)porphyrinato][(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron Complex

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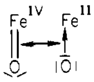
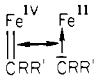
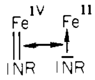
Abstract: Iron(II) porphyrins (porphyrin = P = TPP, TTP and TpClPP) react with 1-amino-2,2,6,6-tetramethylpiperidine, in the presence of either dioxygen or one equivalent of iodosobenzene, to give the corresponding pentacoordinate nitrene complexes $Fe(P)(NNC_9H_{18})$ (P = TPP, **3a**; P = TTP, **3b**; P = TpClPP, **3c**). These complexes, which are also formed by reaction of the iron(II) porphyrins with the free nitrene NNC_9H_{18} at −80 °C in CH_2Cl_2, have been isolated as pure crystalline solids in high yields. The structure of complex **3c** has been fully established by an X-ray structure analysis; it is a pentacoordinate complex with the NNC_9H_{18} nitrene as the axial ligand. Its Fe–N–N sequence is linear, and its Fe–N (1.809 Å) and N–N (1.232 Å) bonds have multiple bond character. It exhibits a marked doming of the porphyrin ring with the iron atom lying 0.54 Å above the mean plane of the porphyrin atoms. Magnetic susceptibility measurements on crystalline complex **3a** (from 100 to 300 K) or on its solution in $CDCl_3$ (307 K) lead to a magnetic moment of $5.1 \pm 0.1\ \mu_B$. ^1H and ^{13}C NMR and Mössbauer studies on complex **3a** are also in favor of a well-defined high-spin ferrous ($S = 2$) state for this complex.

Numerous studies have been concerned in these last few years with the high-valent (porphyrinato)iron–oxo complexes, $Fe^{IV}{=}O$ or $Fe^{V}{=}O$, which are postulated as active intermediates in the catalytic cycle of hydrogen peroxide utilization by peroxidases[1] and of alkane hydroxylation by cytochromes P_{450}.[2] Evidence has been provided for the formation of $Fe^{IV}{=}O$ complexes upon decomposition of (μ-peroxo)iron(III) porphyrin dimers in the presence of imidazoles[3] and for the formation of a π-cation porphyrin $Fe^{IV}{=}O$ complex upon reaction of an iron(III) porphyrin with iodosoarenes.[4] Their carbon and nitrogen analogues are iron–carbene and iron–nitrene complexes, respectively.







Numerous examples of iron–carbene porphyrin complexes have been described,[5] and very recently there has been a growing interest in (porphyrinato)iron–nitrene (or –imido) complexes. First, it has been proposed that the iron–metabolite complexes formed upon metabolic oxidation of 1,1-dialkylhydrazines by hepatic cytochrome P_{450} could involve an iron–nitrene bond.[6] Also, a very recent paper has reported the insertion of a nitrene NSO_2Ar group into a C–H bond of cyclohexane upon reaction of $C_6H_5I{=}NSO_2Ar$ with cyclohexane in the presence of a catalytic amount of an iron or manganese porphyrin.[7]

We have recently reported[8a] preliminary results on the isolation of the nitrene Fe(TPP[9])(NNC_9H_{18}) complex (**3a**) upon aerobic reaction of Fe^{III}(TPP)Cl with 1-amino-2,2,6,6-tetramethylpiperidine (**1**) or anaerobic reaction of Fe^{II}(TPP) with the corresponding nitrene NNC_9H_8 (**2**) at −80 °C. This was not only the first nitrene complex of a metalloporphyrin to be described[8b] but also the first iron complex bearing a nitrene ligand. It is, however, noteworthy that a related analogous structure concerning

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(1) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187.

(2) (a) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315–356. (b) Groves, J. T.; Mc Clusky, G. A.; White, R. E.; Coon, M. J. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 154. (c) Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 68.

(3) (a) Chin, D. H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1448. (b) Chin, D. H.; La Mar, G. N.; Balch, A. L. *Ibid.* **1980**, *102*, 5945–5947. (c) Chin, D. H.; La Mar, G. N.; Balch, A. L. *Ibid.* **1980**, *102*, 4344–4349. (d) La Mar, G. N.; De Ropp, J. S.; Latos-Grazynski, L.; Balch, A. L.; Johnson, R. B.; Smith, K. M.; Parish, D. W.; Cheng, R. J. *Ibid.* **1983**, *105*, 782–787.

(4) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886.

(5) (a) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681–690. (b) Mansuy, D.; Lange, M.; Chottard, J.-C.; Guêrin, P.; Morlière, P.; Brault, D.; Rougée, M.; *J. Chem. Soc., Chem. Commun.* **1977**, 648–649. (c) Mansuy, D.; Lange, M.; Chottard, J.-C.; Bartoli, J.-F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781–782. (d) Mansuy, D.; Lange, M.; Chottard, J.-C. *J. Am. Chem. Soc.* **1978**, *100*, 3213–3214. (e) Mansuy, D.; Guêrin, P.; Chottard, J.-C. *J. Organomet. Chem.* **1979**, *171*, 195–201. (f) Guêrin, P.; Battioni, J.-P.; Chottard, J.-C.; Mansuy, D. *Ibid.* **1981**, *218*, 201–209. (g) Battioni, J.-P.; Chottard, J.-C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056–2062.

(6) (a) Hines, R. N.; Prough, R. A. *J. Pharmacol. Exp. Ther.* **1980**, *214*, 80–86. (b) Prough, R. A.; Freeman, P. C.; Hines, R. N. *J. Biol. Chem.* **1981**, *256*, 4178–4184.

(7) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400–1401.

(8) (a) Mansuy, D.; Battioni, P.; Mahy, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 4487–4489. (b) During the preparation of this paper, the formation of a nitrene–manganese porphyrin complex has been reported: Groves, J. T.; Takahashi, T. *Ibid.* **1983**, *105*, 2073–2074.

(9) TPP, TTP, and TpClPP are the dianions of *meso*-tetraphenylporphyrin, *meso*-tetra-*p*-tolylporphyrin and *meso*-tetra-*p*-chlorophenylporphyrin, respectively.

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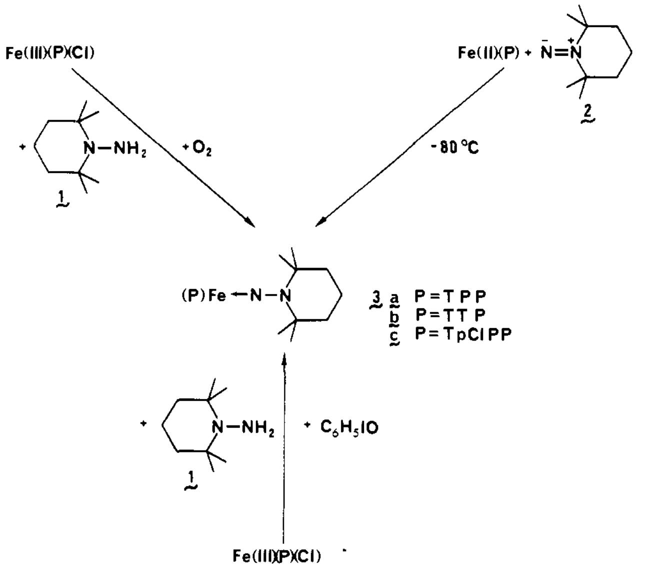
Table I. Compared IR, UV-Vis, and ^1H NMR Spectroscopic Data of Complexes 3a-c

complex	IR (KBr) νFe-N, cm^{-1}	IR (KBr) νN-N, cm^{-1}	UV-vis (CH_2Cl_2) λ, nm (ϵ, mM^{-1}) Soret	α	β	^1H NMR[a] in $CDCl_3$ at 34 °C ($\delta(Me_4Si)$) H_2	CH_3[b]	H_1	H_{pyr}	$H_{o,o'}$	$H_{m,m'}$	H_p	CH_3[c]
3a	1150	1520	436 (186.5)	556 (9.4)	596 (4.6)	81.5	23.5	-15.63	66.8	9.49, 7.89	9.61, 8.81	7.53	
3b	1152	1522	435 (186.7)	556 (10.2)	598 (5.9)	82.4	23.8	-15.00	67.3	9.32, 7.76	9.77, 8.80		4.00
3c	1149	1519	435 (176.3)	557 (10.8)	597 (5.4)	81.4	23.8	-15.15	66.8	9.65, 7.89	9.97, 9.17		

[a] For proton designations see Figure 6. [b] Of the nitrene ligand. [c] Of the porphyrin ring.

Scheme I



a (μ-nitrido)iron porphyrin dimer has been reported.[10]

The present paper describes (i) several preparations of (porphyrinato)[(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron complexes, (ii) the X-ray structure determination of one of them, $Fe(TpClPP)(NNC_9H_{18})$, establishing that it is a pentacoordinate complex with a linear Fe–N–N binding mode for its axial ligand, and (iii) an analysis of the electronic and magnetic properties of these complexes by using magnetic susceptibility measurements as well as Mössbauer and ^1H and ^{13}C NMR spectroscopy, which show an iron(II) high-spin ($S = 2$) structure for these complexes either in solution or in the crystalline state.

Results

Preparation of (Porphyrinato)[(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron Complexes (3a–c). The reaction of chloro(*meso*-tetraphenylporphyrinato)iron(III), Fe(TPP)Cl, 10^{-2} M in aerobic CH_2Cl_2, with 10^{-1} M 1-amino-2,2,6,6-tetramethylpiperidine (**1**)[11] leads, after removal of excess O_2 from the solution by argon bubbling and crystallization upon addition of CH_3OH to the solution, to the formation of the nitrene complex **3a**, $Fe(TPP)(NNC_9H_{18})$ (NC_9H_{18} = 2,2,6,6-tetramethylpiperidyl).[8] Complex **3a** is obtained as purple crystals with a 90% yield.

Complex **3a** can also be prepared by direct interaction of $Fe^{II}(TPP)$ with (2,2,6,6-tetramethyl-1-piperidyl)nitrene (**2**) in anaerobic conditions (Scheme I). This nitrene is stable for hours in anhydrous Et_2O at -80 °C.[12] The reaction of $Fe^{II}(TPP)$, 10^{-2} M in CH_2Cl_2, with a 10-fold excess of nitrene **2** at -80 °C leads quantitatively to complex **3a**.

A third method for the preparation of complex **3a** uses the oxidizing properties of the intermediate active species formed upon reaction of iodosobenzene and Fe(TPP)Cl.[4] Actually, anaerobic oxidation of the hydrazine **1** by Fe(TPP)Cl in the presence of 1 equiv of iodosobenzene at 20 °C gives complex **3a** with a 60% yield after crystallization.

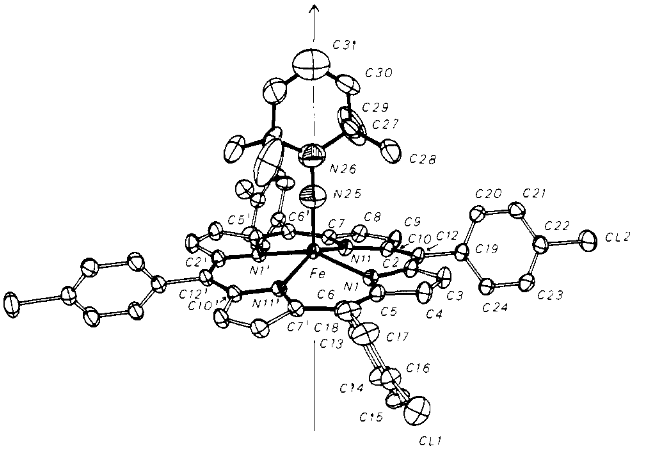


Figure 1. ORTEP plot of complex **3c** with the labeling scheme used. Thermal ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted for clarity.

These three methods have been used for the preparation of the other $Fe(P)(NNC_9H_{18})$ complexes **3b** and **3c** (P = TTP and TpClPP,[9] respectively) (Scheme I).

Characteristics of Complexes 3 in Mass Spectrometry and IR and UV–Vis Spectroscopy. Mass Spectrometry. Upon direct introduction of the complexes at 80 °C (70 eV), one observes the peaks corresponding to the nitrene ligand **2**, $M^+ = 154$ and its fragments, with main peaks at m/e 141 and 126. At 220 °C, the peaks corresponding to iron porphyrin also appear. Neither a lower energy source (30 eV) nor other techniques such as field desorption and chemical ionization (NH_3) allowed us to obtain the molecular peaks corresponding to $Fe(P)(NNC_9H_{18})$. Actually, complexes **3** like other iron porphyrin complexes containing nitrogen-bound ligands such as Fe(TPP)(RNO),[13] are very rapidly decomposed under these conditions.

IR Spectroscopy. The IR spectrum (KBr) of complex **3a** is very similar to those of $Fe(TPP)(Py)_2$, Fe(TPP), and Fe(TPP)Cl except that it exhibits two major additional bands, an intense band at 1150 cm^{-1} and a weaker band at 1520 cm^{-1}, that are lacking in the IR spectrum of the hydrazine (**1**). The former band is located in a region where one could expect a ν Fe–N band. The metal–nitrene complexes described so far[14,15] show ν M–N bands between 1100 and 1300 cm^{-1} and an oxygen analogue of complex **3a**, the $Cr^V(TPP)(O)$ complex, exhibits a ν Cr–O band at 1026 cm^{-1}.[16] The weaker band at 1520 cm^{-1} can be assigned to a N–N stretching vibration, and it is noteworthy that a 1595-cm^{-1} band has been assigned to the N–N stretching vibration of the free nitrene **2**.[17] Coordination of this nitrene to Fe(TPP) would thus lead to a 75-cm^{-1} lowering of the ν N–N frequency. As shown

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(10) (a) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747–1752. (b) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *Ibid.* **1976**, *98*, 6623–6628.

(11) Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228–3235.

(12) Dervan, P. B.; Squillacote, M. E.; Lahti, P. M.; Sylwester, A. P.; Roberts, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 1120–1122.

(13) Mansuy, D.; Battioni, P.; Chottard, J.-C.; Lange, M. *J. Am. Chem. Soc.* **1977**, *99*, 6441–6443.

(14) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(15) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413–486.

(16) Groves, J. T.; Kruper, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 7613–7615.

(17) Hinsberg, W. D.; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608–1610.

Table II. Selected Bond Lengths (Å) and Angles (deg) with Their Estimated Standard Deviations in Parentheses

Fe-N1	2.095 (3)	2.096 (3)
Fe-N11	2.097 (3)	
Fe-N25	1.809 (4)	
N1-C2	1.369 (4)	1.373 (2)
N1-C5	1.375 (4)	
N11-C7	1.372 (4)	
N11-C10	1.378 (4)	
C5-C6	1.405 (5)	1.400 (3)
C2-C12	1.396 (5)	
C12-C10	1.401 (5)	
C2-C3	1.434 (5)	1.431 (3)
C4-C5	1.425 (5)	
C7-C8	1.431 (5)	
C9-C10	1.436 (5)	
C3-C4	1.333 (5)	1.341 (3)
C8-C9	1.349 (5)	
C6-C13	1.489 (5)	1.491 (3)
C12-C19	1.493 (5)	
C11-C16	1.743 (4)	1.740 (3)
C12-C22	1.738 (4)	
N25-N26	1.232 (5)	
N26-C27	1.513 (5)	
C27-C28	1.475 (8)	
C27-C29	1.463 (12)	
C27-C30	1.490 (11)	

mean C···C distance for phenyl rings: 1.374 (3)

N1-Fe-N11	86.6 (1)	
N1-Fe-N11′	86.9 (1)	
N1-Fe-N25	103.0 (1)	103.6 (6)
N11-Fe-N25	104.3 (1)	
C2-N1-C5	106.4 (3)	106.4 (2)
C7-N11-C10	106.3 (3)	
N1-C2-C3	108.9 (3)	109.3 (2)
N1-C5-C4	109.3 (3)	
N11-C7-C8	109.7 (3)	
N11-C10-C9	109.4 (3)	
N1-C5-C6	125.3 (3)	125.3 (2)
N1-C2-C12	125.2 (3)	
N11-C10-C12	125.4 (3)	
C2-C3-C4	107.7 (3)	107.4 (2)
C5-C4-C3	107.5 (3)	
C7-C8-C9	107.3 (3)	
C10-C9-C8	107.2 (3)	
C2-C12-C10	125.3 (3)	125.2 (3)
C5-C6-C7′	125.2 (3)	
C2-C12-C19	117.7 (3)	117.3 (2)
C10-C12-C19	116.9 (3)	
C7-C6-C13	117.6 (3)	
C5-C6-C13	117.1 (3)	
N25-N26-C27	119.3 (3)	
N26-C27-C28	108.3 (4)	
N26-C27-C29	105.8 (5)	
N25-N26-C27	119.3 (3)	
C27-N26-C27′	121.4 (5)	
N26-C27-C30	109.6 (6)	
C30-C31-C30′	113 (1)	

mean C-C-C angle for phenyl rings: 119.9 (1)

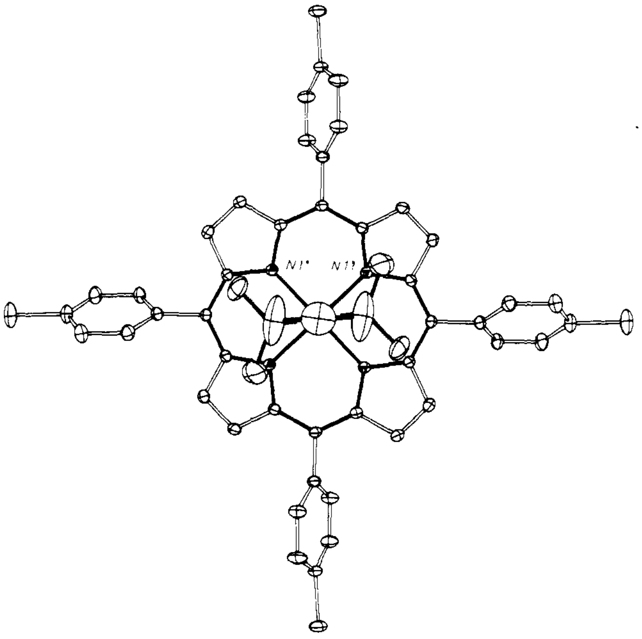

Figure 2. ORTEP plot of complex **3c** viewed along the twofold axis.

in Table I, the position of the 1150- and 1520-cm^{-1} bands are not significantly different in complexes **3b** and **3c**.

UV-Vis Spectroscopy. The unique characteristics of complexes **3** in C_6H_6 are compared in Table I; they all exhibit an unusual red-shifted Soret peak around 440 nm, which has only been previously reported for the Fe(TPP)(2-MeIm) complex[18] (2-MeIm = 2-methylimidazole).

X-ray Structure of Complex 3c. Single crystals of complexes **3a–c** were obtained by slow evaporation of CH_3OH–CH_2Cl_2 solutions at room temperature. Only complex **3c** gave suitable single crystals.

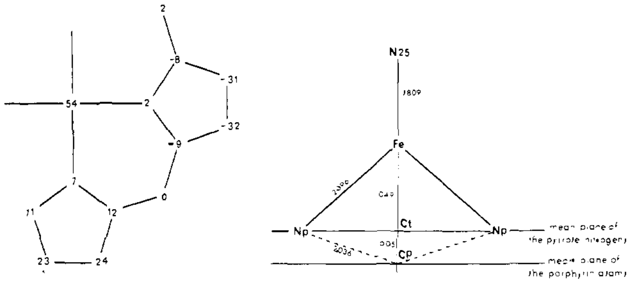

Figure 3. (a) Formal diagram illustrating the perpendicular displacements from the mean plane of the porphyrinato skeleton (in 0.01 Å). (b) Position of the iron atom of complex **3c** above the mean plane of the pyrrole nitrogens and the mean plane of the porphyrin atoms (in Å).

Figure 1 shows the molecule as its exists in the crystal together with the labeling scheme used. The molecule lies on a crystallographic twofold axis, and equivalent atoms by the C_2 axis are labeled with ′. Figure 2 shows the molecule viewed along the twofold axis whereas Figure 3a is a formal diagram illustrating the perpendicular displacements from the mean plane of the core (in 0.01 Å) of the atoms belonging to the crystallographically independent porphyrinato skeleton. Individual bond lengths and angles are given in Table II, and Table III lists the least-squares mean planes of interest.

In complex **3c**, the iron is five-coordinate; it is bound to the four porphyrinato nitrogens and to a nitrogen atom of the axial nitrene ligand. The two independent iron–porphyrinato nitrogen bond distances are equivalent and the average Fe–Np distance is 2.096 Å (Figure 3b). The iron–ligand nitrogen bond length of 1.809 Å is quite short and consistent with a multiple Fe–N bond as in other metal–hydrazido(2–) complexes of known structure.[14] The four pyrrole nitrogens (Np) are approximately coplanar (±0.023 Å) (Table III). The iron atom lies 0.49 Å above this four-Np mean plane (Figure 3b). This displacement is large when compared to those present in the two known five-coordinate

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[18] Rougee, M.; Brault, D. *Biochem. Biophys. Res. Commun.* **1973**, *55*, 1364–1369.

Table III. Least-Squares Mean Planes

	atom	dist,[a] (Å)	equation[b]
PL1	N1°	0.023 (4)	only the y coordinates were used for PL1
	N11°	−0.023 (4)	
	Fe	0.495 (1)	
PL2	N1°	0.070 (3)	
	C2°	0.122 (4)	only the y coordinates were used for PL2
	C3°	0.247 (5)	
	C4°	0.235 (5)	
	C5°	0.108 (4)	
	C6°	−0.009 (4)	
	C7°	−0.098 (4)	
	C8°	−0.321 (5)	
	C9°	−0.312 (5)	
	C10°	−0.084 (4)	
	N11°	0.022 (3)	
	C12°	0.020 (4)	
	Fe	0.542 (1)	
PL3	N1°	−0.012 (3)	
	C2°	0.048 (4)	$-0.0142x - 0.9998y - 0.0172z + 2.4612 = 0$
	C3°	−0.050 (5)	
	C4°	−0.047 (5)	
	C5°	0.048 (4)	
PL4	N11°	−0.006 (3)	
	C10°	0.008 (4)	$0.1411x + 0.9877y - 0.0672z - 2.2837 = 0$
	C9°	−0.003 (5)	
	C8°	0.004 (5)	
	C7°	0.009 (4)	
PL5	C13°	0.019 (4)	
	C14°	−0.005 (5)	$-0.8589x + 0.4112y - 0.3053z + 0.2147 = 0$
	C15°	−0.013 (5)	
	C16°	−0.015 (4)	
	C17°	−0.021 (6)	
	C18°	0.001 (5)	
	Cl1°	0.002 (1)	
PL6	C19°	0.014 (4)	
	C20°	−0.004 (5)	$0.2811x - 0.4828y - 0.8294z + 4.8592 = 0$
	C21°	−0.012 (5)	
	C22°	−0.014 (6)	
	C23°	−0.023 (5)	
	C24°	0.006 (5)	
	Cl2°	0.003 (2)	
PL7	N26°	0	
	C31°	0	$0.2230x + 0y - 0.9748z + 4.0902 = 0$
	C27°	0.600 (6)	
	C30	0.202 (16)	
	C28	1.115 (8)	
	C29	−1.281 (12)	

dihedral angles PL3/PL4 = 171.2

[a] Atoms with the ° sign were used in computing mean plane.
[b] Orthogonalized coordinates were computed according to Blow, D. A. *Acta Crystallogr.* 1980, *13*, 168.

high-spin iron(II) complexes involving a nitrogen-bound axial ligand, Fe(TPP)(2-MeIm) (C_2H_5OH) (0.42 Å)[19] and Fe(TpivPP)(2-MeIm) (C_2H_5OH) (0.399 Å),[20] and is similar to those found for several five-coordinate high-spin thiolate–iron(II) porphyrins.[21,22] The important displacement of the iron atom relative to the four Np mean plane in complex **3c** could be due to the strong multiple Fe–N axial bond[14,15] and to a steric repulsion between the methyl groups of the nitrene and the porphyrin ring. However, no expansion or contraction of the porphyrin core is visible, the mean Np···Cp distance (Figure 3b) of 2.036 Å being in the range found for high-spin five-coordinate iron(II) porphyrin complexes.[23]

Figure 3a shows the displacements of the atoms belonging to the porphyrin core with respect to their mean plane. This mean plane and the mean plane of the four Np are parallel, the latter lying 0.05 Å above the former. Consequently, the iron atom lies 0.54 Å above the porphyrin mean plane. The Ct···Cp distance of 0.05 Å indicates that the stereochemistry of the porphyrin ring has a slightly domed character.[19] However, as shown by Figures 1 and 2, the shape of the ring is not a simple dome but is better described as a flattened saddle. The pyrrole rings, which are individually planar, make dihedral angles of 2.1° and 8.4° with the Np mean plane. This conformation is most probably the result of steric interactions and crystal packing forces.

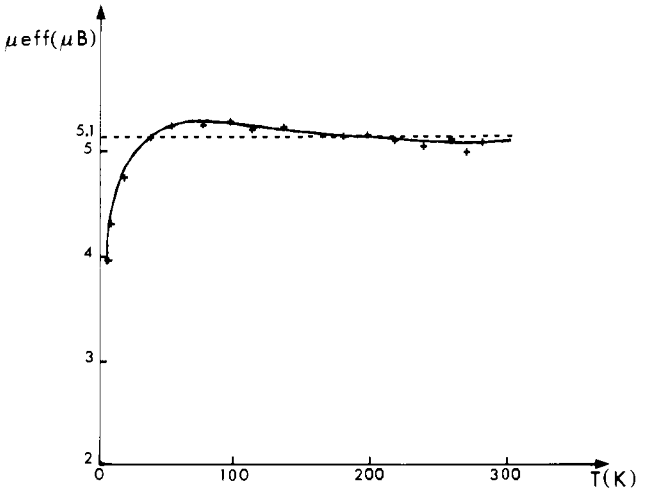

Figure 4. Temperature dependence of the magnetic moment of complex **3a**.

As shown by the data of Table II, the porphyrin bond lengths are normal[24] with mean values of 1.373 (2), 1.400 (3), 1.431 (3), 1.341 (3), and 1.491 (5) Å, respectively for N–C_α, C_α–C_{meso}, C_α–C_β, C_β–C_β, and C_{meso}–C_q (for carbon labeling see Figure 6). The average bond angles are given in Table II. The average of the 12 individually determined C–C bonds in the *p*-chlorophenyl rings is 1.374 Å. The average of the two C–Cl distances is 1.740 Å.

The tetramethylpiperidine ring of the axial ligand does not exactly lie on a staggered position relative to two adjacent Fe–Np bonds (Figure 2), but its mean plane makes an angle of 53° with the direction defined by the two opposite Np, Nl and Nl′. Thus, two methyl groups interact more strongly with two opposite pyrrole rings (Figure 2).

The N_{25}–N_{26} bond distance (1.232 Å) of the axial ligand is indicative of multiple N–N bond character since the N–N bond lengths in the transition-metal hydrazido(2−) complexes already known[14] range from 1.26 to 1.37 Å for bond orders between 1.9 and 1.3.

The piperidine ring has a crystallographic twofold symmetry axis through atoms N_{26} and C_{31} (Figure 1). The ring atoms are not coplanar as shown in Table III (PL7).

Electronic and Magnetic Properties of Complex 3a. Magnetic Susceptibility Measurements. The magnetic moment of crystalline complex **3a** has been found constant between +30 and −200 °C (Figure 4), its value in this range of temperature being $\mu = 5.1 \pm 0.1\ \mu_B$. This result is indicative of an iron complex in a well-defined paramagnetic noninteracting state with $S = 2$. A similar value of $5.1 \pm 0.2\ \mu_B$ has been found by the Evans method[25] for the magnetic moment of complex **3a** in $CDCl_3$ solution at 34 °C. Two electronic structures are consistent with this value of the magnetic moment: either a high-spin Fe(II) or a high-spin Fe(IV) structure.

Mössbauer Spectrum of Complex 3a. The Mössbauer parameters of complex **3a** are indicated (Table VII) and compared with those of iron(II) porphyrin complexes such as Fe^{II}(TPP)[26] or Fe^{II}(TPP)(2-MeIm)[26] and iron(IV) porphyrin complexes such as

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[19] Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 317–380.

[20] Jameson, C. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 6769.

[21] Caron, C.; Mitschler, A.; Riviere, G.; Ricard, L.; Shappacher, M.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7401.

[22] Ricard, L.; Shappacher, M.; Weiss, R., to be published.

[23] Scheidt, R. W.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543–555.

[24] Scheidt, R. W. *Acc. Chem. Res.* **1977**, *10*, 339–345.

[25] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[26] Sams, J. R.; Tsin, T. B. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 425–478.

Table IV. ^{13}C Chemical Shifts[a] of Complex **3a** and of Typical High-Spin Ferrous and Ferric Porphyrin Complexes

complex	C_α	C_β	C_{meso}	$C_{o,o'}$	$C_{m,m'}$	C_p	C_q	CH_3 *p*-tolyl	ref
δ (34 °C), **3a**	941	856	218	232 225	136 134	133	80		this work
δ (26 °C), $Fe^{II}(TTP)(1,2\text{-}MeIm)$	1032	850	125.6	166.8	128.6	137.8	127.7	20	28
δ iso[b] (34 °C), **3a**	790	724	96	97 90	8 6	5	−63		this work
δ iso[b] (34 °C), $Fe^{II}(TPP)(2\text{-}MeIm)$	831	667	0						31
δ iso[b] (34 °C), $Fe^{III}(TPP)(I)$	950	1110	358	299 273	28.5 21.5	16	−215		30

[a] In ppm from TMS ($\delta > 0$ to low field) at 34 °C in CD_2Cl_2; the numbering of carbons is that of Figure 6. [b] Paramagnetic isotropic shifts referenced against $Zn^{II}(TPP)$.[29]

$Fe^{IV}(TPP)(O)(1\text{-}MeIm)$[27] and $Fe^{IV}(TPP)(O)(pyridine)$.[27] The isomeric shift, $\delta = 0.6$ mm/s, found for complex **3a** at 300 K is within the range of the isomeric shifts reported for iron(II) porphyrin complexes, $0.42 < \delta < 0.82$ mm/s, whereas it is very different from those described previously for iron(IV) porphyrin complexes ($\delta \simeq 0.1$ mm/s). These results are in favor of an Fe(II) high-spin ($S = 2$) structure for complex **3a**. It is noteworthy that EPR measurements of complex **3a** are in agreement with this structure. Actually, the EPR spectrum of complex **3a** does not show any significant signal between 4 and 298 K, suggesting an entire spin state $S = 0$, 1, or 2 for the iron of complex **3a** under these conditions.

^{1}H NMR Spectrum of Complex 3a. The ^{1}H NMR spectrum of complex **3a** in $CDCl_3$ at 34 °C has previously been shown in a preliminary communication.[8a] The assignments of its signals have been done by comparison of the spectra of complexes **3a** and **3b** (Table I) and of $Fe(d_{25}TPP)(NNC_9H_{18})$, the analogue of **3a** prepared from a tetraphenylporphyrin completely deuterated on the phenyl rings and partially deuterated on the pyrroles (5/8).[8a] In this deuterated analogue of **3a**, the signals at 9.61, 9.49, 8.81, 7.89, and 7.53 ppm are lacking whereas the intensity of the 66.8 ppm signal is decreased by a factor of $^5/_8$.[8a] The 66.8 ppm signal has thus been assigned to the pyrrole protons and those lying between 7 and 10 ppm to the phenyl protons of the porphyrin ring. Since the 7.53 ppm signal is lacking in the spectrum of complex **3b**, it has been assigned to the para protons of the phenyl rings. Concerning the four other signals of the phenyl-ring protons, those at 7.89 and 9.49 ppm are considerably broader and more separated ($\Delta\delta = 1.6$ ppm) than those at 8.81 and 9.61 ppm ($\Delta\delta = 0.8$ ppm). These properties are expected for the ortho and meta protons of the phenyl rings, respectively, since the ortho protons H_o and $H_{o'}$ are closer to the paramagnetic center than the meta protons and since the ortho protons H_o are closer to the axial nitrene ligand than the meta protons H_m.

Concerning the protons of the axial ligand, the signals at 81.5, 23.5, and −15.63 ppm have been respectively assigned to the H2, CH_3, and H_1 (Figure 5) protons by taking into account their respective integrations (4, 12, and 2 H).

The temperature dependence of the chemical shifts of the protons of complex **3a**, between −70 and 34 °C, corresponds to a Curie law (Figure 5). This is in agreement with a monomeric iron–porphyrin complex in a well-defined paramagnetic noninteracting state. The ^{1}H NMR characteristics of complexes **3a–c** are very similar, as indicated in Table I.

^{13}C NMR Spectrum of Complex 3a. The undecoupled ^{13}C NMR spectrum of complex **3a**, recorded at 34 °C, is shown in Figure 6. Selective decoupling of the pyrrole proton resonances allowed the assignment of the 856-ppm signal to carbons Cβ. Decoupling of the proton resonances of the porphyrin phenyl groups localized the signals of carbons C_o, $C_{o'}$, C_m, $C_{m'}$, and C_p (Figure 6). The specific assignments of these signals indicated in Figure 6 were based on their respective line widths and chemical shifts by comparison to those described previously for high-spin ferrous–porphyrin complexes.[28] Cp gives the sharpest signal, and

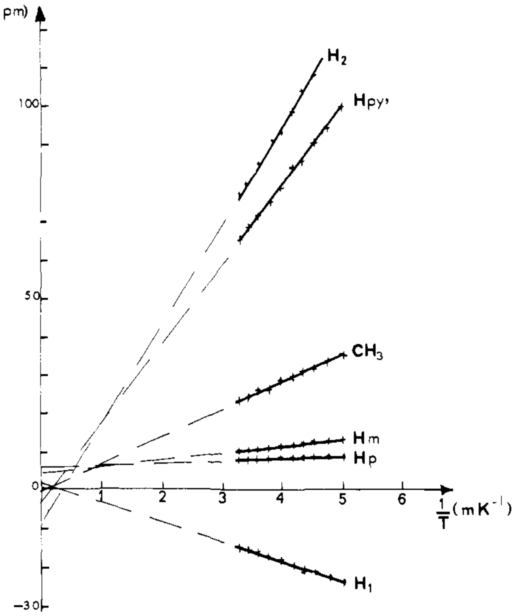

Figure 5. Thermal dependence of the chemical shifts (δ (Me_4Si)) of the protons of complex **3a** (For the labeling of hydrogens, see Figure 6).

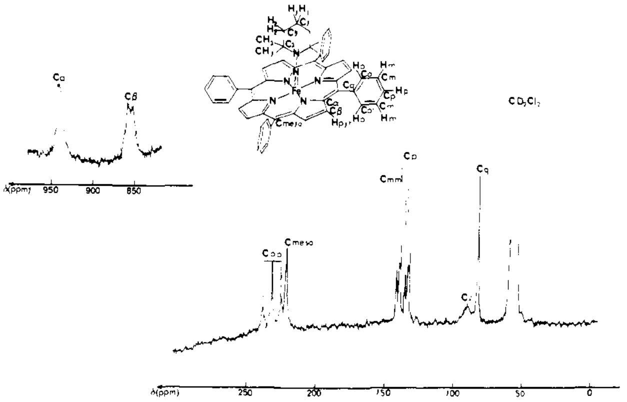

Figure 6. ^{13}C NMR spectrum of complex **3a** in CD_2Cl_2 (25.2 MHz, 34 °C, δ (Me_4Si)).

its chemical shift is similar to those of C_m and $C_{m'}$ but very different from those of C_o and $C_{o'}$. As for the quaternary carbons, the signal of one of these carbons appearing at 941 ppm integrates as eight carbons and was thus assigned to the α carbons of the porphyrin ring. The two other signals at 218 and 80 ppm integrate each as four carbons and should correspond to the meso carbons and the quaternary carbons of the phenyl rings. The specific assignment shown in Figure 6 was based on the respective line width of the corresponding resonances, which is expected to be larger for C_{meso} (40 Hz) than for C_q (20 Hz) because of the difference in their distances from the paramagnetic center.

Only one resonance could be observed for the axial ligand. It was assigned to C2 by proton decoupling. No other resonance

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(27) Simonneaux, G.; Scholtz, W. F.; Reed, C. A.; Lang, G. *Biochim. Biophys. Acta* **1982**, *1*, 716.

(28) Shirazi, A.; Leum, E.; Goff, H. M. *Inorg. Chem.* **1983**, *22*, 360–362.

Table V. Line Widths[a] (in Hz) of the Ring Carbons and of the Pyrrolic Protons (H_{pyr}) Resonances of Complex **3a**, Either Experimentally Observed or Calculated by the Bloemberger–Solomon Equation[35]

	C_α	C_β	C_{meso}	H_{pyr}
λ_{calcd} dipolar contribution	92.5	13	47	59
λ_{calcd} contact contribution	119	100	2	9
total	212	113	49	68
λ_{obsd}	190	135[b]	40	80

[a] At 34 °C, in a magnetic field of 2.35 Tesla. The correlation time was approximated to T_{1e} and was calculated for the best fit between calculated and experimental values ($T_{1e} \simeq 4.10^{-12}$ s). [b] This value was obtained from the simulation of the observed line shape (Figure 6) by the sum of two lorentzian components separated by the C_β–H_{pyr} coupling constant of 170 Hz.

could be detected from −200 to +1500 ppm. Actually it is likely that the lacking resonances, particularly those of C3 and CH_3, are very much broadened because of their proximity to the paramagnetic center and very difficult to detect.

The paramagnetic shifts relative to $Zn^{II}(TPP)$[29] are compared in Table IV with those of a typical high-spin ferric complex[30] and of high-spin ferrous complexes.[28,31] This comparison supports the assignment of a high-spin Fe(II) ($S = 2$) state for complex **3a**. The large downfield pyrrole carbon isotropic shifts are indicative of the half-occupancy of the iron $d_{x^2-y^2}$ orbital.[28,30,32,33] At the same temperature, the mean isotropic shift for the α and β carbons of complex **3a** is very similar to that found for the 2-methylimidazole high-spin ferrous complex of TPP ((757 and 749 ppm, respectively, from Table IV). It is also similar to that of the high-spin iron(III) complex, weighted by the $S(S + 1)$ factor (706 ppm), indicating similar hyperfine coupling constants. However, some differences appear between **3a** and the two other ferrous complexes, which are thought to be related to differences in the π-electron spin distribution on the porphyrin ring. For the three iron(II) complexes, the C_α carbon resonance appears at lower field than that of C_β carbon, in contrast to high-spin ferric complex. The paramagnetic shift of these carbons arises essentially from the contact interaction due to the unpaired electrons delocalized into the σ molecular orbital of the porphyrin ligand, which mixes with the iron $d_{x^2-y^2}$ orbital, and to the π–σ polarization by the π spin densities located at the observed carbon and at the neighboring carbons.[34] These latter two contributions have opposite effects, so that for high-spin ferric complexes (Table IV) the neighboring contributions to the shift of C_α predominate due to the large π spin densities of C_β and C_{meso}.[30] Thus, the reversal of the order of the resonances for the three high-spin ferrous complexes suggests that the π spin density on the porphyrin ring is reduced as compared with the high-spin ferric complexes. This conclusion is also supported by the analysis of the line widths of the resonances of the ring carbons and of the pyrrole protons. Indeed, the line widths calculated for complex **3a** by the Bloemberger–Solomon equation,[35] which does not take into account the effect of local spin densities,[36] approximately agree with the measured ones (Table V), in contrast with what was found for the high-spin ferric complexes.[30,37]

Table VI. Comparison of Metal(M)–N and N–N Bond Lengths and M–N–N Angles in Complex **3c** and Several Mononuclear Hydrazido(2−) Complexes of Transition Metals

complex	M–N, Å	N–N, Å	M–N–N, deg	ref
$Fe(TpClPP)(NNC_9H_{18})$ (**3c**)	1.809	1.232	180	this work
$[Mo_3S_8(NNMe_2)_2](Ph_4P)_2$	2.131	1.162	166	39
$[MoI(dppe)_2(NNHC_8H_{17})]^+I^-$	1.801	1.259	174	40
$[WBr(dppe)_2(NNHCH_3)]^+Br^-$	1.77	1.32	171	41
$VCp_2(NN(SiMe_3))_2$	1.666	1.369	180	42

The isotropic shifts of the meso carbons, the attached phenyl carbons, and the ortho phenyl carbons are different from those of the high-spin Fe(II)(imidazoles) complexes (Table IV). They exhibit, however, the same pattern of alternating shift direction as those described for high-spin iron(III),[30a,32,33] high-spin iron(II),[28] and intermediate-spin iron(II) complexes.[30a] This pattern is thought to be due to the mixing of the σ type orbitals of the phenyl groups with the $2p_z$ meso carbon orbitals,[28,30a] which places σ spin density at the attached phenyl carbon roughly proportional to the π spin density present at the meso carbons. The larger isotropic shifts for the three carbons (meso, quaternary, and ortho) indicate therefore an increased π spin delocalization in complex **3a**, as compared to the imidazoles complexes of $Fe^{II}(TPP)$.[28,31]

The observed isotropic shifts for the pyrrole carbons of complex **3a** are thus a further strong argument in favor of the high-spin ferrous structure proposed for this complex. The isotropic shift of its meso and phenyl carbons indicates a moderate π back-bonding from the iron to the porphyrin plane that places π spin densities at the meso carbons.[38] This π back-bonding is intermediate between that of a typical high-spin ferric complex of the high-spin Fe^{II}(imidazoles) complexes.[28,31]

Discussion

Compounds **3** are both the first nitrene–metalloporphyrin[8] complexes as well as the first mononuclear iron–nitrene complexes to be described. It is, however, noteworthy that hydrazido(2−) complexes of other transition metals[14] as well as compounds containing an imido ligand bridging at least two iron centers[10] have been reported.

As indicated in Scheme I, complexes **3** have been prepared by three different techniques that had never been used for the synthesis of transition-metal–nitrene complexes.

The first one involved the direct reaction of the free nitrene with the iron(II) porphyrin at −70 °C. Naturally, this method cannot be general for the preparation of metal–nitrene complexes since it is restricted to the case of stable nitrenes. The second method could be more general since it involves the oxidation of an amino compound by the high-valent iron–oxo species that is formed upon reaction of an iron porphyrin with the oxygen-atom donor iodosobenzene.[4] At least formally, it corresponds to the replacement of an oxo by an imido ligand (eq 1).

$$R_2NNH_2 + Fe{=}O \rightarrow Fe{=}NNR_2 + H_2O \qquad (1)$$

The third technique also involves the in situ oxidation of the amino group of the hydrazine **1** with O_2 as the oxidant. Although the detailed mechanism of this reaction is not known, it exhibits a certain analogy with the metabolic oxidation of 1,1-dialkylhydrazines by hepatic cyclochrome P_{450}.[6] In both the chemical and enzymatic reactions, dioxygen is used as the oxidizing agent and a stable iron complex is formed. Actually, the results described

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(29) Wüthrich, K.; Baumann, R. *Helv. Chim. Acta* **1973**, *56*, 585–596.

(30) (a) Mispelter, J.; Momenteau, M.; Lhoste, J.-M. *J. Chem. Soc., Chem. Commun.* **1979**, *808*–810. (b) Mispelter, J.; Momenteau, M.; Lhoste, J.-M. *J. Chem. Soc., Dalton Trans.* **1981**, 1729–1734.

(31) Mispelter, J.; Momenteau, M.; Lhoste, J.-M., unpublished results.

(32) Goff, H. M.; Shimomura, E. T.; Phillipi, M. A. *Inorg. Chem.* **1983**, *22*, 66–71.

(33) Phillipi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3904–3911.

(34) Karplus, M.; Fraenkel, G. K.; *J. Chem. Phys.* **1961**, *35*, 1312–1323.

(35) Swift, T. J. In "N.M.R. of Paramagnetic Molecules"; La Mar, G. N., Horrocks, W. W., Holm, R. H., Eds.; Academic Press: New York, 1973; pp 53–83.

(36) Gottlieb, H. P. W.; Barfield, M.; Doddrell, D. M. *J. Chem. Phys.* **1977**, *67*, 3785–3794.

(37) The T_{1e} of the three ring carbons for pentacoordinated 2-methylimidazoles ferrous complexes approximately follow the Bloemberger–Salomon equation.[30]

(38) La Mar, G. N.; Walker, F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61–157.

(39) Dilworth, J. R. Zubieta, J.; Hyde, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 365–367.

(40) Day, V. W.; George, T. A.; Iske, S. D. A.; Wagner, S. D. *J. Organomet. Chem.* **1975**, *112*, C55.

(41) Marsh, F. C.; Mason, R.; Thomas, K. M. *J. Organomet. Chem.* **1975**, *96*, C43.

(42) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 387.

Table VII. Spectroscopic Data of Different Iron Porphyrin Complexes, Including **3a**, That Are Characteristic of Spin and/or Oxidation States

complex	S	μ_{eff}, μ_B	Mössbauer T, K	 δ, mm/s [ref]	 ΔE_q, mm/s	Fe–Np, Å [ref]	^{1}H NMR δ Hpyr (ppm/Me$_4$Si) [ref]	C^{13} NMR (ppm/Me$_4$Si) δ_{iso} C_2 [ref]	 δ_{iso} C_β
Fe^{II}(TPP)(NNC$_9$H$_{18}$) (**3a**)	2	5.1	4.2 77 300	0.72 0.71 0.60 [this work]	1.51 1.51 1.40	2.096^a [this work]	66.8 [this work]	790 [this work]	724
Fe^{II}(TPP)(2-MeIm)	2	5.3 [26]	4.2 77 300	0.93 0.92 0.82 [26]	2.28 2.26 1.74	2.086 [23]	42.3 [45]	831 [31]	667
Fe^{II}(TPP)	1	4.4 [26]	4.2 77 300	0.52 0.50 0.42 [26]	1.51 1.51 1.52	1.972 [23]	4.2 [46]		
Fe^{III}(TPP)Cl	$^5/_2$	5.9	4.2	0.41 [26]	0.46	2.060 [44]	79.4 [47]	950^b [30]	1110^b
Fe^{III}(TPP)(Cl)[C=C(p-ClC$_6$H$_4$)$_2$]	$^3/_2$	3.94 [43a]	4.2 77 300	0.315 0.306 0.225 [43a]	2.85 2.87 2.87	1.990 [43b]			
Fe^{IV}(TPP)(O)(Py)	1		4.2 77	0.11 0.10 [27]	1.26 1.25				
Fe^{IV}(TPP)(O)(1-MeIm)	1	2.9 [3a]	4.2 77	0.10 0.11 [27]	1.56 1.56		5 [3d]		

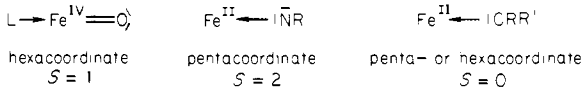
^{a} From X-ray analysis of complex **3c**. ^{b} Values obtained for Fe^{III}(TPP)(I).

above establishing the formation of a nitrene–iron porphyrin complex upon the O$_2$-dependent oxidation of a 1,1-dialkylhydrazine are strong arguments in favor of a similar iron–nitrene structure for the cytochrome P$_{450}$ complexes detected upon microsomal oxidation of the various 1,1-dialkylhydrazines.

The X-ray structure of complex **3c** shows a linear Fe–N–N bonding mode with multiple character in the Fe–N and N–N bonds. The linear arrangement of Fe–N25–N26 atoms is in agreement with the M–N–N angle values already found in hydrazido(2–) complexes of transition metals, which range from 166° to 180° (Table VI). The relatively short Fe–N25 distance (1.809 Å) is characteristic of a Fe–N bond order between 1 and 2. For comparison, previously described hydrazido(2–) complexes of transition metals have M–N bond lengths[14] that range between 1.801 and 1.666 Å for bond orders between 2 and 3 and between 2.131 and 1.801 Å for bond orders between 1 and 2, the N–N bond lengths of hydrazido(2–) complexes of transition metals ranging from 1.369 to 1.162 Å for bond orders between 1.3 and 2 (Table VI).

Various spectroscopic data of different iron–porphyrin complexes including **3a** that are considered as characteristic of spin and/or oxidation states are compared in Table VII. The characteristics of complex **3a** are very similar to those previously reported for high-spin pentacoordinate Fe^{II}(TPP)(imidazole) complexes but very different from those described for high-spin ferric (S = $^5/_2$), intermediate-spin ferric (S = $^3/_2$), intermediate-spin ferrous (S = 1), and low-spin Fe(IV) (S = 1) complexes. Taken altogether, the magnetic moment μ = 5.1 ± 0.1 μ_β, the Mössbauer isomeric shift δ = 0.7 mm/s, the Fe–Np distance (2.09 Å), and the NMR chemical shifts of the pyrrole protons (δ +66.8) and of the pyrrole Cα and Cβ carbons (δ 941 and 856) firmly establish a high-spin ferrous (S = 2) state for complex **3a**. Since (i) the magnetic moments measured at room temperature for crystalline complex **3a** (μ = 5.1 ± 0.1 μ_B) and for its solution in CDCl$_3$ (μ = 5.1 ± 0.1 μ_B) are very similar, (ii) the UV-vis spectrum of a powder of complex **3a** (λ = 448, 563, and 602 nm) exhibits a shape similar to that of complex **3a** 10^{-5} M in C$_6$H$_6$ (the former showing broader bands generally red-shifted as usually found when passing from solution to powder[43a]), it is likely that complexes **3** have a similar structure in solution and in the solid state.

Returning to the analogy between iron(II or IV) porphyrin–oxo, –nitrene, and –carbene complexes (see introduction of this paper), it is noteworthy that the iron–oxo complexes described so far exhibit a low-spin Fe(IV) (S = 1) structure,[3] whereas the iron–carbene[5] and iron–nitrene complexes exhibit respectively a low-spin Fe(II) (S = 0) and a high-spin Fe(II) (S = 2) structure.



This shows that the formally analogous oxene, carbene, and nitrene ligands that bind to iron–porphyrins lead to very different distributions of the electrons involved in the iron–ligand bond. As a result of the greater electronegativity of oxygen compared to nitrogen or carbon, the iron–oxo complexes are the only ones to involve a high-valent Fe(IV).

Experimental Section

Physical Measurements. The experimental operations with iron(II) porphyrins and complexes **3** were performed on a vacuum line. UV-vis spectra were obtained on an Aminco DW2 spectrometer fitted with a temperature regulation system. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 257 spectrometer. Mass spectra were recorded on a Varian CH7 spectrometer (70 eV) at temperatures ca. 220 °C. Elemental analysis were performed by the Service de Microanalyse du CNRS at Gif-sur-Yvette. Cameca 250 operating at 250 MHz and Varian XL100 operating at 100 MHz fitted with a temperature regulation system were used for the ^{1}H NMR spectra.

The ^{13}C NMR spectra were recorded on a Varian XL100 spectrometer operating at 25.2 MHz. Complex **3a** (10^{-1} M) was dissolved in CD$_2$Cl$_2$ (from C.E.A. France) under argon. The spectrum of Figure 6

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(43) (a) Mansuy, D.; Morgenstern-Badarau, I.; Lange, M.; Gans, P. *Inorg. Chem.* **1982**, *21*, 1427-1430. (b) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J.-C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899-2901.

(44) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992-1996.

(45) Mispelter, J.; Momenteau, M.; Lhoste, J. M.; *Mol. Phys.* **1977**, *33*, 1715-1728.

(46) Mispelter, J.; Momenteau, M.; Lhoste, J. M. *Chem. Phys. Lett.* **1978**, *57*, 405-409.

(47) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fager, J. In "Annals of the New York Academy of Sciences"; Boland, B., Monge, M., Cullinan, J., Eds.; New York Academy of Sciences: New York, 1973; Vol. 206, pp 504-514.

was recorded at 34 °C in two parts due to the large chemical shift range. Typically, 300 000 transients were accumulated at a rate of 0.2 s using 90° pulses. The line widths were measured in the absence of decoupling power because this creates temperature instabilities and inhomogeneities to which the paramagnetic carbon resonances are particularly sensitive.

Mössbauer spectroscopy experiments without a magnetic field were performed on powder layers of complex **3a** pressed between two aluminum foils; the proper resonant absorption of the iron contained in the aluminum windows of the sample holder were recorded. The Mössbauer experiments were carried out by using a constant-acceleration electromechanical drive system together with a multianalyzer for collecting and storing the data. ^{57}Co in rhodium was used at room temperature as a source. The velocity calibrations were done with a thin-iron metal absorber, and all the isomeric shifts data given in this paper refer to the symmetry center of the iron metal Mössbauer sextuplet at 300 K.

Reagents and Solvents. For anaerobic reactions, the solvents were deaerated before use by argon bubbling for 0.5 h. CH_3OH, CH_2Cl_2, $CHCl_3$, and other reagents were used as supplied (puriss, grade). Fe(TPP)Cl, Fe(TTP)Cl, and Fe(TpClPP)Cl were prepared according to literature procedures.[48,49] 1-Amino-2,2,6,6-tetramethylpiperidine (**1**) was prepared in two steps as described in the literature.[11] Nitrosation of 2,2,6,6-tetramethylpiperidine by $NaNO_2$ gives 1-nitroso-2,2,6,6-tetramethylpiperidine, bp (7 torr) 97 °C; ^{1}H NMR in $CDCl_3$ δ (Me_4Si) = 1.40 (6 H), 1.58 (12 H) (lit.[11] bp (7–10 torr) 97–98 °C). Further reduction of 1-nitroso-2,2,6,6-tetramethylpiperidine by $LiAlH_4$ gives the hydrazine (**1**), bp (20 torr) 83 °C; IR(KBr) 3350 and 3220 cm^{-1} ($-NH_2$), ^{1}H NMR in $CDCl_3$ δ (Me_4Si) = 1.05 (12 H), 1.47 (6 H), 2.6 (2 H) (lit.[11]) bp (20 torr) = 83 °C, IR (KBr) 3350 and 3220 cm^{-1}; ^{1}H NMR in $CDCl_3$ δ (Me_4Si) = 1.01 (12 H), 1.46 (6 H), 2.6 (2 H).

(2,2,6,6-Tetramethyl-1-piperidyl)nitrene (**2**) has been obtained by oxidation of the hydrazine (**1**) by *t*-BuOCl in the presence of Et_3N, at −80 °C in anhydrous diethyl ether, as described previously.[12]

X-ray Analysis. Suitable single crystals of **3c** were obtained by slow evaporation of dichloromethane solutions at room temperature. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **3c** belong to the monoclinic system.

The unit-cell dimensions and their standard deviations were obtained and defined at room temperature with Cu Kα radiation (λ = 1.5405 Å) by using 25 carefully selected reflections and the standard Phillips software. Final results are as follows: $FeCl_4N_6C_{53}H_{42}$, M = 960.6, a = 16.127 (5) Å, b = 17.969 (6) Å, c = 16.516 (5) Å, β = 95.13 (2), V = 4765 Å^3, Z = 4, d_{calcd} = 1.34 g cm^{-3}, d_{obsd} 1.32 ± 0.02 g cm^{-3}, μ = 49.8 cm^{-1}, $F(000)$ = 1984, space group $C2/c$ or Cc.

A parallelepipedic crystal of 0.16 × 0.30 × 0.16 mm was sealed in a Lindemann glass capillary and mounted on a rotation free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step-scan used was $\Delta\theta = 0.90° +$ (Cu K$\alpha_{1,2}$ splitting) with a step width of 0.05° and a scan speed of 0.02° s^{-1}. A total of 3422 hkl and $hk\bar{l}$ reflections were recorded ($4 < \theta < 57°$). The resulting data set was transferred to a PDP11/60 computer, and for all subsequent computations the Enraf-Nonius SDP/V18 package was used,[50] with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection period showed no significant trend in intensity.

The raw step-scan data were converted to intensities by using the Lehmann-Larson method[51] and then corrected for Lorentz, polarization, and absorption factors; the latter was computed by the numerical integration method of Busing and Levy[52] (transmission factors between 0.40 and 0.56). A unique data set of 2215 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure. An $N(Z)$ cumulative test on $|F_{obs}|$ showed that the most probable space group is $C2/C$.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 8 Å^2, but they were not refined. Full least-squares refinement converged to $R(F)$ = 0.051 and $R_w(F)$ = 0.069 ($\sigma^2(F^2) = (\sigma^2 \text{ count} + (pI)^2)$). A final difference map revealed no significant maxima.

Synthesis of Complexes 3a–c. [(*meso*-Tetraphenylporphyrinato)][(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron(II), Fe(TPP)(NNC_9H_{18}) (3a). To a solution of 0.070 g of Fe^{III}(TPP)Cl in 50 mL of aerobic CH_2Cl_2 at 20 °C, 0.156 g of 1-amino-2,2,6,6-tetramethylpiperidine (**1**) were added. After stirring for 10 min, complex **3a** was completely formed and the solution was then deaerated by argon bubbling. Upon precipitation by addition of 30 mL of deaerated CH_3OH, complex **3a** was obtained as purple shining crystals (yield 0.074 g, 90%). Anal. Calcd for $C_{53}H_{46}N_6Fe{\cdot}0.2CH_2Cl_2$: C, 76.15; H, 5.57; N, 10.02; Cl, 1.61. Found: C, 75.94; H, 5.65; N, 10.05; Cl, 1.61 (the crystallized sample contained 0.2 CH_2Cl_2 per mole of **3a** as shown by ^{1}H NMR spectroscopy).

Complex **3a** was also prepared by reaction of (2,2,6,6-tetramethyl-1-piperidyl)nitrene (**2**) with Fe^{II}(TPP). A solution of 0.070 g of Fe^{III}(TPP)Cl in 50 mL of CH_2Cl_2 was carefully deaerated by argon bubbling, and the iron(III) was reduced by stirring with iron powder (0.1 g). The solution was then filtered under argon, to eliminate the excess of iron powder, and cooled down to −80 °C. A solution of the nitrene **2** in Et_2O at −80 °C, prepared from 0.3 g of hydrazine **1**,[12] was added to the Fe^{II}(TPP) solution previously prepared. Complex **3a** immediately appeared. Crystals of **3a** were obtained by precipitation with CH_3OH (30 mL) (yield 0.080 g, 95%).

Finally, complex **3a** has been obtained by reaction of Fe^{III}(TPP)Cl with the hydrazine (**1**) in the presence of iodosobenzene. Hydrazine (**1**) (0.156 g) in deaerated CH_2Cl_2 (2 mL) were added at 20 °C to a deaerated solution of 0.070 g of Fe^{III}(TPP)Cl in 50 mL of CH_2Cl_2. A solution of C_6H_5IO (0.022 g in 1 mL of CH_3OH) was then added. After a reaction time of 15 min, complex **3a** was precipitated upon addition of 30 mL of deaerated CH_3OH (yield 0.050 g, 60%).

[(*meso*-Tetra-*p*-tolylporphyrinato)][(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron(II), Fe(TTP)(NNC_9H_{18}) (3b). Complex **3b** was prepared as described above, starting from 0.076 g of Fe^{III}(TTP)Cl and 0.156 g of hydrazine (**1**) in the presence of O_2 (first method) (yield 0.080 g, 90%). Anal. Calcd for $C_{57}H_{54}N_6Fe{\cdot}0.2CH_2Cl_2$: C, 76.68; H, 6.12; N, 9.42. Found: C, 76.86; H, 6.20; N, 9.82.

[(*meso*-Tetra-*p*-chlorophenylporphyrinato)][(2,2,6,6-tetramethyl-1-piperidyl)nitrene]iron(II), Fe(TpClPP)(NNC_9H_{18}) (3c). Complex **3c** was prepared starting from 0.084 g of Fe^{III}(TpClPP)Cl and 0.156 g of hydrazine (**1**) in the presence of O_2 (first method). Its structure has been proved by X-ray analysis.

The other characteristics of complexes **3a–c**, mass, UV–vis, ^{1}H NMR, ^{13}C NMR, and IR spectra, have been mentioned in the results.

Registry No. 1, 6130-92-3; **2**, 66337-86-8; **3a**, 82281-71-8; **3b**, 88589-57-5; **3c**, 88589-58-6; O_2, 7782-44-7; C_6H_5IO, 536-80-1; TPP, 917-23-7; TTP, 14527-51-6; TpClPP, 22112-77-2; 2,2,6,6-tetramethylpiperidine, 768-66-1; 1-nitroso-2,2,6,6-tetramethylpiperidine, 6130-93-4.

Supplementary Material Available: Atomic positional and thermal parameters for all atoms with estimated standard deviations (Tables VIII and IX) and listings of structure factor amplitudes (F_o and $F_c \times 10$) (Table X) (14 pages). Ordering information is given on any current masthead page.

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(48) (a) Barnet, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, *30*, 2887–2888. (b) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

(49) Fuhrop, J. H.; Smith, K. M. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 769–774.

(50) Frenz, B. A. "The Enraf-Nonius CAD4-SPD in Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delf Univ. Press: Delf, 1978; pp 64–71.

(51) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *A30*, 580–584.

(52) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–182.