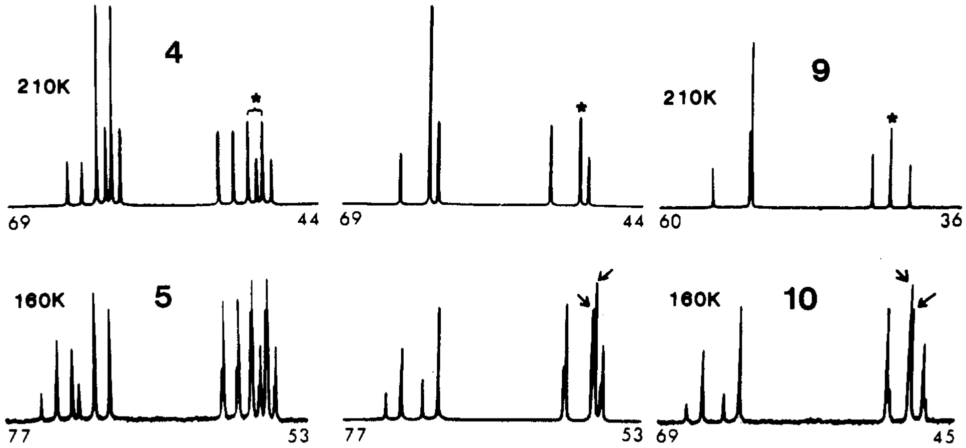

Figure 1. $^{31}P\{^1H\}$ pulsed Fourier transform NMR spectra (101.25 MHz) of complexes **4**, **5**, **9**, and **10** (see text) under conditions of slow rotation about the metal–phosphorus bonds on the NMR time scale. The middle spectra are theoretically computed with ^{103}Rh–^{31}P spin–spin coupling removed and correspond to the spectra of the Rh(I) complexes immediately to the left. An asterisk identifies the least populous subspectrum for complexes **4** and **9**. For an explanation of the arrows (lower spectra) see text. Each spectrum is calibrated at lower left and lower right in ppm.

wire within a 10-min period. An ice bath controlled the reaction. The mixture was stirred for 5 min more at room temperature at which point most of the lithium wire was consumed. Over a 5-min period, di-*tert*-butylchlorophosphine (0.03 mol; Strem Chemicals, Inc.) was added dropwise to the mixture. After refluxing for 1.5 h, the reaction was quenched slowly with water. The ether layer was extracted and dried over Na_2SO_4, and the ether was removed by distillation. The crude phosphine was vacuum distilled to yield a clear colorless liquid in 70% yield (bp 353–356 K (15.5 mm)). Spectral data on the free phosphine: $^{13}C\{^1H\}$ NMR (vinyl chloride, 260 K, 62.9 MHz, Me_4Si reference) δ 31.5 (quaternary, d, $^1J_{PC}$ = 22.2 Hz), 29.8 (*tert*-butyl methyls, d, $^2J_{PC}$ = 13.0 Hz), 15.3 (methyl of ethyl, d, $^1J_{PC}$ = 27.8 Hz), 14.2 (CH_2, d, $^2J_{PC}$ = 20.4 Hz); $^{31}P\{^1H\}$ NMR (vinyl chloride, 260 K, 101.2 MHz, 85% H_3PO_4 reference) δ 33.7 (s); ^1H NMR (vinyl chloride, 260 K, 250.1 MHz, Me_4Si reference) δ 1.33 (CH_2, m, $^3J_{HH}$ = 7.8 Hz, $^2J_{PH}$ = 4.5 Hz), 1.14 (methyl of ethyl, m, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 16.5 Hz), 1.08 (*tert*-butyl, d, $^3J_{PH}$ = 10.0 Hz).

Then, the rhodium complex (**3**) was prepared as described for **1** above by using di-*tert*-butylethylphosphine. Anal. Calcd for $C_{21}H_{46}ClOP_2Rh$: C, 49.0; H, 9.00; Cl, 6.9; P, 12.0. Found: C, 48.9; H, 9.18; Cl, 6.9; P, 12.0.

***trans*-Rh(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$(*n*-C$_4$H$_9$)]$_2$** (**4**) was prepared in the same manner as **1** above using di-*tert*-butyl-*n*-butylphosphine.[12] Anal. Calcd for $C_{25}H_{54}ClOP_2Rh$: C, 52.6; H, 9.53; Cl, 6.2; P, 10.8. Found: C, 52.7; H, 9.50; Cl, 6.3; P, 10.9.

***trans*-Rh(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$C$_6$H$_5$]$_2$** (**5**) was prepared in the same manner described for **1** using di-*tert*-butylphenylphosphine (Strem Chemicals, Inc.).[13] Anal. Calcd for $C_{29}H_{46}ClOP_2Rh$: C, 57.0; H, 7.59; Cl, 5.8; P, 10.1. Found: C, 56.8; H, 7.62; Cl, 6.3; P, 11.2.

***trans*-Ir(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$H]$_2$** (**6**)[5b] was prepared by using a modified version of a previously reported procedure.[14] $IrCl_3 \cdot 3H_2O$ (0.0005 mol; Strem Chemicals, Inc.) was added to 10 mL of 2-methoxyethanol. A stream of carbon monoxide gas was bubbled continuously through the resulting purple solution. The reaction mixture was allowed to reflux for 1 h at which point di-*tert*-butylphosphine was added by syringe to the stirring, hot, clear yellow solution. A gas (CO) was immediately evolved from the reaction. As the reaction mixture slowly cooled, yellow crystals of the iridium(I) complex formed slowly. The iridiun(I) complex was recrystallized from toluene/methanol. Anal. Calcd for $C_{17}H_{38}ClOP_2Ir$: C, 37.4; H, 6.99; Cl, 6.5; P, 11.3. Found: C, 37.8; H, 6.91; Cl, 6.5; P, 11.8.

***trans*-Ir(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$CH$_3$]$_2$** (**7**) was prepared in the same manner as **6** above using di-*tert*-butylmethylphosphine.[15] Anal. Calcd for $C_{19}H_{42}ClOP_2Ir$: C, 39.6; H, 7.35; Cl, 6.2; P, 10.8. Found: C, 39.6; H, 7.35; Cl, 7.9; P, 12.3.

***trans*-Ir(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$C$_2$H$_5$]$_2$** (**8**) was prepared in the same manner as **6** above using di-*tert*-butylethylphosphine.[15] Anal. Calcd for $C_{21}H_{46}ClOP_2Ir$: C, 41.7; H, 7.67; Cl, 5.9; P, 10.2. Found: C, 41.7; H, 7.63; Cl, 5.9; P, 10.0.

***trans*-Ir(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$(*n*-C$_4$H$_9$)]$_2$** (**9**) was prepared in the same manner as **6** above using di-*tert*-butyl-*n*-butylphosphine.[15] Anal. Calcd for $C_{25}H_{54}ClOP_2Ir$: C, 45.5; H, 8.25; Cl, 5.4; P, 9.4. Found: C, 45.3; H, 8.29; Cl, 5.4; P, 9.7.

***trans*-Ir(Cl)(CO)[P(*t*-C$_4$H$_9$)$_2$C$_6$H$_5$]$_2$** (**10**) was prepared in the same manner as **6** above by using di-*tert*-butylphenylphosphine. Spectral data on **10**: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 310 K, 62.9 MHz, Me_4Si reference) δ 171.5 (CO, t, $^2J_{PC}$ = 11.0 Hz), 37.6 (quaternary, t, J_{PC} = 10.1 Hz), 31.1 (*tert*-butyl methyls, s), aromatic carbons at 136.1 (t, J_{PC} = 6.6 Hz), 133.9 (t, J_{PC} = 18.5 Hz), 129.4 (s), 126.6 (t, J_{PC} = 4.1 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 310 K, 101.2 MHz, 85% H_3PO_4 reference) δ 51.5 (s); ^1H NMR ($CDCl_3$, 298 K, 250.1 MHz, Me_4Si reference) δ 1.57 (*tert*-butyl, t, J_{PH} = 6.7 Hz), aromatics at 8.09 (m, 4 H), 7.33 (m, 6 H). Anal. Calcd for $C_{29}H_{46}ClOP_2Ir$: C, 49.7; H, 6.62; Cl, 5.1; P. 8.8. Found: C, 49.6; H, 6.51; Cl, 5.0; P, 8.8.

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Registry No. **1**, 33246-87-6; **2**, 34365-67-8; **3**, 34365-69-0; **4**, 32629-96-2; **5**, 32628-32-3; **6**, 33246-91-2; **7**, 34365-68-9; **8**, 34365-70-3; **9**, 89791-43-5; **10**, 32628-35-6.

Supplementary Material Available: $^{31}P\{^1H\}$ pulsed Fourier transform NMR spectra of complexes **1**–**10** (Figure 1S) (2 pages). Ordering information is given on any current masthead page.

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Control of Spin State in (Porphinato)iron(III) Complexes. Effect of the Porphyrin Ligand

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Changes in spin state of the iron atom of the heme play a major role in the biological activity of the hemoproteins. For example, the change from the high- to the low-spin state accompanying the coordination of dioxygen to deoxyhemoglobin is an essential component of cooperative oxygen binding.[1] The addition of substrate to resting cytochrome P-450$_{cam}$ results in a change in Fe(III) spin state from $S = {}^1/_2$ to 60% $S = {}^5/_2$ at 12 K.[2] This spin-state change is required to allow reduction of the heme by its physiological reductant in the catalytic cycle.[3] Clearly, the factors affecting the spin state of hemes are important and are of interest.

The axial ligands are the primary determinants of spin state.[4] Changes in the heme environment may also effect a change in spin state. Thus, heme proteins with identical axial ligands display markedly different spin-crossover points.[5] The spin state of a heme may also display solvent dependence as in Fe(TPP)(OClO$_3$)[6,7] or a dependence on axial-ligand orientation as in [Fe(OEP)(3-Cl(py))$_2$]ClO$_4$.[8,9] We now wish to report that variation in the porphinato ligand can also systematically affect the spin state of the central iron(III) atom; species with more basic porphyrinate ligands have higher spin multiplicity.

A suggestion of possible spin-state effects of the porphinato ligand was observed[10] in the mixed-axial-ligand complexes Fe(Porph)(NCS)(py), where the OEP derivative is high spin and the corresponding TPP complex essentially low spin. The [Fe(Porph)(X–py)$_2$]ClO$_4$ complexes appear particularly suitable for an examination of the effect of porphyrin ligand on spin state. In solution, the OEP[11,12] and PPIX[13] ferric derivatives have been shown to display temperature-dependent magnetic moments consistent with an $S = {}^1/_2$, $S = {}^5/_2$ spin equilibrium. The 3-Cl(py) complex displays the largest dependence of magnetic moment with temperature.[12] The magnetic susceptibilities for a series of [Fe(Porph)(3-Cl(py))$_2$]ClO$_4$ salts in solution are reported herein. Solution measurements were utilized to avoid solid-state effects on the magnetic moment; we have observed such phenomena in a number of instances.[14]

Tetraarylporphyrins were synthesized by published procedures.[15] Octaethylprophyrin, deuteroporphyrin IX dimethyl ester, and etioporphyrin III were purchased from Strem Chemicals. (Porphinato)iron(III) chloride complexes were prepared by the method of Adler et al.[16] with the modifications suggested by Walker[17] for the *p*-diethylamino-substituted derivative. (Protoporphyrin IX)iron(III) chloride was purchased from Strem Chemicals and converted to the μ-oxo dimethyl ester dimer by a published procedure.[18] The perchlorate species were synthesized by the method of Dolphin et al.[19] with the modifications suggested by Goff et al.[7b] *Caution*! A number of the perchlorates detonated violently during the drying step.

Magnetic susceptibilities were determined by the method of Evans[20] (2–9 mg of Fe(Porph)(OClO$_3$)/mL in 30% 3-chloropyridine in chloroform (v/v) or nitromethane (v/v)).[21]

Table I. Magnetic Moments of [Fe(Porph)(3-Cl(py))$_2$]ClO$_4$ Complexes

Porph[a]	μ_{eff},[b] μ_B	
	CHCl$_3$	CH$_3$NO$_2$
OEP	3.95 (9)	4.37 (3)
Etio	4.32 (10)	4.08 (6)
Deut-DME	3.75 (6)	3.39 (13)
PPIX-DME	3.08 (9)	3.32 (11)
T-*p*-Et$_2$NPP	2.65 (4)	3.07 (4)
T-2,5-Me$_2$PP	2.95 (14)	2.81 (18)
T-*p*-OCH$_3$PP	3.10 (4)	3.18 (2)
T-*p*-CH$_3$PP	3.21 (2)	3.10 (13)
TPP	2.89 (7)	2.94 (6)
T-*p*-ClPP	2.31 (23)	2.77 (12)
T-*m*-NO$_2$PP	2.10 (25)	2.05 (12)
TF$_5$PP	2.12 (6)	2.43 (10)

[a] The porphyrin abbreviations are defined in ref 6. [b] The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.84(\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility and T is 308 K.

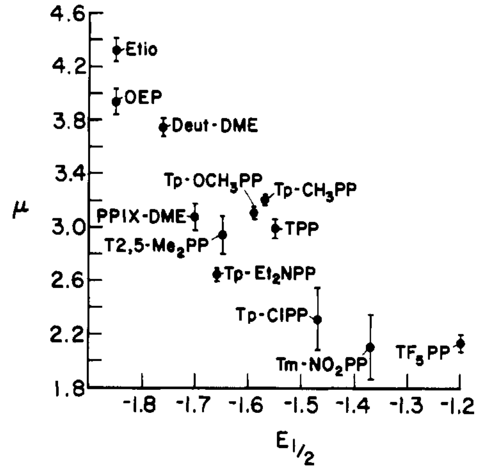

Figure 1. Magnetic moments of [Fe(Porph)(3-Cl(py))$_2$]ClO$_4$ in 30% 3-chloropyridine in chloroform vs. half-wave reduction potentials of the free base. The error bars shown are 1 estimated standard deviation, which is calculated from the several independent measurements.

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(6) Abbreviations used: Porph, any porphyrin; 3-Cl(py), 3-chloropyridine; py, pyridine; X-py, any substituted pyridine; H$_2$OEP, octaethylporphyrin; H$_2$Etio, etioporphyrin III; H$_2$Deut-DME, deuteroporphyrin IX dimethyl ester; H$_2$PPIX-DME, protoporphyrin IX dimethyl ester; H$_2$T-2,5-Me$_2$PP, *meso*-tetrakis(2,5-dimethylphenyl)porphyrin; H$_2$T-*p*-Et$_2$NPP, *meso*-tetrakis(*p*-diethylaminophenyl)porphyrin; H$_2$T-*p*-OCH$_3$PP, *meso*-tetrakis(*p*-methoxyphenyl)porphyrin; H$_2$T-*p*-CH$_3$PP, *meso*-tetrakis(*p*-methylphenyl)porphyrin; H$_2$TPP, *meso*-tetraphenylporphyrin; H$_2$T-*p*-ClPP, *meso*-tetrakis(*p*-chlorophenyl)porphyrin; H$_2$T-*m*-NO$_2$PP, *meso*-tetrakis(*m*-nitrophenyl)porphyrin; H$_2$TF$_5$PP, *meso*-tetrakis(pentafluorophenyl)porphyrin.
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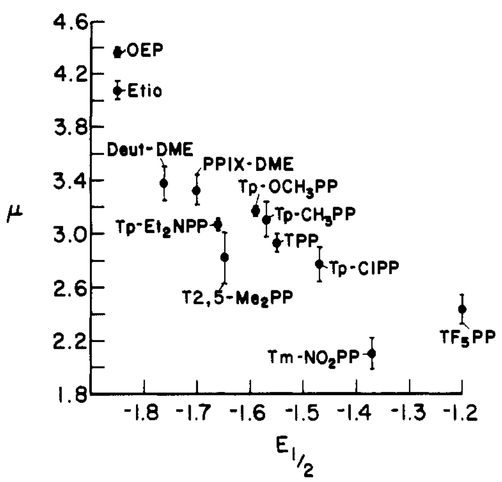

Figure 2. Magnetic moments of $[Fe(Porph)(3\text{-}Cl(py))_2]ClO_4$ in 30% 3-chloropyridine in nitromethane.

A Varian EM-390 NMR spectrometer with a probe temperature of 35 °C was employed. At least three independent measurements were made for each complex. Diamagnetic corrections were applied to all molar susceptibilities and were calculated by direct summations of individual constants[24] or by adding appropriate corrections to the values reported for the free-base porphyrin.[25]

The magnetic moments for the various $[Fe(Porph)(3\text{-}Cl(py))_2]ClO_4$ complexes examined range from 2.0 to 4.4 μ_B and are given in Table I.[26] The results indicate that the porphinato ligand significantly influences the magnetic moment. A reasonable, although not unique, interpretation is that the porphinato ligand affects the amount of the $S = {}^5/_2$ component in an $S = {}^1/_2$, $S = {}^5/_2$ thermal spin equilibrium. The effect of the porphinato ligand on metalloporphyrin chemistry has recently been reviewed.[27] These "cis" effects change redox properties[28] and axial-ligand binding constants[29] and follow Hammet relationships.

The magnetic moment of $[Fe(OEP)(X\text{-}py)_2]ClO_4$ complexes have been shown to be sensitive to the pyridine substituent.[12] A decrease in pyridine basicity results in an increase in high-spin fraction for these $S = {}^1/_2$, $S\ {}^5/_2$ systems. The results presented herein show a dependence on the porphinato-ligand basicity as well. Although direct measurements of porphinato basicity are not available for all species, Hambright et al.[30] have recently compiled extensive lists of half-wave reduction potentials for free-base porphyrins. The reduction potential has been shown to be a good measure of the porphyrin basicity. A linear relationship between these potentials and porphyrin pK_a's has been shown to exist.[30a] A plot of the half-wave reduction potentials of the free-base porphyrins vs. the magnetic moments of the $[Fe(Porph)(3\text{-}Cl(py))_2]ClO_4$ complexes shows the moments to be qualitatively dependent on porphyrin basicity (see Figures 1 and 2). A decrease in the high-spin fraction from approximately 50% to nearly zero is observed as the basicity of the porphyrin decreases.

A possible explanation for the observed porphinato-ligand effect on spin state comes from consideration of a simple charge-attraction model.[7a] The more basic porphyrins donate more electron density to the iron(III) atom and thus decrease its charge attraction for the axial ligands. This results in a decrease of the axial-ligand field, which is known[4] to lead to higher spin multiplicity.

Acknowledgment. The support of the National Institutes of Health (Grant HL-15627) is gratefully acknowledged.

Registry No. $[Fe(OEP)(3\text{-}Cl(py))_2]ClO_4$, 71414-31-8; $[Fe(Etio)(3\text{-}Cl(py))_2]ClO_4$, 89936-65-2; $[Fe(Deut\text{-}DME)(3\text{-}Cl(py))_2]ClO_4$, 89936-67-4; $[Fe(PPIX\text{-}DME)(3\text{-}Cl(py))_2]ClO_4$, 89936-69-6; $[Fe(T\text{-}p\text{-}Et_2NPP)(3\text{-}Cl(py))_2]ClO_4$, 89936-71-0; $[Fe(T\text{-}2,5\text{-}Me_2PP)(3\text{-}Cl(py))_2]ClO_4$, 89936-73-2; $[Fe(T\text{-}p\text{-}OCH_3PP)(3\text{-}Cl(py))_2]ClO_4$, 89936-75-4; $[Fe(T\text{-}p\text{-}CH_3PP)(3\text{-}Cl(py))_2]ClO_4$, 89936-77-6; $[Fe(TPP)(3\text{-}Cl(py))_2]ClO_4$, 72318-32-2; $[Fe(T\text{-}p\text{-}ClPP)(3\text{-}Cl(py))_2]ClO_4$, 89936-79-8; $[Fe(T\text{-}m\text{-}NO_2PP)(3\text{-}Cl(py))_2]ClO_4$, 89936-81-2; $[Fe(TF_5PP)(3\text{-}Cl(py))_2]ClO_4$, 89936-83-4.

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(21) The large excess of axial ligand employed in the measurements ensures that the observed species is six-coordinate. The equilibrium constant for the addition of the second axial ligand to iron porphyrins has been reported to be greater than that of the first for imidazole[22] and pyridine[23] complexes (log β_2 = 6.7 for the addition of 3-Cl(py) to $Fe(TPP)(OClO_3)$).[23a] Furthermore, β_2's increase[22] with increasingly basic porphinates, making it unlikely that the complexes with higher magnetic moments are five-coordinate.

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Molecular Structure of Bis[bis(trimethylsilyl)amido]zinc As Determined by Gas Electron Diffraction

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The synthesis of bis[bis(trimethylsilyl)amido]zinc was first reported by Bürger and co-workers in 1965.[2,3] These authors found the infrared and Raman spectra to be consistent with planar $ZnNSi_2$ fragments and collinear bonds from Zn to the nitrogen atoms, but no conclusions could be drawn about the

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