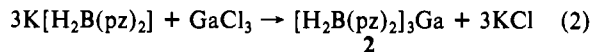


A feature of particular interest is the arrangement of the six-membered GaN_4B rings. As is found typically⁹ in dihydrobis-(pyrazolyl)borate complexes, these rings are in a shallow-boat configuration with Ga–B distances of 3.22 (1) and 3.30 (1) Å. In a number of formally electron-deficient transition-metal complexes of this ligand, a strong agostic B–H...M interaction is observed that can be identified by ¹¹B NMR¹⁰ and IR spectroscopy,^{10,11} as well as short M–B distances in the solid-state structures.^{10,12} In $[\text{H}_2\text{B}(\text{pz})_2]_3\text{Y}$,^{3a} we observed a much weaker agostic interaction, raising the possibility of a similar weak interaction in a main-group complex. Given the long Ga–B distances, no agostic interaction is present in **1**.

Complex **2** is prepared as shown in eq 2.¹³ This complex is



stable in air even in solution and does not react with water. From the equivalence of the pyrazolyl rings in the solution NMR spectrum, this molecule appears to be six-coordinate. We are studying the derivative chemistry of this group of complexes.

Acknowledgment is made to the NIH Biomedical Research Support Grant Award (Grant SO7 RR07160) for support of this research. The NSF (Grant CHE-8411172) and NIH (Grant RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment.

Supplementary Material Available: A table of crystallographic data and full tables of bond distances and angles, positional parameters, and thermal parameters (10 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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- (13) $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (1.58 g, 8.5 mmol) in THF (20 mL, -75°C) was added to GaCl_3 (0.50 g, 2.8 mmol) in THF (10 mL, -75°C). The solution was allowed to warm to room temperature and was stirred over a 5-h period. The solvent was evaporated under vacuum, the residue extracted with CH_2Cl_2 (50 mL), and the solution filtered to remove any insolubles. CH_2Cl_2 was removed under vacuum to yield **2** as a white solid (1.41 g, 2.7 mmol, 96%). This was recrystallized from a CH_2Cl_2 /hexane mixture; mp $155\text{--}157^\circ\text{C}$. ¹H NMR (δ , CDCl_3): 7.65, 6.75 (6, 6; dd, dd; $J = 2.1, 0.7; 2.3, 0.7$ Hz; 3-H, 5-H (pz)); 6.10 (6; t; $J = 2.3$ Hz, 4-H (pz)); 3.5 (broad, BH₂). IR spectrum (benzene, cm^{-1}): 2450 (sh), 2424, 2360 (BH). The high-resolution mass spectrum shows a cluster for $\text{M}^+ - \text{H}$: calcd for $\text{C}_{18}\text{H}_{23}\text{N}_{12}\text{B}_3\text{Ga}$, m/e 509.1704; found, m/e 509.1704. Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_{12}\text{B}_3\text{Ga}$: C, 42.34; H, 4.76. Found: C, 42.24; H, 5.18.

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Reversible CO Binding to Iron(III) Isobacteriochlorins

We² and others^{3–5} have been studying the structural, spectroscopic, magnetic, and chemical properties of iron(II,III) complexes

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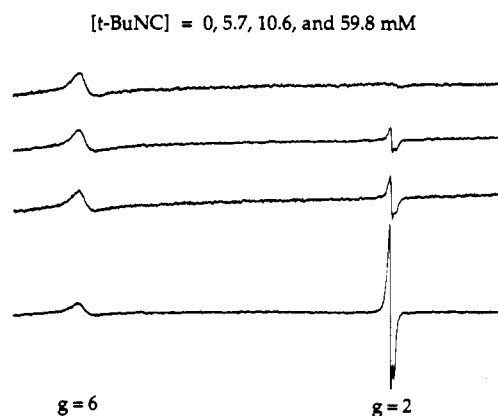
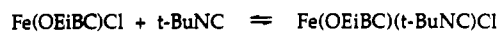


Figure 1. X-Band EPR spectra of 90 K toluene glasses of $\text{Fe}(\text{OEiBC})\text{Cl}$ (0.1 mM) containing varying amounts of $t\text{-BuNC}$. Experimental parameters were as follows: microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 19.9 G. The parameters are a compromise between the optimal settings for high-spin iron(III) and those for a $S = 1/2$ organic radical, and therefore some saturation and distortion of the $g = 2.00$ signal has occurred.

of chlorin and isobacteriochlorin (iBC) macrocycles as models for the heme prosthetic groups in green heme and siroheme proteins and enzymes.^{2a,6} The most dramatic *chemical* differences between iron porphyrins and hydroporphyrins reported to date are electrochemical: reduction potentials for iBC π -oxidation are 250–300 mV less positive than for chlorin π -oxidation and 500–600 mV less positive than for porphyrin π -oxidation.^{2b,3,4e,5e,f,7}

Herein we report that five-coordinate *iron(III)* $\text{Fe}(\text{OEiBC})\text{X}$ complexes exhibit a measurable affinity for CO , $t\text{-BuNC}$, and PF_3 ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{NCS}^-, \text{PhS}^-$).⁸ As far as coordination equilibria

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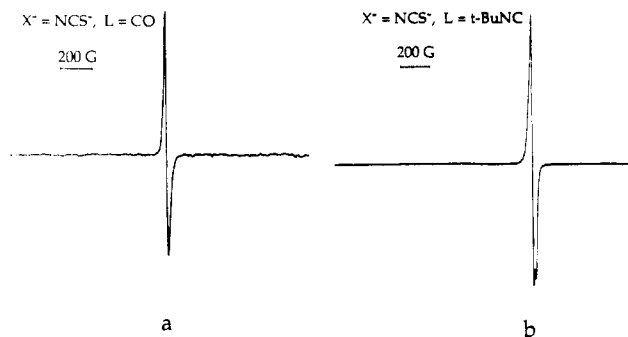
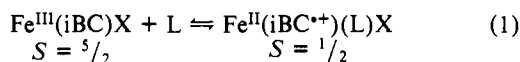


Figure 2. $g = 2$ region of X-band EPR spectra of two representative $\text{Fe}(\text{OEiBC})(\text{L})\text{X}$ complexes (0.1 mM) in toluene glasses at 90 K. Experimental parameters were as follows: microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 2 G.

are concerned, this behavior is more strongly macrocycle dependent (i.e. porphyrin vs hydroporphyrin) than any studied to date: iron(III) porphyrins show *no* detectable affinity for CO. In contrast, the CO affinities of the *iron(II)* complexes $\text{Fe}(\text{OEP})$ and $\text{Fe}(\text{OEiBC})$ only differ by a factor of 2.4, and the CO affinities of $\text{Fe}(\text{OEP})(\text{CO})$ and $\text{Fe}(\text{OEiBC})(\text{CO})$ only differ by a factor of 13.⁹ While some iron(III) porphyrins have been shown to bind alkyl isocyanides, the oxidation state of the metal remains iron(III).¹⁰ However, our data show that the coordination of *t*-BuNC to iron(III) iBCs induces a reversible electronic rearrangement resulting in the reduction of iron(III) to iron(II). Since five-coordinate iron(III) iBC complexes are believed to be the resting state of some siroheme enzymes,^{6a-d} the present results are in harmony with earlier suggestions that enzymatic pathways are possible for iBC-containing enzymes that have no counterpart in classical heme biochemistry.^{2b,3,4,6d}

In a seminal electrochemical study,^{3e} Fajer and Chang showed that the first oxidation of $\text{Fe}^{\text{II}}(\text{POR})(\text{py})(\text{CO})$ or $\text{Fe}^{\text{II}}(\text{CHL})(\text{py})(\text{CO})$ in pyridine/dichloromethane was irreversible, producing free CO and $\text{Fe}^{\text{III}}(\text{POR})(\text{py})_2^+$ or $\text{Fe}^{\text{III}}(\text{CHL})(\text{py})_2^+$, respectively, while the first oxidation of $\text{Fe}^{\text{II}}(\text{iBC})(\text{py})(\text{CO})$ was reversible, producing $\text{Fe}^{\text{II}}(\text{iBC}^+)(\text{py})(\text{CO})$.⁸ Their results suggested to us that a five-coordinate iron(III) iBC complex might bind CO or other π -acid substrates at its vacant (sixth) coordination site by simultaneous oxidation of the macrocycle to a π cation radical and reduction of iron(III) to iron(II), as depicted in eq 1.



We have monitored the equilibrium shown in eq 1 by EPR spectroscopy for combinations of the $\text{Fe}(\text{OEiBC})\text{X}$ complexes and the L π -acid ligands mentioned above (toluene solution or glass). Note that the six-coordinate $S = 1/2$ complex in eq 1 is not charged: the cationic charge on the iBC macrocycle is balanced by X^- . The five-coordinate iron(III) compounds we have used are well-studied high-spin complexes that display characteristic axial (Cl^- , Br^- , NCS^-) or rhombic (PhS^-) EPR spectra at low temperatures.^{2b,4f,11} Addition of CO (NCS^- , PhS^-), *t*-BuNC (all X^-), or PF_3 (Br^-) to samples of these complexes at 296 K, followed

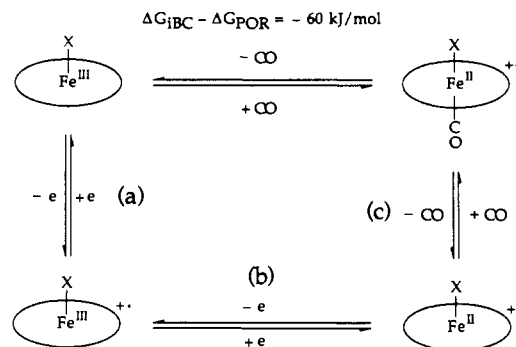


Figure 3. Thermodynamic scheme constructed to estimate $\Delta G_{\text{IBC}} - \Delta G_{\text{POR}}$ for the net reaction shown at the top of the scheme (eq 2 in the text).

by rapid cooling to 90 K, resulted in the decrease of the strong signal in the $g = 6$ region and the concomitant appearance of a relatively sharp signal at $g = 2.00$, as shown in Figures 1 and 2. These spectral changes were reversible if the π -acid ligand was removed from the sample by vacuum distillation.

Figure 1 also shows the effect of addition of incremental amounts of *t*-BuNC to a sample of $\text{Fe}(\text{OEiBC})\text{Cl}$. Double integrations experiments confirmed that the amount of the $g = 2.00$ species that is produced is approximately equal to the amount of the $g = 6$ $\text{Fe}(\text{OEiBC})\text{Cl}$ complex that had been consumed.¹² The evidence that the $g = 2.00$ species are iron(II) iBC π -radicals, as formulated in eq 1, is the following: (i) the $g = 2.00$ signals were at higher field than the average g value for any reported low-spin iron(III) porphyrin¹¹ or hydroporphyrin^{2b} complex; (ii) the $g = 2.00$ signals were much more narrow than the signals for low-spin iron(III) porphyrin and hydroporphyrin complexes; (iii) the $g = 2.00$ signals persisted in fluid toluene solution at 190 K (and in some cases, with a large excess of ligand present, at room temperature), behavior consistent with macrocycle-based radicals and inconsistent with that expected for *any* iron(III) complex; (iv) visible absorption spectra of solutions of $\text{Fe}(\text{OEiBC})\text{Cl}$ and $\text{Fe}(\text{OEiBC})\text{NCS}$ containing *t*-BuNC or CO showed a decrease in intensity of the prominent visible and Soret bands and an overall decrease in intensity throughout the 800–300-nm region, behavior that has been previously reported for $\text{iBC} \rightarrow \text{iBC}^+ + e^-$ oxidations.^{3,4e,6d,13} The persistence of the $g = 2.00$ signals at relatively high temperatures and the tendency of these signals to saturate at microwave power settings greater than 5 mW strongly suggest that the spin state of the iron(II) atom in the proposed $\text{Fe}^{\text{II}}(\text{iBC}^+)(\text{L})\text{X}$ complexes is $S = 0$.

Figure 2 shows the $g = 2.00$ region of EPR spectra of two selected compounds. The sharp signals were generally anisotropic, as in Figure 1 and 2b. Notable exceptions were the spectra of $\text{Fe}^{\text{II}}(\text{OEiBC}^+)(\text{CO})\text{X}$ ($\text{X}^- = \text{PhS}^-$, NCS^-), which appeared to be isotropic, as in Figure 2b. The apparent isotropy is not due to the mixture of OEiBC *trans,cis,trans* (tct) and *trans,trans,trans* stereoisomers in our samples, which could potentially lead to a set of overlapping signals. A spectrum of $\text{Fe}^{\text{II}}(\text{tct-OEiBC}^+)(\text{t-BuNC})\text{Cl}$, prepared from the single stereoisomer *tct*- H_2OEiBC , also exhibited an anisotropic $g = 2.00$ signal like the one shown in Figure 1 for the mixture of isomers. While π -radicals of *some* iBCs exhibit resolvable pyrrole proton hyperfine splitting in EPR spectra (e.g. $\text{H}_2\text{DMOEiBC}^{+14}$), the radical cation H_2OEiBC^+ does not,^{4e} so it is not unexpected that the $g = 2.00$ signals for

- (8) Abbreviations: iBC, any isobacteriochlorinate^{2a} dianion; CHL, any chlorinate^{2a} dianion; POR, any porphyrinate dianion; OEiBC, 2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrinate (octaethylisobacteriochlorinate) dianion; DMOEiBC, 2,7-dihydro-2,7-dimethyl-3,3,8,8,12,13,17,18-octaethylporphyrinate (dimethyloctaethylisobacteriochlorinate) dianion; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinate (octaethylchlorinate) dianion; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinate dianion.
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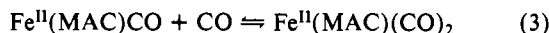
- (12) These experiments were performed in consultation with Professor S. S. Eaton, taking into account any changes in the following parameters, which affect signal intensity: microwave power, modulation amplitude, receiver gain, and spectral scan width. Control experiments were performed to insure that the signal intensities measured were not being altered by saturation. Our determination of the relative concentrations of $S = 5/2$ iron(III) hydroporphyrins and organic radicals is based on unpublished calibration work performed by Professors S. S. Eaton and G. R. Eaton with $\text{Fe}(\text{TPP})\text{X}$ complexes and RNO nitroxyl radicals.
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our OEiBC^{•+} radicals did not exhibit resolvable hyperfine splitting.

Figure 3 shows that the overall reaction eq 2 can be broken down into three separate equilibria (MAC = POR, CHL, or iBC):



(a) oxidation of the Fe^{III}(MAC)X macrocycle by one electron, (b) reduction of the Fe^{III}(MAC^{•+})X to Fe^{II}(MAC^{•+})X by one electron, and (c) binding of CO to Fe^{II}(MAC^{•+})X. We estimate the difference of $\Delta E_{1/2}$ ($E_{1/2}(\text{iBC}) - E_{1/2}(\text{POR})$) for equilibrium a to be -0.60 V, based on the literature values of $E_{1/2}$ for the reversible oxidations of Zn(OEiBC) and Zn(OEP);^{4c} $\Delta E_{1/2}$ for equilibrium b is estimated to be 0.04 V, based on the literature values of $E_{1/2}$ for the reversible reductions of Fe(OEiBC)(py)₂⁺ and Fe(OEP)(py)₂⁺;^{2b} the ratio $K_{\text{eq}}(\text{iBC})/K_{\text{eq}}(\text{POR})$ for equilibrium c is estimated to be 13, based on the literature value of this ratio for the related equilibrium 3.⁹ Equilibrium a obviously



has the most profound effect on the overall reaction (eq 2). When the estimated free energy changes are summed for equilibria a-c, we conclude that $\Delta G_{\text{iBC}} - \Delta G_{\text{POR}}$ is probably equal to approximately -60 kJ mol⁻¹. Therefore, while it is not possible to compare directly the OEiBC and OEP equilibrium constants for eq 2, we conclude that the CO affinity for a five-coordinate iron(III) iBC complex is probably larger by several orders of magnitude than the CO affinity for the corresponding iron(III) porphyrin complex.¹⁵

Recent studies have demonstrated that iron(III) iBC π cation radicals are viable species for at least two reaction states of the hemoprotein subunit of *Escherichia coli* sulfite reductase.^{6d} Together with the results for iron(II) iBC π cation radicals and for nickel(II) and nickel(III) iBC π cation radicals,¹³ the emerging picture is that iBC π -oxidation may be as important, or more important, in siroheme enzymology than porphyrin π -oxidation is in heme biochemistry.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Bruker ER-300 EPR spectrometer was purchased with a grant from the National Science Foundation. We thank Professor S. S. Eaton for stimulating discussions and advice.

(15) K_{eq} for eq 1, measured by a visible spectrophotometric titration, is approximately 10² M⁻¹ for X⁻ = NCS⁻ and L = *t*-BuNC in dichloromethane at -78 °C. Details for this and related experiments will be reported in the full paper.

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Synthesis and Structure of Ti(OAr-2,6Prⁱ)₂(py-4Ph)₃ (OAr-2,6Prⁱ = 2,6-Diisopropylphenoxide; py-4Ph = 4-Phenylpyridine): A Compound Containing both Reduced and Nonreduced 4-Phenylpyridine Ligands Bound to Titanium

The last few years have seen some dramatic developments in the field of low-valent early d-block element chemistry.¹ In particular, the use of sterically demanding oxygen donor ligands, e.g. alkoxides, siloxides and aryloxides, attached to group 4-6 metal centers containing dⁿ ($n = 1-4$) electron configurations results

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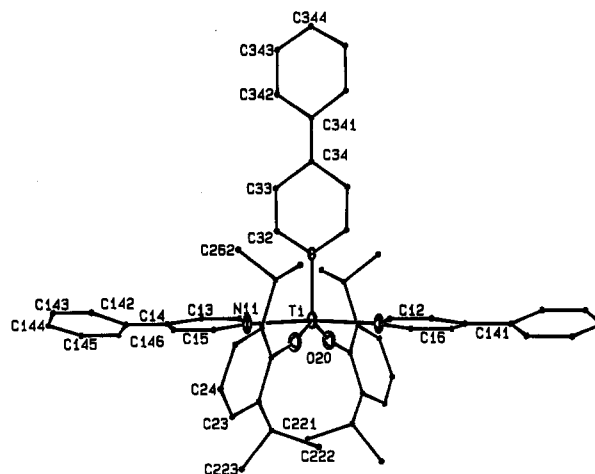
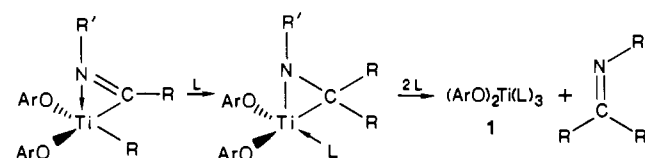


Figure 1. ORTEP view of **1** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) are as follows: Ti-O(20) = 1.864 (4), Ti-N(11) = 2.236 (4), Ti-N(31) = 2.090 (7); O(20)-Ti-O(20)' = 138.2 (3), O(20)-Ti-N(11) = 90.3 (2), O(20)-Ti-N(11)' = 87.6 (2), O(20)-Ti-N(31) = 110.9 (1), N(11)-Ti-N(11)' = 174.2 (3), N(11)-Ti-N(31) = 92.9 (2), Ti-O(20)-C(21) = 165.6 (4).

Scheme 1^a



^a L = py-4Ph; R = CH₂Ph; R' = *tert*-butyl; ArO = 2,6-diisopropylphenoxide.

in metal-based systems capable of carrying out a variety of interesting reduction chemistry.²⁻⁵ During our studies of the chemistry associated with the lower oxidation states of titanium supported by sterically demanding aryloxy ligands, we have demonstrated a ligand-induced reductive-elimination method for the generation of highly reducing titanium(II) compounds.⁵ In this communication, we wish to report on an extension of this work that results in the formation of an interesting compound that structural studies clearly demonstrate as containing both reduced and nonreduced 4-phenylpyridine ligands bound to the same metal center.⁶

The η^2 -imine compound Ti(OAr-2,6Prⁱ)₂[η^2 -Bu^tNC-(CH₂Ph)₂](py-4Ph)⁵ is formed readily by treatment of the η^2 -iminoacyl precursor Ti(OAr-2,6Prⁱ)₂(η^2 -Bu^tNCCH₂Ph)(CH₂Ph)⁷ with 4-phenylpyridine (py-4Ph; 1 equiv) in benzene. Further treatment of the red-orange η^2 -imine with excess 4-phenylpyridine in benzene/hexane (1:1) causes the development of a deep purple color, and after 12 h, long purple needles of a new paramagnetic product of stoichiometry Ti(OAr-2,6Prⁱ)₂(py-4Ph)₃ (**1**) are produced (Scheme I).⁸ Examination of the supernatant of the

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