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Gated Glyoximes: Conformationally Flexible Boron-Linked Superstructure in Iron (Dioximato)borate Complexes

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Macrocyclic ligands which provide a planar tetradentate ligand environment and also incorporate a superstructure capable of through-space effects on axial ligand binding or reactivity have received much attention.[1-4] Here we describe an approach to superstructured nonporphyrinic metal complexes in which boron-linked groups are positioned in close proximity to axial binding sites and function as a flexible "gate" with respect to ligand access to iron.

Boron-derivatized complexes[5] are obtained in high yield by reaction of the substitution-inert[6] $Fe(DMGH)_2(PY)(CO)$ with common boron reagents as shown in eqs 1–3 (DMGH =

$$Fe(DMGH)_2(PY)(CO) + 2BH_3Me_2S \rightarrow Fe(DMGBH_2)_2(PY)(CO) + 2H_2 + 2Me_2S \quad (1)$$

$$Fe(DMGH)_2(PY)(CO) + 2BBN\text{–}H \rightarrow Fe(DMGBBN)_2(PY)(CO) + 2H_2 \quad (2)$$

$$Fe(DMGH)_2(PY)(CO) + (Ph_2B)_2O \rightarrow Fe(DMGBPh_2)_2(PY)(CO) + H_2O \quad (3)$$

dimethylglyoximate, PY = pyridine, BBN–H = 9-borabicyclo[3.3.1]nonane). A alternative route to the $Fe(dmgBPh_2)_2$ system has been previously reported.[7] Subsequent conversion to a variety of axial-ligated derivatives is achieved with complete retention of the boron substituents through ligand substitution reactions exhaustively characterized previously in the $Fe(DMGH)_2$ and $Fe(DMGBF_2)_2$ systems.[6]

Two conformational isomers of the macrocycle arise based on axial vs equatorial orientations of the R groups on each boron. Both C_{2h} and C_{2v} structures have been reported in the solid state.[7a,8] Axially oriented phenyl rings in $Fe(DMGBPh_2)_2$ complexes project over the metal-binding site giving rise to three different ligand environments (Figure 1). In the C_{2h} conformer, found in $Fe(DMGBPh_2)_2(MeIm)_2$,[7a] both ligands face a single phenyl ring. In the C_{2v} confomer, one ligand lies between two parallel phenyl rings while the other experiences a wide open axial environment. The axial phenyl groups resemble the pickets in picket-fence porphyrins[1b] but are in much more intimate contact with metal-bound ligands and "swing" easily in response to entering and leaving ligands. The terms "gates" and "pickets" are appropriate!

The predominant solution conformers in the $Fe(DMGBPh_2)_2$ system are established on the basis of the large upfield shifts of ligand proton resonances (Figure 2) when that ligand lies over the face of an axially directed phenyl group.[9-11] NMR shift mapping and MM2 molecular modeling both place ligand protons within van der Waals contact (3.5 Å) with the face of the axial phenyl groups. Bis-ligated complexes adopt the C_{2h} conformation. When the axial ligands differ, the complex relieves nonbonded contacts by adopting the C_{2v} conformation, directing both axial phenyls toward the smaller ligand. The largest shifts are experienced by CH_3CN in $Fe(DMGBPh_2)_2(PY)(CH_3CN)$ and by pyridine in $Fe(DMGBPh_2)_2(PY)(PMePh_2)$ when these ligands are "sandwiched" between two phenyl rings. These examples illustrate how a ligand may be used in the remote control of the peripheral environment and orientation of the trans ligand.

The barrier for the conformational flip (perhaps <5 kcal/mol as found in diamine chelate rings[12]) places gross movements of boron-linked groups on a much faster time scale than those associated with ligation. The pentacoordinate intermediate, formed along the reaction coordinate for ligand substitution, should adopt a C_{2v} geometry (regardless of reactant conformation[13]) in which both axial phenyls pinch over the vacant site (closing the "gates" following ligand egress). This geometry is predicted by MM2 studies and found in $Co(DMGBF_2)_2(PY)^-$.[8]

The dynamic linkage between axial ligation and conformation is summarized in the free energy profile for the BF_2 and BPh_2

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(10) Pyridine ring orientations are proposed on the basis of the following. In $Fe(DMGH)_2$ and $Co(DMGH)_2$ complexes, axial pyridine and imidazole ligands lie in a plane which bisects the O–H–O groups: Bowman, K.; Gaughan, A. P.; Dori, Z. *J. Am. Chem. Soc.* **1972**, *94*, 727. Lopez, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chem.* **1986**, *25*, 2962. This orientation is prohibited when an axial boron group lies on the same side but is favored on the open face of a C_{2v} conformer.[8b]

(11) Conformational assignments are fully supported by analysis of the phenyl proton resonances. The phenyl protons display a single pair of multiplets in bis complexes consistent with equivalent average environments for all four rings. In mixed complexes two pairs of peaks are found regardless of conformation. Phenyls constrained to face pyridine ligands as in the $PMePh_2$ derivative are the farthest upfield (δ 6.66, 6.38), while those constrained to equatorial sites are the farthest downfield (δ 7.65, 7.35).

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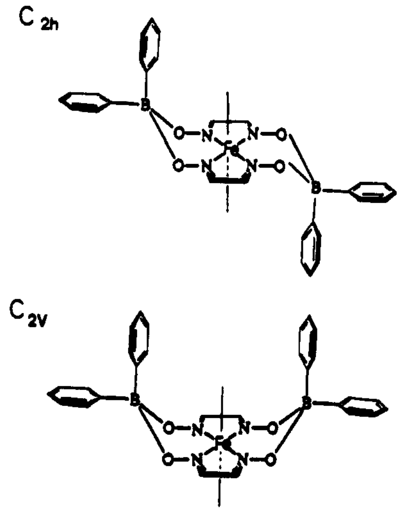

Figure 1. Conformational isomers of $\mathrm{Fe(DMGBPh_2)_2}$. (DMG methyl are groups omitted.)

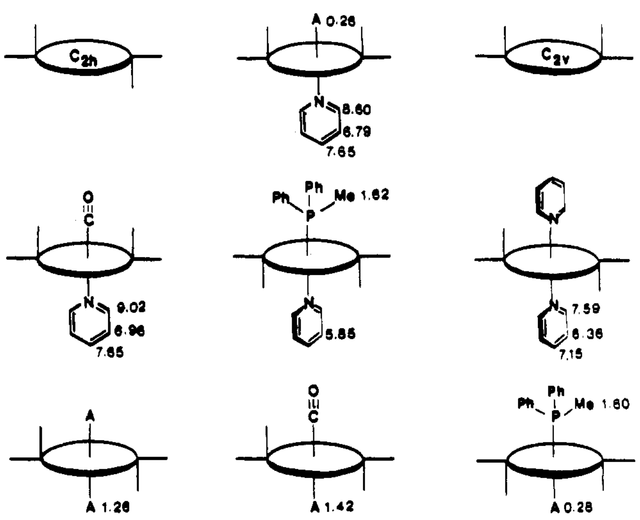

Figure 2. Predominant conformations for ligated $\mathrm{Fe(DMGBPh_2)_2}$ complexes (A = $\mathrm{CH_3CN}$) in $\mathrm{CDCl_3}$. The ^{1}H NMR shifts for pyridine protons and methyl protons in $\mathrm{CH_3CN}$ and $\mathrm{PMePh_2}$ are given.[9,10]

complexes given in Figure 3. Reactant energies are obtained from stepwise constants for pyridine binding (eq 4)[14] measured by spectrophotometric titration.[6b] Transition-state free energies are obtained from flash photolysis studies of reaction 5.[15]

Ground-state destabilizing effects in the $\mathrm{BPh_2}$ complexes arise *only* when axial PY–phenyl contacts are required by conformation. These interactions are avoided in $\mathrm{Fe(CH_3CN)(PY)}$ and Fe(PY)(CO) in the C_{2v} geometry in which the pyridine ligand lies on the open face. As a result, ΔG's differ significantly for the $\mathrm{Fe(PY)_2}$ complexes but not for $\mathrm{Fe(PY)(CH_3CN)}$ or Fe(PY)(CO).

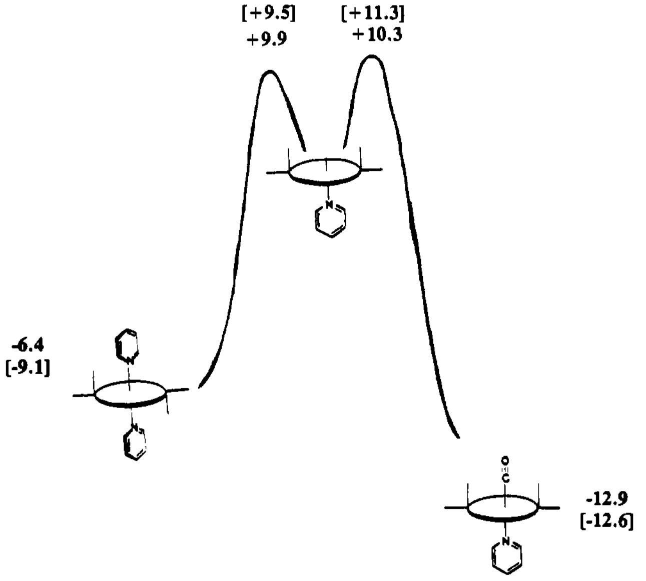

Figure 3. Free energy vs reaction coordinate diagram. Ground- and transition-state free energies (kcal/mol) for $\mathrm{BF_2}$ (in brackets) and $\mathrm{BPh_2}$ complexes are relative to $\mathrm{FeN_4(CH_3CN)_2}$.

$$\mathrm{FeN_4(CH_3CN)_2} \overset{K_1}{\rightleftharpoons} \mathrm{FeN_4(CH_3CN)(PY)} \overset{K_2}{\rightleftharpoons} \mathrm{FeN_4(PY)_2} \qquad (4)$$

$$\mathrm{FeN_4(PY)_2} \underset{k_{+\mathrm{PY}}}{\overset{k_{-\mathrm{PY}}}{\rightleftharpoons}} \mathrm{FeN_4(PY)} \underset{k_{-\mathrm{CO}}}{\overset{k_{+\mathrm{CO}}}{\rightleftharpoons}} \mathrm{FeN_4(PY)(CO)} \qquad (5)$$

Rates of CO binding to $\mathrm{Fe(PY)_2}$ are 500 times faster in the $\mathrm{BPh_2}$ system under conditions of 0.1 M [PY] in CO-saturated dichloromethane ($\mathrm{BF_2}$, $k_{\mathrm{obs}} = 0.0006$ s^{-1}; $\mathrm{BPh_2}$, $k_{\mathrm{obs}} = 0.3$ s^{-1}). This difference can be shown to arise from a combination of "on" ($k_{+\mathrm{CO}}/k_{+\mathrm{PY}}$) and "off" rate effects. Pyridine loss is 44 times faster in the $\mathrm{BPh_2}$ system in part due to repulsive ground-state interaction with axial phenyl groups.

The relative rate of CO vs PY addition to the $\mathrm{Fe(dmg\text{-}BPh_2)_2(PY)}$ intermediate is 10 times larger than for the $\mathrm{BF_2}$ analogue. This result is reflected in the transition-state free energy differences shown in Figure 3. These "on-rate" effects are typical of those associated with blockage of ligand access to iron in hindered hemes.[1a] The facile movement of peripheral phenyl groups, which facilitate ligand access to iron, mimics the mobile nature of distal residues in myoglobin.[16]

The 15 atom $\mathrm{FeN_4C_4O_4B_2}$ unit exemplifies the principles of economy of design within a functional structure.[17] It is potentially a highly adaptable molecular device which may be useful for protein modeling, for fragment positioning,[18] or for the intramolecular control of the peripheral environment around a ligand.

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(14) Stepwise formation constants, $\mathrm{CH_2Cl_2}$, 25 °C, (eq 4): $\mathrm{BPh_2}$, $K_1 = 1.2 \times 10^4$, $K_2 = 4$; $\mathrm{BF_2}$, $K_1 = 1.8 \times 10^4$, $K_2 = 250$; $\mathrm{BH_2}$, $K_1 = 8 \times 10^4$, $K_2 = 450$. Estimated error: 10%. Data analysis is as described previously.[6b]

(15) Kinetic data for eq 5, $\mathrm{CH_2Cl_2}$, 25 °C: $k_{-\mathrm{PY}} = 6.7$, 0.15, and 1.5 s^{-1}; $k_{+\mathrm{PY}}/k_{+\mathrm{CO}} = 2$, 20, and 30 s^{-1}; $k_{-\mathrm{CO}} = 6 \times 10^{-5}$, 2×10^{-5}, and 2×10^{-5} s^{-1} for $\mathrm{BPh_2}$, $\mathrm{BF_2}$, and $\mathrm{BH_2}$, respectively. Estimated errors are 10% for k_- and 20% for $k_{+\mathrm{PY}}/k_{+\mathrm{CO}}$. For the method used, see ref 6b.

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