The reactions of **1** with diazoalkanes (and organic azides) show an amazing structural diversity. The nature of the products depends on subtle electronic and steric factors and on the availability of other electron-donor groups adjacent to the terminal nitrogens.[22]

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Supplementary Material Available: Atomic coordinates (Table I) and crystal data collection statistics (Table II) for $Cp_2Mo_2(CO)_4(\mu\text{-}N_2C(CO_2Et)_2)$ (**8**) and atomic coordinates (Table III) and crystal data collection statistics (Table IV) for $Cp_2Mo_2(CO)_2(NAr)(\mu\text{-}CoN_3Ar)$ (**9**, Ar = 4-*t*-BuC_6H_4) (4 pages). Ordering information is given on any current masthead page.

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(22) Since submission of this manuscript, several pertinent papers have emerged: (a) $Cp^*{}_2Mo_2(CO)_4$ + $RC(O)C(N_2)R$: Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H. *Organometallics* **1982**, *1*, 1673. (b) $Cp^*{}_2Mo_2(CO)_4$ + Me_2CN_2: Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *240*, 381. (c) $Cp^*{}_2Mo_2(CO)_4$ + CH_2N_2: Herrmann, W. A.; Bell, L. K. *Ibid.* **1982**, *239*, C4.

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Hydrogen Bonding from Coordinated Imidazole in Ferric Porphyrin Complexes. Effect on the Fe(III)/Fe(II) Reduction Potential

Sir:

Most heme proteins contain one or more histidine residues bound to the iron through the imidazole imine nitrogen. The acidity of the imidazole NH proton is increased by coordination, e.g., by about 4 pK_a units in methemoglobin and metmyoglobin.[1,2] Several studies involving simple imidazole complexes of ferrous and ferric porphyrins show that hydrogen bonding or deprotonation of the imidazole N_δ–H moiety can have substantial effects on stability constants,[3,4] visible and Raman spectra,[4-7] and addition[8] and substitution[9] kinetics. X-ray structures of several heme proteins suggest that the proximal imidazole NH is hydrogen bonded to electron-rich groups in the protein.[10-13] MO calculations[14] and resonance Raman[15,16] and ESR[17,18] results have also been interpreted in terms of proximal imidazole hydrogen bonding in hemoglobin, cytochrome *c*, and horseradish peroxidase.

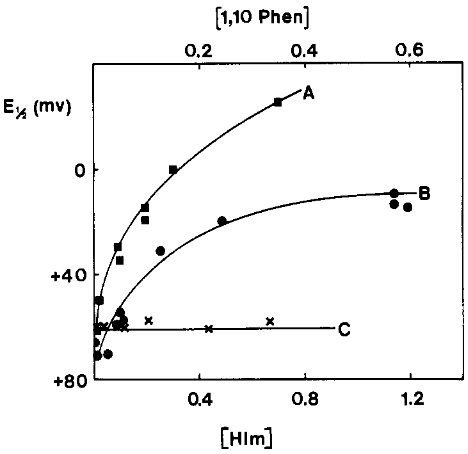

Figure 1. Half-wave potentials of the Fe(III)/Fe(II) couple in acetone at room temperature for (A) [[Fe(TPP)(HIm)$_2$]Cl] = 1.00 × 10^{-3} M, [HIm] = 0.020 M, [phen] as shown; (B) [[Fe(TPP)(HIm)$_2$]Cl] = 1.00 × 10^{-3} M, [HIm] as shown; (C) [[Fe(TPP)(*N*-MeIm)$_2$]Cl] = 1.00 × 10^{-3} M, [*N*-MeIm] = 0.101 M, [phen] as shown.

Several groups have discussed the possible significance of hydrogen bonding from the proximal imidazole in heme proteins. It has been suggested that such hydrogen bonding allows alterations in the electron density at the metal and thereby affects the kinetics and thermodynamics of trans ligand binding, the Fe(III)/Fe(II) reduction potential, and the ease of protein conformational change.[4,14,19,20] These ideas have been suggested to account in part for the cooperative binding of ligands and for the control of the O_2/CO affinity ratio in hemoglobin.[6,8,14,16,17,21,22]

Hydrogen bonding from the proximal imidazole increases the electron density on the metal and therefore would be expected to stabilize the ferric state (relative to ferrous). Changes in the hydrogen-bond strength with the metal oxidation state may be coupled to tertiary structural changes in the protein.[4,14] This provides a mechanism whereby the protein can modulate the redox potential. A correlation of redox potential with the extent of hydrogen bonding to sulfur has been suggested for iron–sulfur proteins.[23,24]

In this report we show that hydrogen bonding from coordinated imidazole in [Fe(TPP)(HIm)$_2$]Cl (**1**; TPP = anion of *meso*-tetraphenylporphyrin; HIm = imidazole) has a substantial effect on the Fe(III)/Fe(II) reduction potential. Walker[3] has shown that excess imidazole forms hydrogen bonds to the coordinated HIm in **1**. It is also known[25,26] that 1,10-phenanthroline (phen) forms similar hydrogen bonds to **1**. phen is a particularly useful base for hydrogen-bonding studies with complexes such as **1** because it is not able to replace the imidazole ligands.[25]

The electrochemistry of complexes **1** and [Fe(TPP)(*N*-MeIm)$_2$]Cl (**2**) was studied by cyclic voltammetry at room temperature in acetone solvent. The metalloporphyrin com-

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plexes were 1.00×10^{-3} M and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. Solutions were deoxygenated with nitrogen presaturated with acetone and blanketed with nitrogen during the experiment. Cyclic voltammograms were recorded with a BAS CV-1B-120 instrument using the standard three-electrode system. The counterelectrode was a Pt wire, and the working electrode was a Pt disk, which was polished before each experiment. The reference electrode consisted of Ag/AgCl in acetone saturated with LiCl. The reference electrode stability was checked daily by measuring the half-wave potential of ferrocene, which was taken to be +0.660 V. The Fe(III)/Fe(II) couple for all solutions was both chemically and electrochemically reversible at scan rates used (400–1000 mV/s). Peak separations were 60 ± 10 mV for all cyclic voltammograms. The anodic and cathodic peak potentials were measured by recording at four scan rates and extrapolating the peak positions to zero current in order to compensate for *iR* drop. Under the conditions used, however, *iR* drop was not a serious problem. Half-wave potentials reported are the average of the anodic and cathodic peak potentials.

The results are given in Figure 1. Curve A was obtained when phen was added to a solution of [Fe(TPP)Cl] containing sufficient HIm to ensure essentially complete formation of the bis(imidazole) complex **1**. The phen addition causes no change in the visible spectrum, and previous studies[25,26] show that the only interaction is hydrogen-bond formation from coordinated HIm. As curve A shows, hydrogen bonding with phen causes a cathodic shift in $E_{1/2}$ of more than 100 mV. The same behavior is seen with excess HIm as the base (curve B), for which the limiting shift in $E_{1/2}$ is about 60 mV. Apparently the hydrogen bonding to phen is somewhat stronger than to free imidazole. Verification that the cathodic shifts in curves A and B are indeed due to hydrogen bonding was established by measuring the dependence of $E_{1/2}$ of **2** as a function of free *N*-MeIm and phen. Hydrogen bonding from **2** is, of course, not possible and as expected there is no dependence of $E_{1/2}$ on the phen concentration (curve C). Solutions of **2** with free *N*-MeIm between 0.1 and 0.8 M also gave a constant $E_{1/2}$ (+60 mV).

Our results show that hydrogen bonding from coordinated imidazole in iron porphyrins stabilizes the ferric state and that this stabilization depends on the acceptor base, and can be quite substantial (ca. 10 kJ with phen and 6 kJ with HIm). It therefore appears reasonable that one mechanism for redox potential modulation in heme proteins may be a coupling of hydrogen-bond strength with tertiary structural changes in the protein.[4,14] Further investigations into these effects are in progress.[27]

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Registry No. 1, 25442-52-8; **2**, 41121-76-0; imidazole, 288-32-4.

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(27) Hydrogen bonding in [Fe(PPIXDME)$(HIm)_2$]Cl has also been observed: O'Brien, P.; Sweigart, D. A., research in progress.

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