the $[Co(phen)_3]^{3+}$ studies[4,7] somewhat surprising. The greater kinetic partitioning[7] of $[Co(phen)_3]^{3+}$ to the acidic site in spinach plastocyanin relative to parsley also suggests greater electrostatic forces in effect here for the spinach protein.

The clear demonstration of multiple electron transfer sites on a protein's surface for a single reacting redox partner gives reason to be cautious in interpreting kinetic parameters for metalloprotein redox processes. In particular, the interpretation of overall activation parameters is hazardous because they may represent averages for very different reactive sites. However, rate studies at several temperatures in the presence of inhibitors at sufficiently high concentration for maximal inhibition combined with similar studies in the absence of inhibitor may allow the correct partitioning of the overall activation parameters between multiple sites since these inhibition studies provide a means of isolating paritcular redox sites. This may provide a better understanding of the solvent and peptide reorganization processes that accompany electron transfer in proteins than has heretofore been possible.

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Registry No. $FeCp_2^+$, 12125-80-3; $(HOCH_2)FeCp_2^+$, 34742-72-8; $(ClHg)FeCp_2^+$, 34742-71-7; $[(NH_3)_5CoNH_2Co(NH_3)_5]^{5+}$, 15771-98-9; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Zr(C_2O_4)_4]^{4-}$, 21392-82-5.

Notes

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Synthesis, Characterization, and Reactivity of New Ruthenium and Osmium N_2O_2 Complexes

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The stabilization[1-11] and reactivity[12-19] of transition-metal–oxo complexes have been topics of much current study. In particular, studies involving (polypyridyl)ruthenium–oxo complexes[13,20] and (phosphine)ruthenium(IV)–oxo complexes[12] have demonstrated the utility of ruthenium–oxo centers as organic substrate oxidation agents and catalysts. In addition, N_2O_2 tetraanionic ligands[21-23] and dianionic ligands[24-26] have been combined with first-, second-, and third-row transition metals, in order to generate new transition-metal complexes in which the metal center displays several accessible oxidation states.

In order to further investigate the effects that ligand systems may have on the stabilization of several oxidation states of ruthenium and osmium complexes, we present the synthesis and the characterization of a set of ruthenium and osmium complexes utilizing an N_2O_2 dianionic ligand originally synthesized by Jager,[27] and selected for this study due to its anticipated redox inertness and chemically robust nature. In addition, the redox reactivity of an $N_2O_2Os^{VI}(O)_2$ complex is examined, where the oxidation of benzyl alcohol to benzaldehyde is observed. An unusual reductive activation of the $N_2O_2Os^{VI}(O)_2$ is necessary for substrate oxidation to occur.

Experimental Section

Materials. $Ru^{II}(PPh_3)_3Cl_2$ and $K_2[Os^{VI}(O)_2(OH)_4]$ were prepared as described in the literature.[28,29] The *N,N'*-o-phenylenebis(2-acetyl-1-amino-1-buten-3-one) ligand (H_2phenba) was synthesized by modifications of literature preparations.[27,30] All solvents were reagent grade unless further purification was indicated.

***trans*-[(phenba)Ru^{II}(PPh$_3$)$_2$].** A 500-mg sample of $RuCl_2(PPh_3)_3$ (0.54 mmol), 177 mg of phenba (0.54 mmol), and 0.15 mL of Et_3N (1.08 mmol) are heated to reflux in 100 mL of degassed THF for 3 h, during which time the solution turns dark red. The solution is cooled and filtered, and then 100 mL of hexanes is added to the filtrate to induce precipitation. A red-brown solid is collected, washed with hexane, and dried; yield 69%. Anal. Calcd for $RuC_{54}H_{48}O_4N_2P_2(H_2O)$: C, 66.79; H, 5.29. Found: C, 66.75; H, 5.54.

***trans*-[(phenba)Ru^{II}(CO)$_2$].** A 250-mg sample of (phenba)Ru^{II} $(PPh_3)_2$ (0.26 mmol) is dissolved in 40 mL of THF. Carbon monoxide is bubbled into this solution until the translucent red-brown solution turns to a transparent orange solution. When the solution is cooled in an ice bath for 15 min, a yellow solid precipitate is formed. Isolation of this

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(1) Arzoumanian, H.; Baldy, A.; Lai, R.; Metzger, J.; Nkeng Peh, M. L.; Pierrot, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1151.

(2) Balch, A. L.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983–2985.

(3) Buchler, J.; Smith, P. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 341.

(4) Budge, J. R.; Gatehouse, B. M. K.; Nesbit, M. C.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1981**, 370.

(5) Calderwood, T. S.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8272–8273.

(6) Leung, T.; James, B. R.; Dolphin, D. *Inorg. Chim. Acta* **1983**, *79*, 180–181.

(7) Griffith, W. P.; Pawson, D. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1315–1320.

(8) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844–3846.

(9) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407–1409.

(10) Che, C. M.; Wong, K. Y.; Leung, W. H.; Poon, C. K. *Inorg. Chem.* **1986**, *25*, 345–348.

(11) Hawkins, J. M.; Dewan, J. C.; Sharpless, K. B. *Inorg. Chem.* **1986**, *25*, 1501–1503.

(12) Marmion, M. E.; Takeuchi, K. T. *J. Am. Chem. Soc.* **1986**, *108*, 510–511.

(13) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310–2312.

(14) Yuan, L. C.; Calderwood, T. S.; Bruice, T. C. *J. M. Chem. Soc.* **1985**, *107*, 8273–8274.

(15) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 507–508.

(16) Kolomnikov, I. S.; Koreshkov, Y. D.; Lobeeva, T. S.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432.

(17) Kress, J.; Wesolek, M.; Le Ny, J. P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1039–1040.

(18) Rappé, A. K.; Goddard W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448–456.

(19) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. S.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515–4516.

(20) (a) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601–3602. (b) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436–444. (c) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106–4115, 5070–5076.

(21) Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198–199.

(22) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472.

(23) Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, *108*, 2088–2090.

(24) Che, M.; Cheng, W. K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703–706.

(25) (a) Nishinaga, A.; Tetsuo, T.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1974**, 896–897. (b) Nishinaga, A.; Tomita, H. *J. Mol. Catal.* **1980**, *7*, 179–199. (c) Nishinaga, A.; Yamazaki, S.; Nagusa, H.; Shimoyama, T.; Matsuura, T. *Nippon Kagaku Kaishi*, **1985**, *3*, 378–386.

(26) Calderazzo, F.; Floriani, C.; Henzi, R.; L'Eplattenier, F. L. *J. Chem. Soc. A* **1969**, 1378–1386.

(27) Jager, E. *Z. Chem.* **1964**, *4*, 437.

(28) Malin, J. M. *Inorg. Synth.* **1980**, *20*, 61–62.

(29) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. S. *Inorg. Synth.* *12*, 237–240.

(30) Riley, D. P.; Stone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1976**, *98*, 1752–1762.

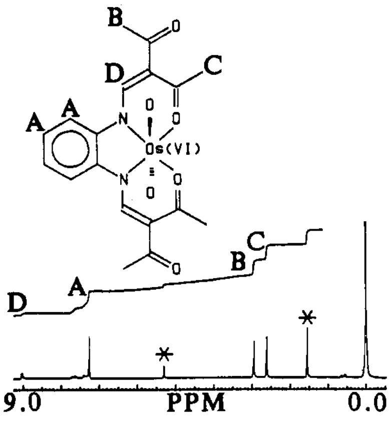

Figure 1. ^1H nuclear magnetic resonance spectrum of [(phenba)Os^{VI}-$(O)_2$]. Peaks marked with an asterisk were determined to be solvents present from the synthesis of [(phenba)$Os^{VI}(O)_2$]. δ(A) = 7.50, δ(B) = 2.94, δ(C) = 2.61, δ(D) = 9.02. Chemical shifts are reported as ppm relative to internal Me_4Si.

yellow solid by suction filtration give the (phenba)$Ru^{II}(CO)_2$ complex in 87% yield. Anal. Calcd for $RuC_{20}H_{18}N_2O_6(2H_2O)$: C, 46.24; H, 4.27. Found: C, 46.06; H, 4.68.

***trans*-[(phenba)$Os^{VI}(O)_2$].** a 61.8-mg sample of $K_2[Os^{VI}(O)_2(OH)_4]$ (0.17 mmol) in 20 mL of methanol is added dropwise into a solution of 55 mg of phenba (0.17 mmol) and 41 mg of benzoic acid (0.34 mmol) in 15 mL of acetone. This solution is stirred for 1.5 h at room temperature and then is cooled in an ice bath for 0.5 h. A dark red, microcrystalline precipitate is isolated, washed with methanol, and dried; yield 78%. Anal. Calcd for $OsC_{18}H_{18}N_2O_6$: C, 39.45; H, 3.48. Found: C, 39.38; H, 3.66.

***trans*-[(phenba)$Os^{II}(PPh_3)_2$].** A 100-mg sample of (phenba)$Os^{VI}(O)_2$ (0.18 mmol) and 954 mg of triphenylphosphine (3.6 mmol) are heated to reflux in 15 mL of degassed benzyl alcohol. The green solution is purified by column chromatography with silica gel as the stationary phase and methylene chloride as the eluent. The green band is collected, and the solution is added to 20 mL of hexanes to induce precipitation. A green solid is collected by suction filtration and washed with hexanes; yield 70%. Anal. Calcd for $OsC_{54}H_{48}O_4N_2P_2(3H_2O)$: C, 59.22; H, 4.97. Found: C, 59.38; H, 4.80.

Gas Chromatography. The reactivity of (phenba)$Os^{VI}(O)_2$ with benzyl alcohol was obtained by utilizing a Shimadzu Gas Chromatograph GC-8A, utilizing a Chromosorb 101 column No. 2406 PC obtained from Alltech Applied Science Labs. The experiment consisted of the addition of 22.5 mg of (phenba)$Os^{VI}(O)_2$ (0.041 mmol) to 5 mL of degassed benzyl alcohol followed by the addition of 10.7 mg of triphenylphosphine (0.041 mmol). The existing solution was stirred for 15 min, and then a sample was analyzed by GC for benzaldehyde content. A GC calibration curve was prepared by quantitatively examining a series of solutions containing various concentrations of benzaldehyde in benzyl alcohol.

Physical Measurements. Elemental analyses were performed by Atlantic Microlabs. IR spectra of Nujol mulls were measured with a Perkin-Elmer 457 grating infrared spectrophotometer (4000–250 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Bausch and Lomb Spectronic 2000 spectrophotometer system. ^1H NMR spectra were measured with a JEOL FX90Q Fourier transform NMR spectrometer, with deuteriated chloroform as the solvent and tetramethylsilane as the internal reference. Cyclic voltammetry experiments were performed by using reagent grade methylene chloride as the solvent, which was dried over calcium hydride and then distilled. The supporting electrolyte was tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) or tetraethylammonium perchlorate (Et_4NClO_4), which was prepared and purified by standard methods[31] and was used in 0.1 M concentrations for all solutions. A platinum working electrode (BAS Bioanalytical Systems), a platinum-wire auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) were used for all electrochemical experiments. Cyclic voltammetry was conducted with an IBM EC/225 voltammetric analyzer and current–voltage curves were recorded with a Houston Instruments Model 164 recorder.

Results and Discussion

Characterization. The use of $K_2[Os^{VI}(O)_2(OH)_4]$ as a starting material for dioxoosmium(VI) complexes is well established[21-23] and has proved convenient for the insertion of osmium into the phenba ligand. The ^1H NMR spectrum of the (phenba)$Os^{VI}(O)_2$ shows the expected resonances characteristic of the phenba ligand, δ 9.02 (methylidene, 2 H, s), 7.50 (phenyl, 4 H, m), 2.94 (methyl, 6 H, s), and 2.61 (methyl, 6 H, s), which results in an integration pattern of 1:2:3:3 (Figure 1). The presence of sharp singlets for the methyl and methylidene protons help support an assignment of C_{2v} symmetry. The UV-vis spectrum of (phenba)$Os^{VI}(O)_2$ (Figure 2) is characterized by one large broad adsorption at 414 nm (ε = 11 000). The infrared spectrum (Figure 4, supplemental material) shows a strong absorption at 848 cm^{-1}, which is consistent with reported examples of osmium dioxo complexes.[21,32] The reaction of (phenba)$Os^{VI}(O)_2$ with triphenylphosphine in benzyl alcohol yielded (phenba)$Os^{II}(PPh_3)_2$. The ^1H NMR of this complex is consistent with the ligand environment: the methyl protons yield singlets (δ 1.85 (6 H), 1.92 (6 H)), the phosphine phenyl protons yield a broad singlet (δ 7.15 (30 H)), the phenba phenyl protons yield resonances that overlap with those from the phosphine phenyl protons (δ 7.15 (4 H)), and the methylidene protons yield a small singlet (δ 8.11 (2 H)). The UV-vis spectrum of (phenba)$Os^{II}(PPh_3)_2$ shows absorptions with λ = 469 (ε = 10 500), 444 (ε = 10 200), and 375 nm (ε = 12 500).

The synthesis of the ruthenium phenba complex ultilizes the $Ru(PPh_3)_3Cl_2$ starting material, which inserts into the ligand in the presence of triethylamine. The UV-vis spectrum of the (phenba)$Ru^{II}(PPh_3)_2$ complex (Figure 2) shows absorptions with λ = 454 (ε = 9700) and 432 nm (ε = 9200). The ^1H NMR spectrum is indicative of the ligand environment (Figure 3) with the methyl protons as sharp singlets (δ 1.84 (6 H), 2.08 (6 H)),

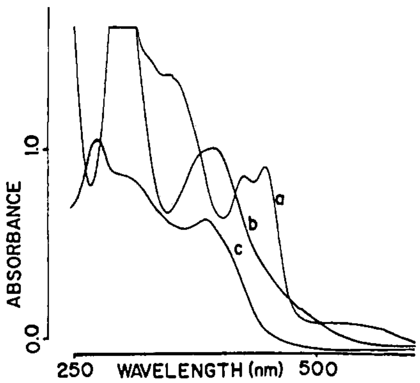

Figure 2. UV-vis spectra of (a) [(phenba)$Ru^{II}(PPh_3)_2$] (9.97 × 10^{-5} M), (b) [(phenba)$Os^{VI}(O)_2$] (9.977 × 10^{-5} M), and (c) [(phenba)$Ru^{II}(CO)_2$] (4.00 × 10^{-5} M) in methylene chloride.

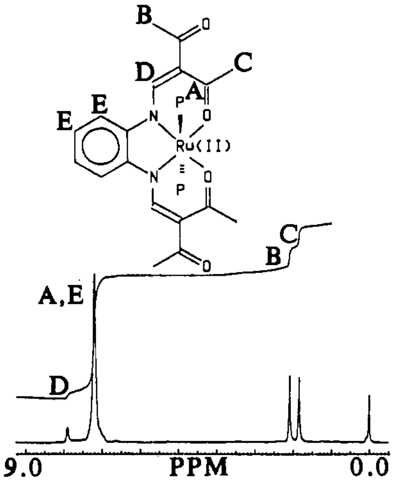

Figure 3. ^1H nuclear magnetic resonance spectrum of [(phenba)Ru^{II}-$(PPh_3)_2$], where P = PPh_3. δ(A, E) = 7.19, δ(B) = 2.08, δ(C) = 1.84, δ(d) = 7.90. Chemical shifts are reported as ppm relative to Me_4Si.

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(31) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; p 212.

(32) Che, C. M.; Poon, C. K.; Chung, W. C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277–1278.

Table I. Infrared Absorbances for Phenba Complexes

	ν,[a] cm^{-1}				
complex	ν(C=O)[b]	ν(C=O)[c]	ν(C=C)	ν(Os=O)	ν(C≡O)[d]
(phenba)Ru^{II}(PPh$_3$)$_2$	1553	1585	1627		
(phenba)Ru^{II}(CO)$_2$	1555	1595	1630		1910
(phenba)Os^{VI}(O)$_2$	1570	1595	1660	848	
(phenba)Os$^{II}_2$(PPh$_3$)$_2$	1573	1595	1619		

[a] The medium used for all infrared spectra was Nujol mull. [b] Infrared absorbance for the coordinated acetyl group. [c] Infrared absorbance for the noncoordinated acetyl group. [d] Infrared absorbance for the coordinated carbon monoxide ligand.

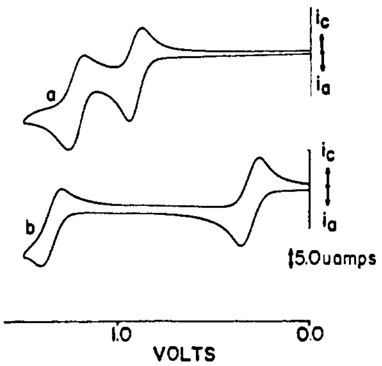

Figure 6. Cyclic voltammograms of (a) [(phenba)Ru^{II}(CO)$_2$] in acetonitrile and (b) [(phenba)Ru^{II}(PPh$_3$)$_2$ in methylene chloride. Scan rate = 100 mV/s.

the phosphine phenyl protons as a broad singlet (δ 7.19 (30 H)), the phenyl protons overlapped with the phosphine phenyl protons (δ 7.19 (4 H)), and the methylidene protons as a small singlet (δ 7.90 (2 H)) (Figure 3).

Starting with (phenba)Ru^{II}(PPh$_3$)$_2$, the ruthenium trans CO complexes is readily synthesized by utilizing a modification of the method for CO insertion used by Wilkinson.[33] The UV-vis spectrum of the (phenba)Ru^{II}(CO)^2 complex (Figure 2) shows one large absorption at 397 nm (ϵ = 17 700). The ^{1}H NMR spectrum shows the resonances expected for the phenba ligand: δ 8.98 (methylidene, 2 H, s), 7.92, 7.26 (phenyl, 4 H, d), 2.55 (methyl, 6 H, s), 2.47 (methyl, 6 H, s).

Table I lists all assignable absorptions in the infrared region for the ruthenium and osmium complexes, and infrared spectra of selected complexes are shown in Figures 4 (supplemental material) and 5 (supplemental material). The assignment of the stretching frequencies in the R$_2$C=O region are based upon observed trends in other metal complexes with similar ligand environments.[34,35] The coordinated acetyl group is found at a lower frequency than that for the noncoordinated acetyl group and both of these absorptions are of lower energy than that for the olefin. The stretching frequencies for the aromatic rings are at slightly lower frequencies, and tend to be under other bands. The (phenba)Ru^{II}(CO)$_2$ complex shows a strong absorbance at 1910 cm^{-1}, which is in the range for a terminal carbon monoxide absorbance.[36]

All of the ruthenium complexes exhibit quasi-reversible waves for the M(III/II) couple (Figure 6). The electrochemical data for the cyclic voltammagrams of reported complexes are as follows: for the ruthenium trans triphenylphosphine complex in methylene chloride, $E_{1/2}$ = +0.29 V, ΔE_p = 85 mV, $I_{p,c}/I_{p,a}$ = 0.92, and scan rate = 100 mV/s; for the ruthenium trans carbon monoxide complex in acetonitrile, $E_{1/2}$ = +0.91 V; ΔE_p = 60 mV; $I_{p,c}/I_{p,a}$ = 0.84, and scan rate = 100 mV/s. The (phenba)Os^{II}(PPh$_3$)$_2$ complex also exhibits a quasi-reversible M(III/II) couple in methylene chloride, with $E_{1/2}$ = −0.03 V, ΔE_p = 60 mV, and $I_{p,c}/I_{p,a}$ = 0.88 at a scan of 100 mV/s.

Reactivity. From the electrochemical data, the N$_2$O$_2$ phenba ligand appears to be a suitable ligand for redox reagent design, in that the ligand is stable when coordinated to ruthenium(II), ruthenium(III), osmium(II), osmium(III), and osmium(VI). In fact, the osmium complex, (phenba)Os^{VI}(O)$_2$, can act as a stoichiometric oxidizer of benzyl alcohol, yielding exclusively benzaldehyde. Notably, (phenba)Os^{VI}(O)$_2$ is not the active oxidizer; it is necessary to first reduce the (phenba)Os^{VI}(O)$_2$ with 1 equiv of triphenylphosphine, generating the potent oxidizer, (phenba)Os^{IV}(Ph$_3$P=O)(O). When benzyl alcohol and (phenba)O^{VI}(O)$_2$ are combined, the production of benzaldehyde is not observed, but when 1 molar equiv of triphenylphosphine is added, benzaldehyde is formed in stoichiometric amounts. The behavior of osmium(IV) as a more potent oxidizer than osmium(VI) is not unexpected, due to the stabilizing effect of *trans*-dioxo ligands with the osmium(VI) complex. In this regard, the potency of lower oxidation state compounds as oxidants can be observed with other elements, such as with the oxides of chlorine and phosphorus.[37] Notably, the suggested osmium(IV) complex is very reactive and presently cannot be isolated or characterized. Cyclic voltammetric and reactivity studies on the proposed intermediate (phenba)Os^{IV}(Ph$_3$P=O)O are under current investigation.

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Supplementary Material Available: Infrared spectra of [(phenba)Ru^{II}(PPh$_3$)$_2$] (Figure 4) and [(phenba)Os^{VI}(O)$_2$] (Figure 5) (2 pages). Ordering information is given on any current masthead page.

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(33) Thornback, J. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 110–115.

(34) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1963.

(35) Bamfield, P. *J. Chem. Soc. A* **1969**, 2021.

(36) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

(37) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.

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^{1}H NMR Study of Iron-Bound Trimethylphosphine in Low-Spin Ferric Complexes of Various Hemoglobins and Myoglobins

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High-resolution nuclear magnetic resonance spectroscopy can be an important tool for characterization of the structure and function of hemoproteins in solution provided that signals corresponding to particular amino acids can be resolved and assigned.[1] These problems can often be eased by NMR investigations of isotopically enriched ligand molecules bound to the heme iron (^{13}CO, ^{13}CNR, C^{15}N$^-$).[2-4] Surprisingly, the attractive properties

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(1) La Mar, G. N. In *Biological Applications of Magnetic Resonance*; Shulman, R. G., Ed.; Academic: New York, 1979; p 305.

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