at time t. The observation of second-order, equal-concentration kinetics shows that reactions 8, 9, and 10 are all stoichiometric as written and that $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ were formed in equal amounts in the separate redox quenching steps. For eq 12, $k(22 \pm 2\ °C) = (2.2 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$ ($I = 0.1$ M).[29]

Conclusions

The flash photolysis experiment shows that the disproportionation of $Ru(bpy)_3^{2+*}$ can be catalyzed in the presence of two different one-electron redox couples. In the experiment, DMA and PQ^{2+} act both as quenchers and, by the enhanced production of DMA^+ and PQ^+, as analytical reagents for the determination of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ once formed. From the potential diagram in Scheme I, it is clear that thermodynamically, the catalyzed disproportionation of $Ru(bpy)_3^{2+*}$ can be achieved by a combination of two one-electron couples or by both oxidized and reduced forms of a single couple. This will be so as long as the reduction potentials involved fall within the disproportionation energy gap (−0.81 to +0.78 V) between the $Ru(bpy)_3^{2+*/+}$ and $Ru(bpy)_3^{3+/2+*}$ potentials.

Acknowledgment. We thank the National Science Foundation for support of this research, under Grant CHE74 14405 A02.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; PQ^{2+}, 4685-14-7; DMA, 121-69-7.

References and Notes

(1) (a) F. E. Lytle and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 253 (1969); (b) K. W. Hipps and G. A. Crosby, *ibid.*, **97**, 7042 (1975), and references therein; (c) R. Benasson, C. Salet, and V. Balzani, *ibid.*, **98**, 3722 (1976).

(2) H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972).

(3) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).

(4) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).

(5) G. S. Laurence and V. Balzani, *Inorg. Chem.*, **13**, 2976 (1974).

(6) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).

(7) F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Chem. Soc., Chem. Commun.*, **901** (1975).

(8) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **19**, 321 (1975), and references therein.

(9) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 396 (1976).

(10) A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 1047 (1976).

(11) C. Creutz and N. Sutin, *J. Am. Chem, Soc.*, **98**, 6384 (1976).

(12) C. P. Anderson, T. J. Meyer, D. J. Salmon, and R. C. Young, *J. Am. Chem. Soc.*, **99**, 1980 (1977).

(13) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976).

(14) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).

(15) T. J. Meyer, *Isr. J. Chem.*, in press.

(16) (a) N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 6582 (1973); (b) T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, **58**, 401 (1975); (c) D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, 1976.

(17) T. J. Meyer, paper presented at the International Workshop on Fundamental Research in Homogeneous Catalysis, Palermo, Sicily, Dec 1976.

(18) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).

(19) J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, **98**, 4853 (1976).

(20) (a) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977). (b) Mentioned in footnote 18 in ref 20a.

(21) J. N. Braddock, Ph.D. Dissertation, The University of North Carolina, 1973.

(22) R. C. Young, Ph.D. Disseration, The University of North Carolina, 1977.

(23) (a) J. F. Wheeler and R. F. Nelson, *J. Phys. Chem.*, **77**, 2490 (1973); (b) A. Yamagishi, *Bull. Chem. Soc. Jpn.*, **48**, 3475 (1975).

(24) F. R. Keene, R. C. Young, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2468 (1977).

(25) E. M. Kosower and J. L. Cottern, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

(26) (a) M. Eigen, W. Kruse, G. Maas, and L. De Maeyer, *Prog. React. Kinet.*, **2**, 285 (1964); (b) R. C. Jarnagin, *Acc. Chem. Res.*, **4**, 420 (1971).

(27) D. Behar and G. Czapski, *Isr. J. Chem.*, **8**, 699 (1970).

(28) In solutions containing both quenchers in high concentration and the excited state as a limiting reagent, competition between quenchers for the excited state would decrease the enhanced production of DMA^+ and PQ^+ below 2. Such a competition is not important here as evidenced by conversion of only ~30% of the $Ru(bpy)_3^{2+}$ (1×10^{-5} M) present initially to redox products (2.4×10^{-6} M; Figure 2) during the whole flash. The quencher concentrations used were relatively low, and the efficiencies of redox product formation for both quenchers are well below 1. A quenching act which leads back to $Ru(bpy)_3^{2+}$ (Scheme II) also leads to $Ru(bpy)_3^{2+*}$ because of the pumping action of the flash.

(29) k was calculated from the slopes of plots of $1/\Delta A$ vs. t where slope $= k/b\Delta\epsilon$, b is the cell path length, and $\Delta\epsilon$ was calculated from $\Delta\epsilon = 1.006 \times 10^4$ at 605 nm.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Preparation of Decacarbonyl[bis(diphenylphosphino)methane]triruthenium and the Elucidation of Its Structure by Dynamic Carbon-13 NMR Spectroscopy

F. Albert Cotton* and Brian E. Hanson

Received July 8, 1977 AIC70490T

Metal carbonyl clusters containing three or more metal atoms have been proposed as models for covered metal surfaces.[1] The mobility of adsorbed carbon monoxide on a metal surface is a phenomenon which is not readily studied by direct experimentation.[2] Carbon monoxide mobility in cluster compounds is well known[3] and easily studied by carbon-13 NMR. Thus, the study of the fluxionality of carbonyl clusters, in addition to its fundamental interest, is worthwhile because it may lead to a better understanding of CO mobility on metal surfaces.

At the present time, however, no study of a metal cluster has revealed a carbonyl exchange process that could be directly applicable to a metal surface. In metal clusters there are exchange processes occurring in the same plane as the metal atoms or involving more than one terminal CO per metal atom, but these can have no direct analogues on metallic surfaces.

We have prepared a derivative of $Ru_3(CO)_{12}$ in which the bidentate ligand, bis(diphenylphosphino)methane, bridges two ruthenium atoms in the equatorial plane. $(dppm)Ru_3(CO)_{10}$ (**1**) executes a CO exchange process that may be regarded as a model for CO migration on a metal surface.

Experimental Section

All operations were performed under argon using standard techniques. THF was distilled prior to use from Na–K benzophenone. Bis(diphenylphosphino)methane and $Ru_3(CO)_{12}$ were purchased from Strem Chemical Co. and used without further purification. Toluene-d_8 was stored over 4-Å molecular sieves and freeze–thaw degassed before use; Freons 12 and 21 were used directly from the lecture bottles.

Synthesis of $(dppm)Ru_3(CO)_{10}$. Triruthenium dodecacarbonyl (160 mg, 0.25 mmol) and dppm (105 mg, 0.27 mmol) were placed in a 100-mL side arm flask and degassed. THF, 50 mL, was added and the resulting solution warmed to 50 °C for 36 h. The solution was then reduced in volume and chromatographed on Florisil, eluting with a 50/50 mixture of THF and hexane. After the removal of a small amount of $Ru_3(CO)_{12}$ a red-orange band was collected. No other bands developed on the column. The fraction collected was reduced in volume and cooled, yielding red-orange crystals of $(dppm)Ru_3(CO)_{10}$. The infrared spectrum in CH_2Cl_2 shows carbonyl stretches at 2080 (m), 2040 (w), 2010 (s), 1988 (sh), and 1960 (m) cm^{-1}. Anal. Calcd for $C_{35}H_{22}O_{10}P_2Ru$: C, 43.4; H, 2.3. Found: C, 43.7; H, 2.5.

The sample used for the carbon-13 NMR measurements was prepared as above using $Ru_3(CO)_{12}$ enriched to ca. 60% in ^{13}CO.

Carbon-13 NMR Spectra. The spectra were recorded on a JEOL PS100/Nicolet 1080 Fourier transform NMR spectrometer operating at 25.0355 MHz. A tilt angle of 30° and a repetition rate of 1.2 s were employed to collect 500–4000 scans/spectrum.

Above 33 °C toluene-d_8 containing 5% THF was the solvent used; from 33 to −83 °C, 30% toluene-d_8 and 70% THF was used; below −83 °C, 15% toluene-d_8, 5% THF, 40% CF_2Cl_2, and 40% $CFHCl_2$ was used. Chemical shifts were referenced to the downfield peak of THF and converted to the Me_4Si scale using $\delta_{Me_4Si} = \delta_{THF} + 68.0$ ppm. No $Cr(acac)_3$ was added to the sample.

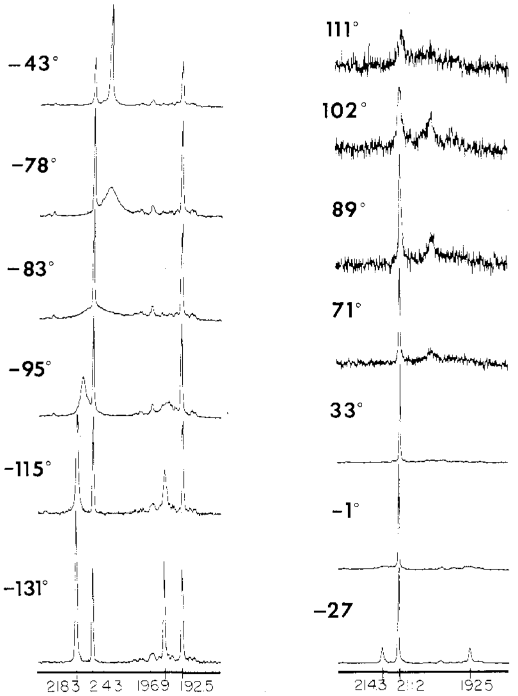


Figure 1. Carbon-13 NMR spectra for $(dppm)Ru_3(CO)_{10}$ at various temperatures. The apparently sharp peak in the spectra at −1 and 33 °C is actually a triplet ($J_{^{13}C-^{31}P}$ = 2.9 Hz).

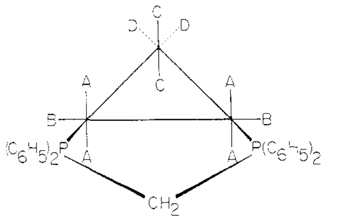


Figure 2. Schematic representation of the solution structure of $(dppm)Ru_3(CO)_{10}$.

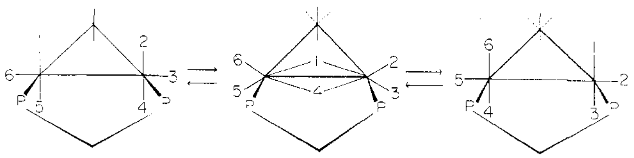
The NMR spectra from −131 to −43 °C were simulated using the program EXCHSYS by G. M. Whitesides and J. K. Krieger.

Results and Discussion

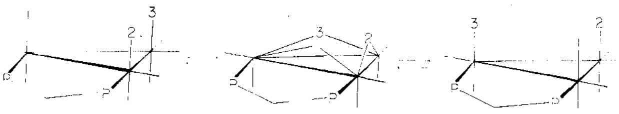
The carbon-13 NMR spectra are shown in Figure 1 from −131 to +111 °C. In the low-temperature limit there are four resonances in the terminal region in the ratio of 4:2:2:2. A four-line spectrum with these intensities could arise from either of two possible structures: (a) one in which dppm is chelated in the equatorial plane to a single Ru atom or (b) one in which dppm bridges two Ru atoms, again with the phosphorus atoms in the equatorial plane. These possibilities were considered in the analogous $(L-L)Ru_3(CO)_{10}$[4] compounds (where L-L is a di(tertiary phosphine or arsine)ligand) although a rigorous choice could not be made. In the compound $(dppm)Fe_2(CO)_7$[5] it was shown crystallographically that dppm bridges the two iron atoms. We conclude that a similar arrangement must also occur in $(dppm)Ru_3(CO)_{12}$ since the observed exchange processes are consistent only with a bridging dppm ligand. It should be noted that for the bridged structure the Ru–Ru–P–C–P ring is puckered so that pairs of axial CO groups above and below the equatorial plane are not instantaneously equivalent. It must be assumed that this envelope configuration flips rapidly enough even at −131 °C to make such pairs of axial CO groups time-average equivalent.

The most facile exchange process in **1** involves the resonances at 218.3 and 196.9 ppm. These are assigned to carbonyl groups at the A and B sites, respectively, in Figure 2.

Scheme I



Scheme II



Coalescence occurs at ca. −80 °C and further warming produces a sharp triplet at 211.2 ppm ($J_{^{13}C-^{31}P}$ = 2.9 Hz at −1 °C). The $^{31}P-^{13}C$ coupling was not resolved in the slow-exchange limit because the lines never became narrow enough. Presumably when the exchange broadening becomes negligible (below about −120 °C) some viscosity broadening has already begun, as in the spectrum at −131 °C. The mechanism for this process is shown is Scheme I. This is the same process observed previously in $Os_3(CO)_{10}(PEt_3)_2$ and $Os_3(CO)_{11}PEt_3$,[6] in which the carbonyls move only in an essentially planar, elliptical path around the two substituted ruthenium atoms. Computer simulation of the line shape for this process gives activation parameters of $E_a = 7.9 \pm 0.1$ kcal mol^{-1}, log $A = 12.3 \pm 0.1$, $\Delta G^\ddagger = 8.5 \pm 0.1$ kcal mol^{-1}, $\Delta H^\ddagger = 7.5 \pm 0.1$ kcal mol^{-1}, and $\Delta S^\ddagger = -3.3 \pm 0.3$ eu.

Local exchange on the unique ruthenium atoms occurs at a relatively high temperature compared to the analogous process in $(C_4H_4N_2)Ru_3(CO)_{10}$ (**2**).[7] Activation energies for CO scrambling, however, are very sensitive to changes in environment[8] so the variation from **1** to **2** is not unduly surprising. Coalescence for this local exchange occurs at ca. 71 °C. However, before the resonance can completely sharpen, the effects of another exchange process which scrambles all carbonyls become apparent. Decomposition became rapid above 111° thus preventing observation of the ultimate fast-exchange spectrum. Line shapes up to 111° were reproducible. The abrupt decrease in signal-to-noise ratio seen in Figure 1 between 33 and 71° is due to the use of a more dilute solution upon changing from a Freon/toluene mixture to a pure toluene solvent.

The high-energy process which is responsible for exchanging carbonyls between the two types of Ru atoms can occur in only one way provided the dppm ligand itself does not move. This process is show in Scheme II. The mechanism involves the concerted formation of three bridges on the face of the triangle of ruthenium atoms. Such a mechanism was considered but found not to occur in **2**.[7] This scrambling process is in a sense the inverse of that proposed by Shapley for the C_{3v} isomer of $(\eta^5-C_5H_5)_3Rh_3(CO)_3$, in which the more stable configuration has three bridging CO groups on the same side of the metal triangle.[9]

Acknowledgment. We thank the Robert A. Welch Foundation for support of this research.

Registry No. 1, 64364-79-0; $Ru_3(CO)_{12}$, 15243-33-1; ^{13}C, 14762-74-4.

References and Notes

(1) (a) R. Ugo, *Catal. Rev.*, **11**, 225 (1975); (b) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
(2) (a) G. C. Bond, "Catalysis by Metals", Academic Press, New York, N.Y., 1962; (b) D. O. Hayward and B. M. W. Trapnell, "Chemisorption", Academic Press, New York, N.Y., 1964.
(3) (a) J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, **44**, 43 (1975); (b) R. D. Adams and F. A. Cotton in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y. 1975, pp 489–520; (c) G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 607 (1977).
(4) W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, **9**, 1839 (1970).

(5) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974).
(6) B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorpp, *J. Chem. Soc., Dalton Trans.*, 1403 (1976).
(7) F. A. Cotton, B. E. Hanson, and J. D. Jamerson, *J. Am. Chem. Soc.*, **99**, 6588 (1977).
(8) C. R. Eady, W. G. Jackson, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Chem. Soc., Chem. Commun.*, 958 (1975).
(9) R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 7433 (1976).

Contribution from the Department of Biochemistry,
Schools of Medicine and Dentistry,
Georgetown University, Washington, D.C. 20007

Kinetics of Reduction of Hemin and the Hemin Bis(pyridine) Complex by Dithionite

James C. Cassatt,* Maria Kukuruzinska, and John W. Bender

Received May 18, 1977 AIC70361C

In order to delineate the important redox reactions of heme proteins, several investigators have studied the kinetics of the redox reactions of various water-soluble metalloporphyrins.[1-6] In this study we report the kinetics of reduction of monomeric hemin, (protoporphyrin IX)iron(III), and the pyridine complex of hemin by dithionite. Since hemin exists as a dimer at neutral pH, it was dissolved in sodium dodecyl sulfate micelles. This procedure had previously been shown to produce monodisperse hemin under the conditions of our experiments.[7]

Experimental Section

Hemin chloride was obtained from Nutritional Biochemicals, sodium dodecyl sulfate from Sigma, and sodium dithionite from Fisher. Dithionite solutions were standardized by reduction of excess potassium ferricyanide under anaerobic conditions. The amount of ferricyanide reduced was determined spectrophotometrically.[3] The samples were found to be 96% pure. All other chemicals were reagent grade or better.

All spectral measurements were carried out on a Beckman Acta CV spectrophotometer. The kinetic experiments were carried out as follows. Solutions of hemin (2×10^{-5} M) were prepared by diluting a stock solution (prepared fresh each day by dissolving hemin in 0.01 M NaOH) into a buffered solution containing 2% sodium dodecyl sulfate. Spectral analysis showed that under these conditions hemin exists as a monomer. Prior to reaction on the stopped-flow apparatus, the solution was deaerated with prepurified N_2. Dithionite solutions were prepared by dissolving the appropriate amount of solid sodium dithionite in a previously deaerated buffered solution also containing 2% sodium dodecyl sulfate. In the case of the reduction of the bis(pyridine) complex, both reactant solutions were brought to 0.05 M pyridine. In general, the solutions were buffered with 0.01 M phosphate or 0.01 M Tris. (At intermediate pHs both buffers were used and identical results were obtained.) Solutions were brought to an ionic strength of 0.1 M with added NaCl. The reactant solutions were then mixed on an Aminco-Morrow stopped-flow apparatus with the temperature controlled to 25 ± 0.1 °C with a circulating water bath.

In the case of the reduction of hemin, the reaction was followed at 570 nm and in the case of the bis(pyridine) complex at 555 nm. All reactions were carried out under pseudo-first-order conditions. Plots of log $|A - A_\infty|$ as a function of time, from which values for the observed rate constant, k_{obsd}, were calculated, were linear for 3 half-lives. All values given are the average of at lease three runs. The average deviation obtained for these runs was less than 10%.

Results

For the reduction of hemin by dithionite, the observed rate constant was determined as a function of dithionite concentration at pH 7 and 9. The results are shown in Figure 1. As is common with a number of dithionite reductions, the observed rate constant is proportional to the square root of the dithionite concentration.[8] These data (at a single pH) are consistent with the mechanism previously proposed for dithionite reductions[8]

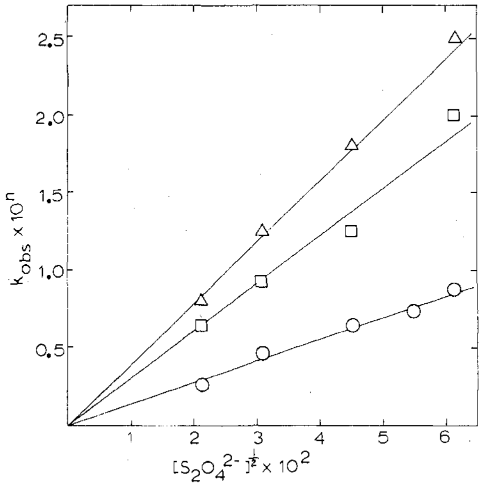


Figure 1. Plot of $k_{obsd} \times 10^{-2}$ as a function of $[S_2O_4^{2-}]^{1/2}$ for the reduction of a bis(pyridine) hemin complex by dithionite, □ (pH 7, [pyridine] = 0.05 M), and $k_{obsd} \times 10^{-1}$ and 10 as a function of $[S_2O_4^{2-}]^{1/2}$ for the reduction of hemin by dithionite at pH 7, ○, and 9, △, respectively. The temperature was 25 °C and ionic strength 0.1 M.

$$S_2O_4^{2-} \overset{K_{eq}}{\rightleftarrows} 2SO_2^-$$

$$SO_2^- + \text{hemin} \xrightarrow{k'} SO_2 + \text{heme}$$

The rate law consistent with this mechanism is

$$\text{rate} = K_{eq}^{1/2}k'[S_2O_4^{2-}]^{1/2}[\text{hemin}] \tag{1}$$

or

$$k_{obsd} = K_{eq}^{1/2}k'[S_2O_4^{2-}]^{1/2} \tag{2}$$

Values for for k' (where $k' = k_{obsd}/K_{eq}^{1/2}[S_2O_4^{2-}]^{1/2}$) were determined as a function of pH at a constant $[S_2O_4^{2-}]$ of 1.0×10^{-3} M and using a K_{eq} of 1.4×10^{-9} M.[8] The rate constant k' was found to be approximately proportional to $[H^+]$. This behavior is consistent with the mechanism

$$H_2O\text{-Hm-}OH_2^+ \overset{K_a}{\rightleftarrows} H_2O\text{-Hm-}OH + H^+$$

$$H_2O\text{-Hm-}OH_2^+ + SO_2^- \xrightarrow{k_1} \text{products}$$

$$H_2O\text{-Hm-}OH + SO_2^- \xrightarrow{k_2} \text{products}$$

The rate law consistent with this mechanism is

$$\text{rate} = \frac{[H^+]k_1 + K_ak_2}{K_a + [H^+]}[SO_2^-][Hm]_T \tag{3}$$

where $[Hm]_T$ is the total hemin concentration and H_2O–Hm–OH_2^+ refers to hemin with two water molecules coordinated in the axial positions.[9] Thus

$$\frac{k'(K_a + [H^+])}{K_a} = \frac{k_1[H^+]}{K_a} + k_2 \tag{4}$$

A spectrophotometric titration of hemin under the conditions of our experiments yielded a value for pK_a of 5.89 (in reasonable agreement with a value of 5.5 determined under somewhat different conditions[10]). A plot of $k'(K_a + [H^+])/K_a$ as a function of $[H^+]$ is shown in Figure 2. From the slope k_1 is equal to $(6.0 \pm 0.7) \times 10^6$ M^{-1} s^{-1}, and from the intercept k_2 is about $(5 \pm 2) \times 10^3$ M^{-1} s^{-1}.

In the case of the reduction of the bis(pyridine) complex, the spectrum of hemin as a function of pyridine concentration was determined prior to the kinetic experiments under the