Figure 1. (a) ^{13}C NMR spectrum of **1** in SbF$_5$/SO$_2$ClF at –90 °C. (b) ^{13}C Satellite spectrum of **1** in SbF$_5$/SO$_2$ClF at –90 °C; δ, equilibrium ^{13}C isotope effect on ^{13}C chemical shift of the averaged methine and cationic carbons.

(**1a** ⇌ **1b**) can be obtained by regular natural abundance ^{13}C spectrum.

Figure 1 shows both the regular ^{13}C NMR spectrum and ^{13}C "satellite" spectrum of **1** obtained in SbF$_5$/SO$_2$ClF at –90 °C.[8] In the satellite spectrum (using the INADEQUATE pulse sequence)[9] both the signals appear as doublets[10] with 180° phase shift in one component of each doublet. The resonance frequency of the carbons in the satellite spectrum can be calculated as the average of the AX doublets. The regular ^{13}C NMR spectrum (Figure 1a) represent the signal from the ion **1a** ⇌ **1b** while the satellite spectrum (Figure 1b) represent the signal from the ion **1c** ⇌ **1d**. The resonance frequency of the peak at $δ_{^{13}C}$ 181 is shifted downfield in the satellite spectrum (Figure 1b) compared to that in the regular spectrum (Figure 1a). The magnitude of the shift is temperature dependent and the values are listed in Table I for the temperature range studied.

In order to determine the intrinsic ^{13}C isotope effect on ^{13}C chemical shift we also studied the *tert*-butyl cation. The difference in the cationic carbon chemical shift between the normal ^{13}C spectrum (which represent the ^{13}C spectrum of **2a**) and the ^{13}C satellite spectrum (which represent the ^{13}C spectrum of **2b**) is less than 2 Hz. Thus the relatively large (23–39-Hz deshielding) ^{13}C isotope effect observed in **1** between –90 and –110 °C is due to the perturbation of the equilibrium due to ^{13}C isotopic substitution. The deshielding of the average peak at $δ_{^{13}C}$ 181 in **1c** ⇌ **1d** compared to that in **1a** ⇌ **1b** indicates that the secondary ^{13}C isotope perturbs the equilibrium toward **1d**. In other words, the positive charge is favored on a carbon next to a ^{13}C isotope (as in **1c**) as opposed to next to a ^{12}C isotope (as in **1d**).

The secondary ^{13}C equilibrium isotope effect (i.e., K_2/K_1) can be determined by $(\Delta + 2δ)/(\Delta - 2δ)$ where Δ is the chemical shift difference between the cationic carbon and the methine carbon in the "frozen out" structure and δ is the chemical shift difference of the average cationic and methine carbon signals between the "normal" spectrum and the ^{13}C satellite spectrum. The values of secondary ^{13}C equilibrium isotope effects (i.e., K_2/K_1) and those of K_2 (calculated using the K_2/K_1 values obtained in this study and K_1 values reported earlier[4]) are listed in Table I. However, to calculate K_2 one need to know K_1, which can be determined only by labeling. The secondary ^{13}C isotope effects (K_2/K_1) range from 1.0066 to 1.0113 over the temperature range studied while K_2 (product of primary and secondary ^{13}C equilibrium isotope effect) range from 1.0203 to 1.0273.

Thus for the first time we have observed the secondary ^{13}C isotopic perturbation of a degenerate equilibrium using natural abundance sample. We have shown that the unsymmetrically positioned ^{13}C isotope does, indeed, produce significant perturbation of the equilibrium which can be conveniently monitored by a change in the ^{13}C chemical shift in the ^{13}C satellite spectrum. These isotope effects are significantly larger compared to intrinsic ^{13}C isotope effect on ^{13}C chemical shift as observed in the *tert*-butyl cation. Our studies are continuing to determine the feasibility of using such secondary ^{13}C isotope effects to distinguish equilibrating systems from bridged ones.

CH$_3$ structure **2a** and **2b**

2a   **2b**

(8) The spectra were recorded on a Varian XL-200 superconducting NMR spectrometer operating at 50-MHz ^{13}C resonance frequency. The field frequency lock was held for the entire duration of the experiment using a coaxial insert containing acetone-d_6. Thus, the "normal" and the "satillite" spectrum can be compared with respect to the transmitter frequency.

(9) The pulse sequence used for the ^{13}C satellite spectra, based on Freeman et al.,[7] is 90°(x)–τ–180°(±y)–τ–90°(x)–Δ–90°(ϕ)–Acq(ψ), where τ ≃ ($2n$ + 1)/4J_{CC}, Δ is a very short delay (~10 μs) needed to reset the radiofrequency phase, and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver, respectively. Optimum setting of τ for direct coupling is when n = 0 and thus set a 7.0 ms (corresponding to a J_{CC} value of ~36 Hz). The repetition rate of this sequence is ~6 s, and reasonable signal to noise ratio was achieved in 8 h of acquisition.

(10) J_{C,CH_3} = 30 ± 1 Hz.

(11) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* 1977, 99, 5026.

(12) Myhre, P. C.; Kruger, J. D.; Hammond, B. L.; Lok, S. M.; Yannoni, C. S.; Macho, V.; Limbach, H. H.; Vieth, M. H. *J. Am. Chem. Soc.* 1984, 106, 6079.

Pentadienyl Compounds of Zirconium, Niobium, and Molybdenum: "U" vs. "S" η^5-2,4-Dimethylpentadienyl Coordination[1]

Lothar Stahl, John P. Hutchinson, David R. Wilson,[2] and Richard D. Ernst*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received March 20, 1985

While metal–pentadienyl compounds have been known since at least 1962,[3] it has only been recently that the utility of these compounds has been appreciated.[4] From a reactivity standpoint, the accessibility of η^5, η^3, and η^1 bonding modes for the pentadienyl ligand (I–III) is a key reason for its utility. As our initial studies

I   II   III
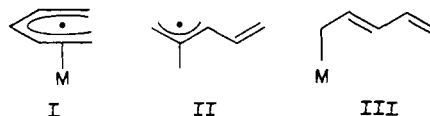
(1) A partial account has been presented: Stahl, L.; Ernst, R. D. "Abstracts of Papers", 40th Southwest Regional Meeting of the American Chemical Society, Lubbock, TX, Dec. 7, 1984; American Chemical Society: Washington, DC, 1984; No. 73.

(2) NSF Predoctoral Fellow, 1980–1983.

(3) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* 1962, 84, 1511.

(4) (a) Ernst, R. D. *Acc. Chem. Res.* 1985, 18, 56. (b) Paz-Sandoval, M. d. l. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* 1984, 3, 1026. (c) Bleeke, J. R.; Kotyk, J. J. *Ibid.* 1985, 4, 194. (d) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* 1981, 208, 189. (e) Lehmkuhl, H.; Naydowski, C. *Ibid.* 1982, 240, C30. Leyendecker, M.; Kreiter, C. G. *Ibid.* 1983, 249, C31.

Communications to the Editor

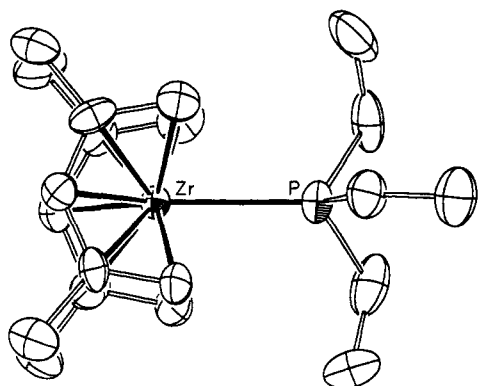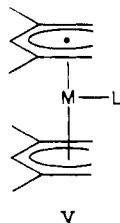*J. Am. Chem. Soc., Vol. 107, No. 17, 1985* 5017

Figure 1. Perspective view of the triethylphosphine adduct of bis(2,4-dimethylpentadienyl)zirconium, emphasizing the syn-eclipsed conformation. The niobium compound is isostructural.

emphasized sterically crowded bis(pentadienyl) compounds of first-row transition metals, it appeared that greater versatility might be achieved with larger second- and third-row metal systems. Herein we report our initial results for zirconium, niobium, and molybdenum including, to our knowledge, the first demonstration of an inherent preference by a metal for η^5-coordination by an S pentadienyl ligand, IV.

IV

The reactions of $[ZrCl_3(P(C_2H_5)_3)_2]_2$[5] or $MCl_4(P(C_2H_5)_3)_2$[5],[6] (M = Zr, Nb, Mo) with 6 or 4 equiv, respectively, of the 2,4-dimethylpentadienyl anion $(2,4-C_7H_{11}^-)$ in THF at -78 °C under nitrogen lead to the remarkably facile formations of the respective $M(2,4-C_7H_{11})_2(P(C_2H_5)_3)$ complexes in reasonable yields (generally exceeding 45%). Each has been thoroughly characterized by appropriate techniques (e.g., elemental analysis, ^1H and ^{13}C NMR spectroscopy, ESR spectroscopy, IR and mass spectroscopy, magnetic susceptibility, and single-crystal X-ray diffraction).[7] The zirconium and niobium compounds are similar in that they are bright green solids, slightly soluble in hydrocarbon solvents, and extremely air sensitive. The ^1H and ^{13}C NMR spectra for the zirconium compound display four resonances due to the 2,4-dimethylpentadienyl ligand, characteristic of the syn-eclipsed conformation (e.g., V) found in related titanium and vanadium CO

V

and PF_3 complexes.[8] This assignment was confirmed by structural

Figure 2. Perspective view of the triethylphosphine adduct of bis(2,4-dimethylpentadienyl)molybdenum.

determinations for the zirconium and niobium compounds (Figure 1).[9]

In notable contrast, the molybdenum complex is a yellow solid, extremely soluble in hydrocarbons and virtually air stable. Its ^1H and ^{13}C NMR spectra are quite different from those for the zirconium complex in that there are 14 resonances present for the 2,4-dimethylpentadienyl groups, indicative of nonequivalent ligands in unsymmetric environments. The X-ray diffraction result, necessary for structural assignment, can be seen in Figure 2.[10] Each molybdenum atom is bound by two 2,4-dimethylpentadienyl ligands in η^5 fashion: however, only one of these is observed to be in the normal U conformation. Surprisingly, the other 2,4-dimethylpentadienyl group has adopted the unusual S (sickle) conformation. The phosphine ligand is essentially situated by the open faces of the η^5-"U"-2,4-dimethylpentadienyl ligand and of the "cis-butadiene" portion of the η^5-"S"-2,4-dimethylpentadienyl ligand.

The structural data for the molybdenum compound provide the first opportunity to examine the geometric characteristics of an η^5-bound S pentadienyl ligand.[11] As can be seen in Figure 2, the "handle" end of the sickle is quite nonplanar, with the C(3)–C(2)–C(1) plane twisted, relative to the "butadiene" plane, toward the metal atom by ca. 52° and the C(3)–C(2)–C(6) plane twisted away from the metal atom by ca. 71°.[12] The relative Mo–C bond distances are also informative, being 2.285 (19), 2.164 (14), 2.208 (16), 2.390 (15), and 2.349 (16) Å respectively for atoms C(1)–C(5). Both the ligand nonplanarity and the very short Mo–C(2) and Mo–C(3) bond distances can best be attributed to geometric constraints required for effective η^5 coordination.

While η^5-bound S pentadienyl ligands have been identified in cationic tricarbonyliron complexes by Pettit, Lillya, Sorensen, and

(5) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.

(6) (a) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Ibid*, **1984**, *23*, 3592. (c) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc. Dalton Trans.* **1975**, 2639.

(7) Satisfactory analytical data (C,H) have been obtained. ^1H and ^{13}C NMR spectra for the zirconium and molybdenum compounds (also for hafnium and tungsten analogues) are consistent with the proposed formulations. For the niobium compound, magnetic susceptibility measurements demonstrate the presence of a single unpaired electron (1.61 μ_B), and the ESR spectra demonstrate coupling to the single niobium nucleus ($I = {}^9/_2$, hyperfine splitting = 120.6 G, g = 1.984) but not to the phosphorus nucleus.[8]

(8) (a) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257. (b) Ernst, R. D. *Struct. Bond (Berlin)* **1984**, *57*, 1.
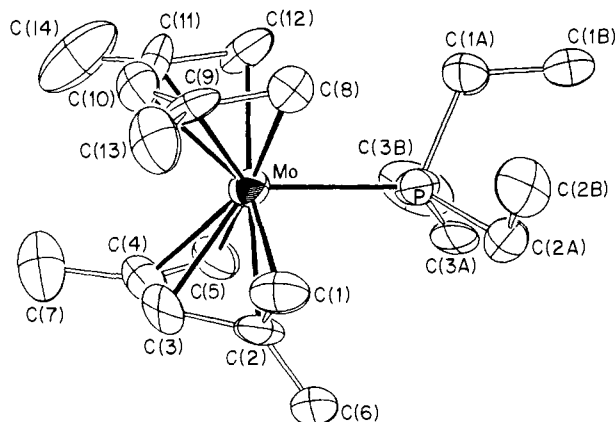
(9) The zirconium and niobium compounds are isomorphous, space group C_i^1-$P\bar{1}$ No. 2), with a = 7.988 (4) Å, b = 8.631 (4) Å, c = 15.649 (7) Å, α = 87.98 (4)°, β = 103.46 (4)°, γ = 91.70 (4)° and a = 7.936 (2) Å, b = 8.735 (2) Å, c = 15.511 (5) Å, α = 87.82 (2)°, β = 103.79 (2)°, γ = 92.12 (2)°, respectively. Data were collected out to 60° and 50°, leading to 4642 and 2593 unique observed ($I > 2.5\sigma(I)$) reflections, respectively. The final agreement indices are $R = 0.081$ and $R_w = 0.097$ for zirconium and $R = 0.051$ and $R_w = 0.052$ for niobium. The structural determinations were somewhat complicated by twinning.

(10) The molybdenum compound belongs to space group D_{2h}^{15}-*Pbca* (No. 61), with a = 11.244 (2) Å, b = 14.516 (2) Å, c = 24.963 (4) Å. Data were collected out to 50°, resulting in 1803 unique observed ($I > 3\sigma(I)$) reflections. The final agreement indices are $R = 0.084$ and $R_w = 0.096$.

(11) (a) A highly modified pentadienyl ligand, prevented from adopting the U configuration by its partial fusion into a lactone ring, has also been observed to bond in η^5 fashion to molybdenum. The bonding differs considerably from that noted here and was described more in terms of η^5-vinylallyl coordination. The ligand was formed by a coupling reaction involving two acetylene molecules and two CO ligands.[11b] (b) Allen, S. R.; Green, M.; Norman, N. C.; Paddick, K. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1625.

(12) For comparison, the "U" 2,4-dimethylpentadienyl ligands in these structures are essentially planar, the largest deviation being a tilt by the methyl groups of ca. 1–4° toward their respective metal atoms. The carbon–carbon bond distances in the "S" ligand, beginning at C(1), are 1.37 (2), 1.48 (2), 1.33 (3), and 1.38 (2) Å.

Brookhart,[13] in general these complexes readily rearrange to the more stable U conformation. However, for the (1,1,5-trimethylpentadienyl)iron tricarbonyl cation, steric interactions between substituents on the 1- and 5-positions lead to an equilibrium between η^5-bound U and S conformations.[13c] However, the 2,4-dimethylpentadienyl group is known to favor the U conformation when bound to lithium, potassium, or magnesium[14,15] (contrary to other pentadienyl groups used in the above-mentioned studies). Thus, while the 1,1,5-trimethylpentadienyl ligand bound to Fe(CO)$_3^+$ *partially* adopts the S conformation *due to* its particular substituents, one of the 2,4-dimethylpentadienyl ligands in Mo(2,4-C$_7$H$_{11}$)$_2$(PEt$_3$) is *totally* present in the S form *despite* an inherent bias for the U conformation. Clearly a powerful driving force is operative here in favor of the unusual η^5-"S" form. Exactly why this preference occurs here is not clear, however. Molybdenum is smaller than zirconium or niobium (the average M–P bond distances are 2.520 (3), 2.721 (2), and 2.628 (2) Å, while the average M–C bond distances involving the "U" 2,4-C$_7$H$_{11}$ ligands are 2.309 (6), 2.460 (3), and 2.399 (2) Å, respectively), and thus the greater interligand repulsions in a syn-eclipsed "U" structure could be reduced if one ligand adopted the "S" conformation. However, the marked contrast between the zirconium or niobium complexes and the molybdenum complex, particularly the apparent absence of any S ⇌ U equilibria,[16] may be indicative of some electronic influences. In this regard, the present situation is reminiscent of the occurrence of η^4-butadiene complexes involving both cis and trans conformations.[17] Much more remains to be learned about these systems, and further studies are under way.

(13) (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963,** *85,* 3955. (b) Clinton, N. A.; Lillya, C. P. *Ibid.* **1970,** *92,* 3065. (c) Sorensen, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970,** *25,* C62. (d) Lillya, C. P.; Sahatjian, R. A. *Ibid.* **1970,** *25,* C67. (e) Brookhart, M.; Harris, D. L. *Ibid.* **1972,** *42,* 441.

(14) (a) Schlosser, M.; Rauchschwalbe, G. *J. Am. Chem. Soc.* **1978,** *100,* 3258. (b) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980,** *53,* 1089. (c) Yasuda, H.; Ohnuma, Y.; Nakamura, A.; Kai, Y.; Yasuoka, N.; Kasai, N. *Ibid.* **1980,** *53,* 1101.

(15) It is interesting to note that (1,3,5-tris(trimethylsilyl)pentadienyl)-lithium exists in the sickle conformation in THF.[15b] (b) Yasuda, H.; Nishi, T.; Lee, K.; Nakamura, A. *Organometallics* **1983,** *2,* 21.

(16) (a) It might be expected that the implementation of a more normal pentadienyl ligand, *i.e.,* one for which the S conformation is favored relative to the U conformation, might lead to an η^5-bound S pentadienyl ligand for the less crowded zirconium and/or niobium compounds. Preliminary ^{1}H and ^{13}C NMR data for Zr(C$_5$H$_7$)$_2$(P(C$_2$H$_5$)$_3$) indicate that two η^5-"U"-pentadienyl ligands are present; however, the situation regarding niobium has not been resolved yet. (b) While the most obvious way to form the η^5-"S"-pentadienyl ligand would involve simple rotation around an "internal" carbon–carbon bond of the pentadienyl fragment, alternatives do exist, e.g.:
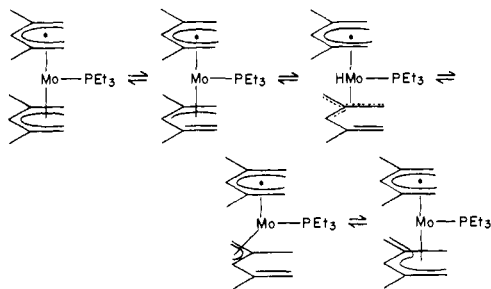
Similar reactions are known for (pentadienyl)cobalt compounds.[16c] (c) Wilson, D. R.; Ernst, R. D.; Kralik, M. S. *Organometallics* **1984,** *3,* 1442.

(17) (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980,** *102,* 6344. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982,** *1,* 388. (c) Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985,** *107,* 1791.

Control of Heme Protein Redox Potential and Reduction Rate: Linear Free Energy Relation between Potential and Ferric Spin State Equilibrium

Mark T. Fisher and Stephen G. Sligar*

*Department of Biochemistry, University of Illinois
Urbana, Illinois 61801*

The cytochrome P-450$_{cam}$ monooxygenase system isolated from *Pseudomonas putida* grown on camphor is an ideal system to study the regulation of electron transfer between two redox centers on separate protein molecules. Cytochrome P-450 catalyzed monooxygenation reactions require an external source of two electrons (SH + O$_2$ + 2e$^-$ + 2H$^+$ → SOH + H$_2$O), which are transferred from NADH to the heme iron of cytochrome P-450$_{cam}$ through the combined action of the FAD-flavoprotein putidaredoxin reductase and the iron–sulfur protein putidaredoxin.[1] The mechanisms of regulation of the first electron-transfer step (ferric to ferrous reduction) in the various P-450 systems has been the subject of intense interest.[2] In the case of the camphor monooxygenase system, camphor binding produces dramatic changes in the visible and near-UV regions of the heme optical spectrum.[1] Mössbauer[3] and electron spin resonance studies[4] have linked these optical changes to a shift in the spin state of the heme iron from a low spin ($S = \frac{1}{2}$) configuration in the absence of substrate to a high spin ($S = \frac{5}{2}$) configuration for the substrate-bound hemoprotein. This dynamic spin state change has also been observed for cytochrome P-450 model metalloporphyrin compounds.[5] In addition, experimentation has shown that camphor binding in-

(1) Gunsalus, I. C.; Meeks, J. R.; Lipscomb, J. D.; Debrunner, P. G.; Munck, E. "Molecular Mechanisms of Oxygen Activation"; Academic Press: New York, 1974; p 559.

(2) (a) Sligar, S. G. *Biochemistry* **1976,** *15,* 5399. (b) Sligar, S. G.; Cinti, D. L.; Gibson, G. G.; Schenkman, J. B. *Biochem. Biophys. Res. Commun.* **1979,** *90,* 925. Light, D. R.; Orme-Johnson, N. R. *J. Biol. Chem.* **1981,** *256,* 343. (c) Backes, W. L.; Sligar, S. G.; Schenkman, J. B. *Biochemistry* **1982,** *21,* 1324. (d) Ristau, O.; Rein, H.f Greschner, S.; Janig, G.; Ruckpaul, K. *Acta Biol. Med. Ger.* **1979,** *256,* 6686. (e) Gould, P. V.; Gelb, M. H.; Sligar, S. G. *J. Biol. Chem.* **1981,** *256,* 6686. (f) Sligar, S.; Gunsalus, I. C. *Proc. Natl. Acad. Sci. U.S.A.* **1976,** *73,* 1078. (g) Sligar, S.; Gunsalus, I. C. *Biochemistry* **1979,** *18,* 2290. (h) Sligar, S.; Cinti, D.; Gibson, G.; Schenkman, J. *Biochem. Biophys. Res. Commun.* **1979,** *90,* 925. (i) Hintz, M. J.; Mock, D. M.; Peterson, L. L.; Tuttle, K.; Peterson, J. A. *J. Biol. Chem.* **1982,** *257,* 14324. (j) Hintz, M. J.; Peterson, J. A. *J. Biol. Chem.* **1981,** *256,* 6721. (k) Gugenrich, F. P. *Biochemistry* **1983,** *22,* 2811.

(3) (a) Sharrock, M.; Munck, E.; Debrunner, P. G.; Marshall, V.; Lipscomb, J. D.; Gunsalus, I. C. *Biochemistry* **1973,** *12,* 258. (b) Sharrock, M.; Debrunner, P. G.; Schulz, D.; Lipscomb, J. D.; Marshall, V.; Gunsalus, I. C. *Biochem. Biophys. Acta* **1976,** *420,* 8. (c) Champion, P. M.; Lipscomb. J. D.; Munck, E.; Debrunner, P.; Gunsalus, I. C. *Biochemistry* **1975,** *14,* 4151.

(4) Tsai, R. L.; Yu, C.-A.; Gunsalus, I. C.; Peisach, J.; Blumberg, W. E.; Orme-Johnson, W. H.; Beinert, H. *Proc. Natl. Acad. Sci. U.S.A.* **1970,** *66,* 1157.

(5) Coleman, J. P.; Sorrell, T. N.; Hodgson, K. O.; Kulshrestha, A. K.; Strouse, C. E. *J. Am. Chem. Soc.* **1977,** *99,* 5180.