Table I

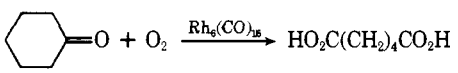
Solvent	Yield CO_2[a] (mmol)	Solvent oxidation	Remaining O_2 (%)
None	Trace	None	100
Cyclohexane	Trace	None	100
Cyclohexene	5	*b*	10
Acetone	20	CH_3CO_2H(1.5 mmol)	10
Cyclohexanone	17	$(CH_2)_4(CO_2H)_2$ (1 mmol)	10
Dimethoxyethane	9	*b*	20
Dimethyl sulfoxide[c]	10	*d*	10

[a] From CO (32 mmol) and O_2 (16 mmol). [b] Solvent decomposition to several unidentified compounds occurred. [c] No $Rh_6(CO)_{16}$ could be recovered, but the resulting solution remained catalytically active. [d] Unidentified acidic products were formed.

tion, and proceeding with the catalysis. Oxidation continued, and a homogeneous solution remained when the mixture was finally assayed.

In a typical reaction $Rh_6(CO)_{16}$ ($\sim 10^{-2}$ mmol) was suspended in 10 ml of solvent in a glass vial and the mixture stirred at 100° under a pressure of 34 atm (35 ml volume). The ratio of CO:O_2 was 2:1 and the reaction was complete within 24 hr. The quantities of CO_2 formed and O_2 remaining were measured by mass spectrometer, after thorough mixing of the vented gases with a known amount of argon. Gas quantities were obtained from the peak areas by comparison to a standard curve after contributions from interfering ions were subtracted out. The peaks used for these analyses were 32 for O_2, 40 for Ar, and 44 for CO_2.

The volume of O_2 consumed in acetone as solvent is in excess of that required for the conversion of the CO into CO_2. The other product, along with very minor unidentified components, is acetic acid. The acetic acid was identified by gas chromatography and assayed by titration. This homogeneous oxidation of acetone to acetic acid must occur by a catalytic C–C bond cleavage reaction. In order to identify the fate of the other methyl group on acetone the reaction was carried out in cyclohexanone as solvent. Oxidation of CO to CO_2 was again facile and the acid now formed was adipic acid. This result implies that the other product from acetone is formic acid, which would not be stable under the condition of the reaction. In order to increase the yield of adipic acid the reaction was carried out under the same total pressure but with a partial pressure ratio of 3:1 for



$$CH_3COCH_3 + O_2 \xrightarrow{Rh_6(CO)_{16}} CH_3CO_2H + \text{"}HCO_2H\text{"}$$

O_2:CO. The yield of adipic acid in this run was 1000 mmol.[1] At the end of the reaction a red solution remained, but no $Rh_6(CO)_{16}$ was present. The hexameric cluster compound could be regenerated, however, by restoring a substantial pressure of CO and O_2 over this solution at 100°. Attempts to obtain the ketone oxidation under pure oxygen were unsuccessful due to decomposition of the cluster; nevertheless, $Rh_6(CO)_{16}$ could again be regenerated by the above procedure.

Previous work has shown that when $Rh_6(CO)_{16}$ is refluxed in acetic acid a dimer, $Rh_2(OAc)_2(CO)_4$, is obtained.[5] It appears therefore that under the conditions of our reaction there will be considerable conversion of the cluster into a carboxylate bridged dimer. In agreement with this rationale we have found that $Rh_2(OAc)_2(CO)_4$ is readily converted into $Rh_6(CO)_{16}$ under CO pressure. The carboxylate complex is not necessary for the catalytic conversion of CO into CO_2 since the reaction occurs in cyclohexene as solvent without any formation of acidic products. The oxidation of CO has been carried out in a range of solvents as shown in Table I.

When $Rh_2Cl_2(CO)_4$ was used as catalyst little conversion of CO to CO_2 occurred, and this corresponded with the formation of a small quantity of $Rh_6(CO)_{16}$. With $Rh_4(CO)_{12}$ catalysis was facile because of its ready conversion to $Rh_6(CO)_{16}$.

This work shows that the compound $Rh_6(CO)_{16}$ is effective as an oxidation catalyst in addition to being a useful hydrogenation and hydroformylation catalyst.[6-8] This oxidation reaction, however, is particularly interesting because of the accompanying unique homogeneously catalyzed C–C bond cleavage reaction of ketones.

Acknowledgments. This research was supported in part by the National Science Foundation under Grant No. GP-38775, and acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Nuclear Magnetic Resonance Study on Ligand–Metalloporphyrin Complexation. A Study of Equilibria and Paramagnetism in a Ferriprotoporphyrin–Cyanide System

Sir:

A large number of studies of the effect of ligands on the high to low spin transitions of ferrous and ferric porphyrins have been reported.[1-4] Despite the wide variety of NMR studies,[1,2] relatively little is known concerning the equilibria and kinetics of ligand binding to the iron of porphyrins. We report here a study of ferriprotoporphyrin (hemin)–cyanide complexation in DMSO-d_6[5] in which we show: (i) the cyanide ligation to hemin is a two-step binding process (see eq 1 and 2) with the binding constant K_1 greater than K_2 (see eq 3 and 4), (ii) the first step involves formation of the previously unknown monocyano adduct of hemin, paramagnetic susceptibility measurements show this adduct to be low

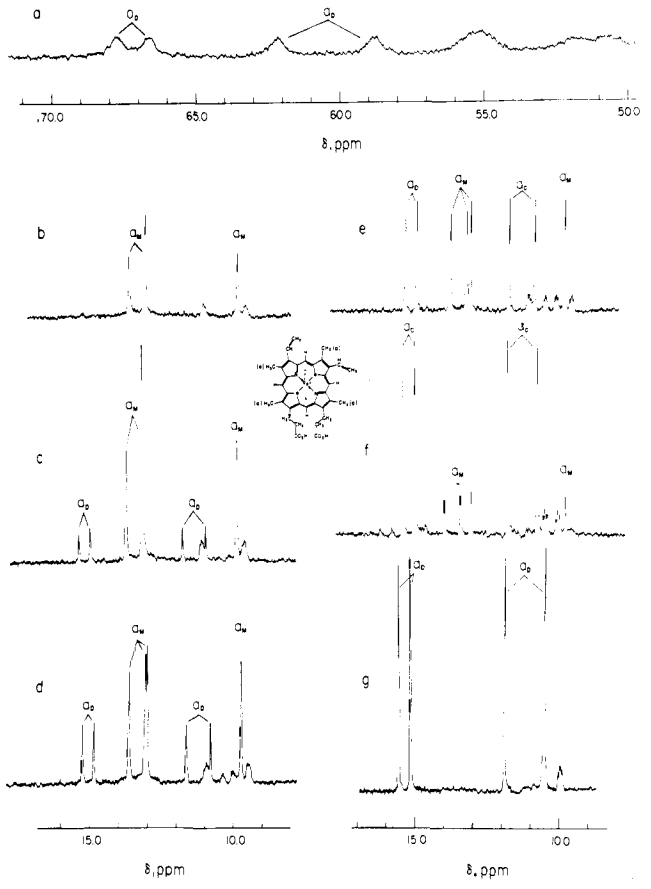

Figure 1. Room temperature (20°) 220-MHz ^1H spectra of a 0.02 *M* ferriprotoporphyrin·Cl (hemin) in DMSO-d_6 solution at various potassium cyanide concentrations. Only the methyl protons of porphyrin are shown here. The cyanide concentrations are (a) 0.00 *M*, (b) 0.01 *M*, (c) 0.02 *M*, (d) 0.025 *M*, (e) 0.03 *M*, (f) 0.04 *M*, and (g) 0.05 *M*. a_0, a_M, and a_D are assigned as the methyl resonances from the hemin, monocyanohemin, and dicyanohemin species, respectively.

spin, and (iii) the rate of exchange among the three hemin species is slow on the NMR time scale.

$$\underset{1}{\text{hemin}^+} + CN^- \rightleftharpoons \underset{2}{\text{hemin}\cdot CN} \quad (1)$$

$$\text{hemin}\cdot CN + CN^- \rightleftharpoons \underset{3}{\text{hemin}\cdot (CN)_2^-} \quad (2)$$

$$K_1 = \frac{[\text{hemin}\cdot CN]}{[\text{hemin}^+][CN^-]} \quad (3)$$

$$K_2 = \frac{[\text{hemin}\cdot (CN)_2]}{[\text{hemin}\cdot CN][CN^-]} \quad (4)$$

The observation of transition from high spin hemin (**1**) to low spin monocyanohemin (**2**) and dicyanohemin (**3**) in solution is illustrated in Figures 1 and 2. Figure 1 shows the proton NMR spectra of the four porphyrin methyls of hemin at various potassium cyanide concentrations. In the absence of cyanide (Figure 1a), only the high spin hemin, which has DMSO as its fifth and sixth ligands,[6] exists in the solution. The methyl protons (labeled as a_0) of **1** exhibit a large paramagnetic shift to low field at 50–70 ppm relative to TMS. Upon addition of cyanide to the solution the areas under these four methyl resonances decrease and finally disappear with the concomitant appearance of a new group of resonance peaks (labeled as a_M in Figure 1b–f) at 10–20 ppm. These new peaks reach a maximum intensity at a cyanide–hemin ratio of about 1:1 and then decrease thereafter, finally disappearing at about a 2:1 ratio. A second

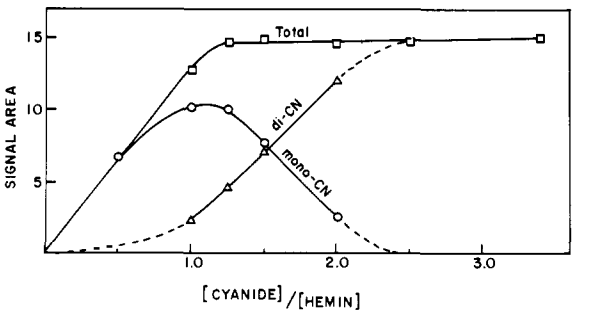

Figure 2. Variation of the methyl resonance signal area of monocyanohemin (○), dicyanohemin (△), and their sum (□) from a 0.02 *M* hemin in DMSO-d_6 solution as a function of the cyanide–hemin ratio.

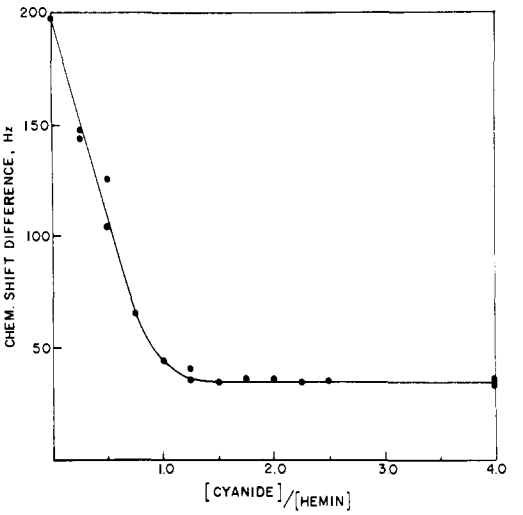

Figure 3. Variation of the chemical shift difference between a 1% TMS in DMSO-d_6 (in an internal capillary) and similar solutions containing hemin (0.02 *M*) and varying amounts of cyanide. Chemical shifts were measured at 20° on a Varian HR-220 spectrometer.

group of peaks (labeled as a_D in Figure 1c–g) were also noted in the same chemical shift region. These peaks first appear at a cyanide–hemin ratio of about 1:1, reaching a maximum at about a 2:1 ratio and then remain constant at higher cyanide–hemin ratios. The resonances of a_M and a_D are assigned to the methyl protons of **2** and **3** species, respectively.

A plot of the intensity of the resonances, a_M, as a function of the cyanide to hemin ratio (Figure 2) shows a maximum at about 1:1, i.e., demonstrates the stoichiometry of the complex as 1:1. The second complex, a_D, does not reach its maximum value until the ratio of cyanide–hemin is 2, i.e., a 2:1 complex. These observations suggest that the binding constants K_1 and K_2 are large and the former greater than the latter. Using eq 3 and 4, and the concentrations of three hemin species obtained at various cyanide concentrations, K_1 and K_2 were calculated to be $1.9 \pm 0.3 \times 10^4$ and $1.1 \pm 0.2 \times 10^3\ M^{-1}$ at 20°, respectively.[7] These values are comparable to those reported by Shack and Clark ($K_1 \sim 2.2 \times 10^6$ and $K_2 \sim 0.63$),[8a] and by Kaziro et al. ($K_1 \sim 4.8 \times 10^4$ and $K_2 \sim 3.4 \times 10^2$)[8b] in a pyridine solution using the spectrophotometric method. The overall $K(=K_1K_2) \sim 10^7$ is found larger than those reported for the complexations of imidazole ($K \sim 10^5$)[9] and *N*-methylimidazole ($K \sim 10^3$)[2] to TPPFe·Cl.[10]

The spin states of hemin (**1**) and its complexes, where the fifth and sixth positions are coordinated by strong field ligands (e.g., dicyanide and diimidazole), have been reported.[4,11] A mono-*N*-methylimidazole adduct of hemin was suggested to be in a high spin form based on indirect evidence.[2] The assignment of a spin state for monocyanohe-

min has not been previously reported. We now assign unequivocally the monocyanohemin to a low spin state from measurements of the paramagnetic susceptibility using the method described by Evans.[12] Figure 3 shows the chemical shift difference between a 1% TMS in DMSO-d_6 (in an internal capillary) and similar solutions containing hemin (0.02 M) and varying amounts of cyanide. The chemical shift difference, which is directly related to the bulk paramagnetic susceptibility of the hemin solution, decreases linearly with added cyanide until a 1:1 ratio (cyanide:hemin) is reached and becomes constant thereafter. This demonstrates that both **2** and **3** have the same paramagnetism and, therefore, are in the low spin state ($S = \frac{1}{2}$). The close resemblance in the proton spectra between **2** and **3** also supports this assignment. Using the equation described by Brault and Rougee,[13] the effective magnetic moments (μ_{eff}) of iron(III) in **1** and **2** (or **3**) in DMSO-d_6 were determined to be 5.0 and 2.1 BM, respectively. These values are in good agreement with the reported high spin (μ_{eff} = 5.1–5.8 BM) and low spin (μ_{eff} = 1.7–2.5 BM) values in other ferriporphyrin systems.[4,11]

The presence of all three hemin spectra in the DMSO-d_6 solution requires that they are in the NMR slow exchange limit region. Based on our data, the rate of exchange is calculated to be slower than 160 sec^{-1} at 65°. A value of 60 sec^{-1} at 30° was reported for the TPPFe·Cl-*N*-methylimidazole system.[2]

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$$\chi_M = \frac{3}{4\pi}\frac{\Delta\nu}{\nu}\frac{1000}{C} + \chi_0 M - \chi_D$$

rather than the equation

$$\chi_M = \frac{3}{2\pi}\frac{\Delta\nu}{\nu}\frac{1000}{C} + \chi_0 M - \chi_D$$

which is used when the axis of the cylindrical sample is perpendicular to the field.

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Binding and Activation of Enzymic Substrates by Metal Complexes. II. Delocalized Acetylene Complexes of Molybdenum[1]

Sir:

In previous communications,[2-4] we reported the synthesis and reactivity of several oxomolybdenum complexes containing *N,N*-dialkyldithiocarbamate and alkylxanthate ligands, emphasizing possible relationships to molybdoenzymes, particularly nitrogenase. The oxidative addition of diazenes (RN=NR) to $OMo(S_2CNR_2)_2$ and subsequent hydrolysis of the 1:1 adduct to yield a substituted hydrazine (RNHNHR) and $O_2Mo(S_2CNR_2)_2$ is thought to be particularly relevant. However, as these oxomolybdenum(IV) complexes added only highly activated multiple bonds, we sought more reactive entities and have investigated the reactivity of some d^4 Mo(II) compounds. These have increased basicity, no oxo ligands, and also the capability of effecting a four-electron reduction of substrate (as opposed to the d^2 Mo(IV) species). Herein we describe the preparation, characterization, and reactivity of a Mo(II) dithiophosphinate complex.

Reaction of $Mo(CO)_4Cl_2$ (ref 5) with $HS_2P(i\text{-}Pr)_2$ (ref 6) in methanol gave a deep orange-red solution which changed to green on concentration in vacuo. Further concentration yielded green crystals of **1**. After washing (MeOH) and drying in vacuo, elemental analysis (Calcd for $C_{14}H_{28}O_2P_2S_4Mo$: C, 32.7; H, 5.45. Found: C, 32.4; H, 5.78), molecular weight (calcd, 514; found, 525, cryoscopy), CO evolution data (1.95 mol/mol of complex), and ir spectroscopy (ν(CO) 1960, 1860 cm^{-1}) showed **1** to be *cis*-$Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$. **1** is diamagnetic (NMR, $CDCl_3$).

Addition of CO to a CH_2Cl_2 solution of **1** caused a change from green (λ_{max} 468 (ϵ 480), λ_{max} 688 nm (ϵ 900)) to red (λ_{max} 469 nm (ϵ 456)) with the concomitant production of three carbonyl bands (2040, 1990, and 1940 cm^{-1}). When CO was removed in vacuo, the original visible and ir spectra returned. Such data are consistent with formation of $Mo(CO)_3[S_2P(i\text{-}Pr)_2]_2$ (**2**) and provide conclusive evidence for the reversibility of the CO uptake. Similar observations[7] have been reported for other Mo(II) complexes, with dramatic color changes as CO is evolved or complexed. Attempts to isolate pure, crystalline **2** have been unsuccessful.[8] Evaporation of a solution of **2** in a stream of CO yields a red oil.

Similarly, concentration of a reaction mixture containing **1** and Ph_3P gave red $Mo(CO)_2(Ph_3P)[S_2P(i\text{-}Pr)_2]_2$ (**3**), which was characterized by elemental analysis (calcd for $C_{32}H_{53}O_2P_3S_4Mo$: C, 49.5; H, 5.54. Found; C, 48.9; H, 5.61.) and ir spectroscopy (ν(CO) 1950, 1865 cm^{-1}). Dissolution of **3** in CH_2Cl_2 (ca. 10^{-3} M) gave a *green* solution whose visible spectrum (λ_{max} 480 (ϵ 437), 689 nm (ϵ 705)) indicated the following equilibrium to be shifted far to the right under these conditions.

$$Mo(CO)_2PPh_3[S_2P(i\text{-}Pr)_2]_2 \rightleftarrows Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2 + PPh_3$$