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 ($\mu_{\text{eff}} = 5.1$–5.8 BM) and low spin ($\mu_{\text{eff}} = 1.7$–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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$$\chi_{\mathrm{M}} = \frac{3}{4\pi}\frac{\Delta\nu}{\nu}\frac{1000}{C} + \chi_0\mathrm{M} - \chi_{\mathrm{D}}$$

rather than the equation

$$\chi_{\mathrm{M}} = \frac{3}{2\pi}\frac{\Delta\nu}{\nu}\frac{1000}{C} + \chi_0\mathrm{M} - \chi_{\mathrm{D}}$$

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, $CDCl_3$).

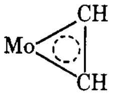
Addition of CO to a CH_2Cl_2 solution of **1** caused a change from green ($\lambda_{\max}$ 468 (ϵ 480), $\lambda_{\max}$ 688 nm (ϵ 900)) to red ($\lambda_{\max}$ 469 nm (ϵ 456)) with the concomitant production of three carbonyl bands (2040, 1990, and 1940 cm^{-1}). When CO was removed in vacuo, the 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 ($\lambda_{\max}$ 480 (ϵ 437), 689 nm (ϵ 705)) indicated the following equilibrium to be shifted far to the right under these conditions.

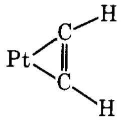
$$Mo(CO)_2PPh_3[S_2P(i\text{-}Pr)_2]_2 \rightleftarrows Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2 + PPh_3$$

At room temperature in CH_2Cl_2, **1** reacted with acetylene (one mol per Mo) and the solution became light yellow-green. Removal of the solvent in vacuo and recrystallization (CH_2Cl_2-hexane) yielded the yellow-green solid, $Mo(CO)(C_2H_2)[S_2P(i\text{-}Pr)_2]_2$ (**4**). Anal. Calcd for $C_{15}H_{30}O_3P_2S_4Mo$: C, 35.2; H, 5.91. Found: C, 34.8; H, 6.27. The ir spectrum of **4** had bands at 1950 (ν(CO)), 3070, 3150, and 745 cm^{-1} (assigned to the C–H of the coordinated acetylene). No carbon–carbon stretch was observed in the usual region,[9] suggesting a significant perturbation of the triple bond. Thermal decomposition (GLC injection port) showed C_2H_2 only, indicating the acetylene to be bound as a monomer.

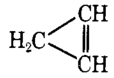
The NMR spectrum ($CDCl_3$) of **4** exhibited, in addition to a complex signal for the isopropyl groups, a sharp singlet 12.33 ppm *downfield* from TMS, which was assigned to the two protons of the coordinated acetylene. This extreme downfield shift (free acetylene is at 2.3 ppm) may be indicative of a delocalized, 2-π aromatic system,



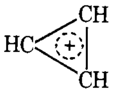
which could result if C_2H_2 behaved as a four-electron donor with both π bonds interacting with appropriate empty metal orbitals.[10] In contrast, similar delocalization cannot occur for $Pt(PPh_3)_2(C_2H_2)$, generated in situ,[11] due to the lack of empty metal orbitals. The acetylenic protons of the complex appear in the 7.3 ppm region, indicating that this compound represents the more-localized double bond arrangement,



This correlation is consistent with carbon analogs; e.g., similar relative shifts are found on comparing the localized double bond of cyclopropene,



(olefinic protons at 7.01 ppm[12]) with the aromatic cyclopropenyl cation,



(ring protons at 11.2 ppm[13]) although some of the deshielding in the latter case must result from the positive charge. The acetylenic protons in recently reported[14] $(C_5H_5)_2Mo(C_2H_2)$ appear at 7.68 ppm. This chemical shift, together with the fact that a C═C stretch is observed at 1613 cm^{-1}, suggests that the stereochemical and/or electronic properties of this complex are unsuitable for the delocalized interaction suggested for **4**.

1 also reacts with a variety of substituted acetylenes including $HC{\equiv}CPh$, $CH_3C{\equiv}CPh$, $PhC{\equiv}CPh$, $CH_3O_2CC{\equiv}CCO_2CH_3$, and $HC{\equiv}CCO_2CH_3$ to yield analogs of **4**. Adducts containing terminal acetylenic protons exhibit similar low field (12-13 ppm) resonances, suggesting delocalized bonding. Unlike the platinum and molybdocene systems, **1** does *not* react with ethylene, nor will this olefin displace acetylene from **4**.

Addition of HCl gas to a CH_2Cl_2 solution of **4** immediately produces ethylene (GLC and mass spectrometry). Only ~20% of the bound acetylene is converted, however, and current work is directed to explaining this result. Although *cis*-2-butene has been produced by acidification of both $(C_5H_5)_2Mo(CH_3C_2CH_3)$ (ref 15) and $Pt(PPh_3)_2(CH_3C_2CH_3)$ (ref 16), our system is the first reported where acetylene itself is reduced to ethylene via the two-step sequence of (i) oxidatively adding C_2H_2 to form an isolable complex and (ii) protonation of this intermediate to yield ethylene.

We believe that these reactions with acetylenes are relevant to the mechanism of nitrogenase catalysis. The $Mo(CO)[S_2P(i\text{-}Pr)_2]_2$ core may be considered as a coordinatively unsaturated 14-electron species, and thus may be related to the N_2-reducing titanocene system.[17] The driving force for formation of these acetylene (but not olefin) complexes may be that Mo is attaining an inert gas configuration by acceping four π-electrons, a situation not possible with ethylene. Such reactivity parallels that of nitrogenase,[18] and, as such, we suggest that the active site of the enzyme may also consist of a 14-electron, coordinatively unsaturated moiety. Thus N_2 would also have to interact as a four-electron donor in order to be reduced. The recently reported[19] $[C_5(CH_3)_5]_2TiN_2$, suggested to involve "side on" bound N_2, may be an example of such an interaction.

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