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Use of $[MoFe_3S_4]^{3+}$ Single Cubanes in the Catalytic Reduction of Acetylene to Ethylene and Ethane. Identification of Molybdenum and Iron Atoms as Catalytic Sites during Substrate Reduction and Implications for Nitrogenase Action

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Abstract: The reactivity modeling of the nitrogenase enzyme is currently being pursued in our laboratory using various single cubanes possessing the $[MFe_3S_4]^{3+}$ core as catalysts for the reduction of enzymatically relevant substrates ($M = Mo$, $n = 3$; $M = V$, $n = 2$). One such substrate, acetylene, is catalytically reduced by $(NEt_4)_2[(Cl_4\text{-cat})(CH_3CN)MoFe_3S_4Cl_3]$ (**I**: Cl_4-cat = tetrachlorocatecholate dianion) to ethylene and small amounts of ethane in the presence of added protons (lutidine hydrochloride) and reducing equivalents (cobaltocene). Gas chromatography was employed to monitor the progress of the reaction. Catalysis in excess of 15 turnovers has been demonstrated over a period of 24 h. A kinetics study reveals saturation kinetics to be operating at high substrate concentrations; however, at lower, optimum substrate levels initial reaction velocities v_0 may be obtained and further used in a double reciprocal plot, v_0^{-1} vs $[C_2H_2]^{-1}$, to determine $K_m \approx 17.9$ mM and $V_{max} \approx 1.1 \times 10^{-4}$ M/min. A study of this reaction at five temperatures indicates a moderate activation energy ($E_{act} = 9(1)$ kcal mol^{-1}) but a large entropy of activation ($\Delta S^{\ddagger} = -32(2)$ cal K^{-1} mol^{-1}) which extrapolates to a significant Gibbs free energy ($\Delta G^{\ddagger} = 19(1)$ kcal mol^{-1}). The large negative $\Delta S^{\ddagger\, i}$ is consistent with an ordered transition state. Considerable evidence has been amassed which directly implicates the Mo atom of **I** as the primary catalytic site. Replacement of the Mo bound solvent molecule of **I** with non-labile ligands acts to suppress the observed rate of reaction. In addition, the Fe sites on the catalyst have been found to effect substrate reduction albeit at a *markedly* reduced rate compared to the heterometal. Catalyst integrity has also been demonstrated by a variety of techniques, primarily EPR spectroscopy which identifies the characteristic $S = {}^3/_2$ signal of cubane **I** after at least 18 h of reaction time. The geometry of addition across the substrate triple bond has been shown to be *cis* by the use of C_2D_2 which results in the formation of *cis*-1,2-$C_2H_2D_2$ as the predominant isomer. Implications for the action of the nitrogenase enzyme are also addressed.

Introduction

As a result of recent single-crystal X-ray studies on the Fe−Mo protein component of nitrogenase the structure of the Fe/Mo/S active site has been revealed to near atomic resolution.[1,2] This site is a Fe_7MoS_9 cluster and consists of two corner-voided cubane-like subunits bridged by three sulfide ligands. The $MoFe_3S_3$ and Fe_4S_3 subunits lack a full complement of terminal ligands and the structure contains six coordinatively unsaturated FeS_3 sites with their central Fe atoms located in a trigonal prismatic arrangement. The remaining Mo and Fe atoms, capping the trigonal faces of the Fe_6 prism, serve as cluster anchor points and in the protein are coordinated to a histidine (imidazole) and a cysteine (thiolate) residue (Figure 1).

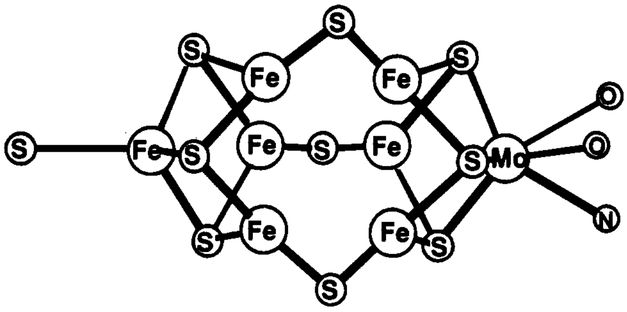

Figure 1. The structure of the Fe/Mo/S site in nitrogenase (refs 1 and 2).

Prior to the MoFe protein structure determination, numerous attempts to obtain synthetic analogs for the nitrogenase active site have resulted in the synthesis of a great variety of Fe/Mo/S clusters. Included among these clusters are (a) the oligonuclear Fe/M/S (M = Mo, W) complexes,[3,4] (b) the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{3-,4-}$ clusters derived from the hexagonal prismatic $[Fe_6S_6L_6]^{n-}$ clusters,[5] (c) polynuclear, Fe−M−S clusters that contain as a common structural feature the MFe_3S_4 cubane-type units[4] (M = Mo, W), and (d) clusters obtained from the reactions of the $[Fe_2S_2(CO)_6]^{2-}$ dianion with various Mo sources.[6]

The clusters that contain the $MoFe_3S_4$ cubanes as structural units are represented by three general structural types: the double cubanes[7a] that contain two bridged MFe_3S_4 cubane units such as $[Mo_2Fe_6S_9(SR)_8]^{3-}$,[7a,b] $[Mo_2Fe_6S_8(SR)_9]^{3-,4-}$,[7c] [Mo2-

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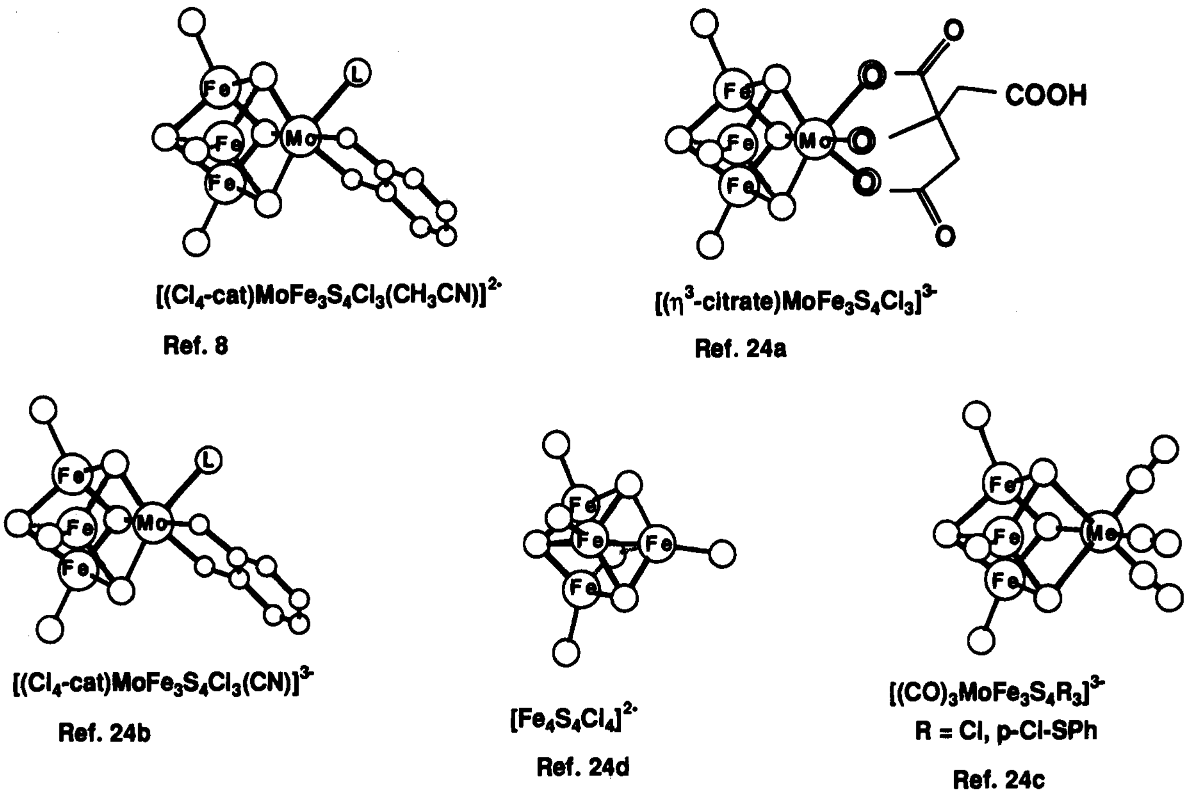

$[(Cl_4\text{-cat})MoFe_3S_4Cl_3(CH_3CN)]^{2-}$ Ref. 8

$[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ Ref. 24a

$[(Cl_4\text{-cat})MoFe_3S_4Cl_3(CN)]^{3-}$ Ref. 24b

$[Fe_4S_4Cl_4]^{2-}$ Ref. 24d

$[(CO)_3MoFe_3S_4R_3]^{3-}$ R = Cl, p-Cl-SPh Ref. 24c

Figure 2. Single cubanes used as catalysts in the reduction of acetylene to ethylene.

$Fe_6S_8(OMe)_3(SR)_6]^{3-}$,[7b] $[Mo_2Fe_7S_8(SR)_{12}]^{3-,4-}$,[7c] and $[Mo_2Fe_6S_8(SR)_6(3,6\text{-}R'_2cat)_2]^{4-}$,[7d] the single cubanes such as $[Mo(3,6\text{-}R'_2\text{-cat})(L')Fe_3S_4(L)_3]^{2-,3-}$ ($L = RS^-$, Cl^-; R' = allyl, *n*-Pr; L' = DMSO, DMF, CH_3CN, PR_3, RS^-, CN^-, RO^-),[4,7d,8] and the doubly-bridged double-cubane clusters $[[MoFe_3S_4Cl_2(Cl_4\text{-cat})]_2(\mu_2\text{-}S)(\mu_2\text{-}L)]^{n-}$ ($L = N_2H_4$, $n = 4$; $L = OH^-$, CN^-, N_3^-, $n = 5$; and $L = S^{2-}$, $n = 6$).[9-11] None of the above Fe/Mo/S complexes have the correct stoichiometry or structure to qualify as synthetic analogs for the nitrogenase site. Nevertheless, many of these compounds possess structural features similar to those found in the Fe/Mo/S site in nitrogenase.

This is particularly true for the synthetic Fe/Mo/S clusters that contain the MFe_3S_4 structural units.[4] In the latter the six-coordinate Mo atoms show first and second coordination sphere environments similar to those found in the nitrogenase center. This similarity, previously suggested by comparative Mo-EXAFS analyses,[12] offers a unique opportunity for reactivity studies on Mo centers structurally relevant to the nitrogenase site. The importance of such reactivity studies derives from (a) the scarcity of functional analogs for the nitrogenase active site and (b) from unanswered questions regarding the role of the coordinatively saturated Mo atom in nitrogenase in substrate reduction.

Recently we initiated studies on the reactivity of synthetic Fe/Mo/S clusters and we reported on the catalytic reduction of hydrazine to ammonia by specific $[MoFe_3S_4]^{3+}$ single cubanes.[13] As an extension of these studies to other nitrogenase substrates we report herein on the effective use of the same cubanes (Figure 2) in the catalytic reduction of acetylene to ethylene. Previous studies on the abiological reduction of C_2H_2[14-23] suffer from major drawbacks including incomplete catalyst identifica-

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tion,[14,15,17] the use of mononuclear or binuclear Mo complexes of little relevance to the nitrogenase problem,[16-22] and substoichiometric, non-catalytic, substrate reduction.[23] In the present study we provide substantial evidence that identifies the $[MoFe_3S_4]^{3+}$ cubanes as catalysts in the reduction of acetylene to ethylene and implicates both the Mo and Fe sites in acetylene reduction.

Experimental Section

Syntheses. The compounds $(Et_4N)_2[(Cl_4\text{-cat})(CH_3CN)MoFe_3S_4Cl_3]$[8] (**I**), $(NEt_4)_3[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]$,[24a] $(NEt_4)_3[(Cl_4\text{-cat})(CN)MoFe_3S_4Cl_3]$,[24b] $(NEt_4)_3[(CO)_3MoFe_3S_4R_3]$[24c] (R = Cl, *p*-Cl-SPh), and $(NBu_4)_2[Fe_4Cl_4]$[24d] were all synthesized by published procedures. Cobaltocene and anhydrous DMF were obtained from Aldrich Chemical Co. the former was used without further purification, the latter was extensively degassed and placed over 3 Å molecular sieves prior to use. The anaerobic reaction of 2,6-lutidine with 1 M ethereal HCl results in the precipitation of white, hygroscopic 2,6-lutidine hydrochloride (Lut·HCl) in quantitative yields.

Physical Measurements. Gas-chromatographic analyses of C_2H_2, C_2H_4, and C_2H_6 were carried out on a Hewlett Packard 5980 Series II instrument employing a Porapak N (6 ft) porous polymer column and a flame ionization detector. Hydrogen was detected using a Perkin Elmer 8500 gas chromatograph fitted with a 5 Å molecular sieve (3 ft) column (Hewlett Packard) and a thermal conductivity detector. EPR studies were performed using a Varian E-Line Century Series instrument operating at X-band frequency with the cavity temperature at 20 K. Infrared spectra were obtained using a Nicolet 740 FT-IR spectrophotometer and processed on a Nicolet 680-DSP spectral workstation. Microanalyses were obtained through the University of Michigan Chemistry Department analytical services.

Catalytic Reductions. All manipulations were carried out using a Vacuum Atmospheres Dri-Lab glovebox or standard Schlenk techniques. In a typical acetylene reduction experiment, $Co(Cp)_2$ (0.145 g, 0.77 mmol) and Lut·HCl (0.11 g, 0.77 mmol) were weighed into a 25-mL vial fitted with a septum. Catalyst **I** (1.0 mL of a 9.6 mM solution in DMF) was added concomitantly with fresh DMF to a total volume of 10 mL. Immediately following this, C_2H_2 (5 mL) was injected, ensuring that the final vial pressure never exceeded 1 atm. The reaction was stirred at 20 °C and periodically analyzed (GC) by withdrawal of a 100-μL sample of the head space gas. The NMR spectra of the DMF solutions after 20 h did not show the presence of other hydrocarbon molecules or higher oligomers of acetylene.

Results and Discussion

Kinetic experiments on catalytic reductions of C_2H_2 to C_2H_4 (and traces of C_2H_6) were carried out at 20 °C using cubane **I** as the catalyst and cobaltocene and 2,6-lutidine hydrochloride, Lut·HCl, as sources of electrons and protons, respectively. Initial catalyst concentration was maintained at 0.96 mM while substrate excess over catalyst was varied from 5-fold to 80-fold. In addition, a $C_2H_2:H^+:e^-$ ratio of 1:4:4 was employed in the initial stages of the reaction. Kinetics data are contained in Table 1. The initial-rate method, whereby the condition [catalyst] ≪ [substrate] always holds,[25] yields reaction velocities, v_0 (M/min). These were obtained at less than 5% substrate consumption (Table 1). The present system obeys saturation kinetics, as found for enzyme catalysis. Reaction rates remain constant for C_2H_2:cubane ratios ≥ 30:1, indicating zero-order substrate dependence past the 30:1 ratio (Figure 3). At low concentration of C_2H_2 (that prevail at C_2H_2:cubane ratios < 30:1) the reaction is first order in substrate. A double reciprocal plot, v_0^{-1} vs $[C_2H_2]^{-1}$, is linear at optimum substrate concentration (Figure 4) and is consistent with preequilibrium kinetics.[25] From this plot the Michaelis–Menten constant, K_m = 17.9 mM, and the maximum velocity, $V_{max} \approx 1.2 \times 10^{-4}$ M/min, are calculated. The K_m value is considerably larger than the value obtained for the catalytic reduction of acetylene to ethylene by a dimeric Mo cysteine complex[17] (K_m = 0.33 mM) and the approximate value reported for nitrogenase[27] (K_m = 0.1–0.3 mM).

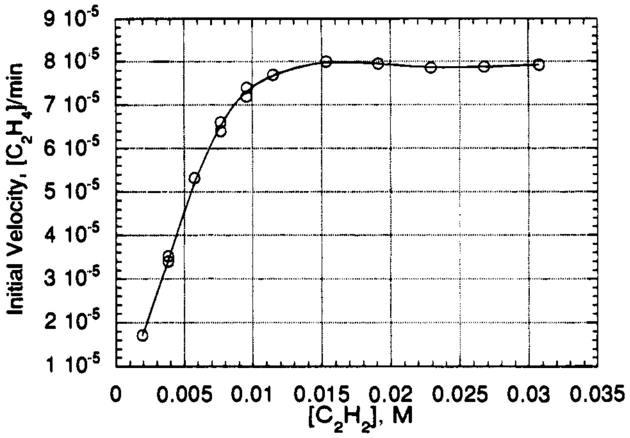

Figure 3. Plot of reaction velocity, v_0, vs $[C_2H_2]$, indicating saturation kinetics for the reduction of C_2H_2 by cubane **I**. At low C_2H_2 concentrations there is first-order substrate dependence, whereas at higher C_2H_2 concentrations the reaction pathway is zero order in acetylene.

Table 1. Kinetic Data for the Reduction of Acetylene to Ethylene Catalyzed by Cubane I[a]

C_2H_2:**I**	v_0 (M/min)[b] (×10^5)	$[C_2H_2]$ (mM)[c]	% reaction completion[d]	$1/v_0 \times 10^{-4}$ (optimum $[C_2H_2]$ range)[e]
5:1	1.7(1)	4.77	6.4	
10:1	3.4(2)	9.58	4.6	
15:1	5.3(1)	14.4	4.0	1.9(1)
20:1	6.6(3)	19.1	5.2	1.5(3)
25:1	7.4(3)	23.9	5.2	1.4(3)
30:1	7.7(2)	28.8	4.2	1.3(2)
40:1	8.0(1)	38.3	4.8	1.2(1)
50:1	7.9(2)	47.8	3.6	1.2(2)
60:1	7.8(2)	57.5	2.9	
70:1	7.8(2)	67.0	2.8	
80:1	7.9(3)	77.0	2.9	

[a] Experiments are performed in DMF solvent at 20 °C using $Co(Cp)_2$ and Lut·HCl as sources of electrons and protons, respectively. [b] Initial velocity, v_0, is obtained as the slope from $[C_2H_4]$ (M) vs *t*(min) which obeys a straightline relationship during the initial stages of the reaction. [c] Determined by GC analyses of the DMF reaction solutions. The amount of C_2H_2 in the solution phase accounted for >98% of the total C_2H_2 added. This is consistent with the reported solubility studies[26] that show C_2H_2 soluble in DMF to 1.2 M. [d] Consumption of C_2H_2 as a percentage of the initial $[C_2H_2]$. The initial rate method for determining v_0 is optimum to ca. 5% reaction completion (see ref 25). [e] The Double Reciprocal Plot (DRP), v_0^{-1} vs $[C_2H_2]^{-1}$, is obtained in the optimal $[C_2H_2]$ range, typically, K_m = 0.33–2.0 mM. At high $[C_2H_2]$, K_m = 3.3–20 mM, the reaction is zero-order in C_2H_2 and the DRP is essentially horizontal. At low $[C_2H_2]$, K_m = 0.033–0.2 mM, the reaction is first order in C_2H_2 and the DRP intercepts both axes too close to the origin to allow K_m and V_{max} to be determined accurately (see ref 25).

The catalytic reduction of C_2H_2 by **I**, under a saturating concentration of C_2H_2 (1.25×10^{-1} M), proceeds with a first-

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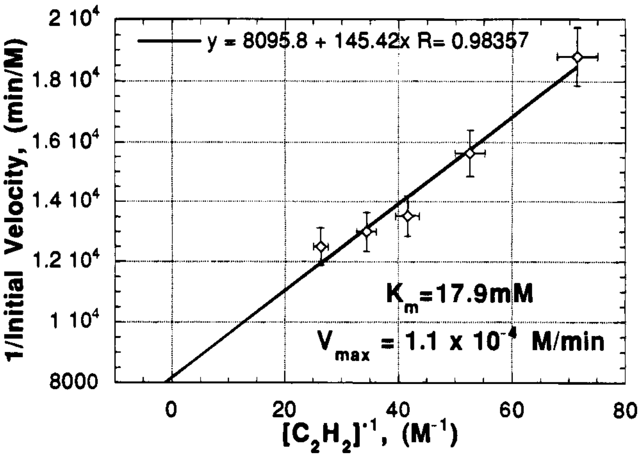

Figure 4. Double reciprocal (Lineweaver–Burk) plot, v_0^{-1} vs $[C_2H_2]^{-1}$, exhibiting linearity at the optimum substrate concentration range. $K_m \approx 17.9$ mM and $V_{max} \approx 1.1 \times 10^{-4}$ M/min are obtained from this plot.

Table 2. Activation Parameters For the Reduction of Acetylene to Ethylene Catalyzed by Cubane I[a,b]

E_{act}	9(1) kcal mol^{-1}
$\Delta H^{\ddagger}$	9(1) kcal mol^{-1}
$\Delta S^{\ddagger}$	−32(2) cal K^{-1} mol^{-1}
$\Delta G^{\ddagger}$ [c]	19(1) kcal mol^{-1}

[a] Experiments are performed in DMF solvent using $CoCp_2$ and Lut·HCl as sources of electrons and protons, respectively. [b] Activation energy is calculated from the Arrhenius treatment of data in which $\ln(v_0)$ vs T^{-1} is plotted for T = 30, 35, 40, 45, and 50 °C, where v_0 = initial reaction velocity. $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ were calculated from an Eyring plot in which $\ln(k_1/T)$ vs T^{-1} is plotted (Figure 6) for T = 30, 35, 40, 45, and 50 °C. [c] Value given for T = 40 °C (313 K).

order dependence on proton concentration and a zero-order dependence on reductant concentration (Figure 5). A plot of initial reaction velocity v_0 vs $[H^+]$ exhibits the expected linear relationship from which a first-order proton dependence may be deduced. At high H^+ concentration, saturation effects ensure a leveling off of reaction velocity at *ca.* $v_0 = 1.75 \times 10^{-4}$ M/min. A similar plot of v_0 vs [reductant], however, yields an essentially horizontal line for the same ordinate scale, consistent with a process where the rate-determining step does not involve electron transfer from reductant to catalyst/substrate.

Initial reaction velocities, v_0 (M/min), were obtained from the reduction of acetylene catalyzed by cubane **I** at 30, 35, 40, 45, and 50 °C. An Arrhenius plot (ln (v_0) vs T^{-1}) allows for the calculation of the activation energy E_{act} of 9(1) kcal mol^{-1}. An Eyring plot ($\ln(k_1/T)$ vs $1/T$, where k_1 is the rate constant at a given catalyst concentration under substrate saturating conditions) reveals (Figure 6) the expected straight-line relationship. This plot was used to derive $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 9(1) kcal mol^{-1} and −32(2) cal K^{-1} mol^{-1} which extrapolate to a Gibbs free energy of activation, $\Delta G^{\ddagger}$, of 19(1) kcal mol^{-1} (Table 2). The Gibbs free energy of activation ($\Delta G^{\ddagger}$ = 19(1) kcal mol^{-1}) shows that a considerable amount of the energy required for the process is associated with the large negative entropy of activation ($\Delta S^{\ddagger}$ = −32(2) cal K^{-1} mol^{-1}). The latter indicates significant bond formation and an ordered transition state. Such a transition state may involve the interaction between catalyst, substrate, and very likely one or both of the protons involved in substrate reduction.

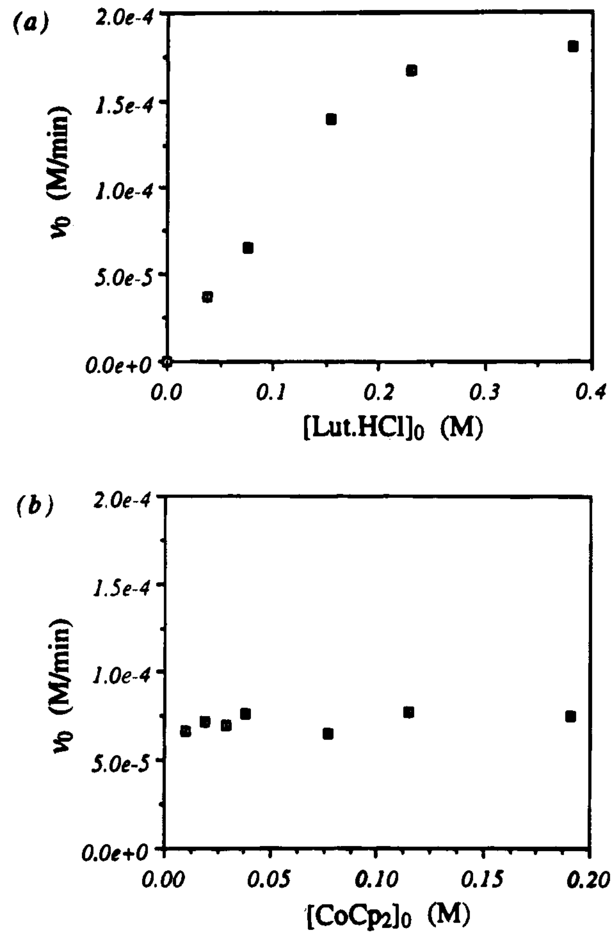

Figure 5. Plots of initial reaction velocity (v_0) versus proton concentration (graph a), and reductant concentration (graph b) at saturating $[C_2H_2]$ (1.25×10^{-1} M). The former indicates the rate-determining step to be first order in protons at low proton concentration and zero order at higher proton concentrations, while the latter shows the rate-determining step to be zero order in reductant for all concentrations of cobaltocene. The same ordinate scale has been chosen for both graphs to emphasize the differences in line shape.

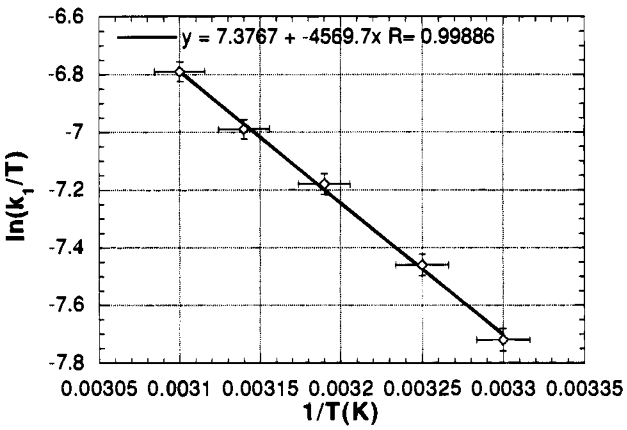

Figure 6. Eyring plot of $\ln(k_1/T)$ vs T^{-1} (K^{-1}) from which the activation parameters E_{act}, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ were calculated as 9(1) kcal/mol, −32(2) eu, and 19(1) kcal/mol, respectively. The rate constant, k_1 (rate = k_1[catalyst]) was obtained for [catalyst] = 9.6×10^{-4} M under substrate saturation conditions, 1.25×10^{-1} M.

The activation energy of 9(1) kcal mol^{-1} determined for the reduction of acetylene by **I** is similar to the estimated value reported[27b] for C_2H_2 reduction by nitrogenase (14 kcal mol^{-1}) and the one reported[17] for the Mo_2-cys catalyst (13 kcal mol^{-1}). It should be noted that, in nitrogenase, hydrolysis of MgATP is coupled to substrate reduction and serves as a source of energy.

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(27) (a) Hardy, R. W. F.; Knight, E. *Prog. Phytochem.* **1968**, *1*, 407. (b) Hardy, R. W. F.; Burns, R. C.; Parshall, G. W. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; pp 745–793.

Table 3. Initial Velocities (v_0) for the Reduction of Acetylene to Ethylene Catalyzed by Various Cubanes[a]

cubane catalyst	v_0 (M/min)[b] ($\times 10^5$)	v_0 normalized to cubane **I**
I	6.6(3)	1.0
$[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$	6.4(2)	0.97
recovery cubane[c]	2.7(3)	0.41
$[Fe_4S_4Cl_4]^{2-}$	1.3(3)	0.20
$[(Cl_4\text{-cat})MoFe_3S_4Cl_3(CN)]^{3-}$	1.6(1)	0.24
$[(CO)_3MoFe_3S_4Cl_3]^{3-}$	1.5(2)	0.23
$[(CO)_3MoFe_3S_4R_3]^{3-}$ $R = p\text{-}S\text{-}C_6H_4\text{-}Cl$	1.1(3)	0.17
I + PEt_3 (1:2)[d]	1.3(2)	0.20
blank (no catalyst)[e]	0.011	0.002

[a] Experiments are performed in DMF solvent at 20 °C using $CoCp_2$ and Lut·HCl as sources of electrons and protons, respectively. The initial substrate:catalyst ratio used is 20:1. [b] Initial velocity obtained as outlined in Table 1 (footnote *b*). [c] "Recovered cubane" is the form of the active catalyst isolated following acetylene reduction (see Results/Discussion section and ref 28). [d] Acetylene reduction performed using cubane **I** as the catalyst in the presence of PEt_3 such that Mo:PEt_3 = 1:2. [e] Typical acetylene reduction conditions except for the absence of catalyst.

The integrity of the catalyst following substrate reduction was established by EPR spectroscopy. The characteristic EPR spectrum of complex **I** ($S = {}^3/_2$) persists after at least 18 h of reaction time. The spectral line-shape and *g* values of pure **I** are indistinguishable from those obtained from the reaction solution following substrate reduction. Quantitation of the EPR spectra obtained from **I** before and after reaction with acetylene shows no loss of signal intensity (within the detection accuracy of the instrument). These results strongly suggest that the $[MoFe_3S_4]^{3+}$ cubane core remains structurally intact during the reaction and that cubane **I** may be considered the actual catalyst in the reduction of acetylene.

The active catalyst may be isolated from the reaction mixture following reduction of acetylene.[28] This cubane (termed "recovered cubane") is essentially unchanged and has been characterized by EPR and IR spectroscopy as well as elemental analysis.[28] The EPR spectrum shows the unique signal characteristic of the $S = {}^3/_2$ ground state of the cubane species and indicates that the core of the catalyst has remained unchanged. The IR spectrum of the "recovered cubane" shows DMF ligation to the Mo atom as well as the presence of $[Co(Cp)_2]^+$ which apparently has replaced NEt_4^+ as the cluster cation. Elemental analysis[28] of the "recovered cubane" corresponds to the formulation $[CoCp_2]_2[(Cl_4\text{-cat})(DMF)MoFe_3S_4Cl_3]$, which is a plausible species in view of the reaction conditions. Clearly, the core structure of the cubane retains its integrity during the course of the reaction. The "recovered cubane" has been found to be active in the catalytic reduction of acetylene (Table 3) albeit at a marginally slower rate compared to pure catalyst **I** (Figure 7). The slower rate may be due to the reduced solubility of the "recovered cubane" in DMF as a result of the $[Co(Cp)_2]^+$ cations.

The stereochemistry of addition across the substrate triple bond was investigated using gaseous FT-IR spectroscopy (Figure 8). In a typical experiment, the use of deuterated acetylene (C_2D_2) results in the formation of solely *cis*-1,2-$C_2D_2H_2$ which was identified by its characteristic IR absorption, ν_7 = 842 cm^{-1}.[29] No evidence for *trans* substituted ethylene was found (IR absorption at 988 cm^{-1}). This result is consistent with a transition state intermediate in which substrate acetylene is side-on bonded to the Mo atom in **I**. Such an arrangement would permit multiple protonation of the alkyne from the same side; resulting in formation of *cis*-1,2-$C_2D_2H_2$. Nitrogenase-catalyzed reduction of acetylene also proceeds with a high degree of stereoselectivity resulting in *cis* addition across the triple bond.[30]

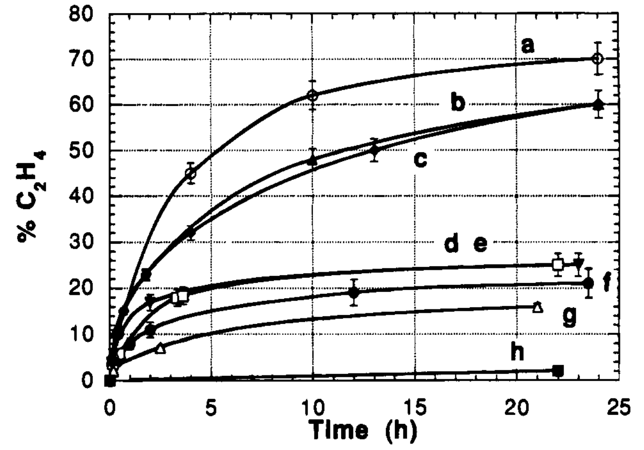

Figure 7. Ethylene production in DMF solvent at 20 °C from the following reaction, $20C_2H_2 + 80Lut{\cdot}HCl + 80Co(Cp)_2$ + 1 catalyst. Graph a: catalyst = cubane **I**. Graph b: catalyst = η^3-citrate cubane. Graph c: catalyst = "recovered cubane" cubane. Graph d: catalyst = CN cubane. Graph e: catalyst = $[Fe_4S_4Cl_4]^{2-}$. Graphs f (R = Cl) and g (R = *p*-S-C_6H_4-Cl): catalyst = $[R_3Fe_3S_4Mo(CO)_3]^{3-}$. Graph h: Blank reaction (no catalyst).

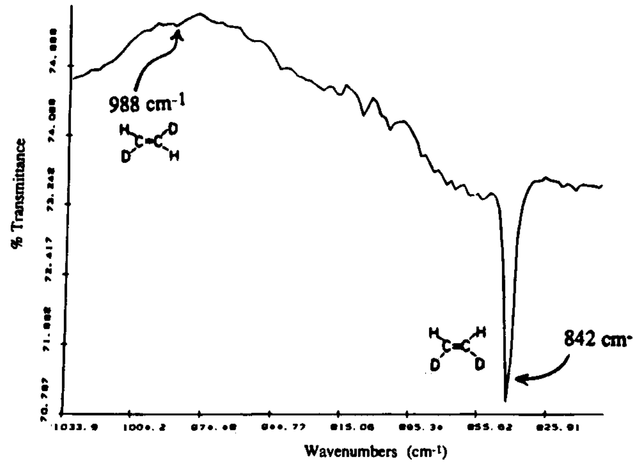

Figure 8. Gas FT-IR spectrum of the product from the reduction of C_2D_2 catalyzed by cubane **I**. The predominant stereoisomer is *cis*-1,2-$C_2D_2H_2$ (ν = 842 cm^{-1}).

Evident in Figure 9 is the production of small amounts of ethane (2−10%) during normal catalysis. The total amount of ethane produced was found to be dependent on proton concentration. The mechanism by which acetylene is reduced to ethane is intriguing since *catalyst I is totally ineffective in the reduction of ethylene to ethane.* The addition of 4 electrons and 4 protons to substrate C_2H_2 may be either a concerted process which occurs on **I** at a fraction of the rate of ethylene production or a process catalyzed efficiently by a very small amount of a cluster

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[28] Following acetylene reduction after a period of time the reaction may be stopped by the addition of a vast excess of ether. Filtration of the precipitates and thorough washing with THF, ethanol, and ether removes unreacted starting materials as well as cobaltocinium and 2,6-lutidine byproducts. The solid material may be further recrystallized from DMF/ether to yield a pure sample of the "recovery cubane" as the $[CoCp_2]_2[(Cl_4\text{-cat})(DMF)MoFe_3S_4Cl_3]$ salt. Anal. Calcd for $C_{29}H_{27}Co_2Cl_7Fe_3MoNO_3S_4$ (MW = 1195.31): C, 29.2; H, 2.30; N, 1.17; Fe, 14.0. Found: C, 30.8, H, 2.80; N, 1.32; Fe, 13.5.

[29] (a) Crawford, B. L., Jr.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1953**, *21*, 678. (b) Arnett, R. L.; Crawford, B. L., Jr. *J. Chem. Phys.* **1950**, *18*, 118.

[30] Hardy, R. W. F.; Holsten, R. D.; Jackson, E. K.; Burns, R. C. *Plant Physiol.* **1968**, *43*, 1185.

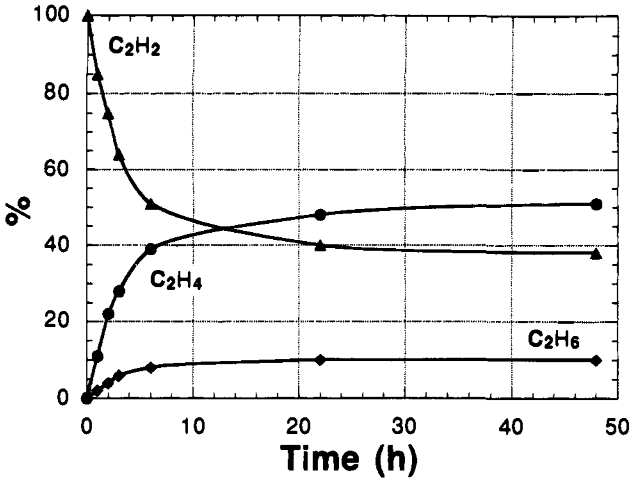

Figure 9. Plot of a typical acetylene reduction experiment showing the consumption of substrate C_2H_2 and the production of C_2H_4 and C_2H_6. Catalyst = cubane **I**.

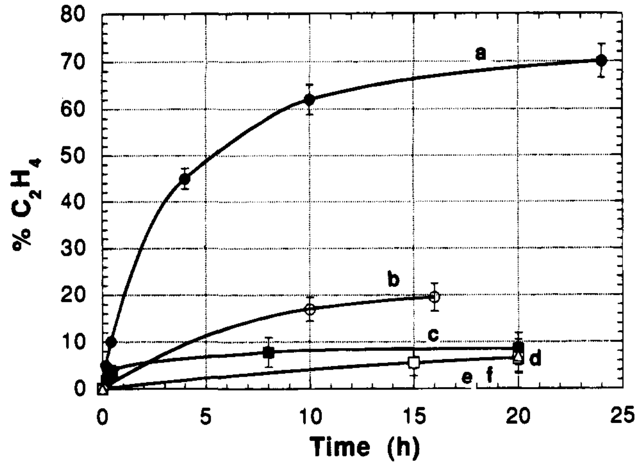

Figure 10. Ethylene production in DMF solvent at 20 °C from the following reaction, $20C_2H_2 + 80Lut{\cdot}HCl + 80Co(Cp)_2 + 1$ catalyst + $xPEt_3$. Graph a: catalyst = cubane **I**, x = zero. Graph b: catalyst = $[Fe_4S_4Cl_4]^{2-}$, x = zero. Graph c: catalyst = cubane **I**, $x = 2$. Graph d: catalyst = cubane **I**, $x = 10$. Graph e: catalyst = $[Fe_4S_4Cl_4]^{2-}$, $x = 10$. Graph f: catalyst = cubane **I**, x = zero, under CO atmosphere.

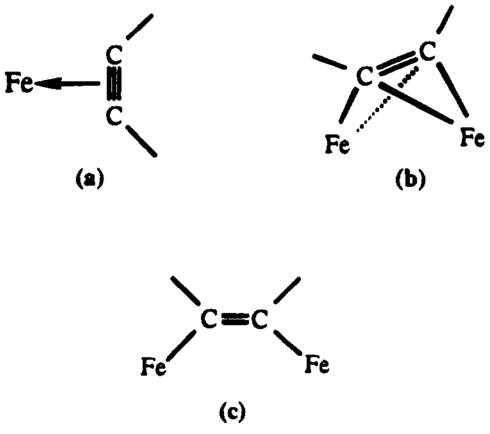

Figure 11. Various binding modes of C_2H_2 to cubane Fe sites, suggested by McMillan *et al.*[23]

decomposition product. By comparison, acetylene reduction by the "MoFe" nitrogenase yields ethane in negligible quantities, producing the alkane at *ca.* 0.01% compared to ethylene production.[31] The "Fe only" nitrogenase, however, is capable of reducing C_2H_2 to C_2H_6.[31]

The importance of the Mo atom in acetylene reduction is revealed by modification of the coordination sphere around the Mo atom (Figure 7) and the rate of ethylene production varies considerably depending on the availability of Mo coordination sites (Table 3). Replacing the bidentate Cl_4-cat ligand in **I** with η^3-citrate[24a] effects a slight reduction of reaction rate. This is in contrast with a previous study in our laboratory in which hydrazine was used as the substrate.[13] Catalytic reduction of N_2H_4 was found to be enhanced by the substitution of the Cl_4-cat ligand with the η^3-citrate ligand at the Mo center. The enhanced reactivity of the citrate cubane was rationalized in terms of a hapticity change of the tridentate citrate ligand following protonation as well as hydrogen bonding between substrate N_2H_4 and the citrate ligand. A similar mechanism does not appear to be advantageous or possible in the reduction of acetylene.

In attempts to block the Mo site from catalytic acetylene reduction (vide infra) it was discovered (Table 3) that some reduction did take place. We interpret the results as indicative that the Fe atoms on cubane **I** also are competent in substrate reduction albeit at a slower rate. Typically all the Fe sites combined completed 2-3 turnovers in a 24-h period, while the entire cluster, with the Mo site free for substrate binding, was capable of at least 16 turnovers in the same time. The use of $[NBu_4][Fe_4S_4Cl_4]$ as the catalyst shows essentially the same reaction rate or overall yield as cubane **I** with the Mo atom "blocked" from substrate binding/reduction. The results indicate that the rate of reaction varies considerably depending on the reaction site, Mo *vs* Fe, the former being decidely more competent in mediating acetylene reduction. This is especially true during the initial stages of the reaction ($t < 3$ h) (Figure 10) where proton and electron concentrations are optimal and where kinetic data are obtained. Ethane is also produced in very small quantities (~2%) when $[NBu_4]_2[Fe_4S_4Cl_4]$ is used as the catalyst in acetylene reduction. This result, coupled with the observation that the "Fe only" nitrogenase[31] is capable of reducing C_2H_2 to C_2H_6, may suggest that in the catalytic reactions that employ **I** or other variants C_2H_6 is produced at the Fe sites. Acetylene reduction at the Fe sites of $[Fe_4S_4(SR)_4]^{2-}$ cubanes has been reported previously by McMillan *et al.*[23] This study, in which the sub-stoichiometric substrate reduction (*cis* addition) was described, considered various binding modes of C_2H_2 to cubane, including mononuclear, side-on bonding as well as C_2H_2 bridged units (Figure 11).

A significant decrease in the reaction rate is observed when CN^- is used as the terminal ligand in **I** in place of CH_3CN or DMF (Figure 7). The non-labile cyanide ligand precludes binding of substrate acetylene to the Mo atom thereby restricting substrate reduction to the Fe sites. Indeed ethylene production with **I**-CN proceeds at a rate comparable to that observed with the $[Fe_4S_4Cl_4]^{2-}$ cubanes. A similar result is obtained when the $[(CO)_3MoFe_3S_4R_3]^{3-}$ (R = Cl, *p*-S-C_6H_4-Cl) cluster[24c] is used as a catalyst. In the latter the stable tricarbonyl-Mo(0) fragment does not undergo dissociation of CO and does not allow acetylene binding/reduction on the Mo atom. A small change in reaction rate is observed upon variation of the terminal ligands on the Fe atoms (R = Cl vs *p*-S-C_6H_4-Cl). The reason for this may be associated with steric effects or the relative effectiveness of acetylene to displace terminal ligands coordinated to the Fe atoms.

An inhibition study of the Mo and Fe substrate binding sites using PEt_3 revealed that both centers are adversely affected by the phosphine (Figure 10). The affinity of PEt_3 for the

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[31] Burgess, B. K. In *Molybdenum Enzymes, Cofactors, and Model Systems*; Stiefel, E. J., Coucouvanis, D., Newton, W. E., Eds.; ACS Symp. *Ser.* No. 535; American Chemical Society: Washington, DC, 1993; p 144.

heterometal in cubane **I** is well-documented[32] and our work now shows that at sufficiently high concentrations PEt_3 also serves to block the Fe sites on **I** from reducing acetylene. Similar results are obtained when $[NBu_4]_2[Fe_4S_4Cl_4]$ is used as the catalyst. We have not isolated any Fe−PEt_3 adduct from these reactions. Such species may only be transiently involved.

Catalytic C_2H_2 reduction by cubane **I** is effectively prevented if the reaction is carried out under a CO atmosphere (Figure 10). The overall yield of C_2H_4 and C_2H_6 products is diminished to approximately that of the background level (no catalyst present). This suggests that CO precludes C_2H_2 binding to the Mo atom of **I**. It has been reported previously that the solvated oxidized clusters with $[MoFe_3S_4]^{3+}$ cores similar to **I** do not bind to CO. The reduced cubane, $[((C_3H_2)_2\text{-cat})(CH_3CN)\text{-}MoFe_3(p\text{-S-}C_6H_4)_3]^{3-}$, however, with a $[MoFe_3S_4]^{2+}$ core, binds to CO irreversibly.[33] It appears that CO inhibition of the catalytic C_2H_2 reduction by **I** is due to binding of CO to the one electron reduced form of **I** (eq 1).

$$\mathbf{I}^-\text{−DMF} + \text{excess CO} \rightarrow \mathbf{I}^-\text{−CO} + \text{DMF} \qquad (1)$$

Interestingly, a saturated CO atmosphere also appears to block substrate reduction at the secondary (Fe) catalytic sites (*vide infra*) on **I**. A mechanism for this inhibition may involve CO binding to the Fe atoms in a terminal or bridging fashion (Figure 11), possibly across an Fe_2S_2 face of **I**. The overriding factor, however, in CO inhibition of C_2H_2 reduction by catalyst **I** is undoubtedly the vast concentration excess of CO over substrate and catalyst alike.

An important contrast can be made between the present work and our previous report of catalytic N_2H_4 reduction by **I**,[13] in which $[Fe_4S_4Cl_4]^{2-}$ cubanes were shown to be totally ineffective in the catalytic reduction of hydrazine to ammonia. The catalytic function of **I** in the reduction of two different substrates shows substrate-dependent site selectivity. This finding raises the possibility that either or both Fe and Mo sites in nitrogenase may be important during the stepwise reduction of a given substrate. This possibility also has been suggested in a theoretical study of dinitrogen binding[34] to nitrogenase.

In the catalytic reduction of C_2H_2 by **I**, H_2 also was detected as a reaction byproduct. A semiquantitative analysis of proton reduction found catalysts **I** and $[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ to be equally competent in this process. A control experiment ($[Co(Cp)_2]^+$, Lut·HCl, but no catalyst present) showed hydrogen production (background) in amounts approximately 50% of that seen for catalysis with **I** or the η-citrate cubane. The use of $[Fe_4S_4Cl_4]^{2-}$ as the catalyst shows approximately the same level of hydrogen production as **I**. This observation and the fact that production of H_2 (at the same level) also takes place with **I** under an atmosphere of CO suggest that likely sites of H^+ reduction in these clusters are common structural features such as the core $\mu_3\text{-}S^{2-}$ ligands. It is assumed that protonation of the Fe-coordinated Cl^- ligands is an unlikely event. The reduction of protons concomitant with the reduction of substrates is a process that also is known to occur during normal turnover of nitrogenase.

The inhibition and changes in the rate of substrate reduction observed in the presence of various ligands show that reduction of acetylene by the $MoFe_3$ cubanes occurs at both the Mo and the Fe sites with the latter showing much slower rates than the former. A mechanistic description of the more efficient acetylene reduction by the Mo site in **I** requires as a first step the introduction of acetylene to the Mo coordination sphere. Whether this requires one or two binding sites on the Mo atom is not immediately clear. However, the availability of two coordination sites for substrate coordination in **I** is possible only with a change in coordination mode of the catecholate ligand from bidentate to monodentate. This event does not seem very likely in view of the apparent lack of lability of the Cl_4-cat ligand. An investigation of **I** by NMR spectroscopy shows that even under protic conditions and in the presence of vast excesses of various catecholate ligands the Cl_4-cat ligand remains bound to the Mo atom. The Cl_4-cat ligand, although non-exchangeable under the conditions of the experiment, has available lone pairs on the oxygen donor atoms and is likely to be protonated at least transiently during turnover. This may facilitate proton transfer to Mo bound substrate and may account for the superior performance of the heterometal in C_2H_2 reduction compared to the Fe sites of the cubanes.

The use of $[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ as the catalyst effects *no appreciable slowing of the reaction compared to cubane **I**.* The η^3-citrate ligand is likely to be protonated under the conditions of the reaction, thus adopting a bidentate configuration about the Mo atom and liberating a coordination site for substrate binding and reduction. Double protonation of the η^3-citrate ligand and, consequently, monodentate binding to the Mo is an *unlikely* event, hence, under the conditions of the reaction, the catalyst $[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ may be assumed to be in the η^2-citrate form and consequently substrate reduction must occur at a single coordination site on the Mo atom.

In a previous study,[17] a mechanism for C_2H_2 reduction by mononuclear Mo−cysteinyl complexes was based on the premise that two metal coordination sites were occupied by the substrate. The results from the present study although in favor of one-site substrate binding cannot rule out a two-site substrate binding and reduction.

The catalytic effectiveness of the $[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ cubane, with an apparently coordinatively saturated Mo site, has interesting implications regarding the reactivity of the coordinatively saturated, homocitrate bound Mo atom in nitrogenase. *Protonation of the Mo bound homocitrate ligand of FeMoco may liberate a coordination site for substrate binding and at the same time facilitate proton transfer to the substrate.* A similarly unusual catalytic reactivity of the $[(\eta^3\text{-citrate})MoFe_3S_4Cl_3]^{3-}$ cubane also has been found in the reduction of hydrazine to ammonia. The latter reaction proceeds at a rate nearly an order of magnitude faster than the rate observed with **I** as a catalyst.

By varying the acid source (Lut·HCl, Lut·HBF_4, Lut·$HBPh_4$, Lut·HPF_6)[35] used in acetylene reduction experiments, we have been able to detect an active "cobalt" species which derives from the $Co(Cp)_2$. *In the absence of Cl^- and catalyst **I**,* this "cobalt" compound, which we have not attempted to identify as yet, effects sub-stoichiometric reduction of acetylene to ethylene (Figure 12). In the presence of Cl^- (either from Lut·HCl or from added NEt_4Cl) the "cobalt" species is rendered totally inactive toward acetylene reduction. In light of these findings, the catalytic, kinetic, studies of acetylene reduction by **I**, reported herein, were restricted to the use of Lut·HCl as the proton source.

A possible pathway for the reduction of acetylene by the "Co" species may involve protonation and change in hapticity of one

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(32) Palermo, R. E.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 4310.

(33) Mascharak, P. K.; Armstrong, W. H.; Mizobe, Y.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 475.

(34) Dance, I. G. *Aust. J. Chem.* **1994**, *47*, 979.

(35) (a) Lut·HPF_6 was isolated from the stoichiometric reaction of $NaPF_6$ and Lut·HCl in ethanol. (b) Lut·$HBPh_4$ precipitated from an ethanolic mixture of stoichiometric quantities of Lut·HCl and $NaBPh_4$. Re-extraction into MeCN and treatment with ether afforded the pure product. (c) Lut·HBF_4 may be synthesized from a stoichiometric reaction in ether between 2,6-lutidine and ethereal HBF_4.

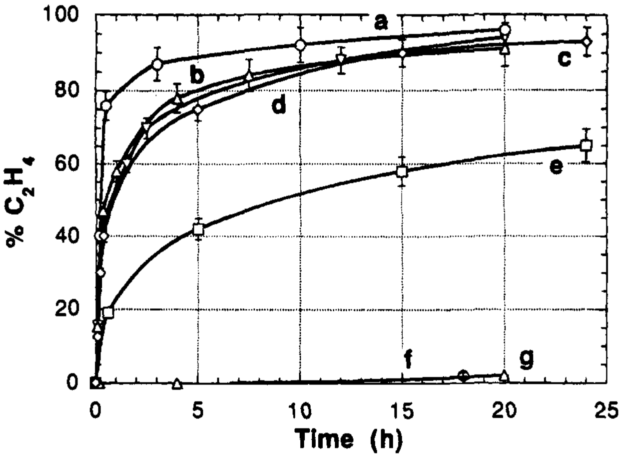

Figure 12. Ethylene production in DMF solvent at 20 °C from the following reaction, $20C_2H_2$ + 80Lut·H"X" + $80CoCp_2$ + 1 catalyst + yNEt$_4$Cl. Graph a: catalyst = cubane **I**, "X" = BPh_4^-, y = zero. Graph b: blank (no catalyst), "X" = BPh_4^-, y = zero. Graph c: blank (no catalyst), "X" = BF_4^-, y = zero. Graph d: blank (no catalyst), "X" = PF_6^-, y = zero. Graph e: catalyst = cubane, **I**, "X" = BPh_4^-, y = 80 (H^+:NE$_4$Cl = 1:1). Graph f: blank (no catalyst), "X" = Cl^-, y = zero. Graph g: blank (no catalyst), "X" = BPh_4^-, y = 80 (H^+:NEt$_4$Cl = 1:1).

of the cyclopentadienyl rings in $Co(Cp)_2$, thereby creating a potential substrate binding site. It appears that C_2H_2 access to such a site in the presence of Cl^- is effectively blocked. The exact nature of this interesting reaction must await further studies.

Summary and Conclusions

The $[MoFe_3S_4]^{3+}$ cubanes arguably are partial models[4] for the Fe/Mo cofactor of nitrogenase since they possess fundamentally important structural features as well as relevant reactivity characteristics. We have used these synthetic cubanes to demonstrate the catalytic reduction of acetylene to ethylene and small amounts of ethane. Hydrogen also has been detected as a product in a reaction parallel to acetylene reduction. The latter proceeds with first-order dependence on proton concentration and zero-order dependence on reductant concentration. The integrity of catalyst **I** following the catalytic reduction has been evaluated. The solution after many turnovers of acetylene reduction, and within the limits of EPR spectroscopy, shows quantitatively the retention of the characteristic $S = {}^3/_2$ $[MoFe_3S_4]^{3+}$ core. The catalyst following a number of turnovers of acetylene reduction has been isolated and analyzed. This same "recovered" catalyst was effectively "re-cycled" in catalysis.

The alkene product from reduction of C_2D_2 has been identified by gas-infrared spectroscopic measurements as the *cis* stereoisomer. The Mo center has been shown to be the principal site of substrate reduction while the Fe sites also have been implicated in the reaction process, however, at a markedly reduced rate. Both metal sites on cubane **I** may be inhibited toward acetylene reduction by the use of PEt_3 or a saturating CO atmosphere.

Notwithstanding overall reaction rates and turnover numbers orders of magnitude slower compared with the nitrogenase system, the present results suggest varying affinities of the Mo and Fe sites on catalyst **I** for substrate acetylene. This phenomenon may be manifest in the enzyme such that both the Fe and Mo centers of FeMoco may be involved at some point during normal catalysis based on the affinity of reaction intermediates for each metal site.

Acknowledgment. The support of this work by a grant from the National Institutes of Health (GM-33080) is gratefully acknowledged. We thank S. Malinak for determining the solubilities of C_2H_2 in DMF solutions and R. Sands and W. R. Dunham for obtaining EPR spectra.

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