6 H). The arsonium salt **7** reversibly yields 1,1-dimethyl-λ^5-arsabenzene **3** on treatment with dimsyl anion in Me_2SO. The proton NMR spectrum illustrated in Figure 1 shows signals for H_3, H_5 as a multiplet centered at δ 6.63, for H_4 as an 8 Hz triplet at 4.43 partially overlapping with 10 Hz doublet at 4.34 for H_2, H_6, while the methyl groups are at δ 1.5. ^{13}C NMR (Me_2SO) δ 138.6 (for C_3, C_5), 91.8 (for C_4), 70.3 (for C_2, C_6) 22.4 (for CH_3). Again four ring protons of **7** at H_2, H_4, and H_6 are washed out with D_2O–Me_2SO and base.[6]

In the NMR spectra of **1b** and **3** the H_2, H_4, and H_6 protons have chemical shift values well outside the aromatic region and are markedly upfield from the range of olefinic protons of their conjugate acids, **5** and **7.** On the other hand the H_3 and H_5 protons of **1** and **3** are relatively highly deshielded. However, the signals for these protons occur approximately half a part per million upfield from the corresponding H_3 protons of conjugate acids **5** and **7.** The absences of any shift to lower fields for H_3 and H_5 as well as the large upfield shift of H_2, H_4, and H_6 suggest that there are no appreciable ring current effects in λ^5-phosphabenzenes and λ^5-arsabenzenes.[7] In fact the NMR spectra, together with proton exchange data, strongly suggest that C_2, C_4, and C_6 bear a high electron density. Thus we must view the ring carbon atoms as favoring a pentadienyl anion which is stabilized largely by electrostatic interaction with the positive heteroatom.

The C NMR spectral data on **1** and **3** further support these conclusions.[7] Signals for C_2 and C_6 occur more than 60 ppm upfield from the signals of C_3 and C_5.[8] As in the proton NMR spectra the signal for C_4 is not shifted as far upfield. Very likely this is a consequence of polarization of the carbanionic pentadienyl system by the positive heteroatom.[9] It is striking that the chemical shift values of ylides **1** and **3** are very nearly identical with those of anions **8** and **9,** available from deprotonation of **1** and **3.**[4,10] It seems highly likely that the electron density at each carbon is very similar. In contrast to the near identity of chemical shift values of anions and ylides, the ^{31}P–^{13}C and ^{31}P–^{1}H coupling constants are markedly divergent for **1** and **8,**[4,11] an expected consequence of the different hybridization at P in the two systems.

^1H and ^{13}C NMR spectra of 1,1-dimethyl-λ^5-phosphabenzene and 1,1-dimethyl-λ^5-arsabenzene present strong presumptive evidence that these compounds are ylidic in character. In this respect they strongly resemble the thiabenzenes.[9,12,13] Several bonding proposals have been put forward for λ^5-phosphabenzenes[13] and similar cyclic systems[15,16,17] conjugated via d–p π-bonding to higher row elements. Our findings do not rule out the use of the ultimate arsenic and phosphorus d orbitals in bonding of the λ^5-phosphabenzenes and the λ^5-arsabenzenes, but they do strongly argue against any bonding proposal in which appreciable electron density is donated from carbon to the heteroatoms.

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(6) The H NMR spectrum showed only singlets at δ 7.0 (1 H), 6.2 (1 H), and 2.2 (6 H), while there was a strong peak at δ 4 for HOD.
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(10) The ^{13}C NMR spectrum of **8** consists of doublets at δ 71.8 (3 Hz) for C_2, 133.0 (8 Hz) for C_3, and 96.5 (9 Hz) for C_4, while signals for **9** occur at δ 72.9 for C_2, 132.1 for C_3, and 92.6 for C_4. See ref 4.
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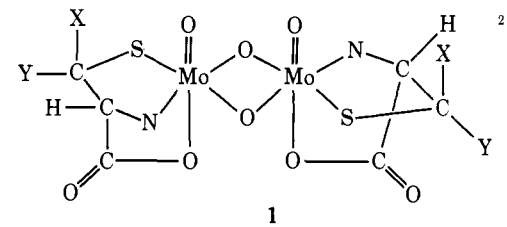
Ligand Effects and Product Distributions in Molybdothiol Catalyst Systems

Sir:

The reduction of acetylene to ethylene is one of the reactions catalyzed by nitrogenase and is commonly used to assay for the activity of this enzyme.[1] The complex, $Mo_2O_4(cys)_2^{2-}$, **1** (X = Y = H),[2] is reported to mimic the enzyme in this re-



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spect,[3-6] catalyzing the formation of ethylene (but with small amounts of ethane), the reducing power being supplied either by $NaBH_4$[3,4] or electrolytically.[5] Although complexes of molybdenum seem superior as catalysts to those of other transition metals,[6] structural variations in the ligand have not been systematically pursued. We have therefore initiated a program of preparation and testing of Mo complexes containing cysteine-related ligands as potential catalysts. These studies reveal several rather striking results. Even with the cysteine complex, we find the major reduction product of acetylene in borate buffer to be 1,3-butadiene (C_4H_6), not ethylene. The production of C_4H_6 presumably went unnoticed in all previous investigations. Further, we observe that seemingly minor changes in ligand or buffer have profound effects on the product distribution and/or catalytic activity.

Typical reactions were run in 15-ml "Hypovials" (Pierce Chemical Co.) as follows: Septum-sealed vials containing 25 mg of complex and 3.5 ml of pH 9.6 buffer (0.1 M $Na_2B_4O_7 \cdot 10H_2O$ or 0.2 M Na_2CO_3) were flushed with acetylene and kept at 30 °C for 4–6 h[7] before initiating the reaction by injection of 0.10 ml of 2 M $NaBH_4$ in DMF.[8] Reaction mixtures were then shaken[9] (30 °C bath) and the gas phase analyzed[10] by GC on Porapak N (temperature programming). The results are summarized in Table I.

Butadiene (C_4H_6) was found to be a major product for those complexes in Table I which were catalytically active in the reduction of acetylene. A preparative scale reaction using **1** (X = Y = H) yielded sufficient C_4H_6 for characterization by methods other than GC. The product was separated by trapping at −50 °C and confirmed to be butadiene by its NMR and mass spectra. Its formation constitutes an overall two-electron reductive dimerization of acetylene.

Our first attempts at ligand variation involved methyl sub-

Table I. Acetylene Reduction by Molybdocomplex Systems[a]

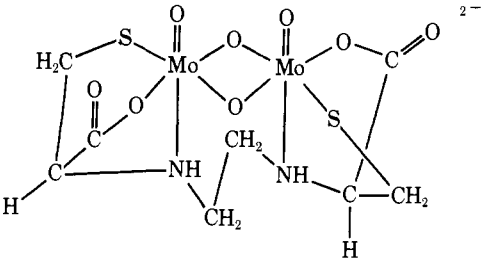
Complex (ligand)	Gas phase (μmol)			
	C_2H_4	C_2H_6	C_4H_6	C_2H_2
1 (X = Y = H) (cys)	52.5	0.6	142	362
1 (X = Y = H) (cys)[b]	130	4.8	27	450
1 (X = Y = CH_3) (pen)	4.0	1.1	3.7	668
1, X = CH_3; Y = H (*threo*-β-Me)	52.9	1.3	149	345
1, X = H; Y = CH_3 (*erythro*-β-Me)	8.0	1.3	10.0	672
2 (edta)	4.9	0.9	0.6	672
3 (edcys)	0.6	0.3	0.1	668

[a] 25-min reaction times and borate buffer (pH 9.6) were used unless noted otherwise. At the catalyst level employed, ca. 80 μmol of reduction products correspond to one turn-over per Mo *atom*. That no other major product has escaped detection is clear from consideration of material balance. Control experiments lacking Mo or ligand yield less than 0.14 μmol of reduced products. [b] 0.2 M carbonate buffer, pH 9.6. A similar effect is seen using the threo complex.

stitution of cysteine at the β position. The complexes, prepared by standard methods,[11] are extremely similar to $Mo_2O_4(cys)_2^{2-}$ in properties and are presumed to have structure **1**. Remarkably, the complex $Mo_2O_4(pen)_2^{2-}$, **1** (X = Y = CH_3),[12] was found ineffective in catalyzing acetylene reduction. The presence of the two methyl groups in the β position has clearly compromised the reactivity of the complex.

To probe the nature of this effect, we prepared both the threo and erythro forms of β-methylcysteine[13] and their corresponding $Mo_2O_4L_2^{2-}$ complexes. These isomeric complexes have identical electronic and very similar infrared spectra. Remarkably, the threo complex (**1**) (X = CH_3, Y = H) behaves quite like the cysteine complex in the reduction of acetylene (in both product yield and distribution) while the erythro complex (**1**) (X = H, Y = CH_3) resembles the penicillamine complex and has little activity. Because the two isomeric β-methylcysteine ligands are likely to have similar electronic influences in these complexes, a steric factor must be responsible for the observed phenomenon. Inspection of molecular models reveals a probable explanation, if dissociation of carboxylate is assumed necessary for activity. To produce an accessible metal site by carboxylate dissociation requires a twist of the C–C bond in the five-membered MoNCCS chelate ring. In the case of the inactive erythro complex, this twist is accompanied by eclipsing of the methyl and carboxylate groups, a 1–2 interaction which may be sufficiently unfavorable to hinder the dissociation process. In the active threo isomer eclipsing of these groups does not occur and the dissociation of carboxylate should be energetically more favorable. Moreover, even if the carboxylate dissociation does occur, the β-methyl group of the erythro form can partially block the position trans to Mo–O_t, while in the threo form there is a clearly accessible metal site. In either event the open site in the threo form may be more accessible to nucleophilic attack, which could aid in the dissociation of the dimer to catalytically active monomers (see below). A specific buffer ion could be the nucleophile in question, for, as shown in Table I, the product distribution is profoundly affected by changing the buffer ion from borate to carbonate. The true nature of this effect awaits elucidation through additional experiments.

One of the hypotheses resulting from earlier ligand variation studies is that sulfur-donor ligands are required for activity.[6] The lack of activity of $Mo_2O_4(edta)^{2-}$, **2**, is thus ascribed to absence of thiolate. Moreover, detailed electrochemical studies reveal that while the cysteine complex dissociates on reduction, the dinuclear edta complex remains intact.[14,15] It is possible, however, that the ethylenediamine (en) linkage bridging the two Mo atoms in the edta complex may be in part responsible for the lack of activity. To test this idea we prepared the *N,N'*-ethylenedicysteine[16] complex, $Mo_2O_4(edcys)^{2-}$, **3** (of



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proposed structure[12] shown), wherein an ethylene bridge links the cysteine units on each Mo atom. We find that this complex resembles the edta complex in both electrochemistry and lack of activity in C_2H_2 reduction (Table I). It would appear that despite the presence of thiol ligands, the bridging en group does not allow dissociation into the discrete monomeric units apparently needed for activity. Furthermore, the little activity that is present leads to the formation of a substantial proportion of C_2H_6, indicating the ability of the reduced dinuclear complex to effect the required four-electron reduction.

Finally, in view of our finding of extensive 1,3-butadiene formation in the "model" system, one must ask the question: does nitrogenase produce C_4H_6 from C_2H_2? It is notable that at high levels of acetylene, the reduction of C_2H_2 by nitrogenase shows substrate inhibition (at least insofar as production of ethylene is concerned).[17] The possibility of nitrogenase catalyzing the production of C_4H_6 from C_2H_2 was therefore investigated. Using 1 atm of C_2H_2 and conditions where the Mo–Fe protein has a specific activity of 1600 nmol of C_2H_4 produced (mg of enzyme)$^{-1}$ min^{-1} [18] there was no detectable butadiene (i.e., <0.3 nmol min^{-1} (mg of enzyme)$^{-1}$). Therefore, it is clear that the molybdothiol model system does not mimic nitrogenase in this important respect.

The results presented in this communication illustrate both pitfalls and promise in the model approach. They emphasize the need to look at the chemistry of a system as a whole and not solely at those aspects which happen to mimic the enzyme. Further, the observation that subtle variations of the ligand in the molybdothiol complex have large effects on catalytic activity opens the possibility that the optimal activity for such systems has not yet been achieved.

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(7) In the catalytic systems the "activity" increases substantially over 4–5 h. For those data in Table I, a 5-h "incubation" period was used. An effect of incubation time on activity has been previously noted and attributed to dissociation.[4] Yields of products in the noncatalytic systems were relatively independent of this effect.

(8) The use of DMF had no effect on the product yields.
(9) Without shaking, the cysteine complex yielded C_2H_4 and C_4H_6 (borate buffer) in about equal amounts, probably due to depletion of acetylene in the liquid phase.
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Novel Thioxo-β-lactams from Thiosulfinates Derived from Penicillin Sulfoxides

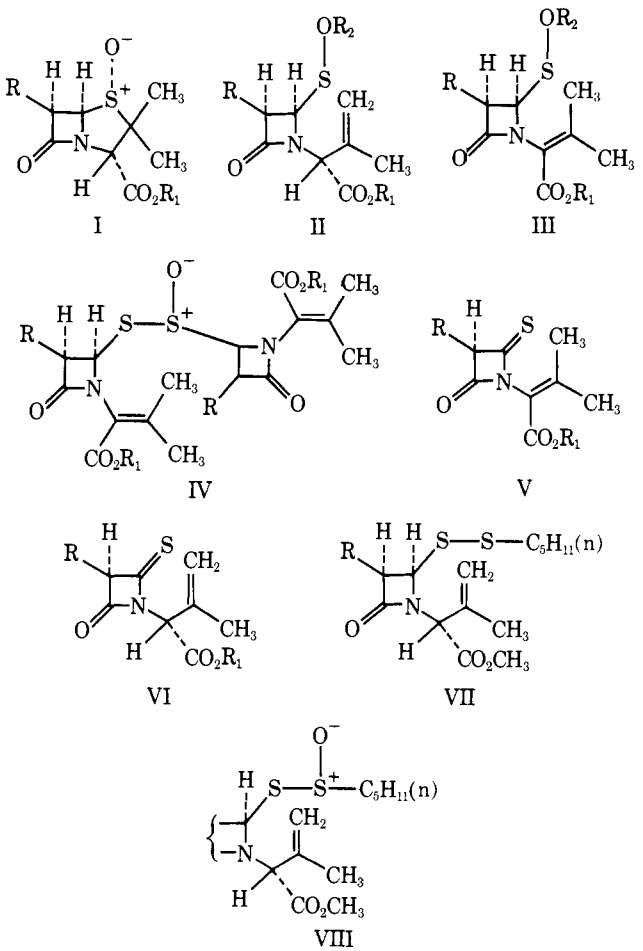
Sir:

Recent publications[1] revealed the utilization of the trimethylsilyl (Me_3Si) group in the isolation and crystallization of β-lactam sulfenic acids II and III (R_2 = H, R_1 = CH_3, *p*-$NO_2C_6H_4CH_2$) generated thermally from penicillin sulfoxides. The Me_3Si group distinguished itself from other acid protecting groups in that it is hydrolyzed readily to permit the generation of the β-lactam sulfenic acids in situ and, therefore, provided a way of studying the chemistry of this reactive species.

The nucleophilic nature of the sulfur atom in the sulfenic acid is well known;[2] thus, sulfenic acid II (R_2 = H) obtained from hydrolysis of the Me_3Si ester (II, R_2 = Me_3Si) will add to the vinylic double bond under neutral conditions to regenerate the penicillin sulfoxides. However, due to the lack of reactivity of the conjugated double bond of the α,β-unsaturated ester (III) to the intramolecular 1,4 addition,[3] a characteristic intermolecular condensation reaction of the sulfenic acid moiety is allowed to take place.[4] Therefore, when sulfenic acid III (R_1 = CH_3, R_2 = H), generated from its Me_3Si ester (III, R_1 = CH_3, R_2 = Me_3Si) by the treatment of methanol, was allowed to stand at room temperature for several hours, this condensation reaction occurred readily and the resulting thiosulfinate crystallized from chloroform–ether to give a colorless crystalline solid IV (R_1 = CH_3): mp 156–157 °C; $[\alpha]^{27}_D$ +56° ($CHCl_3$); IR ($CHCl_3$) 1795, 1785, 1735, and 1115 cm^{-1}; NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.15 (s, 3 H), 2.21 (s, 3 H), 2.35 (s, 3 H), 3.76 (s, 3 H), 3.81 (s, 3 H), 5.62 (d, 2 H, *J* = 4.5 Hz), 5.70 (ABq, 2 H, *J* = 4.5 and 34 Hz) and 7.82 (s, 8 H). Similarly, treatment of III (R_1 = CH_3, *p*-$NO_2C_6H_4CH_2$, Me_3Si; R_2 = Me_3Si) in chloroform with methanolic HCl resulted in the instantaneous precipitation of IV (R_1 = CH_3, *p*-$NO_2C_6H_4CH_2$, H, respectively) in high yield.

The thiosulfinate IV (R_1 = CH_3), after brief heating or prolonged standing at room temperature in an inert solvent, produced the novel thioxo-β-lactam V (R_1 = CH_3).[5] This monocyclic thione lactam will not polymerize and can be crystallized from methanol as light yellow prisms, mp 126–127 °C, in 67% yield.[6,7] The presence of an azetidine carbonyl group and a thiocarbonyl carbon in V (R_1 = CH_3) was indicated respectively by an absorption in the IR ($CHCl_3$) at 1835 cm^{-1} and by a chemical shift at 200.5 ppm downfield from tetramethylsilane in the ^{13}C NMR ($CDCl_3$).[8] In addition, the ^{13}C NMR also indicated the presence of $2CH_3$ (δ 22.0, 23.4), $1OCH_3$ (δ 52.3), 1CH (δ 65.7), 2C=C (δ 117.1, 161.8), 1 NC=O (δ 165.9), 1 ester C (δ 167.2), and a phthaloyl group. A ^1H coupled ^{13}C spectrum verified that the thiocarbonyl carbon is within three bonds of only one proton. The proton NMR ($CDCl_3$) of V had signals at δ 2.18 (s, 3 H), 2.42 (s, 3 H), 3.78 (s, 3 H), 5.92 (s, 1 H), and 7.84 (m, 4 H), and was also consistent with the structure.[9] Using the same method, the thioxo-β-lactams (V, R_1 = H, *p*-$NO_2C_6H_4CH_2$) can be prepared from the respective thiosulfinates (IV, R_1 = H, *p*-$NO_2C_6H_4CH_2$).

We theorized that the corresponding thioxo-β-lactam (VI) in the β,γ-unsaturated ester series could be prepared if the sulfenic acid II could be intercepted by an external sulfur nucleophile. Treatment of I (R_1 = CH_3) with *n*-pentyl mercapton afforded a high yield of VII, NMR ($CDCl_3$) δ 5.74 (ABq, 2 H, *J* = 4.5 and 10 Hz), 5.10–5.35 (m, 3 H, characteristic of the vinylic CH_2 and the allylic methine H), 2.32–2.80 (m, 2 H, $-SCH_2-$) and 2.12 (s, 3 H).[10] Subsequent oxidation of VII with *m*-chloroperbenzoic acid–CH_2Cl_2 gave selectively the thiosulfinate VIII, NMR ($CDCl_3$) δ 5.8–6.4 (m, 2 H), 2.8–3.2 (m, 2H, $OSCH_2-$), and 2.0 (s, 3 H).[11] Heating VIII in re-



I, II, III, IV, V, VI, VII, VIII

R = phthalimido
R_1 = CH_3, *p*-nitrobenzyl (*p*-$NO_2C_6H_4CH_2$), H, trimethylsilyl (Me_3Si)
R_2 = H, Me_3Si