two solvents. Electron transfer within this molecule is known to be significantly nonadiabatic, and tunneling is an important mechanism.

Figure 1 shows the dependence of E_{op} on the reduction potential of the oxidant used to generate the mixed-valence species I from the fully reduced (II,II) complex. As before,[27] in order to observe the correlation, it was necessary to measure the ionic strength dependence of each oxidant and extrapolate the line so obtained to the value at zero ionic strength ($E_{op}°$). All ruthenium complexes were isolated as the NO_3^- salts, and NH_4NO_3 was employed to adjust the ionic strength. The solvent was dimethyl sulfoxide.

There are two mechanisms by which a dependence of the E_{op} value on the potential of the incoming oxidant may be rationalized. This depends on whether the reduced oxidant is interacting symmetrically or unsymmetrically with the two metal ions in the mixed-valence species. If it is interacting symmetrically, then the actual shape of the potential energy wells must be affected by this interaction, the depth of the wells being dependent upon the potential of the oxidant employed (or its charge since the potential and charge of the oxidant molecules also correlate with each other). If the interaction is unsymmetrical, then the observed shift in E_{op} as a function of the oxidant employed may result from a zero-point energy difference which changes in response to the oxidant present.

In either case, the complexes must exist as a solvent-caged ion aggregate long enough for the reduced oxidant to modify favorably the molecular orbitals involved in transferring the electron in the binuclear. Conductance measurements showed a strong ion aggregation between the oxidant and the reduced binuclear which is surprising in view of the 7+ overall charge of this aggregate.

We are further exploring these ideas especially with regard to more strongly electronically coupled systems to see if this work is, in fact, symptomatic of a more general problem, or if this behavior will be displayed only by systems which are markedly nonadiabatic, as is true of most biological redox processes.

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Oxidative Cyclization Chemistry Catalyzed by Clavaminate Synthase

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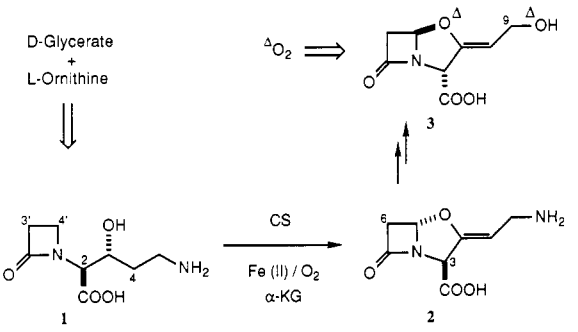
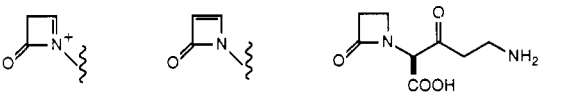
Clavaminate synthase plays a central role in the biosynthesis of the potent lactamase inhibitor clavulanic acid (**3**). This enzyme has been purified to homogeneity and found to carry out the double oxidative cyclization of proclavaminic acid (**1**) to clavaminic acid (**2**) in the presence of ferrous ion, dioxygen, and α-ketoglutaric acid.[1,2] In this communication we describe the first mechanistic studies of this enzyme which indicate that conventional hydroxylase activity has been replaced by oxidative cyclization chemistry having parallels to biochemical sulfur introduction[3] characteristic of e.g., biotin, lipoate, penicillin, and cephalosporin biosynthesis.

The oxazolidine oxygen of clavulanic acid (**3**) has been established to be derived from molecular oxygen ($^{\Delta}O_2$, Scheme I).[4] The dioxygenase cofactors of clavaminate synthase (CS) suggest

Scheme I



that the ring oxygen could be introduced at this stage from molecular oxygen. Alternatively, this oxygen could be retained from an earlier ornithyl hydroxylation step leading to the formation of proclavaminic acid (**1**). In the course of the CS reaction, oxidation takes place at C-4′, that, a priori, could be visualized in terms of either one-electron or two-electron processes. A subset of the latter mechanistic possibilities would invoke the intermediacy of an acylimine **4** leading to cyclization with a C-3 alcohol or enolate in a 5-*endo*-TRIG sense[5] or, alternatively, in a 5-*exo*-TRIG[6] fashion through the intervention of an azetinone **5**.



Furthermore, in the course of the CS reaction, C-3 of proclavaminate attains the oxidation state of a ketone. These mechanistic possibilities involve formal loss and/or potential exchange of hydrogen at C-2 and C-3′ in addition to the obvious losses at C-3, C-4, and C-4′. Moreover, apart from proton loss through enolization, a 3-keto intermediate, e.g., **6**, may undergo oxygen exchange prior to formation of clavaminic acid.

The potential loss or exchange of hydrogen at C-2 and C-3′ in proclavaminate was examined in two experiments. [2-^{2}H,3-^{13}C]Proclavaminic acid (**11**, prepared by condensation of glycyl β-lactam **7**[7] after deuterium exchange and aldehyde **9**, which was available from [1-^{13}C]-β-alanine[4])[8,9] was combined with [3-^{13}C]proclavaminic acid and purified by preparative HPLC. Two enhanced resonances in a 1:1.2 ratio were observed in the $^{13}C\{^1H\}$ NMR spectrum (0.61 Hz resolution) of this mixture at δ 69.58 and δ 69.51 (Δδ 0.07 ppm), the upfield signal owing to a β-deuterium isotopic shift.[10,11] Incubation[12] of this labeled mixture with purified CS[2] gave a sample of clavaminic acid whose C-2 resonance was significantly enhanced above natural abundance and showed a pair of signals at δ 159.35 and δ 159.32 (Δδ 0.03

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(9) The details of these syntheses will be reported elsewhere.

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(11) Vederas, J. C. *Nat. Prod. Rep.* **1987**, *4*, 277-337.

(12) Stirred reactions at ambient temperature contained in a volume of 2.5 mL; 25 mM MOPS buffer pH 7.0, 0.5 mM dithiothreitol, 0.1 mM ascorbate, 0.01 mM ferrous ammonium sulfate, 5 mM α-KG, and 3 mM proclavaminate. Enzyme (0.5 mg) was added in two portions over a 6-h incubation period and removed by ultrafiltration prior to analysis.

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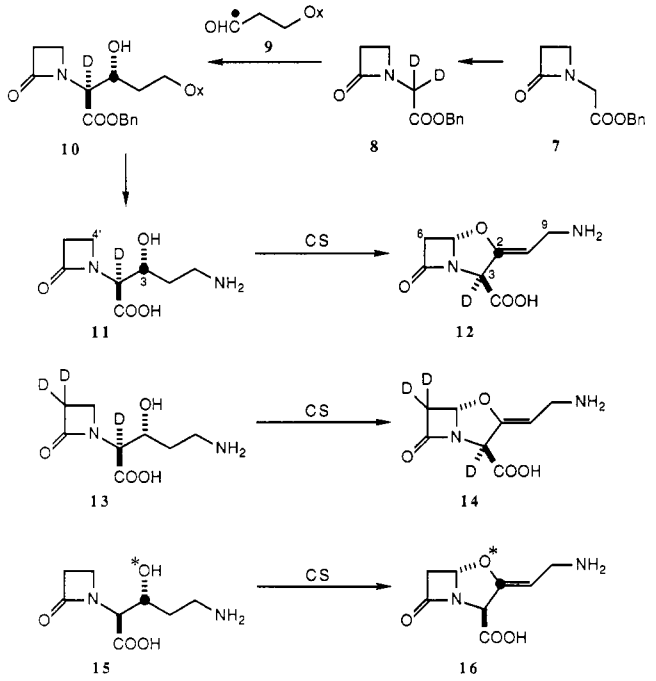
Scheme II



ppm) in the identical 1:1.2 ratio indicating no detectable deuterium loss at C-3 in **12**. The absence of loss from C-2 of proclavaminate was further verified and the fate of the C-3′ hydrogens was examined by converting [2-^{2}H,3′-^{2}H$_2$]proclavaminic acid (**13**; EIMS: <1% d_1, 12% d_2, 87% d_3)[9] to clavaminic acid (**14**). The latter was purified by reverse phase HPLC, derivatized by reaction with ethyl chloroformate and diazomethane, and analyzed for its deuterium content by ^{1}H NMR and CIMS (4% d_1, 12% d_2, 84% d_3). We attribute the slight apparent loss of label evident in the d_1 species (CIMS) to be an artifact of the higher background of this ionization technique relative to EIMS and to minor chemical exchange at C-3 during chromatographic isolation of the methyl ester derivative.[13]

Determination of the origin of the oxazolidine oxygen from the C-3 hydroxyl of proclavaminic acid or from molecular oxygen was addressed through the preparation of [3-^{13}C,^{18}O]proclavaminic acid (**15**) and monitoring the fate of heavy oxygen in clavaminate by means of its well-established isotopic shift on the directly bound ^{13}C-reporter nucleus.[11] Aldehyde **9** was exchanged in dry THF containing a small amount of ^{18}O-water (*O), crystallized and condensed with **7** to afford **15**, after N,O-deprotection. Examination of the carbinol resonance of **15** by ^{13}C{^{1}H} NMR spectroscopy (0.11 Hz resolution) gave signals at δ 69.58 and δ 69.56 ($\Delta\delta$ 0.022 ppm) in a very nearly 1:1 ratio for the ^{16}O/^{18}O species. Incubation of the doubly labeled **15** with CS gave a sample of labeled clavaminic acid (**16**) whose corresponding NMR analysis showed a pair of signals at δ 159.35 and δ 159.33 ($\Delta\delta$ 0.020 ppm) clearly indicating an unchanged 1:1 mixture of ^{13}C/^{16}O and ^{13}C/^{18}O species.

In conclusion, proclavaminic acid (**11**/**13**) is oxidatively cyclized by clavaminate synthase to **12**/**14** without loss of deuterium labels at C-2 and C-3′ in the former. The oxygen of the oxazolidine rings of clavaminic acid (**2**/**16**) and clavulanic acid (**3**) is that present at C-3 in proclavaminate (**1**/**15**) and originates at an earlier stage in the biosynthesis from molecular oxygen[4] (see Scheme I). Remarkably, although the oxidation state at C-2 of clavaminate is that of a ketone, no exchange of this labeled oxygen or of the adjacent hydrogen at C-2 is evident. These observations suggest either that oxidative oxazolidine ring formation precedes desaturation or that oxidation at C-3 in **1**/**15** occurs in a manner such that the substrate oxygen remains differentiated or isolated from exchange by the enzyme prior to its oxidative cyclization to **2**/**16**.

Clavaminate synthase bears fundamental similarities to two other enzymes important in β-lactam antibiotic biosynthesis, isopenicillin N synthase (IPNS), and deacetoxycephalosporin C (DAOC) synthase. IPNS catalyzes the formation of isopenicillin N from a cysteine-containing tripeptide[14] in the presence of ferrous ion and 1 equiv of dioxygen,[15] while DAOC synthase carries out the oxidative ring expansion of penicillin N to deacetoxycephalosporin C and requires Fe(II), O_2, and α-ketoglutarate.[16] These three enzymes catalyze intramolecular bond formation between heteroatomic and carbon sites contained in their substrates in the absence of hydrogen exchange at adjacent positions. Molecular oxygen utilized in all of these processes, however, does not appear in the products, although reactive hydroxylated intermediates may be involved transiently in product formation.[17] These enzymes, therefore, are not conventional oxygenases in spite of their cofactor requirements. The pattern evident in the penam/cephem series for sulfur has now been extended to oxygen in the clavams and may point to an interaction of potential heteroatomic ligands in the substrate with iron at the active sites of these enzymes to divert typical hydroxylase activity to oxidative (desaturative) cyclization chemistry. Participation by oxygen in this manner may have wider significance, for example, in the biosynthesis of polyether antibiotics[18] and marine toxins.[19]

Acknowledgment. We are grateful to Dr. J. L. Kachinski (JHU) for carrying out the mass spectral analyses essential to the work described and to the NIH (research Grant AI 14937 and postdoctoral fellowship GM 12119 to S.P.S.) for financial support.

(13) ^{1}H NMR spectroscopic analyses revealed no change in deuterium levels at C-6 in **14** in the conversion of **13** to **14**, ca. 98% site. The CIMS analysis was performed by using methane as the reagent gas (use of ammonia led to significant exchange at C-3 in derivatized **14**).

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Dynamic ESR Study of the 19-Electron $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ Complex (L_2 = 2,3-Bis(diphenylphosphino)maleic Anhydride). Measurement of the Barrier to Ring Rotation

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Fluxional processes in transition-metal organometallic complexes are typically studied by NMR spectroscopy.[1] Stable paramagnetic organometallic complexes are becoming increasingly common,[2] however, and NMR methods cannot, in general, be used for studies of these molecules. ESR spectroscopy has been used to study stereochemical nonrigidity in organic radicals,[3] but there are a few instances of it being used to study fluxional behavior in paramagnetic organometallic complexes.[4] In this communication we report the results of a variable-temperature ESR study of the 19-electron[5] $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ radical complex (L_2 = the chelating phosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride).[7] From an analysis of the spectra, we were able to determine the activation parameters for rotation of the C_5Ph_4H ring about the bonding axis.

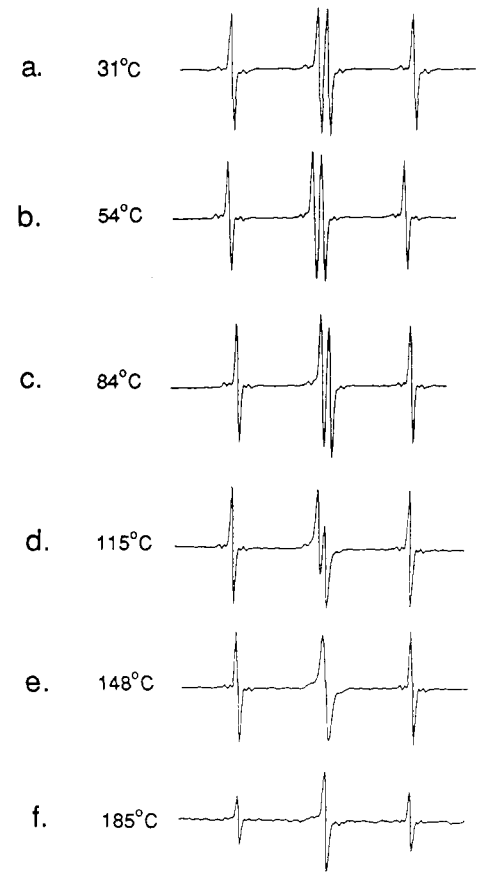

Figure 1. ESR spectra of $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride) in *o*-dichlorobenzene at various temperatures.

Figure 1 shows the ESR spectrum[8] of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ complex in *o*-dichlorobenzene at various temperatures. At 31 °C (Figure 1a) the two phosphorus atoms are magnetically inequivalent because the spectrum shows four well-resolved lines (g_{iso} = 2.0058; a_{P_1} = 9.01 G, a_{P_2} = 9.94 G). As the temperature increased, the two middle lines began to overlap (Figure 1b,c,d) and eventually (at 148 °C) broadened into a single line (Figure 1e). When the temperature was increased further, this broad middle line began to sharpen and eventually the spectrum became a 1:2:1 triplet (a_P = 8.92 G),[9] indicative of magnetically equivalent

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(5) Nineteen-electron complexes with the L_2 ligand are essentially 18-electron complexes with a reduced ligand.[6] Prof. T. L. Brown (University of Illinois) coined the term "18 + δ" to describe these types of complexes. Examples of 18 + δ complexes are increasingly numerous, see: (a) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504-505. (b) Creber, K. A. M.; Wan, J. K. S. *Trans. Met. Chem.* **1983**, *8*, 253-254. (c) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101-2102. (d) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *241*, 313-319. (e) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144-4151. (f) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442-3448. (g) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171-178. (h) Kaim, W. *Inorg. Chim. Acta* **1981**, *53*, L151-L153. (i) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365-3368. (j) Alegria, A. E.; Lozada, O.; Rivera, H.; Sanchez, J. *J. Organomet. Chem.* **1985**, *281*, 229-236.

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(7) Synthesis of $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$. $[(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3]_2$ (1.0×10^2 mg; 9.1×10^{-2} mmol) and L_2 (85 mg; 1.8×10^{-1} mmol) were added to 30 mL of THF. The solution was stirred and irradiated ($\lambda > 520$ nm; high pressure Hg arc lamp from the Oriel Corp.) for ~24 h. (The undissolved $[(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3]_2$ did not affect the reaction because it dissolved as the reaction proceeded.) During the irradiation, a stream of N_2 was passed through the reaction vessel so that any CO formed in the reaction was swept out. As the reaction proceeded, the color of the solution turned from red to purple and eventually to green. The green solution was then concentrated to about 10 mL by pumping off the solvent, followed by the addition of pentane or hexane to precipitate the green product $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$; yield: 75%. The product was recrystallized from THF/hexane. ν(CO) (THF) 1958 (s), 1887 (s), 1741 (s), 1673 (s). Anal. Calcd for $C_{59}H_{41}MoO_5P_2\cdot C_4H_8O$: C, 71.39; H, 4.66; P, 5.84. Found: C, 71.29; H, 4.38; P, 5.89.

(8) All ESR spectra were measured on a Varian E-109 spectrometer operating at X-band frequency with 100 kHz magnetic field modulation and equipped with Varian E-272B field/frequency lock assembly. The temperature at the sample was controlled by a Varian E-4557-9 variable-temperature accessory, and DPPH was used as *g*-marker and for magnetic field calibration.

(9) Ideally, the ^{31}P coupling constant in the fast-exchange limit (8.92 G) should be the average of the two coupling constants in the slow-exchange limit (9.01 and 9.94 G). We attribute the nonideal behavior observed with this molecule to a decrease in the electron-withdrawing ability of the $\eta^5\text{-}C_5Ph_4H$ ligand as the temperature is increased. We suggest that, as the temperature is increased, the electron-withdrawing ability decreases because rapid dynamic rotation of the phenyl rings destroys the extensive conjugation in the ligand. The decreased electron-withdrawing ability of the $\eta^5\text{-}C_5Ph_4H$ ligand will polarize the unpaired electron toward the oxygen atoms of the L_2 ligand. Consequently, there will be less unpaired electron spin density on the two phosphorus atoms at higher temperature, and the ^{31}P coupling constants will be smaller than at lower temperatures. (The $^{95,97}Mo$ coupling constant should also decrease with increasing temperature. However, this coupling constant is so small that we were unable to measure a decrease within experimental error; $a_{Mo,-14°C}$ = 0.85 ± 0.02 G; $a_{Mo,185°C}$ = 0.81 ± 0.02 G.) In support of this explanation, we note that our previous study of the 19-electron $Co(CO)_3L_2$ complex and its substituted derivatives $(Co(CO)_2L'L_2)$ showed that the phosphorus coupling constants decreased as the electron-donating ability of the substituting ligands increased.[6b] In addition, NMR spectroscopic results on diamagnetic complexes containing the $\eta^5\text{-}C_5Ph_4H$ ligand are consistent with the proposal that phenyl ring rotation increases with increasing temperature. Thus, Castellani and Trogler[10] showed that the proton signal in the $\eta^5\text{-}C_5Ph_4H$ ligand shifted upfield as the temperature increased. The upfield shift was attributed to phenyl ring rotation; the rotation caused the loss of deshielding from the ring currents of adjacent coplanar phenyl rings.

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