constant for the buildup of the T_1 state of phenazine was measured to be 7×10^{10} s^{-1} in isooctane.[22] Fast decay of the transient absorption of $FADH^0$ in photolyase is probably due to the intersystem crossing of the same type (Figure 2): that from D_1 ($\pi\pi^*$) to Q_1 ($n\pi^*$) or to Q_k ($n\pi^*$) which lies between D_1 and Q_1. If D_1 is the $n\pi^*$ state, then we have to consider the intersystem crossing from D_1 ($n\pi^*$) to Q_1 ($n\pi^*$) or to Q_k ($n\pi^*$). In this case, vibronic coupling between D_1 ($n\pi^*$) and its neighboring D_n ($\pi\pi^*$) or between the lowest $\pi\pi^*$ quartet state Q_1 ($\pi\pi^*$) and $Q_i(n\pi^*)$ or $Q_k(n\pi^*)$ is necessary to cause the spin-orbit coupling. Fast intersystem crossing processes in the picosecond time region which presumably include vibronic couplings have been observed for aromatic ketones.[23-27]

In summary we conclude that intersystem crossing is a major relaxation process of the D_1 state of $FADH^0$ and that the excited states of lifetimes of ca. 100 ps and 1 μs we observe with nanosecond and picosecond flash photolysis, respectively, correspond to D_1 and Q_1 states of photolyase-bound flavin radical. Further experiments to prove this conclusion by transient spectroscopy of the flavin radical in solution and by quenching the doublet with heavy atoms are in progress.

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π-Heterocyclic Complexes of Pentaammineosmium(II) and the Metal-Induced Cycloaddition of Pyrrole and Maleic Anhydride

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The isostructural heterocycles pyrrole, furan, and thiophene show markedly different reactivity toward cycloaddition to dienophiles.[1] Whereas furan reacts with maleic anhydride in a matter of seconds at room temperature,[1b] thiophene does so only at severe pressures,[1c] and the nitrogen analogue altogether fails to form cycloadducts without the addition of a catalyst.[1d] Judging from our previous experiences,[2] we anticipated that the intermediate $[(NH_3)_5Os]^{2+}$ would form stable π complexes with these heterocycles and, thus, we undertook an investigation of their reactivity toward cycloaddition.

When $(NH_3)_5Os(OTf)_3$ is reduced over Mg^0 in the presence of an excess of the desired heterocycle, the complexes $[(NH_3)_5Os(2,3\text{-}\eta^2\text{-}L)]^{2+}$ are obtained in high yield (L = pyrrole, **1**; furan, **2**; thiophene, **3**).[3] ^1H NMR spectra for these cations feature four inequivalent hydrocarbon resonances,[4] thereby ruling out η^1-coordination at the heteroatom. Contrary to what is observed for **2** or **3**, the pyrrole complex **1** displays resonances which are significantly broadened at room temperature; homonuclear decoupling at −25 °C reveals a dynamic process in which the metal tautomerizes between the 2,3- and 4,5-η^2-positions of the pyrrole ring.[5]

Scheme I. Cycloaddition Products for the Reaction of $[Os(NH_3)_5(pyrrole)]^{2+}$ and Maleic Anhydride

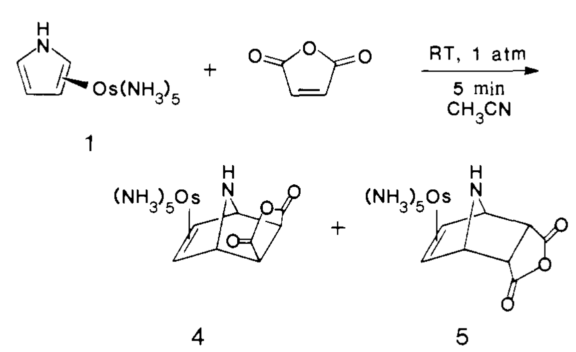
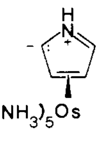


Chart I. The Azomethine Ylide Intermediate for the Complex $[Os(NH_3)_5(pyrrole)]^{2+}$



A ^1H NMR spectrum of an acetonitrile-d_3 solution containing the furan complex **2** (21 mM) and excess maleic anhydride (750 mM) shows no reactivity, even after 10 days. In an analogous experiment the thiophene complex **3** also fails to react over this time period. However, a rapid reaction occurs when **1** at the same concentration as above is exposed to 1 equiv of maleic anhydride in acetonitrile-d_3, as evidenced by the ^1H NMR spectrum of the mixture. After 5 min, the broad aromatic resonances originally observed for **1** have been completely replaced by three sharp singlets at 4.20 (2 H), 3.45 (2 H), and 3.14 (2 H) ppm (**4**) and another set of lines at 4.15 (dd, 2 H), 3.60 (dd, 2 H), and 3.23 (s, 2 H) ppm (**5**) in a 4:1 ratio.[6] The disappearance of the aromatic pyrrole resonances[7] and the observed NMR pattern point to the formation of two osmium(II) isomers containing 1:1 symmetrical cycloadducts of pyrrole and maleic anhydride.[8] When the reaction is performed with maleic anhydride-d_2, the resonances at 3.45 and 3.60 are absent; the high field peaks at 3.14 and 3.23 ppm agree well with the η^2-ethylene chemical shifts in $[(NH_3)_5Os(\eta^2\text{-}CH_2{=}CH_2)]^{2+}$ (3.22 ppm) and can thus be assigned to the coordinated olefin protons of the adducts, and the remaining, low field resonances to bridgehead protons. From the splitting patterns it is concluded that **4** and **5** correspond to the *exo*- and *endo*-maleic anhydride isomers, respectively, with the metal moiety bound in the exo configuration for both species, as shown in Scheme I.

The cycloaddition reaction at −30 °C under the same conditions yields **4** and **5** in a ratio of 2:1; when the product solution is allowed

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(3) Synthesis of **1**: Pyrrole (1.5 mL) and Mg^0 (2 g) were added to a stirred suspension of $(NH_3)_5Os(OTf)_3$ (250 mg) and NaOTf (35 mg) in 5 mL of DME. Addition of CH_2Cl_2 (3 mL) to the filtered reaction mixture after 45 min resulted in a bright yellow precipitate which was either used without further purification (OTf salt) or purified by aqueous ion exchange chromatography and precipitated as a tetraphenylborate salt. E_p (acetonitrile, TBAH, ν = 200 mV/s) = −0.05 V (NHE). **1**: Calcd for $C_{52}H_{60}OsN_6B_2$: C, 63.67; H, 6.17; N, 8.57. Found: C, 63.44; H, 6.38; N, 8.40. Complexes **2** and **3** were prepared in similar manner by substituting DMA (0.5 mL) for NaOTf. **2**: $E_{p,a}$ = 0.67 V; Calcd for $C_{52}H_{59}OsO_1N_5B_2$: C, 63.61; H, 6.06; N, 7.13. Found: C, 63.37; H, 6.43; N, 6.89. **3**: $E_{p,a}$ = 0.45 V; Calcd for $C_6H_{19}OsS_3F_6O_6N_5$: C, 10.96; H, 2.91; N, 10.65; S, 14.63. Found: C, 11.09; H, 2.93; N, 10.57; S, 14.46.

(4) ^1H NMR in acetone-d_6 **1** (t = −25 °C): 7.47 (H_a, b, 1 H), 6.81 (H_b, d, 1 H), 6.65 (H_c, d, 1 H), 5.68 (H_d, t, 1 H), 5.36 (H_e, t, 1 H), 4.52 (b, 3 H); 3.32 (b, 12 H). **2** (20 °C): 7.50 (d, 1 H), 6.96 (d, 1 H), 6.18 (t, 1 H), 5.12 (t, 1 H), 4.76 (b, 3 H), 3.50 (b, 12 H). **3** (20 °C): 6.78 (d of d, 1 H), 6.75 (d of d), 6.05 (d of d, 1 H), 5.58 (d of d, 1 H), 4.90 (b, 3 H), 3.55 (b, 12 H).

(5) Partial spin saturation exchange was observed between H_b–H_c and H_d–H_e, an observation which indicates that the specific rate of tautomerization at −25 °C is on the order of seconds.

(6) Relative intensities were integrated against tetraphenylborate anion. *Cis*- and *trans*-ammine peaks at 3.05 (b, cis) and 3.80 (b, trans) are superimposed for **4** and **5**.

(7) No Michael addition products were detected in this reaction.

(8) A solid can be obtained by the addition of ether to the solution of the OTf^- salt. Analyses: Calcd for $C_8H_{22}OsS_2F_6O_9N_6$: C, 16.26; H, 3.00; N, 11.38. Found: C, 16.64; H, 3.21; N, 11.09.

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to stand at room temperature, no changes in the relative amounts of the isomers can be detected, even after 12 h, and hence it can be inferred that the distribution of exo and endo products is under kinetic control.

The lack of reactivity of the furan complex **2** toward maleic anhydride ($>10^4$ decrease in the pseudo-first-order rate constant compared to the free ligand) is expected upon metal 2,3-η^2-coordination, which causes loss of diene character in the ring. However, the pyrrole complex **1**, albeit also forming a 2,3-η^2-species with pentaammineosmium(II), displays unprecedented facile reactivity with maleic anhydride. The contrasting reaction patterns for the isostructural species **1** and **2** may be ascribed to their differing intramolecular dynamics. In contrast to what is observed for **2**, complex **1** undergoes a rapid 2,3- $\leftrightarrow$ 4,5-η^2-tautomerization, passing through an isomer in which the 2- and 5-positions are available for cycloaddition.

If the metal were to isomerize to the ring nitrogen, Diels–Alder addition of maleic anhydride to the diene fragment could ensue, and this might be followed by an N $\rightarrow$ π rearrangement. However, this hypothesis loses validity in view of the reactivity observed for the η^2-bound *N*-methylpyrrole analogue:[9] in this complex, both the tautomerization and the cycloaddition rates are at least twice as fast as those observed for **1**, thereby making an attack at the hindered nitrogen an unlikely possibility. Alternatively, an intermediate is shown in Chart I which would be stabilized by the π-basic metal center. Addition of maleic anhydride to the 2- and 5-positions of **6** could fully account for the observed products, the reaction taking the form of a 1,3-dipolar cycloaddition to the azomethine ylide portion of the complex. The failure of the furan complex (**2**) to undergo cycloaddition can be understood by considering the decreased stability of the corresponding oxonium intermediate.

Our attempts to liberate the cycloadduct from either osmium(II) or osmium(III) have thus far been unsuccessful.

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[9] The complex $[(NH_3)_5Os(\eta^2\text{-}N\text{-methylpyrrole})]^{2+}$ was prepared as for **1**.

Detection of Reaction Intermediates in the Conversion of Cyclohexane to Benzene on Pt(111)

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Dehydrogenation reactions catalyzed by transition-metal surfaces have long been of great interest because of their importance in petroleum processing.[1] In the conversion of cyclohexane to benzene on Pt, cyclohexene has been suggested as an intermediate, but it has never been directly detected.[1-10] Presented here is the first direct observation of cyclohexene as an intermediate in this reaction. In addition, a second intermediate which is believed to be a bis(alkylidene) species is also detected.

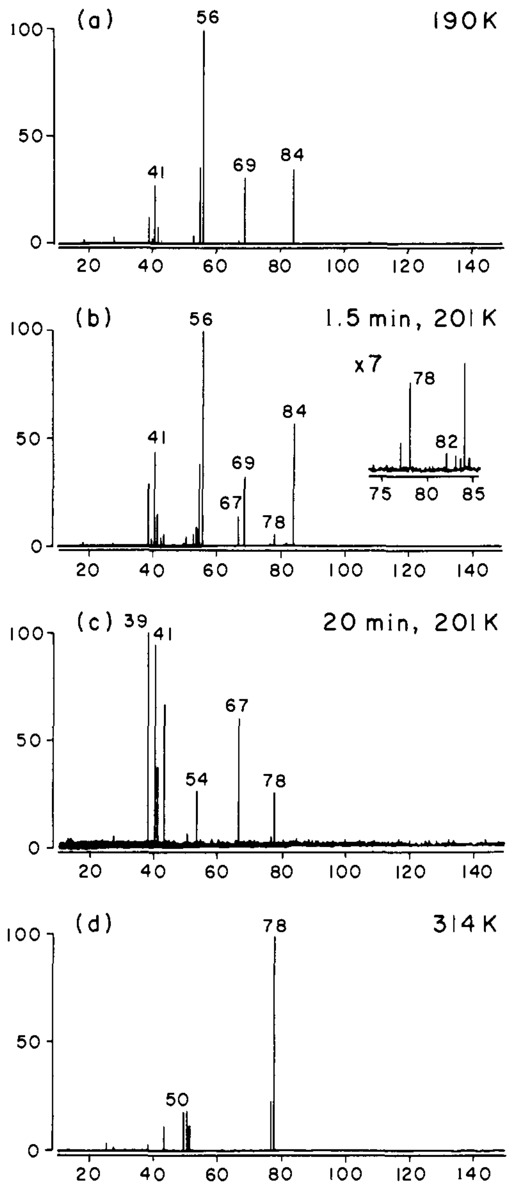

Figure 1. Laser-induced thermal desorption Fourier transform mass spectra, each resulting from a single laser shot at a fresh spot, obtained from a Pt(111) crystal surface after dosing with less than one molecular layer of cyclohexane. (a) After about 3 min at 190 K showing only molecular cyclohexane. (b) Shortly after warming to 201 K, showing the presence of cyclohexane at *m*/*z* 84 and benzene at *m*/*z* 78 (using the same scaling as 1a) and, cyclohexene, in the inset (with scaling expanded by a factor of 7) at *m*/*z* 82. (c) After 20 min at 201 K, cyclohexane and cyclohexene are gone, but benzene and another intermediate, 1,6-hexadialkylidene, remain. (d) Warming to 314 K gives only benzene.

The reaction is studied as a function of temperature and time by laser-induced thermal desorption and Fourier transform mass spectrometry (LITD/FTMS).[11-16] In the experiments described

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