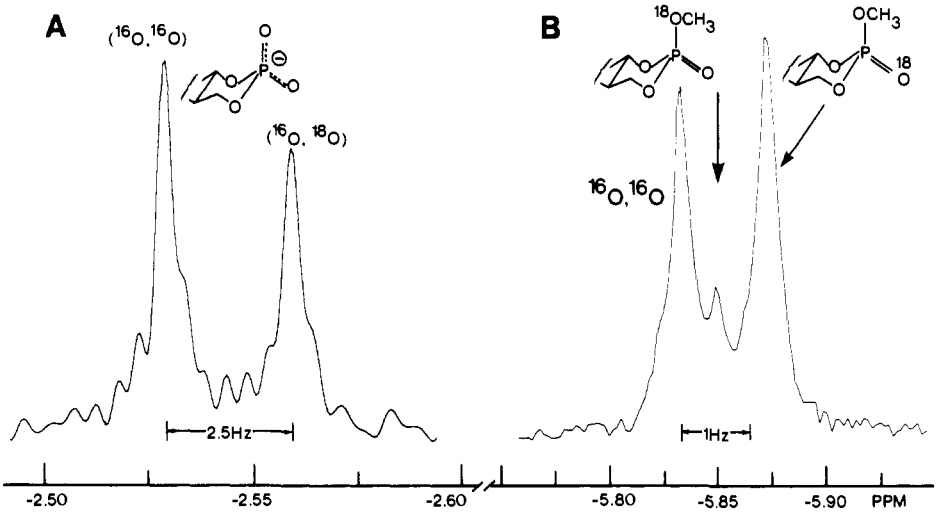

Figure 1. (A) 80.9-MHz ^{31}P NMR spectrum of 45% ^{18}O-enriched 1,3,2-dioxaphosphorinane diester (**2**) (^{18}O label in exocyclic oxygens). The upfield signal at −2.563 ppm represents the monooxygen-18 labeled diester. Spectral conditions on the Nicolet NTC-200 spectrometer: 444 scans, 1.7-s recycle time, 56° pulse width, 20% D_2O/H_2O solvent. (B) 32.4-MHz ^{31}P NMR spectrum of the axial epimer of 2-methoxy-1,3,2-dioxaphosphorinane (**3**). Total monooxygen-18 enrichment into the exocyclic oxygens is 61%. Spectral conditions on the Bruker WP-80 spectrometer: 6000 scans, 8-s recycle time, 67° pulse width, $CDCl_3$ solvent.

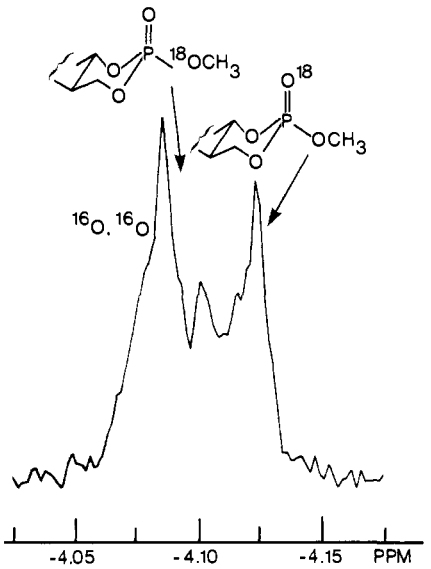

Figure 2. 32.4-MHz ^{31}P NMR spectrum of the equatorial epimer of 2-methoxy-1,3,2-dioxaphosphorinane (**3**). Total oxygen-18 enrichment into exocyclic oxygens is 59%, 4950 scans.

Cohn and Hu[10] have shown that a rough linear correlation exists between the magnitude of the ^{18}O isotope ^{31}P shift and the bond order between phosphorus and the isotopically substituted atom. In ADP and ATP, ^{18}O substitution on a single P–O bond produces a 0.0166-ppm upfield shift, and ^{18}O substitution on a P–O bond with half single-bond character and half double-bond character is 0.0285 ppm. Utilizing these two numbers and extrapolating to ^{18}O substitution on a full double bond yields a calculated ^{18}O isotope shift of 0.0404 ppm. As shown in Figure 1B, the shift between the two larger ^{31}P signals is 0.040 ppm and that between the downfield and middle signals is 0.015 ppm. The furthest upfield signal is thus associated with ^{18}O isotopic substitution into a full equatorial P=O bond and the middle signal ^{18}O substitution into a single bond. Hydroxide attack on the axial epimer of 2,4-dinitrophenyl ester (**1**) yields 82% inversion, assuming no epimerization occurs during the methylation reaction.

These assignments were confirmed by a similar study of the stereochemistry for ^{18}O hydroxide catalyzed hydrolysis of the equatorial epimer of the (*p*-methoxyphenoxy)dioxaphosphorinane **1**. Mass spectral analysis of the methyl triester indicates 59 ± 5% ^{18}O enrichment. The ^{31}P NMR spectrum of this equatorial triester sample is shown in Figure 2, and integration of the $^{16}O,^{18}O$ signals at −4.100 and −4.123 ppm indicates 51 ± 5% ^{18}O enrichment. The methyl triester ^{18}O signal distribution indicates that hydroxide attack proceeds with 59% inversion.

The stereochemistry for hydroxide attack in the *p*-methoxyphenoxy ester differs significantly from the stereochemistry for methoxide attack in methanol. Thus, the methoxide displacement proceeds with only 9% inversion,[6a] while 59% inversion is observed in the hydroxide reaction. In contrast, the 2,4-dinitrophenoxy triester yields 82–83% inversion for both hydroxide and methoxide displacement.[6a]

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A New Process for Sensitization of Ketone Photoreduction: Exploitation of Low-Lying Metal-to-Ketone Charge-Transfer Excited States

Sir:

Sensitizing organic reactions to longer wavelengths of light than absorbed by reactants is an important objective of photochemistry research.[1] We report a new mechanism for sensitizing the photoreduction of ketones by exploiting absorption that populates a low-lying metal-to-ketone charge-transfer excited state in complexes of the formula *fac*-$[XRe(CO)_3L_2]$ (X = Cl and L = 4-benzoylpyridine or X = I and L = 4-acetylpyridine). The process also depends on (i) electron-transfer quenching of the excited state and (ii) substitution lability of the Re-bound photoreduction products. Numerous examples[2-6] of photoredox processes via

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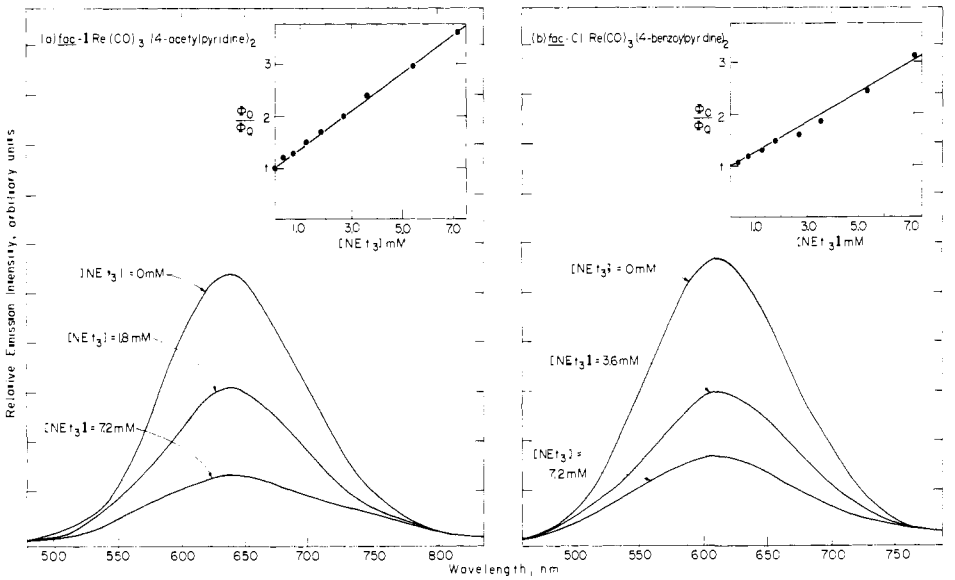

Figure 1. Quenching of luminescence of (a) *fac*-[IRe(CO)$_3$(4-AcPyr)$_2$] and (b) *fac*-[ClRe(CO)$_3$(4-BzPyr)$_2$], respectively, in degassed benzene/CH_2Cl_2 (50:50 by volume) solution at 25 °C. The excitation wavelength was 436 nm. Spectra shown are uncorrected for detector response.

MLCT excited states now exist, but the results reported here are the first involving MLCT for L being a ligand undergoing redox reactions.

We have previously reported[7] the synthesis and characterization of the 4-benzoylpyridine complex; the 4-acetylpyridine species is a derivative and has properties that are quite similar to those for L = 4-benzoylpyridine. The ReLCT excited state is the lowest excited state for both ketone complexes, and both complexes are emissive in most solvents. Emission of the Re complexes as a function of the concentration of Et_3N is shown in Figure 1; quenching obeys the Stern–Volmer equation,[1] and from the lifetime of the complexes ($\sim$0.5 μs) we conclude that the quenching constant, k_q, is $\sim 10^9$ M^{-1} s^{-1}. The ReLCT excited state of *fac*-[XRe(CO)$_3$L$_2$] should be a powerful enough oxidant to effect the oxidation of Et_3N. This conclusion is based on the fact that the cyclic voltammetry of the Re complexes exhibits a reversible one-electron reduction wave at $\sim$−1.2 V vs. SCE in CH_3CN/0.1 M [*n*-Bu_4N]ClO_4, and the onset of the emission is at $\sim$2.5 eV, giving an excited-state potential (Re*)/Re^-· of $\sim$+1.3 V vs. SCE. The peak potential for the oxidation of Et_3N is +1.0 V vs. SCE in the same solvent/electrolyte system. Similar Re complexes have been found to be quenched somewhat below diffusion-controlled rates by electron transfer when the free-energy change is of a similar magnitude.[8,9] Since Et_3N has no low-lying excited states, it would appear that quenching of the photoexcited ReLCT state (eq 1) is via the process represented by eq 2.

$$fac\text{-}[XRe(CO)_3L_2] \xrightarrow[436\text{ nm}]{\text{ReLCT}} fac\text{-}[XRe(CO)_3L_2]^* \quad (1)$$

$$fac\text{-}[XRe(CO)_3L_2]^* + Et_3N \xrightarrow{k_q = 10^9\ M^{-1}\ s^{-1}} fac\text{-}[XRe(CO)_3L_2]^{-}\cdot + Et_3N^{+}\cdot \quad (2)$$

Quenching of the ReLCT excited state is accompanied by permanent chemical change (eq 3). The Re-containing product is ultimately the bis(alcohol) complex; this has been established

$$fac\text{-}[XRe(CO)_3L_2] \xrightarrow[Et_3N\text{ in }CH_2Cl_2]{436\text{ nm}} fac\text{-}[XRe(CO)_3LL'] \xrightarrow[Et_3N\text{ in }CH_2Cl_2]{436\text{ nm}} fac\text{-}[XRe(CO)_3L_2'] \quad (3)$$

X = Cl, L = 4-BzPyr [(ν_{ketone}) 1669 cm^{-1}], L′ = Ph-4-PyrCHOH [(ν_{OH}) 3380 cm^{-1}]

$\Phi_{436} = 0.20 \pm 0.02$

X = I, L = 4-AcPyr [(ν_{ketone}) 1696 cm^{-1}], L′ = Me-4-PyrCHOH [(ν_{OH}) 3360 cm^{-1}]

$\Phi_{436} = 0.18 \pm 0.02$

by independent synthesis by reduction of the ketones with $NaBH_4$ to L′ = phenyl- or methyl-4-pyridylmethanol and reaction of L′ with $XRe(CO)_5$ to generate *fac*-[XRe(CO)$_3$L$_2$′].[7] Small infrared spectral changes occur in the metal–carbonyl stretching region consistent with the stepwise formation of the bis(alcohol) complexes according to eq 3. Oxidation products from Et_3N are found; Et_2NH and CH_3CHO are observed, presumably via hydrolysis of the primary oxidation product as has been observed previously.[10] The 436-nm quantum yields given are for the disappearance of *fac*-[XRe(CO)$_3$L$_2$] to form *fac*-[XRe(CO)$_3$LL′] under conditions where Et_3N (0.2 M) quenches all of the emission. The concentration of Re complex was typically 3–10 mM.

Irradiation (436 nm) of *fac*-[XRe(CO)$_3$L$_2$] (typically 3–10 mM) in the presence of Et_3N (typically 0.5 M) and added L (typically 0.2 M) in CH_2Cl_2 yields more L′ than can be accounted for on the basis of the amount of L initially bound to Re (eq 4).

$$L + Et_3N \xrightarrow[fac\text{-}[XRe(CO)_3L_2]]{436\text{ nm}} L' + (Et_3N\text{–oxidation products}) \quad (4)$$

The only light-absorbing species under these conditions is the Re complex. Greater than 20 molecules of L′ have been generated per Re complex initially present. Thus, the Re complexes can be used to sensitize the photoreduction of the pyridyl ketones, since the ketones themselves do not absorb visible light. Near-ultraviolet, 355 nm, irradiation of L in CH_2Cl_2 in the presence of 0.2 M Et_3N yields L′ with a 0.3 (±0.03) quantum yield. Such ketone pho-

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toreduction processes are well-known.[10] The alcohol product, L′, has been established by ^{1}H NMR and mass spectra data compared to the authentic samples of L′ synthesized independently.[11] The main result here is that visible light irradiation of the Re complexes results in the same chemistry as from direct ultraviolet irradiation of the ketones.

Sensitized photoreduction of excess ketone (ketone not initially bound to Re) requires a ligand-substitution process to exchange the reduced material for the unreacted ketone, since free ketone does no quenching of the ReLCT or ReL′CT excited state. The *fac*-[XRe(CO)$_3$L$_2$] complexes sluggishly undergo substitution reactions at 25 °C. From measurements of the rate of the reaction represented by eq 5, it would appear that dissociation of L′ (L′

$$fac\text{-}[XRe(CO)_3L_2'] + \text{1,10-phen} \rightarrow fac\text{-}[XRe(CO)_3(\text{1,10-phen})] + 2L' \quad (5)$$

= methyl-4-pyridylmethanol, phenyl-4-pyridylmethanol) from Re occurs with a rate constant of $\sim 10^{-7}$ s^{-1}. At 50 °C, the rate constant is $\sim 10^{-4}$ s^{-1}. Thus, the ligand-exchange rate may be the rate-limiting step in the overall sensitization process, depending on the rate of excitation (light intensity) and temperature. At 25 °C and at our typical intensities of $\sim 10^{-7}$ einstein/min, thermal exchange of L′ is rate limiting. This was proven by irradiating *fac*-[IRe(CO)$_3$(4-AcPyr)$_2$] in the presence of 4-benzoylpyridine and Et$_3$N. The coordinated ketone undergoes photoreduction before any 4-benzoylpyridine is reduced.

To summarize, we find that the pyridyl ketones can be photoreduced by irradiation with wavelengths longer than absorbed by the ketones themselves. The same products and similar quantum yields are obtained from direct and sensitized photoreaction. The sensitization process involves binding the ketone to a metal to induce a low-lying M → ketone CT absorption, electron donation to the complex from some reducing agent, H$^+$/H· transfer chemistry to yield the alcohol, and exchange of the reduction product for unreacted ketone (eq 1, 2, 6, and 7).

$$fac\text{-}[XRe(CO)_3L_2]^{-}\cdot \rightarrow fac\text{-}[XRe(CO)_3LL'] \quad (6)$$

$$fac\text{-}[XRe(CO)_3LL'] \xrightarrow[\Delta]{L} fac\text{-}[XRe(CO)_3L_2] + L' \quad (7)$$

The H$^+$/H· transfer reactions giving the alcohol presumably parallel those in the direct irradiation. A difference in the Re-complex sensitization is that the odd electron in *fac*-[XRe(CO)$_3$L$_2$]$^-$· may not be totally localized on the ketone as it would be in the direct reaction (eq 8).[12] Electrochemical experiments

$$[\text{ketone}]^* + Et_3N \rightarrow [\text{ketone}]^{-}\cdot + Et_3N^{+}\cdot \quad (8)$$

show that the ketone complexes are 0.35–0.5 V more easily reduced than the free ketones, consistent with greater delocalization of the added electron density. The sensitization process outlined here should be applicable to many other photoredox reactions, and the wavelength response can be controlled, in principle, by the functionality on the metal fragment other than the L.

Acknowledgment. We thank the National Science Foundation for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975–1980.

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Methyl Reactivity in Deazalumazines[1]

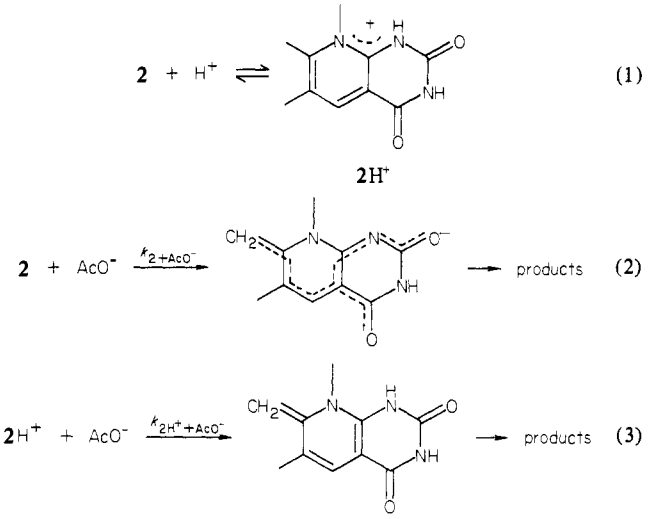
Sir:

6,7-Dimethyllumazines (e.g., **1**) give flavins both in vivo and in vitro via a mechanism involving initial proton loss from the highly reactive C-7 CH_3 group.[2] We have examined a series of 5-deazalumazines (**2**–**7**) in order to learn more about the activation process at C-7, since replacing N at position 5 with CH gives more opportunities for structural variation. Furthermore, 5-deazaflavins have recently been shown to be involved in the biological reduction of carbon dioxide to methane,[3] and the analogous 5-deazalumazines are of interest as possible precursors. We report herein an unusual effect of methyl substitution adjacent to the reaction site.

Compounds **2**, **3**, **5**, and **7** were prepared[4] by condensing 6-methylaminouracil with the appropriate dicarbonyl compound (or its acetal), essentially by the method of Paterson and Wood;[5] **4** and **6** were similarly prepared[4] by using the unsaturated aldehyde or acetal. These authors prepared a series of compounds closely related to those used herein and noted that both C-5 and C-7 CH_3 groups in deazalumazines exchange their hydrogen atoms in D_2O.

The structures of the isomers **2** and **4**, and **5** and **6**, made on the basis of NMR shifts and synthesis arguments, were confirmed by using the nuclear Overhauser effect. Irradiation of the N–CH_3 protons gave a 38% enhancement of the ring proton for **4** and a 20% enhancement of the C-7 CH_3 group of **5**. Assignment of the signals for the two exchanging groups in **3** was similarly made, the upfield group that was assigned to C-7 CH_3 giving a small enhancement (6%).

We have determined the general base- and acid-catalyzed rate constants in water for the C-5 and C-7 methyl groups (the C-6 and N-8 methyl groups do not react) by iodometry and deuterium exchange (NMR).[6] See, for example, reactions 1–3. Partitioning



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