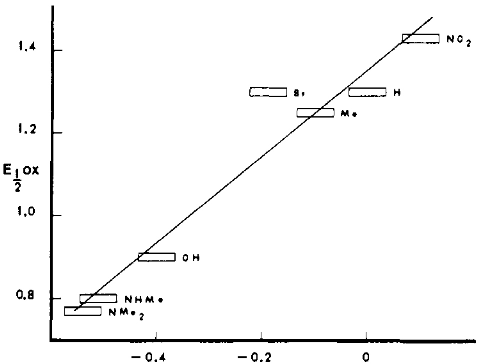

Figure 1. A plot of the Ru(III/II) reduction potentials ($E_{1/2}$OX) vs. $\sigma_R{}^0$. Values of $\sigma_R{}^0$ are taken from ref 6. Error limits are ±0.01 V in $E_{1/2}$(OX) and ±0.03 for $\sigma_R{}^0$ values (ref 23).

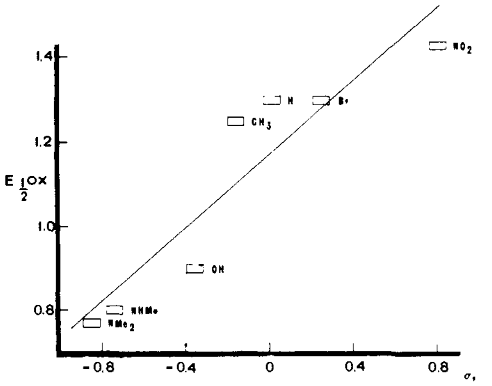

Figure 2. A plot of the Ru(III/II) reduction potentials ($E_{1/2}$OX) vs. σ_p. Values for σ_p are taken from ref 6. Error limits as in Figure 1.

uent groups are directly attached to the aromatic ring.[20]

The Ru(II) nitrosoarene complexes are stable in acetonitrile solution, and, as is the case in metal carbonyl and nitrosyl complexes, the Ru-N(O)Ar linkage may be largely π-bonding in character. This is consistent with the relative instability of first-row transition metal complexes of nitrosoarenes,[21] and the surprising, relatively high lability of some of the Ru(III) nitrosoarene complexes.[22] The chemical evidence and the correlation in Figure 1 are consistent with extensive π-back-bonding from Ru(II), and the effect of -X is probably transmitted mainly through the π-system of the ligand.

Acknowledgments are made to the Army Research Office Durham under Grant No. DA-ARO-D-31-124-73-G104 and to the National Science Foundation under Grant GP42846X for support of this work, to Professor W. E. Hatfield for helpful discussions, and to Kim Nordquest for providing samples of the nitrosoarenes.

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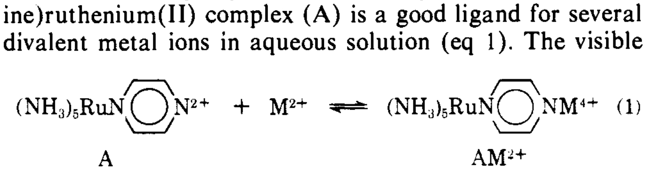
Electron Transfer Photochromism. The Flash Photolysis of the Binuclear Complex (NH$_3$)$_5$Ru^{II}(μ-pyrazine)Cu^{II}

Sir:

Recent studies[1-4] have demonstrated that the metal-to-ligand charge transfer excited states of Ru(bpy)$_3{}^{2+}$ can undergo electron transfer to metal complexes and other oxidants in solution. Observations with several other complexes indicate similar behavior resulting from MLCT excitation.[5,6] Photostimulated electron transfer can be separated into two general classes: in the first, light accelerates a thermodynamically favored reaction (e.g., the photocatalyzed reaction between Ru(bpy)$_3{}^{2+}$ and Tl^{3+})[2] or a reaction giving products which decompose irreversibly (e.g., the proposed reduction of cobalt(III) ammines by excited Ru(bpy)$_3{}^{2+}$).[7] The second category includes those photostimulated electron transfers to produce thermodynamically less favored species which undergo the reverse reaction to regenerate the starting materials.[3,7c] The term *electron transfer photochromism* describes the latter case. Here we report the first demonstration of *intramolecular* electron transfer photochromism between two metal ions of a polynuclear complex.

It was recently reported[8] that the pentaammine(pyrazine)ruthenium(II) complex (A) is a good ligand for several divalent metal ions in aqueous solution (eq 1). The visible

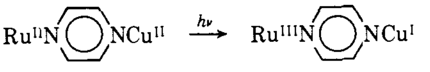


$$(NH_3)_5RuN\bigcirc N^{2+} + M^{2+} \rightleftharpoons (NH_3)_5RuN\bigcirc NM^{4+} \quad (1)$$

A AM^{4+}

(M^{2+} = Cu^{2+}, Zn^{2+}, Ni^{2+})

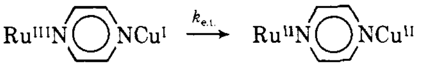
spectrum of A is dominated by an intense MLCT absorption band (λ_{max} 472 nm) and association with H$^+$ or M^{2+} shifts this to the red (508 nm for Cu^{2+}, 489 nm for Zn^{2+}, 493 nm for Ni^{2+}, 529 nm for H$^+$).[8,9] Continuous photolysis of A in the MLCT region leads to low photoreaction quantum yields ($\Phi \sim 10^{-3}$). AH$^+$ is an order of magnitude less photoactive.[10,11] Flash photolysis of A or AH$^+$ does not indicate the formation of any transient species and net photoreaction under these conditions is very minor. However, while the continuous photolysis of ACu^{2+} shows very little net photodecomposition ($\Phi \sim 10^{-4}$), flash photolysis demonstrates efficient transient bleaching of the MLCT absorption band at 508 nm ($\Phi > 0.2$) followed by regeneration of the starting material. Since the Ru(III) pyrazine complex is virtually colorless,[9] we believe this transient bleaching represents the photostimulated electron transfer process:



(2)

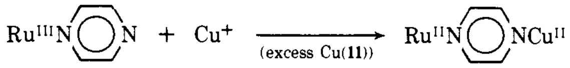
B

followed by regeneration of ACu^{2+} according to the redox reactions:



(3)

and/or

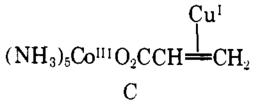


(4)

Attempts to observe directly absorptions corresponding to the presence of a species such as B proved inconclusive probably as a result of the strongly absorbing character of the initial solutions. Transient bleaching was the only phenomenon seen by kinetic flash photolysis over the monitoring wavelength range 360-620 nm. Transient absorption was apparent at 640 nm; however, at this and longer wavelengths the optical density is very high owing to the $Cu^{2+}(aq)$ in solution, thus the significance of this transient absorption is questionable.

The solution subjected to flash photolysis contained excess Cu^{2+} (conditions: $[Ru(II)] = 1.4 \times 10^{-5}\ M$, $[Cu^{2+}] = 0.33\ M$, pH $\sim$6, $\mu = 1.0\ M$, $T = 25°$, $\lambda_{flash} > 405$ nm). Therefore, the question remains whether the photostimulated electron transfer is inner sphere as in eq 2 or is outer sphere as in the electron transfer reactions from excited $Ru(bpy)_3{}^{2+}$. The following observations support the conclusion that the transient bleaching results from an inner sphere electron transfer. First, not only do A and AH^+ fail to show flash induced transient bleaching but also the zinc and nickel complexes, AZn^{2+} and ANi^{2+}, show no significant photoreaction when subjected to flash photolysis under similar conditions. Only the relatively easily reduced Cu^{2+} displays this pathway. Second, flash photolysis of the 4-acetylpyridine complex, $(NH_3)_5Ru(pyCOCH_3)^{2+}$ (λ_{max} 523 nm), in the presence of the 0.35 M Cu^{2+} displays no transient bleaching. Since this complex has a MLCT band comparable in energy to that of ACu^{2+} and there is no evidence for association of Cu^{2+} with the 4-acetyl complex, we conclude that inner sphere association between the Ru^{II} complex and Cu^{2+} is necessary for efficient photostimulated electron transfer.

Photostimulated intramolecular electron transfer has been reported for species C (and related complexes)[6] and is implied by the photodecomposition noted for species D;[5]



$$(NH_3)_5Co^{III}O_2CCH\overset{Cu^I}{\overset{|}{=\!=}}CH_2$$

C

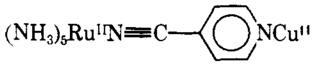
$$(NH_3)_5Co^{III}(\mu\text{-}4,4'\text{-bpy})Fe^{II}(CN)_5$$

D

however, these cases represent irreversible electron transfer steps owing to the rapid dissociation of the Co(II) product. In contrast, the transient bleaching of species ACu^{2+} is followed by its regeneration on a millisecond time scale; therefore, the system is photochromic. For a related system, it was reported[12] that $Ru(phen)_2(CN)_2$ (phen = 1,10-phenanthroline) forms complexes with Cu^{2+} in aqueous solution and that these complexes are responsible for a static quenching pathway of the ruthenium complex charge transfer luminescence. Without additional data (e.g., flash photolysis results), one cannot differentiate between energy transfer or electron transfer pathways for the static quenching mechanism. However, our flash photolysis results with ACu^{2+} plus the observed redox reactivity of excited $Ru(bpy)_3{}^{2+}$ make the electron transfer quenching pathway an attractive possibility.

Formulation of the photoproduct as B introduces another dimension of the interest to this system. B is a precursor complex[13] of the reverse inner sphere electron transfer reaction (eq 3). Despite the extensive activity in the study of electron transfer reactions between metal ion centers, precursor complexes of inner sphere paths have been rarely observed,[5,6,14] and measured rate constants of inner sphere redox reactions generally are the product of the formation constant of the precursor complex and the rate constant $k_{e.t.}$. Based on the flash photolysis results, it is difficult to conclude that the back reaction is in fact a monomolecular decay of the precursor complex (eq 3). Cu^I is expected to be substitution labile, and the back reaction conceivably would represent a bimolecular path eq 4 or a combination of eq 3 and 4. However, the regeneration curves are linear over several half-lives when plotted ln $(A_\infty - A_t)$ vs. t and the resulting first-order rate constants k_1 are independent of the flash intensity ($k_1 = (7.8 \pm 0.7) \times 10^3$ sec^{-1} at 25°) and of the concentration of B generated. Although plots according to second-order kinetics ($(A_\infty - A_t)^{-1}$ vs. t) are also approximately linear for the first half-life, the second-order rate constants (k_2) obtained are not independent of flash intensity. Therefore it appears that regeneration of ACu^{2+} from B (eq 3) is faster than dissociation of Cu^+ from B, and that electron transfer relaxation is unimolecular. We are currently initiating stopped flow kinetic measurements of the reaction between aqueous Cu^+ and the Ru(III) pyrazine complex generated separately to confirm this conclusion. A second-order rate constant of $\sim 10^9\ M^{-1}$ sec^{-1} would be necessary to account for electron transfer relaxation of flash induced transients by a bimolecular process.

Similar behavior under flash photolysis has been observed for related systems (e.g. E), and these are being investigated further in this laboratory.



E

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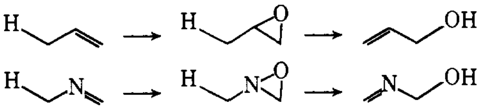
The Oxidative Deamination of Amines to Ketones via Oxaziridines

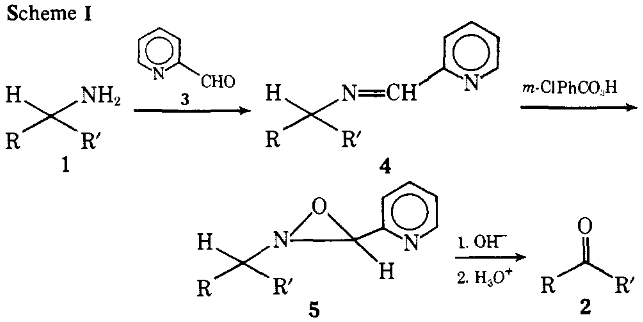
Sir:

The transposition of a carbon-nitrogen double bond plays a pivotal role in the enzymatic oxidative deamination of α-amino acids to pyruvic acids mediated by pyridoxal pyrophosphate.[1] In developing synthetic methodology for the oxidative deamination of amines **1** to ketones **2**,[2] we have sought to mimic this biochemical process.[3] The conversion of olefins to allylic alcohols via epoxides proceeds with concomitant carbon-carbon double bond transposition[4] and suggests that oxaziridines could be utilized to effect carbon-nitrogen double bond transposition.



We now wish to report an oxidative deamination procedure which incorporates this approach (Scheme I).

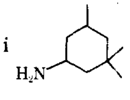
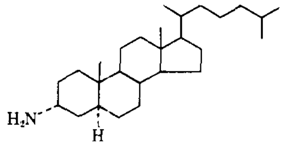
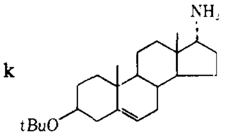
Scheme I



The condensation of 2-pyridinecarboxaldehyde[5] (**3**) (1.0 equiv) with amines **1** in THF (5 ml/mmol of **1** at 25° for 2 hr) over 5A molecular sieves furnished imines **4** in high yield (Table I). The selection of **3** bearing no α hydrogens circumvented any problems in the regioselectivity of oxaziridine ring opening later in the sequence. The *m*-chloroperoxybenzoic acid oxidation[6] (1 equiv/CH_2Cl_2/0° for 0.5 hr) of imines **4** provided a mixture of *E* and *Z* isomers[7] of oxaziridines[8] **5** in good yield[9] (Table I). The formation of nitrones or pyridine *N*-oxides was not problematical.

The base-catalyzed ring opening of oxaziridines was reported to liberate ammonia in high yield[10] but to afford carbonyl compounds in low yield.[11] The desired ring opening of an oxaziridine **5** would regenerate 2-pyridinecarboxaldehyde (**3**) as well as liberate a ketone **2** according to the postulated mechanism shown below. To allow for the efficient conversion of oxaziridines **5** to ketones **2** required the suppression of two competing reactions: the rearrangement of **5** to amide **6**[12] and the Aldol condensation of the ketone **2** and 2-pyridinecarboxaldehyde (**3**).

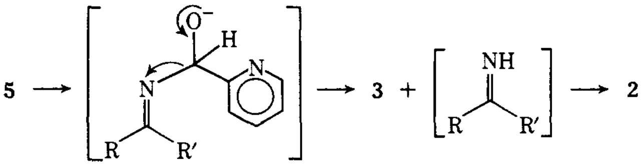
Table I. The Oxidative Deamination of Amines (RR′CHNH$_2$) **1** to Ketones (RR′C=O) **2**

			% isolated yields			
	R	R′	Imine 4	Oxaziridine 5	Cosolvent (Time, hr)	Ketone 2
a	n-C_5H_{11}	n-C_5H_{11}	91	88	DMF (18)	73
b	n-C_6H_{13}	n-C_6H_{13}	97	86	DMF (21)	73
c	$-CH_2(CH_2)_4CH_2-$		89	82	MeOH (1.5)	64[b]
d	$-CH_2(CH_2)_5CH_2-$		92	77	DMF (6.5)	44
e	$-CH_2(CH_2)_9CH_2-$		92	80	DMF (14)	66
f	$-C_2H_5$	$-CH_2CH_2Ph$	92	78	MeOH (2.5)	74
g	H	Ph	93	...	MeOH (1)	64[a]
h	CH_3	Ph	94	...	MeOH (0.25)	42[a]
i			93	90	MeOH (3)	47[b]
j			99	89	DMF (23)	77
k			100	...	DMF (16)	44[a,c]

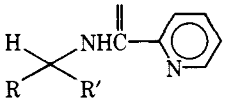
[a] Oxaziridine too labile to isolate by thick layer chromatography. [b] Isolated as the 2,4-dinitrophenylhydrazone derivative. [c] Oxaziridine generated at −78° by inverse addition of *m*-ClPhCO$_3$H to imine.

Table II. Base-Catalyzed Ring Opening of Oxaziridine **5b**

		% isolated yields	
Base (equiv)	Conditions	Ketone 2b	Amide 6b
KOH(10)	H_2O–DMF–acetone	73	...
KOH(10)	H_2O–MeOH–acetone	64	3
NaOMe(1.5)	THF	22	12
KO-*t*-Bu(1.5)	THF	20	3
Li-N(*i*-Pr)$_2$(1.5)	THF		56
Cu(OAc)$_2$(1.0)	H_2O–MeOH		68



We have found that the ring opening of **5** to ketones **2** proceeds smoothly using potassium hydroxide in an aqueous acetone solution containing methanol or *N,N*-dimethylformamide as a cosolvent[13] (Table I). The dramatic influence of other bases on the course of the reaction is summarized in Table II. In marked contrast to the effective use of dialkylamides and alkoxides in the ring opening of epoxides,[4] only hydroxide ion proved suitable in the ring opening of oxaziridines **5** to ketones **2**.[14] Finally, acetone[15] served to trap the regenerated **3** as the enone **7**. The pyridine ring in **7** allowed for the facile removal of this contaminant (and any unreacted **3**) in an acidification step.



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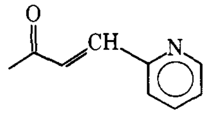

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In several cases, we have found that our oxidative deamination sequence is superior to literature procedures. For example, application of our procedure to **1j** provided **2j** in 66% yield (without isolation of the intermediate imine or oxaziridine) but application of the mesitylglyoxal procedure[3c] af-