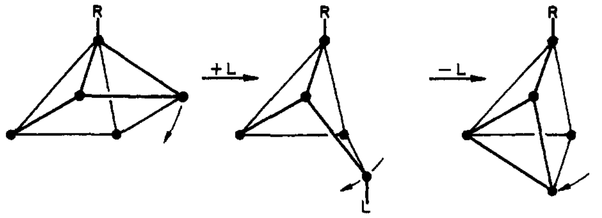
isolation of the adduct $CH_3B_5H_8 \cdot N(CH_3)_3$ described here provides strong support for this idea. In 1963 Onak, Gerhart, and Williams[10] proposed a structure similar to structure II for the possible intermediate. In view of the anticipated tautomerism of hydrogens[10,15] in these boron hydride structures and the lack of evidence for the positions of hydrogens in the newly isolated adduct, the two structures may be considered essentially the same at the present stage. The isomerization may be visualized as illustrated below



It is suggested here that the steric problem that would be introduced in going from the intermediate trigonal-bipyramid arrangement to the final structure may be relieved by rearranging the relative position of the base. Thus, the selective formation of the 2,3 isomer from $1,2\text{-}(CH_3)_2B_5H_7$[12] may be explained by the addition of the base to the basal boron atom which does not carry methyl group. The chemistry of the adduct, $CH_3B_5H_8 \cdot N(CH_3)_3$, and the related systems will be published elsewhere upon completion of the study.

Acknowledgments. This work has been supported by a grant from the National Science Foundation (GP 32079). The author is grateful to Professor Robert W. Parry for his cooperation.

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Intermediates Generated in the Charge Transfer to Ligand Photochemistry of Ruthenium(II) Pyridine and Bipyridyl Complexes[1]

Sir:

It is a rather interesting contrast in gross photochemical behavior that irradiation of charge transfer to ligand (CTTL) absorption bands of $Ru(NH_3)_5py^{2+}$ should lead to extensive ligand aquation[2] while irradiation of the same type of transition in $Ru(bipy)_3{}^{2+}$ should lead to no detectable photochemistry and appreciable phosphorescent emission at room temperature in fluid solution.[3,4] In fact, the latter complex is so photochemically inert that it is an exceptionally useful triplet sensitizer.[4,5] In the present report we wish to call attention to what appears to be a new reaction pathway in the photochemistry of coordination complexes; a photochemical pathway shared by $Ru(NH_3)_5py^{2+}$ and $Ru(bipy)_3{}^{2+}$.

In the course of our studies with the triplet sensitizer, $Ru(bipy)_3{}^{2+}$, we have had occasion to flash photolyze solutions containing this species. We have observed a transient bleaching[6] of the CTTL absorption (λ_{max} 450 nm) of this substrate. The substrate absorptivity is regenerated with a pH ($1 \leq pH \leq 3$) dependent pseudo-first-order rate constant, $k_{obsd} = 0.1[H^+]^{-1}\ sec^{-1}$. Very similar behavior is exhibited by $Ru(phen)_3{}^{2+}$, $Fe(bipy)_3{}^{2+}$, and $Fe(phen)_3{}^{2+}$. The extent of the bleaching (or transient yield) and the lifetime of the bleached intermediate species do not change appreciably on replacing bipyridyl (bipy) by 1,10-*o*-phenanthroline (phen), but the intermediate lifetimes are about four times greater in the case of the ruthenium complexes than observed for the iron complexes. The transient produced from $Ru(bipy)_3{}^{2+}$ reacts with $Co(HEDTA)Cl^-$ to produce $Ru(bipy)_3{}^{3+}$ and presumably Co^{2+} with a second-order rate constant, $k \simeq 7 \times 10^5\ M^{-1}\ sec^{-1}$.

In order to further elucidate the nature of the observed intermediate species, we flash photolyzed some of the $Ru(NH_3)_5L^{2+}$ complexes which have been photochemically examined by Ford and coworkers.[2,7] In the cases that L = pyridine and benzonitrile we find again a transient bleaching of the characteristic CTTL absorption bands[8,9] of the ruthenium(II) complex. In each of these cases, however, the total substrate absorbance is not regenerated, consistent with some photoaquation of ligands L.[2] The variations in observed aquation parallel the pH dependencies of ϕ_L reported by Ford, *et al.*[2] In the case of $Ru(NH_3)_5py^{2+}$ we find again a pseudo-first-order, pH-dependent regeneration of substrate absorptivity, $k_{obsd} = (32 + 6.8[H^+]^{-1})\ sec^{-1}$, in the range $0 \leq pH \leq 3.5$, and for $\mu = 0.2$ ($LiClO_4$). Using published values of ϕ_{py}[2] we estimate a primary yield (extrapolated to zero time) of (0.2 ± 0.1) for bleached species. In the case of $Ru(NH_3)_5NCC_6H_5{}^{2+}$ the transient species has a pH-independent limetime of 0.1 sec.

To accommodate the similar photochemical behavior of these several complexes requires some similar features in each of the intermediate species; thus, for example, a one-ended dissociation of bipyridyl would yield a species differing little in absorptivity from $Ru(bipy)_3{}^{2+}$,[10] cannot be extended to the case of $Ru(NH_3)_5py^{2+}$, and would not function as an electron-transfer reducing agent. There seems no viable alternative to the conclusion that the species with diminished CTTL absorptivity must contain oxidized metal centers. Since ruthenium(III) is substitution inert[11] and since the original substrate is readily regenerated, it seems evident that the radical anion (py^-, $bipy^-$, etc.) must remain coordinated. Thus taking $Ru(NH_3)_5py^{2+}$ as prototype for the class of compounds, a relatively simple mecha-

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[1] Partial support of this research by the National Science Foundation (Grant GP 24053) is gratefully acknowledged.

[2] P. C. Ford, D. A. Chaisson, and D. H. Stuermer, *Chem. Commun.*, 530 (1971).

[3] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, 26, 72 (1968).

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[6] We have made observations in several spectral regions between 600 and 300 nm; however, the substrate absorptivity is generally much too high and the transient yield too low to permit detection of the transient absorption spectrum.

[7] P. C. Ford, D. H. Stuermer, and C. P. McDonald, *J. Amer. Chem. Soc.*, 91, 6209 (1969).

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[9] P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968).

[10] D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, 48, 1853 (1968).

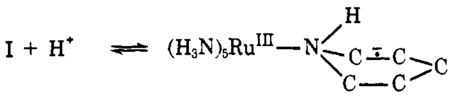
[11] P. C. Ford, *Coord. Chem. Rev.*, 5, 75 (1970).

nism may be proposed to account for these observations.

$$Ru(NH_3)_5py^{2+}\ (^1A_1) + h\nu \longrightarrow Ru(NH_3)_5py^{2+}\ (^*CT)$$

$$^*CT \longrightarrow {}^1A_1$$

$$^*CT \longrightarrow \underset{\text{I}}{Ru^{III}(NH_3)_5(py^-)} \qquad (1)$$



(2)

II

$$\text{I} \longrightarrow {}^1A_1 \qquad (3)$$

$$\text{II} + H_2O \longrightarrow Ru(NH_3)_5OH_2^{2+} + Hpy^+ \qquad (4)$$

At present it is not clear whether the pH-independent path for pyridine aquation occurs from I in competition with back-electron transfer (3) or whether the net ligand aquation reactions are to be associated with the population of other (*e.g.*, ligand field) excited states. Our observations do require that $pK_a \geq 4$ for II; it also appears that the acid-independent term of k_{obsd} is to be associated with pyridine aquation as indicated in (4).

It is to be observed that an intermediate analogous to I has been observed in the pulse radiolysis of $(H_3N)_5CoO_2CC_6H_4NO_2^{2+}$.[12] The lifetime of the electron adduct of nitrobenzoate coordinated to cobalt(III) varies from 10^{-2} to 2.5×10^{-6} sec for the ortho and meta isomers, respectively.[12] The similarly long lifetimes for aromatic radical anions coordinated to either cobalt(III) or ruthenium(III) suggest a significant activation barrier[13,14] to the intramolecular electron-transfer reactions which generate the stable divalent metal complex. At least for the systems we have studied it seems reasonable to attribute this barrier to structural changes in the ligand such as the change in hybridization of the pyridine nitrogen which we have indicated in I. In the case of $Ru(NH_3)_5py^{2+}$ the proposed intermediate I also provides a convenient means of accounting for the pH dependence of the transient lifetime.

Although the transient species which we have observed must be regarded as primary photochemical products, they apparently decay largely in a way which regenerates the original substrate. In the case of the triplet sensitizers, $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$, any significant photoreaction, particularly a long-lived bleaching reaction, could affect estimates of the number of triplet states populated in sensitization reactions.[15] To estimate product yields we have used a solution of naphthalene in ethanol as a filter for the flash lamps to ensure irradiation of only the low-energy CTTL bands. Using pyridine aquation from $Ru(NH_3)_5py^{2+}$ as an approximate actinometric reference, we estimate that the yields of transient from CTTL irradiation of $M(bipy)_3^{2+}$ and $M(phen)_3^{2+}$ are approximately 10^{-3}. Thus even in 1 *M* [H⁺], a correction would only be significant in the $Ru(bipy)_3^{2+}$ sensitized product yields obtained if absorbed light intensities were greater than about 10 einsteins $l.^{-1}$ sec^{-1}.

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[12] (a) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **94**, 1757 (1972); (b) M. Z. Hoffman, private communication.

[13] In their analogous studies on cobalt complexes, Hoffman, *et al.*,[12] have postulated that relatively long-lived (compared to the case of $Co(NH_3)_5O_2CC_6H_5^{2+}$ where no transient is observed) transients result due to localization of the electron at NO_2. However, it does not seem that electron localization far from the metal center is a sufficient condition as the intrinsic barriers to reduction of cobalt(III) complexes seem generally very small.[14] It seems more likely to us that long-lived transients can only be observed, regardless of the central metal, when electron capture by the ligand results in some structural change within the ligand.

[14] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, **94**, 394 (1972); (b) D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, in press; (c) *J. Amer. Chem. Soc.*, submitted for publication; (d) J. F. Endicott, R. R. Schroeder, and D. R. Ferrier, *J. Phys. Chem.*, submitted for publication.

[15] It should also be noted that net production of $Ru(bipy)_3^{3+}$ can be a complication when $Ru(bipy)_3^{2+}$ is used as a sensitizer. This may come about through electron transfer from $Ru^{III}(bipy)_2(H^+\text{-}bipy^-)$ as noted above or through the oxidation of $Ru(bipy)_3^{2+}$ by radical fragments.

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The Stereoselective and Stereospecific Thermal Isomerizations of *trans*-1,2-Di(prop-1′-enyl)cyclopropanes

Sir:

Pioneering studies by Vogel[1,2] and by Doering and Roth[3,4] on the thermal isomerizations of *cis*-divinylcyclopropanes have been extended spectacularly, leading to new concepts and examples of fluxional isomerism and degenerate rearrangements. The discovery that *trans*-1,2-divinylcyclopropane may be converted at 190° to cyclohepta-1,4-diene[5] has not been pursued with a similar vigor. Whether the rearrangement involves a diradical-mediated Cope process, or an epimerization followed by a conventional Cope isomerization,[5] has been an unaddressed question.

Natural products derived from the essential oil of *Dictyopteris*, an odiferous seaweed, and from the female gametes of the brown alga *Ectocarpus siliculosus* have revived interest in *trans*-1,2-dialkenylcyclopropanes.[6-14] In the course of this work Pettus and Moore[14] provided the first data pertinent to the mechanism of the Cope rearrangement of *trans*-dialkenylcyclopropanes, by demonstrating that dictyopterenes A and B rearrange thermally to the cyclohepta-1,4-dienes **1** and **2** with some degree of stereoselectivity;[15]

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