Efficient Upper Excited-State Ligand Photochemistry in Pentammineruthenium(II)–Acylpyridine Complexes

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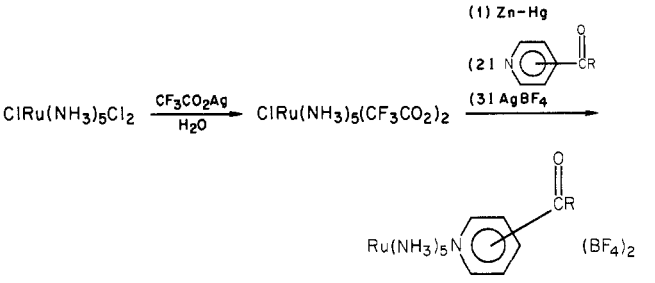
Efficient photochemistry from upper excited states is relatively rare,[1] except when such states are in thermal equilibrium with the lowest excited state.[2,3] The rarity results from the necessity for a relatively rapid chemical reaction to compete with a relatively slow internal conversion process. There has been particular interest in such processes in organometallic complexes. Wrighton has provided several clear examples of efficient ligand photochemistry when the locally excited ligand (IL) excited state is the lowest in the compound.[4] However, the situation is not so clear when an IL excited state of an organic ligand lies higher in energy than a metal–ligand charge transfer (CT) state. Whitten first reported cis–trans isomerizations in some $Ru^{II}(bpy)_2$–stilbazole complexes[5] and Wrighton more recently reported competitive ligand and CT emissions in $XRe(CO)_3$–benzoylpyridine complexes.[6] In neither case was the competition between excited ligand reaction and internal conversion characterized.

We report here that several $Ru^{II}(NH_3)_5$–acylpyridine complexes with lowest MLCT excited states undergo 100% efficient Norrish type II elimination[7] from excited ligand. These complexes were chosen for study because of the known rapidity of excited-state type II reactions,[7] the absence of other easily excited ligands, and the well-characterized photochemistry of such complexes.[8] The complexes were synthesized along the lines outlined by Taube and co-workers[9] as shown in Scheme I. The reduction was best achieved by passing the yellow solution containing the Ru(III) complex[10] through a column packed with zinc–mercury amalgam into a flask containing an aqueous solution of acylpyridine. Addition of $AgBF_4$ precipitated the complex which was recrystallized from ether in high yield and then from water in lower yield. All reactions were carried out under argon.

The crystalline complexes gave correct elemental analyses and IR and UV spectra consistent with those of comparable reported complexes.[9,11] Figure 1a compares the electronic spectrum of the blue *m*-valerylpyridine complex with that of meta-valerylpyridinium hydrochloride; Figure 1b compares the purple *p*-valerylpyridine complex with the hydrochloride. As already reported,[9,11] a MLCT transition occurs in the visible region with d–d transitions in the near-UV[9] region and the ligand π–π^* transition at 260–270 nm. The ligand hydrochloride salts show extinction coefficients at 313 nm of 50 ± 13 (meta) and 62 ± 4 (para) which represent primarily n–π^* excitation. The extinction coefficients at 313 nm for the complexes are 360 ± 110 (meta) and 310 ± 50 (para).[12] We assume that complexation does not affect n–π^* extinction coefficients and that the enhanced complex absorption at 313 nm reflects competing d–d transitions.

Irradiation of degassed acetonitrile solutions of several such acylpyridine complexes at 313 nm, where some 14% (meta) or 20% (para) of the absorbed light excites an IL transition, results in measurable type II photoelimination. No such reaction occurs upon visible irradiation. Table I lists the compounds studied and

Scheme I



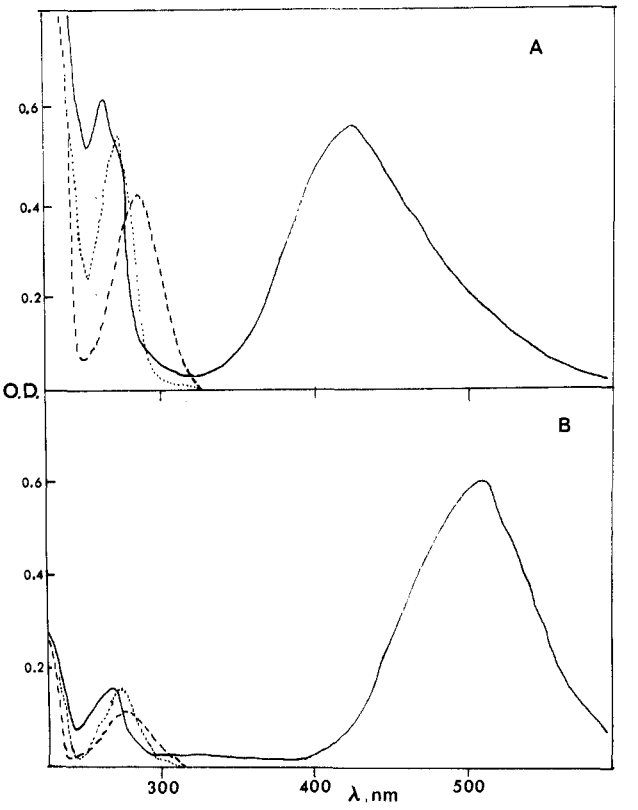
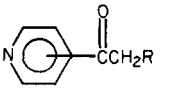


Figure 1. (A) UV–visible spectra in acetonitrile of 1.3×10^{-4} M *m*-valerylpyridine: (---) free ligand; (···) HCl salt; (—) $(NH_3)_5Ru$ complex. (B) Same for 5×10^{-4} M *p*-valerylpyridine.

Table I. Photokinetic Data for $(NH_3)_5Ru(II)$ Complexes and Hydrochloride Salts of Acylpyridines[a]



		$(NH_3)_5Ru$			HCl		
position	R	Φ_{II}	$k_q\tau$, M^{-1}	$10^{-8}/\tau$, s^{-1}	Φ_{II}	$k_q\tau$, M^{-1}	$10^{-8}/\tau$, s^{-1}
meta	$CH(Me)_2$	0.020	22	4.8	0.19	13.1	7.5
meta	CH_2Et	0.020	10	10.0	0.23	4.9	20.
para	$CH(Me)_2$	0.023	13	7.5	0.16	7.4	14.
para	CH_2Et	0.019	6.6	15.	0.12	3.0	33.
para	CH_2-*i*-Pr	0.020	5.7	18.	0.13	2.1	50.

[a] Degassed acetonitrile solutions, 0.01 M in Ru complex or 0.05 M in HCl salt, irradiated at 313 nm. All data represent averages of duplicate runs with precision of ±5%.

(1) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.
(2) (a) Wagner, P. J.; May, M. L.; Haug, A.; Graber, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 5269. (b) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *Ibid.* **1973**, *95*, 5604.
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(4) (a) Wrighton, M. S.; Morse, D. A.; Pdungsap, L. *J. Am. Chem. Soc.* **1975**, *97*, 2073. (b) Giordano, P. J.; Wrighton, M. S. *Ibid.* **1979**, *101*, 2888.
(5) Zarnegar, P. P.; Bock, C. R.; Whitten, D. S. *J. Am. Chem. Soc.* **1973**, *95*, 4367.
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(8) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.
(9) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.
(10) Allen, A. D.; Bottomley, F.; Harris, R. O.; Reinslau, V. P.; Senoff, C. V. *J. Am. Chem. Soc.* **1967**, *89*, 5595.
(11) Chaison, D. A.; Hintze, R. E.; Stuermes, D. H.; Peterson, J. D.; McDonald, D. P.; Ford, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 6665.
(12) As other workers have noted,[9] it is difficult to measure extinction coefficients of such compounds with high precision.

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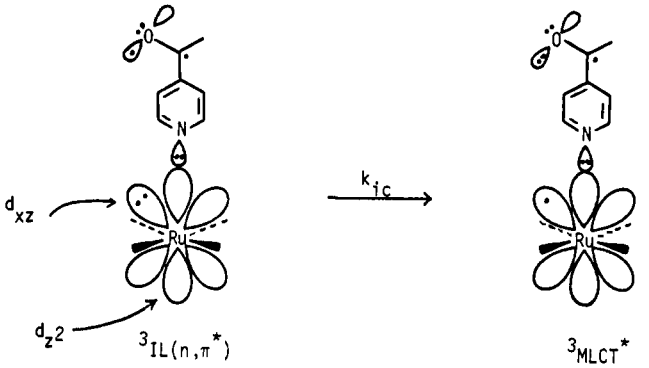
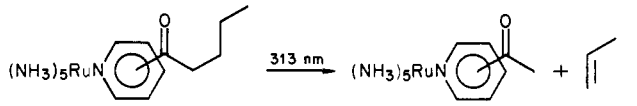
Scheme II



the photokinetic results. Since the ligand could not be displaced thermally from the complex, olefin formation was monitored by GC analysis. The reaction was quenched by conjugated dienes. Slopes of linear Stern-Volmer plots[13] and the triplet lifetimes calculated therefrom[14] are also listed in Table I. No other volatile products were obtained from the para complexes; free ligand, but no acetylpyridine, was formed in low quantum yields from the meta complexes. This selective displacement is consistent with Ford's observations.[8] The complete lack of acetylpyridine formation from any of the complexes indicates that all of the type II reactions come from complexed acylpyridine.



Comparable data were obtained for the acylpyridine hydrochlorides, chosen as the best available model for the complexed ligands.[4] Table I compares the parallel behavior of the protonated and complexed acylpyridines. When the observed quantum yields for the complexes are corrected for only partial absorption by ligand, the complexes and salts are seen to have comparable quantum yields. In each case, quantum yields are low but independent both of γ C-H bond strength and of triplet lifetime. Such behavior proves that triplet lifetimes are determined solely by rates of γ-hydrogen abstraction.[15] The facts that ligand quantum yields are independent of triplet reactivity and equal to those in the uncomplexed ligands indicate that internal conversion from the triplet IL to the lower lying MLCT states does not compete with triplet ligand reaction. Therefore we can conclude that *the rate of internal conversion* (k_{ic}) *in these complexes is less than* 10^8 s^{-1}.

So few k_{ic} values are known that it is difficult to discuss the relatively low value for these complexes. Liu concluded that k_{ic} for T_2 (E_T = 74 kcal) to T_1 (E_T = 43 kcal) in several anthracenes is $\sim 5 \times 10^9$ s^{-1}.[16] The value for S_2 (81 kcal) to S_1 (41 kcal) in azulene is 10^9 s^{-1}.[17] These transitions are relatively slow because of large energy gaps, even though the π,π^* excited states occupy the same space. The energy gaps in the complexes are comparable or smaller; $E_T(n,\pi^*)$ = 71-73 kcal and E_T(MLCT) = 40-50 kcal.[18] The much lower value of k_{ic} must then reflect poor orbital overlap. The MLCT transition is primarily a d-π^* transition, and the lowest π^* orbital in phenyl ketones is localized largely on the carbonyl.[2b] Therefore, k_{ic} really measures a d_{xz}-n_O electron demotion as shown in Scheme II. Although the CO and Ru centers are not very far apart, the coplanar n and d_{xz} orbitals are highly directed and almost perpendicular to each other. Therefore both poor orientation and the intervening nuclei of the pyridine ring combine to minimize orbital overlap.

The fact that absorption-corrected quantum yields for the Ru-complexed acylpyridines are comparable to those for the simple protonated acylpyridines indicates that internal conversion from *singlet* ligand n,π^* to MLCT state does not compete significantly with ligand intersystem crossing. Such intersystem crossing is very rapid ($k > 10^{10}$ s^{-1}).[19] The low quantum yields from these positively charged acylpyridines indicate that the 1,4-biradical intermediates revert to ground-state ketones much more efficiently than usual,[20] behavior which we do not fully understand.

The actual k_r values for the complexed acylpyridine triplets are half those of the protonated ketones and 2-4 times those of the free acylpyridines.[7b] The correctness of this order depends on k_q being equal for all these types of compounds.[14] The order is reasonable if the variation reflects primarily an inductive effect; the pyridine nitrogen in the complexes is only partially positive, the Ru^{2+} charge being spread over six ligands.

We are currently studying complexes with less reactive acylpyridine ligands to pinpoint k_{ic} values more accurately.

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Reaction of $(CH_3)_3SnM$ and Ph_3SnM (M = Li, Na, K) with Optically Active 2-Octyl Tosylate, Chloride, and Bromide[1]

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Traditionally, investigations of the mechanism of substitution reactions have been greatly aided by stereochemical studies. The application of classical experimental procedures (i.e., polarimetry) to such studies require that the maximum rotation of the product also be known; this fact has prevented the general application of this procedure to the elucidation of most organometallic reaction mechanisms, since the optical resolution of such substances is frequently impractical.[2] Optical resolution becomes unnecessary, however, if the product in question can be synthesized stereospecifically. We report here the stereospecific synthesis of two such mechanistically significant compounds, trimethyl- and triphenyl(2-octyl)tin (**1** and **2**), together with several related findings.

On the basis of our previous observation that the reaction of $(CH_3)_3SnM$ (M = Li, Na, K) with either *cis*- or *trans*-4-*tert*-butylcyclohexyl tosylate proceeds with essentially complete (>99%) *inversion* of configuration,[3] it seemed reasonable to expect that

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(2) Alternative procedures have been developed which circumvent this difficulty by employing diastereomeric rather than enantiomeric substrates; however, such techniques are not without their own shortcomings. Cf.: Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826 and references therein.

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