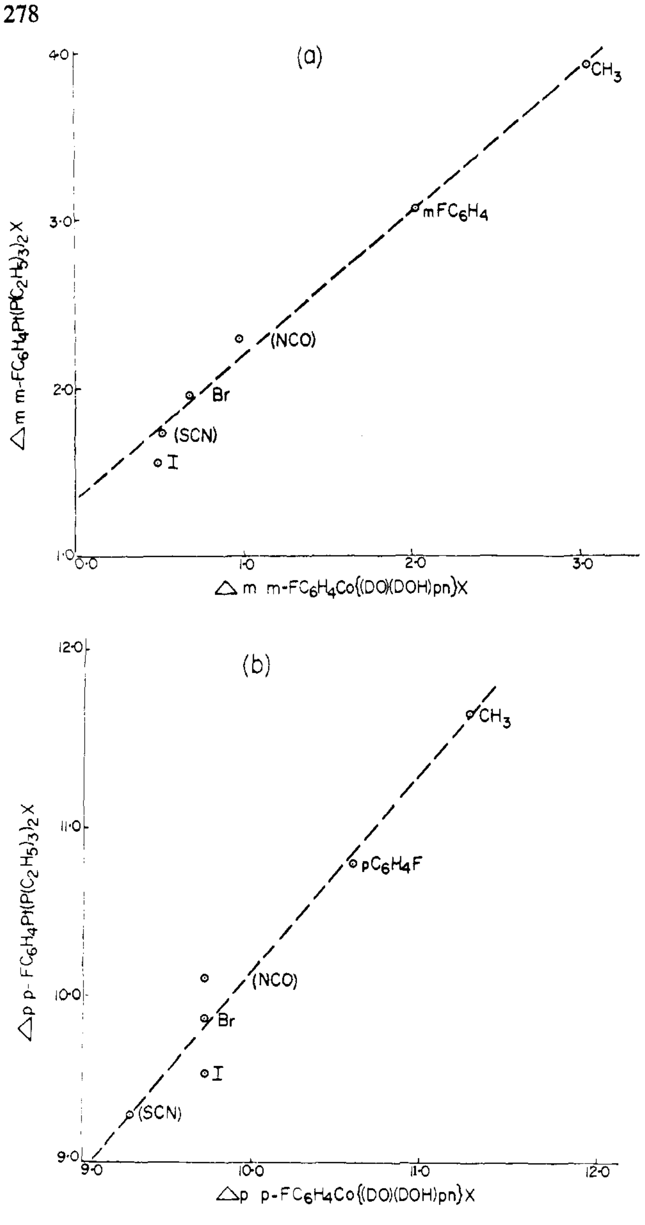

Figure 1. Plot of the ^{19}F chemicals shifts (ppm) of (a) m-$FC_6H_4Co\{(DO)(DOH)pn\}X$ in $(CH_3)_2SO$ *vs.* m-$FC_6H_4Pt(P(C_2H_5)_3)_2X$ in $(CH_3)_2CO$ and (b) p-$FC_6H_4Co\{(DO)(DOH)pn\}X$ in $(CH_3)_2SO$ *vs.* p-$FC_6H_4Pt(P(C_2H_5)_3)_2X$ in $(CH_3)_2CO$.

σ-donor properties of the ligand were mainly responsible for the observed ^{1}H chemical shifts. Differences between the Co(III) and Pt(II) complexes are more apparent in Δ_p values, since they include both σ and π interactions (Figure 1b). The π-electron-effect parameters, $(\Delta_p - \Delta_m)$, Table II, imply that the Co(III) complexes are better π donors (poorer π acceptors) than the Pt(II) complexes and, interestingly, show a greater sensitivity to the trans ligand X. The donor properties of the metal complexes have different dependence on X: for Co(III), I > Br > SCN(NCS) > OCN(NCO) > CH_3; for Pt(II), I > Br > OCN(NCO) > CH_3 > SCN(NCS). The different orders may be accounted for if it is assumed that the thiocyanate ligand acts as a π donor in the Co(III) complexes and a π acceptor in the Pt(II) complexes.

These results suggest that σ-bonding effects in cobalt(III) and platinum(II) complexes are similar; that there is extensive π interaction with aryl ligands coordinated in complexes of *both* metals which is modified by the trans ligand; and that the two metal ions are differently sensitive to the influence of the trans ligand X in as far as it affects the π interaction with the aryl ligand.

Acknowledgments. We wish to thank Professor G. Costa and Dr. G. Mestroni for their advice. One of us (K. G. M.) thanks the Science Research Council for a research studentship and we are grateful to NATO for financial support.

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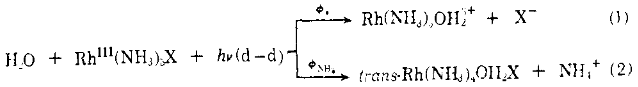
Structure and Photochemical Reactivity of Excited States of Halopentaamminerhodium(III) Complexes[1]

Sir:

The photochemical behavior of rhodium(III)–ammine complexes is of interest both for its uniqueness and for its similarities to the behavior of other nd^6 complexes. For example, features which seem common to the photochemistries of nd^6 complexes (especially of cobalt, rhodium, and platinum) are wavelength-dependent product yields and oxidation–reduction reactions subsequent to the irradiation of charge transfer to metal bands.[2,3]

A feature of great potential significance in the photochemistry of rhodium(III) is the relatively high product yields which result from irradiation of ligand field absorption bands.[3–5] It is the purpose of this report to call attention to some unanticipated inferences which may be made based on the photochemical behavior which results from the ligand field excitation of $Rh^{III}(NH_3)_5X$ (X = Cl, Br, I) complexes. It has been reported that ligand field excitation of $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5I^{2+}$ [3] results in predominantly (*i.e.*, >90%) halide or ammonia aquation, respectively (eq 1 and 2). We have now found that $Rh(NH_3)_5Br^{2+}$ exhibits intermediate behavior, *i.e.*, Br^-, NH_4^+, *trans*-$Rh(NH_3)_4OH_2Br^{2+}$, and $Rh(NH_3)_5OH_2^{3+}$ result from the irradiation of the ligand field absorption bands of this complex (see Table I).



$$H_2O + Rh^{III}(NH_3)_5X + h\nu(d-d) \begin{cases} \xrightarrow{\Phi_X} Rh(NH_3)_5OH_2^{3+} + X^- & (1) \\ \xrightarrow{\Phi_{NH_3}} trans\text{-}Rh(NH_3)_4OH_2X + NH_4^+ & (2) \end{cases}$$

All three halopentaammine complexes of rhodium(III) quench the biacetyl phosphorescence but do not affect the fluorescence at room temperature. Stern–Volmer quenching plots are linear and consistent with similar studies of the sensitized photolysis of coordination complexes.[2,6,7] However, for these rhodium(III) com-

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(1) Support of this research by the National Science Foundation (Grant GP24053) is gratefully acknowledged.

(2) For a comprehensive recent review, see V. Balzani and V. Carassitti, "The Photochemistry of Coordination Complexes," Academic Press, New York, N. Y., 1969.

(3) (a) T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, **92**, 5733 (1970); (b) *ibid.*, in press.

(4) L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967).

(5) (a) R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 2437 (1968); (b) *Inorg. Chem.*, **8**, 2231 (1969).

(6) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970).

(7) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *ibid.*, **93**, 339 (1971).

Table I. Product Yields Resulting from the Ligand Field Photolysis of $Rh^{III}(NH_3)_5X$ Complexes

X	*T*, °C	Wavelength irradiated,[a] nm	Assignment[b]	Direct photolysis product yields[c] ϕ_X	ϕ_{NH_3}	Biacetyl sensitized product yields[d] ϕ_X	ϕ_{NH_3}
Cl	25	350	$^1A_1 \rightarrow {}^1T_1$	0.16 ± 0.01[e]	$<10^{-3}$	0.16	$<10^{-3}$
	75			0.18 ± 0.01	$<10^{-3}$		
Br	25	360	$^1A_1 \rightarrow {}^1A_2$	0.019 ± 0.001	0.18 ± 0.02	0.02	0.20
	75			0.021 ± 0.001	0.34 ± 0.03		
I	25	385	$^1A_1 \rightarrow {}^1A_2$	0.01	0.82 ± 0.08	<0.01	0.90
	75			0.01	0.83 ± 0.04		

[a] Bandwidth ± 20 nm. [b] T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971); C. K. Jorgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962. [c] Based on 3–30 determinations with varying periods of irradiation. [d] Precision 10–20%. [e] Moggi[4] reported $\phi_{Cl} = 0.14$ on irradiating this band at 380 nm.

plexes we obtain the same products and product yields from the sensitized and direct (ligand field) photolysis. This indicates that in each case the intersystem crossing yield (ligand field singlet → triplet), ϕ_{isc}, is 1.0 and that all the products arise from a "ligand field" excited state with triplet spin multiplicity. Thus the different product yields cannot be attributed to different intersystem crossing yields or different populations of singlet and triplet excited states. The single simplest inference is that there are two photochemically active excited states of triplet spin multiplicity which differ little in (vibrationally equilibrated) energy, but which are very different in geometry; one state must involve a greatly lengthened Rh(III)–halide bond, the other a greatly lengthened Rh(III)–ammonia bond (note that all excited states are considered to have electron density in antibonding orbitals). In Figure 1 we have designated these states as ^3Y and ^3X, respectively. The state leading to ammonia aquation, ^3X, appears to have an intrinsically high yield for product formation (*i.e.*, to be nearly dissociative at room temperature). In fact, the product yields for $Rh(NH_3)_5Br^{2+}$ depend on temperature in a manner which suggests that ^3X is higher in energy than ^3Y (energy difference of about 300 cm^{-1}, assuming that the intrinsic product yield from ^3X is about 1)[8] for this complex. In the case of $Rh(NH_3)_5Cl^{2+}$, the energy gap appears to be sufficiently large ($\geq 10^3$ cm^{-1}) that there is not significant thermal activation of the corresponding ^3X state while in $Rh(NH_3)_5I^{2+}$ it would appear that ^3X must have the same or lower energy than ^3Y.

Our inference that there are two distinct photochemically active rhodium(III) excited states of similar energy but differing in geometry and in chemical reactivity, suggests that any simple, limiting strong field description is inappropriate for the excited states of coordination complexes. For example, since *trans*-ammonia and halide aquation appear as uncoupled processes in the ligand field photochemistry of these complexes, the photochemically important excited states are not usefully described in terms of electron density in orbitals of either "d_{z^2}" or "$d_{x^2-y^2}$" symmetry.

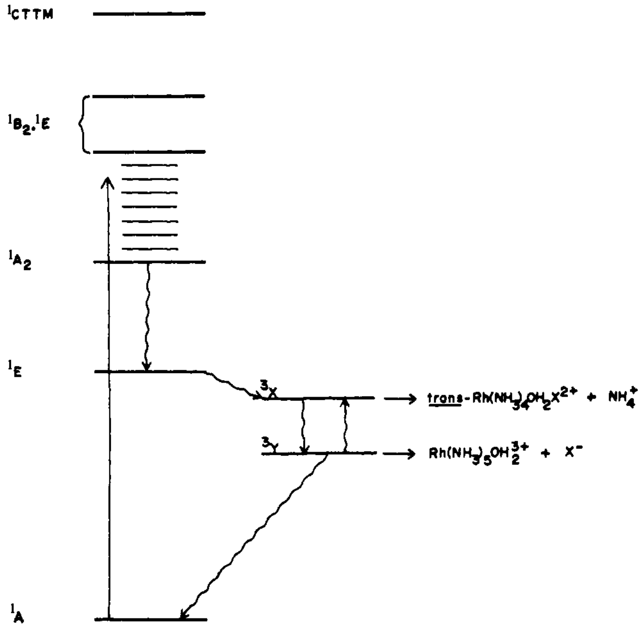

Figure 1. Relative energy level scheme for $Rh^{III}(NH_3)_5X$. Nonradiative activation and deactivation processes are indicated by wavy lines. The higher energy ligand field transitions (B_2, E^1) are obscured by the CTTM transition when X = Br or I. For illustrative purposes the ordering of the photochemically active states, ^3X and ^3Y, is that inferred for X = Br or Cl. Assignments based on T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971).

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(8) Actually if the intrinsic product yield from ^3X is about 1, then the energy gap would be greater than 300 cm^{-1} since the population of ^3X and ^3Y could not then be in equilibrium. The actual product yields according to our proposed model must depend on the intrinsic rate constants of the competitive processes

$$^3X \longrightarrow {}^3Y$$

$$^3X \longrightarrow \text{products}$$

$$^3Y \longrightarrow {}^3X$$

$$^3Y \longrightarrow \text{products}$$

$$^3Y \longrightarrow \text{nonradiative deactivation}$$

This kinetic argument will be developed in detail elsewhere.

An Organic Transition State[1]

Sir:

The geometrical isomerization of cyclopropane is one of the simplest organic reactions. Since its discovery in 1958[2] many attempts have been made to elucidate its mechanism[3–8] as well as that of related

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(1) The material on which this communication is based was presented in a plenary lecture at the 23rd IUPAC Congress, Boston, Mass., July 1971. The proceedings of this congress appear in: Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem., Suppl.* (*23rd Congr.*), **1**, 197 (1971).

(2) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(3) F. T. Smith, *ibid.*, **29**, 235 (1958).