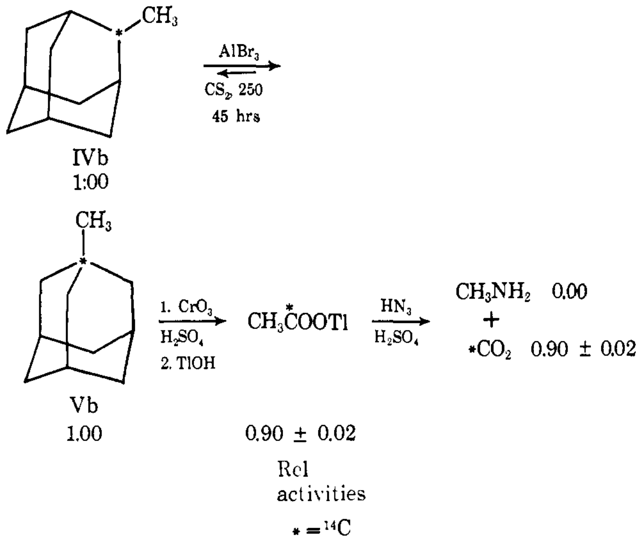

These results demonstrate that *the methyl group remains attached predominantly to the same carbon atom during the rearrangement of 2-methyladamantane (IV) to 1-methyladamantane (V).* Direct 1,2-methyl shifts (mechanism 3) do not take place to a significant extent. Mechanism 3 involving skeletal rearrangement, however, is perfectly consistent with the labeling patterns observed.[24] It seems probable that this type of mechanism is a general one for many adamantane rearrangements[7] and for those involving molecules not possessing favorable geometry for direct 1,2 shifts.

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[24] Control experiments[25] have shown that not more than 1–3% of label scrambling occurs in the adamantane nucleus during the AlBr$_3$ treatment and the Kuhn–Roth degradation of 1-methyladamantane-*1* (or *2*)-^{14}*C*.

[25] S. H. Liggero, Z. Majerski, P. v. R. Schleyer, A. P. Wolf, C. S. Redvanly, H. Wynberg, J. A. Boerma, and J. Strating, *J. Label. Compounds*, in press; Z. Majerski, S. H. Liggero, P. v. R. Schleyer, and A. P. Wolf, submitted for publication, and unpublished results.

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Charge-Transfer Photochemistry of Rhodium(III)[1]

Sir:

Although there have been many studies of the photochemistry of cobalt(III) complexes, studies of the rhodium(III) and iridium(III) analogs are rare.[2] Of the existing reports only Moggi's study[3] of Rh(NH$_3$)$_5$Cl^{2+} can be regarded as definitive. Much of this previous work has involved irradiation of metal-centered absorption bands and the net photochemical reactions have involved the exchange of coordinated ligands with solvent species.[2–4] To the present there have been no reports of photoredox behavior in rhodium(III) or iridium(III) complexes. In fact there have been some attempts to compare the photochemistry of rhodium(III) and iridium(III) to that of chromium(III), even to the extent of suggesting that rules for predicting photochemical reactions of chromium[2a,5] are also applicable to complexes of these heavier metals.[4] A consideration which heretofore has been neglected is that photoreduction of either rhodium(III) or iridium(III) complexes would produce a pair of *bulk* radicals, the corresponding divalent metallo complex, and an oxidized ligand, which ought to recombine. Thus net product yields are expected to show only ligand exchange and that only to the extent that the divalent complexes may equilibrate during their short lifetimes. No *net* photoreduction should be observed.

We report here our preliminary observations in the first study of the charge-transfer photochemistry of rhodium(III). We have chosen Rh(NH$_3$)$_5$I^{2+} for this study because the I$^-$→Rh(III) bands occur at relatively low energy,[6] but also because the primary oxidized product, I, forms a well-characterized easily detected complex ion, I$_2^-$.[7]

The continuous 254-nm irradiation of Rh(NH$_3$)$_5$I^{2+} in the absence of free I$^-$ produces high yields of NH$_3$[8] and aquated iodoammine complexes of rhodium(III)[9] as well as a small yield of *trans*-Rh(NH$_3$)$_4$I$_2^+$ (Table I). In the presence of small amounts of I$^-$ the yields of *trans*-Rh(NH$_3$)$_4$I$_2^+$, ϕ_t, and NH$_3$, ϕ_{NH_3}, are identical within the limits of experimental error. It is very significant that these same products are obtained under conditions where irradiation of I$^-$ produces e$^-$(aq),[10–12] which can react with nonabsorbing amounts of Rh-

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[1] (a) Support of this research by the National Science Foundation (Grant No. GP 17082) is gratefully acknowledged; (b) presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[2] For recent reviews see (a) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968); (b) D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968); (c) V. Balzani, L. Moggi, F. Scandola, and V. Carassitti, *Inorg. Chem. Acta Rev.*, **1**, 7 (1967); (d) E. L. Wehry, *Quart. Rev., Chem. Soc.*, **21**, 213 (1967).

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

[5] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

[6] C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962.

[7] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

[8] W. Bollster, C. Bushman, and P. Tiduell, *Anal. Chem.*, **33**, 592 (1961).

[9] This complex elutes from a cation-exchange resin (Dowex 50 W-2X H$^+$ form, 200–400 mesh) as a 2+ ion slightly ahead of Rh(NH$_3$)$_5$I^{2+}. Elemental analysis of the eluted material shows Rh:N:I = 1:3.6:1, indicating a mixture of aquoammine complexes. The spectral maxima of the eluted material are red shifted from those of Rh(NH$_3$)$_5$I^{2+}.

[10] G. Stein, *Advan. Chem. Ser.*, No. 50, 230 (1965).

[11] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **67**, 2613 (1963).

[12] For the conditions of concentration employed in the continuous photolysis of I$^-$,Rh(NH$_3$)$_5$OH$_2^{3+}$ (Table I) one would anticipate some ion-pair formation and probably some ion-pair photolysis. In such case the reactions listed under photoreduction (b) below may be regarded as short circuited; *i.e.*, the photoelectron would not be expected to have a significant lifetime in the bulk solvent. The spectral properties of these systems suggest that I$^-$ is the predominant absorbing species. In the complementary flash-photolysis work [I$^-$] is necessarily small enough that ion-pair formation is unlikely.

Table I. Representative Product Yields From the Charge-Transfer Photochemistry of $Rh(NH_3)_5I^{2+}$[a]

Primary absorbing species	$10^3 \times$ [Rh(III)], M	$[I^-]$,[b] M	N[c]	ϕ_t[d]	ϕ_{NH_3}	Range of $10^4 \times I_a$, einsteins $l.^{-1}$ min^{-1}
$Rh(NH_3)_5I^{2+}$	2.0	0	3	0.035 ± 0.006	0.29 ± 0.03	5–6
	1.0[e]	0	3	0.025 ± 0.006	0.27 ± 0.02	2–5
	1.0	0	2	[f]	0.32 ± 0.03	0.33
	1.0	1.0×10^{-3}	2	0.15 ± 0.02	0.16 ± 0.01	2–3
I^- [g]	1.0	0.10	8	0.44 ± 0.05[h]	0.4[h,i]	0.26–3.3

[a] 25°, pH 1 ($HClO_4$), except as indicated. [b] Initial concentration. [c] Number of determinations. [d] Yield of *trans*-$Rh(NH_3)_4I_2^+$. [e] pH 1–3. [f] Too small to detect. [g] At pH 3; rhodium(III) present initially as $Rh(NH_3)_5OH_2^{3+}$. [h] Quantum yields based on maximum yield of rhodium(II) formed from reaction of e_{aq}^- with $Rh(NH_3)_5OH_2^{3+}$, using 0.29 as the yield of solvated electrons (ref 10). [i] One determination.

$(NH_3)_5OH_2^{3+}$ (Table I), although there is no *net* photooxidation of I^- in these cases.

Flash photolysis of $Rh(NH_3)_5I^{2+}$ in iodide-free solutions produces no detectable transient (the high-intensity transitions of I atoms lie in the far-uv), but when small amounts of I^- are present in bulk solution a transient (λ_{max} 380 nm) identified as I_2^- is observed. This transient is also observed on flashing I^- in solutions containing $Rh(NH_3)_5OH_2^{3+}$. The I_2^- transient (regardless of the absorbing species) is shorter lived (*i.e.*, has about seven-tenths the characteristic lifetime of I_2^-) under conditions which produce rhodium(II) than when rhodium(II) is absent.

By placing filter solutions between the flash lamps and the sample solution we have been able to demonstrate (Table II) that the I_2^- transient is produced only when the charge-transfer-to-metal (CTTM) bands are irradiated. The relative redox yield is highest (at least 30%) when the σ CTTM band is irradiated. The photochemical changes which do occur on irradiating other spectral regions have not yet been fully characterized.

Table II. Wavelength Dependence of Transient Yields in Flash Photolysis of $Rh(NH_3)_5I^{2+}$

Wavelength region irradiated,[a] nm	Type of absorption bands[b]	$([I_2^-] + [I])$[c] $\times 10^7$, M	% redox[d]
230–250	CTTM (σ)	10.6	30
250–270	CTTM ($\pi + \sigma$)	3.0	7
270–320	CTTM ($\pi + \sigma$)	0.6	0.6
320 and longer	d–d + CTTM (π)	<0.1	<0.1

[a] Filter solutions were used to eliminate the shorter wavelength spectral regions. Product yields are actually differences in yields obtained using the succession of filter solutions. [b] See ref 6. [c] [I] obtained from the observed I_2^- yields and the reported formation constant for $I + I^- \rightleftarrows I_2^-$ (ref 7). [d] $([I_2^-] + [I])$ divided by the observed decrease in $[Rh(NH_3)_5I^{2+}]$. Spectral changes indicate large changes in $[Rh(NH_3)_5I^{2+}]$ for every region irradiated.

These observations demonstrate that photoreduction is an important process in photochemistry of rhodium(III). The net product yields (and the transient decay kinetics) are compatible with facile recombination reactions, provided the five ammonia ligands of the rhodium(II) produced are not all equivalent; *i.e.*, that rhodium(II) is tetragonally distorted to the extent that four ammines have relatively long coordinated lifetimes. Thus, the three basic steps in the charge-transfer photochemistry may be represented as follows.[13] For photoreduction (a) with $Rh(NH_3)_5I^{2+}$ as the absorbing species

$$Rh(NH_3)_5I^{2+} + h\nu \longrightarrow Rh(NH_3)_4^{2+} + NH_3 + I \qquad (\phi I_a)$$

or (b) with I^- as the absorbing species[10,11]

$$I^- + h\nu \longrightarrow I + e_{aq}^-$$

followed by

$$e_{aq}^- + RH(NH_3)_5OH_2^{3+} \longrightarrow Rh(NH_3)_4^{2+} + NH_3$$

for complexation

$$I + I^- \rightleftarrows I_2^-$$

and for recombination

$$Rh(NH_3)_4^{2+} + I_2^- \longrightarrow trans\text{-}Rh(NH_3)_4I_2^+$$

or

$$Rh(NH_3)_4^{2+} + I + H_2O \longrightarrow Rh(NH_3)_4OH_2I^{2+}$$

Although I_2^- is clearly very reactive toward $Rh(NH_3)_4^{2+}$, it is not at all evident that both iodide ligands of *trans*-$Rh(NH_3)_4I_2^+$ originated in I_2^-.

This work demonstrates that photoredox behavior is important in the photochemistry of rhodium(III). It appears that the principal differences between the photochemistry of cobalt(III) and rhodium(III) are the higher product yields[14,15] on irradiation of d–d absorption bands and the higher energy of charge-transfer transitions of the latter complexes, together with some differences in the chemical behavior of cobalt(II) and rhodium(II).

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[13] Note that this mechanistic discussion is based on the observed *bulk* radicals. We are not yet in a position to propose a detailed mechanism for the formation of these bulk radicals. The mechanism is proposed for the redox steps only.

[14] By analogy with what seems to be generally the case for cobalt(III), d–d irradiation would not be expected to result in photoredox behavior in rhodium(III) complexes.

[15] It should be noted that few investigators have bothered to look for ammonia in the photochemistry of cobalt(III) complexes, so even this difference may not be entirely general.

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Paramagnetic Induced Shifts in the Proton Magnetic Resonance Spectra of Alcohols Using Tris(dipivalomethanato)europium(III)

Sir:

The initial discovery by Hinckley[1] of the effectiveness of the dipyridine adduct of the rare earth complex tris(dipivalomethanato)europium(III) $[Eu(DPM)_3 \cdot 2py]$

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, 91, 5160 (1969).