species as **1**. The intense band at 900 $cm^{-1}$ is probably due to an out-of-plane CH bend (848 $cm^{-1}$ in homoadamantene[12]), but a definitive assignment will have to await the results of experiments on deuterated material. A very weak band appears at ~3015 and could be attributed to olefinic C—H stretch. Several very weak bands occur in the 1520–1650-$cm^{-1}$ region where a C═C stretch would be expected; unfortunately this region is obscured in our spectra by absorptions owing to trace amounts of water.

When the argon matrix is warmed and the residue subjected to GC-MS analysis, only two major peaks appear. By comparison with authentic samples, the first is identified as due to the starting dihalide, the second as due to the [2 + 2] dimers of adamantene. The two peaks have comparable areas. In addition, several much smaller GC peaks are present. One of the larger of these has the mass spectrum expected for a biadamantyl. These results agree exactly with expectations based on previous reports[1-3] and leave little doubt that the new product whose IR spectrum is observed at 10 K indeed is **1**.

We can now interpret the ESR results obtained with **2** and **3**. We propose that the small amounts of the 1-adamantyl radical formed originate in a gas-phase reaction in which **1** abstracts a hydrogen from **2** or **3**. This process will also account for the formation of biadamantyls (1,1-biadamantyl is the dominant isomer[1]). A close analogy is found in the gas-phase dehalogenation reactions of iodinated benzenes, run under similar conditions, in which benzene is one of the main products.[8]

From the properties of **1** observed so far, we conclude that its severely distorted double bond still is best viewed as a double bond rather than a biradical: the dimerization of **1** is not diffusion controlled at 70 K, monohaloadamantyl radicals apparently fragment readily at 120 °C, and the CH out-of-plane bend region in the IR spectrum resembles that of trisubstituted olefins more than that of the isopropyl radical (out-of-plane CH bend at 375 $cm^{-1}$).[13] However, the double bond undoubtedly has a partial biradicaloid character: after all, ordinary olefins do not dimerize nor do they abstract hydrogen atoms, even from good donors.[14]

**Acknowledgment.** Support of this work by the National Science Foundation is gratefully acknowledged. We thank M. Jones, Jr., and D. J. Martella for a communication of unpublished results.

## References and Notes

(1) D. J. Martella, M. Jones, Jr., and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **100,** 2896–2897 (1978).

(2) W. Burns, D. Grant, M. A. McKervey, and G. Step, *J. Chem. Soc., Perkin Trans. 1*, 234–238 (1976), and references therein.

(3) D. Lenoir, *Tetrahedron Lett.*, 4049–4052 (1972); D. Lenoir and J. Firl, *Justus Liebigs Ann. Chem.*, 1467–1473 (1974).

(4) A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047–3049 (1973).

(5) J. E. Gano and L. Eizenberg, *J. Am. Chem. Soc.*, **95,** 972–974 (1973).

(6) For a review, see B. G. Gowenlook, C. A. F. Johnson, and J. E. Parker, in "Comprehensive Chemical Kinetics", Vol. 18, C. H. Bamford and C. F. G. Tipper, Eds., Elsevier, New York, 1976, Chapter 4 ("Selected Elementary Reactions"). For a survey of preparative applications, see M. J. McGlinchey and P. S. Skell in "Cryochemistry", M. Moskovits and G. A. Ozin, Eds., Wiley, New York, 1976, Chapter 4.

(7) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99,** 4840–4842 (1977).

(8) D. Otteson, R. Sustmann, F. H. Walker, K. B. Wiberg, and J. Michl, unpublished results. Similar dehalogenation reactions occur in the surface on cold matrices (see, e.g., J. E. Bennett, B. Mile, and A. Thomas, *Proc. R. Soc. London, Ser. A*, **293,** 246–258 (1966)) and with photoactivation, in the bulk (P. H. Kasai, *Acc. Chem. Res.*, **4,** 329 (1971)).

(9) At low temperatures, the ESR spectrum is very poorly resolved, but at ~45 K and above, we observe ~60 of the lines reported: P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94,** 995–997 (1972).

(10) D. J. Martella and M. Jones, Jr., private communication.

(11) The temperature readings in our ESR and IR experiments are only approximate since they were taken at the cold heads of an Air Products Displex cryostat rather than in the matrices themselves. The differential error between the ESR and the IR cryostat is <10° as judged by events such as disappearance of hydrogen gas from an argon matrix or of the argon matrix itself.

(12) D. J. Martella, M. Jones, Jr., P. v. R. Schleyer, and W. F. Maier, *J. Am. Chem. Soc.*, preceding paper in this issue.

(13) J. Pacansky, D. E. Horne, G. P. Gardini, and J. Bargon, *J. Phys. Chem.*, **81,** 2149–2154 (1977).

(14) *trans*-Cyclohexene appears to abstract hydrogen atoms from ether solvent: P. J. Kropp, H. G. Fravel, Jr., and T. R. Fields, *J. Am. Chem. Soc.*, **98,** 840 (1976).

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*Received June 28, 1979*

## Mechanism of the Formation of Dihydrogen from the Photoinduced Reactions of Tris(bipyridine)ruthenium(II) with Tris(bipyridine)rhodium(III)

*Sir:*

The properties of the metal to ligand charge-transfer excited state of tris(2,2′-bipyridine)ruthenium(II) ($^*Ru(bpy)_3{}^{2+}$) have been extensively studied[1] and the use of $Ru(bpy)_3{}^{2+}$ in various solar energy conversion schemes has been proposed.[2-5] Recently $Ru(bpy)_3{}^{2+}$ has been employed successfully as a mediator in the photoreduction of water to dihydrogen in both heterogeneous [6-9] and homogeneous systems.[10] The report of Lehn and Sauvage[6] concerning hydrogen production from aqueous solutions containing $Ru(bpy)_3{}^{2+}$, triethanolamine (TEOA), $RhCl_3$, $K_2PtCl_6$, and 2,2′-bipyridine (bpy) evoked our interest and led us to a detailed study of a closely related system. We find that visible light irradiation of aqueous solutions of $Ru(bpy)_3{}^{2+}$, $Rh(bpy)_3{}^{3+}$, TEOA/$TEOAH^+$ (pH 8.1), and $K_2PtCl_4$ (or $K_2PtCl_6$) yields dihydrogen with a quantum yield of up to 0.11 ± 0.01 mol $einstein^{-1}$ depending on the conditions used.[11] The dihydrogen is the end product of a sequence of electron-transfer reactions: $^*Ru(bpy)_3{}^{2+}$ formed by visible light absorption is oxidized by $Rh(bpy)_3{}^{3+}$ to produce $Rh(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{3+}$. The latter is rapidly reduced by TEOA. In the absence of platinum the rhodium(II) disproportionates to give rhodium(III) and rhodium(I); in the presence of platinum the rhodium(II) may either disproportionate or yield dihydrogen. Here we report our observations on the photochemical and dark reactions in this system.

Continuous photolysis (450-W xenon lamp, λ 450 ± 20 nm, $I_0 = 2 \times 10^{-8}$ einstein $s^{-1}$) of solutions containing 0.005–3.0 $\times 10^{-4}$ M $Ru(bpy)_3{}^{2+}$, 2–5 $\times 10^{-3}$ M $Rh(bpy)_3{}^{3+,12}$ and 0.2 M TEOA at pH 8.1 ($\mu = 0.5$ M, $Na_2SO_4$), but no $PtCl_6{}^{2-}$ or $PtCl_4{}^{2-}$, gives no dihydrogen; instead a pink species is formed. The pink species is identified as a Rh(I) complex containing two bpy ligands[13] from the following experiments. An aqueous solution of $Rh(bpy)_2(OH_2)_2{}^{3+}$ [14] was reduced with amalgamated zinc to give a pink-brown stock solution A. The spectra observed when this solution is diluted in various media are similar to those produced in photolysis experiments under the same conditions (see Figure 1).[15] Solution A was treated with excess $Os(bpy)_3{}^{3+}$ and the $Os(bpy)_3{}^{2+}$ produced was calculated from the absorbance increase at 480 nm to be (2.0 ± 0.2)Os(II) per $Rh(bpy)_2(OH_2)_2{}^{3+}$ present in the solution before reduction.[16] Thus the rhodium species in solution A is Rh(I). Since no bpy could be extracted into chloroform from solution A, two bpy groups must be attached to Rh(I). From the $Rh(bpy)_2{}^+$ molar absorptivity[15] the quantum yield for Rh(I) formation (conditions as above) is 0.11 ± 0.01 mol $einstein^{-1}$ and the ratio of Rh(I) to bpy produced in the photoinduced reduction of $Rh(bpy)_3{}^{3+}$ is 1.1 ± 0.1 (eq 1).

$$Rh(bpy)_3{}^{3+} + 2e \rightarrow Rh(bpy)_2{}^+ + bpy \qquad (1)$$

Since TEOA and $Rh(bpy)_3{}^{3+}$ do not absorb light in the visible region, the primary product of irradiation of the

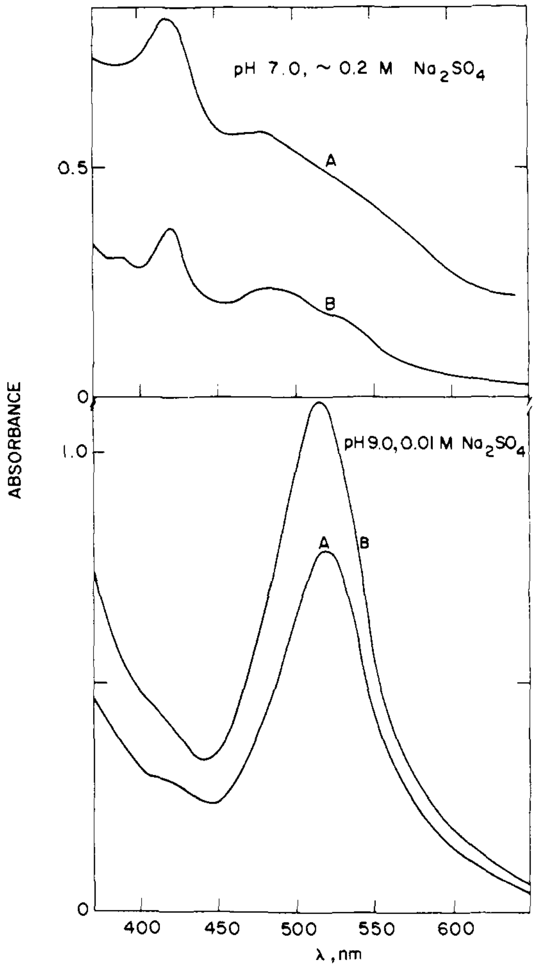

**Figure 1.** Spectra of $Rh(bpy)_2^+$ solutions produced (A) by reduction of ~$2 \times 10^{-4}$ M $Rh(bpy)_2(OH_2)^+$ using amalgamated zinc (1-cm cell) in (top) 0.01 M phosphate buffer and (bottom) 0.02 M TEOA; (B) by photolysis of (top) $5 \times 10^{-6}$ M $Ru(bpy)_3^{2+}$, $5 \times 10^{-3}$ M $Rh(bpy)_3^{3+}$, 0.1 M $(TEOAH)_2SO_4$, pH 7 for 20 min (5-cm cell), and (bottom) $5 \times 10^{-5}$ M $Ru(bpy)_3^{2+}$, $5 \times 10^{-3}$ M $Rh(bpy)_3^{3+}$, 0.02 M TEOA, pH 9 for 30 min (2-cm cell), with λ 450 ± 10 nm.

$Ru(bpy)_3^{2+}$-$Rh(bpy)_3^{3+}$-TEOA mixtures is $^*Ru(bpy)_3^{2+}$. Laser flash photolysis[17,18] and steady-state emission techniques[18] were used to ascertain the fate of the excited $Ru(bpy)_3^{2+}$. The rate constant for quenching of $^*Ru(bpy)_3^{2+}$ by $Rh(bpy)_3^{3+}$ is $6.2 \times 10^8$ $M^{-1}$ $s^{-1}$ (25 °C, 0.5 M $H_2SO_4$), while triethanolamine, as also noted by others,[7] does not quench detectably ($k_q < 1 \times 10^6$ $M^{-1}$ $s^{-1}$). Following 530-nm flash excitation of a solution $5 \times 10^{-5}$ M in $Ru(bpy)_3^{2+}$ and $4.0 \times 10^{-3}$ M in $Rh(bpy)_3^{3+}$ in 0.5 M $H_2SO_4$, bleaching of (ground state) $Ru(bpy)_3^{2+}$ absorption in the 450-500-nm range with a quantum yield of 0.15 ± 0.03 is observed. Subsequently the preflash absorption is restored with a second-order rate constant $k_t = 3 \times 10^9$ $M^{-1}$ $s^{-1}$. By contrast, when $Ru(bpy)_3^{2+}$ and $Rh(bpy)_3^{3+}$ are flashed in a solution containing 0.01 M TEOA/0.01 M $TEAOH^+$ at pH 8.1, the $Ru(bpy)_3^{2+}$ absorption is very rapidly restored with a pseudo-first-order rate constant of ~$10^5$ $s^{-1}$. These observations establish that quenching of $^*Ru(bpy)_3^{2+}$ by $Rh(bpy)_3^{3+}$ yields the electron-transfer products $Ru(bpy)_3^{3+}$ and $Rh(bpy)_3^{2+}$; the relatively low quantum yield (0.15) for the formation of these products is a consequence of the very rapid rate of thermal back-reaction within the cage.[18] The $Ru(bpy)_3^{3+}$ that escapes from the cage may either undergo reduction by $Rh(bpy)_3^{2+}$ ($k_t = 3 \times 10^9$ $M^{-1}$ $s^{-1}$) or by TEOA ($k = 2 \times 10^7$ $M^{-1}$ $s^{-1}$).[19]

The fate of the $TEOA^+$ radical produced on oxidation of TEOA by $Ru(bpy)_3^{3+}$ was ascertained by using methylviologen chloride ($MVCl_2$, $MV^{2+}$ = *N,N'*-dimethyl-4,4'-bipyridinium cation). The latter is not reduced to the blue $MV^+$ radical by $Rh(bpy)_2^+$ below pH 10; exponential formation of $MV^+$ is, however, observed with $k = (4 \pm 1) \times 10^8$ $M^{-1}$ $s^{-1}$ when $0.3$-$3.0 \times 10^{-4}$ M $MVCl_2$ is added to a $Ru(bpy)_3^{2+}$ ($3 \times 10^{-5}$ M)/$Rh(bpy)_3^{3+}$ ($5 \times 10^{-3}$ M) mixture in 0.1 M TEOA at pH 7 or 8. The quantum yield for $MV^+$ formation is 0.33 ± 0.04, so that the ratio of $MV^+$ to $Rh(bpy)_3^{2+}$ produced in the quenching is 2.2 ± 0.2. The $TEOA^+$ radical is thus acting as a reductant. On the basis of the time profile for $MV^+$ formation, we conclude that, under the flash photolysis conditions used, $Rh(bpy)_3^{3+}$ is reduced by the $TEOA^+$ radical to give a second $Rh(bpy)_3^{2+}$; $Rh(bpy)_3^{2+}$ and oxidized TEOA are thus the sole photolysis products present after ~0.1 ms.

The Rh(I) identified in the continuous photolysis must arise from disproportionation of the Rh(II) produced in the photochemical step. However, we have not obtained evidence for rate-determining disporportionation of $Rh(bpy)_3^{2+}$ either in flash-photolysis or in pulse-radiolysis experiments in which $Rh(bpy)_3^{2+}$ is reduced by hydrated electrons.[18,20,21] In both types of experiment there is a slow first-order formation of $Rh(bpy)_2^+$ with $k_{obsd} = 2 \pm 1$ $s^{-1}$ independent of the concentrations of $Rh(bpy)_3^{2+}$ and $Rh(bpy)_3^{3+}$. Evidently ligand loss on Rh(II) is rate determining (i.e., eq 2[22] with $k_1 = 2 \pm 1$ $s^{-1}$) and is followed by rapid reduction of $Rh(bpy)_2^{2+}$ by $Rh(bpy)_3^{2+}$ (eq 3). This sequence (eq 2, 3) is supported by the bpy/Rh(I) ratio of ~1 obtained in the continuous photolysis and by the fact that rapid second-order formation ($k \sim 10^8$ $M^{-1}$ $s^{-1}$) of $Rh(bpy)_2^+$ (presumably according to eq 3) is observed in the pulse radiolysis of $Rh(bpy)_3^{3+}$-$Rh(bpy)_2(OH)_2^+$ mixtures.[21]

$$Rh(bpy)_3^{2+} \xrightarrow{k_1} Rh(bpy)_2^{2+} + bpy \qquad (2)$$

$$Rh(bpy)_3^{2+} + Rh(bpy)_2^{2+} \xrightarrow{k_2} Rh(bpy)_3^{3+} + Rh(bpy)_2^{+} \qquad (3)$$

Dihydrogen is produced when the photolysis of $Ru(bpy)_3^{2+}$-$Rh(bpy)_3^{3+}$-TEOA (0.2 M, pH 8.1) mixtures is conducted in the presence of $0.5$-$2 \times 10^{-4}$ M $K_2PtCl_6$ or $K_2PtCl_4$ (λ 450 ± 20 nm, $\phi_{H_2} = 0.11 \pm 0.01$ mol einstein$^{-1}$ [11]). During the photolysis brown solutions mixed with a fine dark solid (>95% platinum, by analysis) are produced; spectral maxima characteristic of Rh(I) are absent. Variable amounts of bpy are obtained and the $H_2$/bpy ratio varies from 0.5 to ~20, increasing with the photolysis time. Here the major unknowns are the nature of the $H_2$ precursor (reductant) and the identity of the species which catalyzes the formation of $H_2$. It is likely that the active catalyst in the $PtCl_6^{2-}$ and $PtCl_4^{2-}$ solutions is colloidal Pt(0): other platinum sources, including commercial platinum black, $PtO_2$ (after an induction period), and colloidal platinum,[23] also lead to $H_2$ production. When Pt(II) is used, the time profile for $H_2$ exhibits an induction period corresponding to ~18 einstein per Pt(II). From flash experiments no detectable redox products arise from quenching of $^*Ru(bpy)_3^{2+}$ by either $PtCl_6^{2-}$ ($k_q = 7.2 \times 10^9$ $M^{-1}$ $s^{-1}$, 25 °C, $\mu$ = 0.5 M)[24] or $PtCl_4^{2-}$ ($k_q = 2.6 \times 10^9$ $M^{-1}$ $s^{-1}$, 25 °C, $\mu$ = 0.5 M).[25] Since $PtCl_6^{2-}$ and $PtCl_4^{2-}$ are rapidly reduced by $Rh(bpy)_2^+$, the induction period likely corresponds to formation of Rh(I) (and bpy) followed by reduction of Pt(II) to colloidal Pt. This process would require 20 einstein per Pt(II).

From a number of considerations it can be shown that $Rh(bpy)_2^+$ is not the $H_2$ precursor in this system. The high $H_2$/bpy ratios found in the extended photolyses require either that $H_2$ be formed from a $Rh(bpy)_2^+$ precursor prior to bpy loss or that bpy be consumed in the reactions of $Rh(bpy)_2^+$ that produce $H_2$. The latter explanation is ruled out by the fact that the catalyzed reduction of water to $H_2$ by $Rh(bpy)_2^+$ is not observed: solutions of $Rh(bpy)_2^+$ generated photochemically or by amalgamated zinc reduction of $Rh(bpy)_2(OH)_2^+$ are decolorized slowly by platinum (gauze, black, or colloidal[23]) at pH 8.1 but yield no (<1% in 20 h) free $H_2$. Nor does $H_2$ result at pH 5 or pH 1 in the presence or absence of colloidal platinum. Furthermore, potentiometric measurements indicate that the formal potential for the $Rh(bpy)_2(OH)_2^+ + 2e = Rh(bpy)_2^+$ couple is ca. $-0.25$ V at pH 8.[26] As the $H_2O/H_2$ couple is more negative ($-0.47$ V at pH 8[27]), reduction of water to $H_2$ by $Rh(bpy)_2^+$ is thermodynamically unfavorable at this pH. On the basis of these experiments we conclude that $Rh(bpy)_2^+$ is not the $H_2$ precursor. Possible candidates for the $H_2$ precursor include a form of $Rh(bpy)_2^+$ different from the one characterized here[28] and a rhodium(II) species, probably $Rh(bpy)_3^{2+}$. The reduction potential for the $Rh(bpy)_3^{3+/2+}$ couple is ca. $-0.8$ V vs. SCE in acetonitrile[29,30] and ca. $-0.7$ V in aqueous solution[26] so that $Rh(bpy)_3^{2+}$ is a strong enough reductant to reduce water to $H_2$ up to about pH 11. In rough accord with this potential is the pH dependence of the $H_2$ quantum yield (pH 8.1, 0.11; pH 9.0, 0.03; pH 10, $<10^{-3}$).

If the $H_2$ precursor in the present system is indeed Rh(II), the detailed mechanism for $H_2$ production must strongly resemble that in the $Ru(bpy)_3^{2+}$/methylviologen/TEOA (or EDTA) system[7-9] with Rh(II) fulfilling the role of a one-electron storage system analogous to the methylviologen radical. If this is the case, there is no particular advantage of the rhodium-based system over other water-photoreduction systems requiring the presence of heterogeneous catalysts.[7-9] Indeed the rhodium system is more expensive than that based on methylviologen and is subject to efficiency-lowering side reactions. In fact, the side reactions which arise from the rich chemistry of the low oxidation states of rhodium are a potentially valuable aspect of this system. These are the focus of ongoing work in this laboratory.[31]

**Acknowledgment.** This work was performed at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences. We gratefully acknowledge the assistance of Mrs. Mei Chou, Mr. D. Comstock, Dr. Bruce S. Brunschwig, and Dr. Tadashi Matsubara.

## References and Notes

(1) For recent reviews see: Sutin, N.: Creutz, C. *Adv. Chem. Ser.* **1978,** No. 168, 1. Sutin, N. *J. Photochem.* **1979,** *10*, 19–40.

(2) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975,** *72*, 2858.

(3) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science* **1975,** *189*, 852.

(4) (a) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976,** *80*, 77. (b) Durham, B.; Meyer, T. J. *J. Am. Chem. Soc.* **1978,** *100*, 6287.

(5) Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975,** *97*, 4781.

(6) Lehn, J.-M.; Sauvage, J.-P. *Nouv. J. Chim.* **1977,** *1*, 449.

(7) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978,** *61*, 2720.

(8) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978,** *2*, 547.

(9) Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1979,** 381. DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979,** *101*, 4007.

(10) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979,** *101*, 1298.

(11) Observed quantum yields have been corrected for the fraction of $^*Ru(bpy)_3^{2+}$ quenched by $Rh(bpy)_3^{3+}$ (typically a 30% correction) and, when necessary, for the induction period encountered as Pt(IV) or Pt(II) is reduced to Pt(0) (normally a 20% correction). The cage escape yield of $Rh(bpy)_3^{2+}$ (0.15) imposes an upper limit of 0.15 mol einstein$^{-1}$ on bpy, Rh(I), and $H_2$ quantum yields in terms of our mechanism (vide infra). The $H_2$ quantum yields could be slightly low since they have not been corrected for light scattered by the turbid solutions. $H_2$ was determined by gas chromatography[10] or volumetry and the light intensity by ferrioxalate actinometry.

(12) $Rh(bpy)_3^{3+}$ was prepared according to the procedure given by DeArmond, K.; Halper, W. *J. Phys. Chem.* **1971,** *75*, 3230. Before use in these experiments, solutions of the perchlorate salt were passed through an anion-exchange column in the bisulfate form.

(13) $[Rh(bpy)_2]ClO_4$ has been described: (a) Martin, B.; McWhinnie, W. R.; Waind, G. M. *J. Inorg. Nucl. Chem.* **1961,** *23*, 207. (b) Oliver, F. D.; Miller, J. D. *J. Chem. Soc., Dalton Trans.* **1972,** 2473.

(14) $[Rh(bpy)_2(OH_2)_2](ClO_4)_3$ was prepared according to the procedure given by Gidney, P. M.; Gillard, R. D.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1972,** 2621. Before use, the perchlorate salt was converted into the bisulfate salt by treatment with anion exchange resin.

(15) As is evident in Figure 1, the spectrum of $Rh(bpy)_2^+$ is exceedingly medium sensitive. Martin et al.[13a] and Oliver and Miller[13b] have reported that the spectrum of the perchlorate salt of $Rh(bpy)_2^+$ prepared by $NaBH_4$ or $H_2$ reduction has maxima at 557 nm ($\epsilon$ $3.55 \times 10^3$ M$^{-1}$ cm$^{-1}$) and 520 nm in 25% ethanol–water. Here we find $\lambda_{max}$ 516 nm at pH 9 with $2 \times 10^{-2}$ M TEOA, $1 \times 10^{-2}$ M $Na_2SO_4$; $\lambda_{max}$ ~500, 420 nm at pH 8.1 with 0.1 M TEOA/0.1 M $TEAOH^+$, 0.13 M $Na_2SO_4$, etc. These and other observations suggest that the nature of Rh(I) is both pH and Rh(I) dependent. The best estimate for the intensity of the visible band is that determined for electrolytically produced Rh(I) in 0.05 M NaOH ($\lambda_{max}$ 518 nm ($\epsilon$ 8600 ± 800 M$^{-1}$ cm$^{-1}$): T. Matsubara, unpublished work). The intensity of this band is reduced by 35% in the pH 8.1 TEOA medium used in the photochemical studies.

(16) This conclusion is confirmed by the results of exhaustive electrolysis (graphite electrode, applied voltage $-1.25$ V vs SCE) of $1 \times 10^{-3}$ M $Rh(bpy)_2(OH)_2^+$ in 0.05 M NaOH: 1.97 ± 0.04 electrons per Rh(III) were consumed (T. Matsubara, work in progress).

(17) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976,** *98*, 6536.

(18) Hoselton, M. A.; Lin, C.-T.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978,** *100*, 2383.

(19) The value reported here for 25 °C, $\mu = 0.5$ M, may be compared with that of $4.7 \times 10^7$ M$^{-1}$ s$^{-1}$ reported in ref 7 for an unspecified medium.

(20) The instrumentation and technique are described in Dodson, R. W.; Schwarz, H. A. *J. Phys. Chem.* **1974,** *78*, 892. Typically solutions containing $1 \times 10^{-4}$ M $Rh(bpy)_3^{3+}$ and 0.02 M TEOA (pH 7–9) were scrubbed with argon. TEOA is an effective hydroxyl scavenger; Rh(III) is rapidly reduced to Rh(II) by the hydrated electron. Formation of Rh(I) was monitored at 450–550 nm.

(21) Creutz, C.; Schwarz, H. A., work in progress.

(22) Here "$Rh(bpy)_2^{2+}$" could be four-coordinate $Rh(bpy)_2^{2+}$, five-coordinate $Rh(bpy)_2H_2O^{2+}$, or six-coordinate $Rh(bpy)_2(H_2O)_2^{2+}$ and the configuration of the bpy's may be either cis or trans. The formation of "$Rh(bpy)_2^{2+}$" almost certainly proceeds via a monodentate $Rh(bpy)_2bpy^{2+}$, which is formed from $Rh(bpy)_3^{2+}$ with a rate constant of $\sim 10^5$ s$^{-1}$.

(23) Rampino, L. D.; Nord, F. F. *J. Am. Chem. Soc.* **1941,** *63*, 2745.

(24) At 0.5 M ionic strength. This may be compared with the value $10^{10}$ M$^{-1}$ s$^{-1}$ reported for $2 \times 10^{-3}$ M ionic strength by Bolletta, F.; Maestri, M.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1974,** *78*, 1374.

(25) At 0.5 M ionic strength. This may be compared with the value $1.7 \times 10^{10}$ M$^{-1}$ s$^{-1}$ (zero ionic strength) reported by Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1976,** *98*, 5800.

(26) Matsubara, T., work in progress.

(27) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N. J., 1964.

(28) Since the $Rh(bpy)_2^+$ solutions which we obtain may contain polymeric species, we cannot exclude the possibility that "nascent" monomeric $Rh(bpy)_2^+$ (cis or trans) is the hydrogen precursor.

(29) The electrochemical behavior of $Rh(bpy)_3^{3+}$ and $Rh(bpy)_2(OH)_2^+$ in alkaline aqueous solutions is complex. Results obtained from cyclic voltammetry on pyrolytic graphite (adsorption is severe on mercury) show that one-electron reduction of $Rh(bpy)_3^{3+}$ occurs at ca. $-0.75$ V vs. NHE in 0.05 M NaOH and is followed by a rapid chemical reaction, probably the formation of monodentate $Rh(bpy)_2bpy^{2+}$ with $k > 3 \times 10^2$ s$^{-1}$ at 25 °C.[26] Kew, DeArmond, and Hanck[30] found analogous behavior for $Rh(bpy)_3^{3+}$ in acetonitrile.

(30) Kew, G.; DeArmond, K.; Hanck, K. *J. Phys. Chem.* **1974,** *78*, 727.

(31) After this paper had been submitted, a recent paper came to our attention: Kirch, M.; Lehn, J.-M.; Sauvage, J.-P. *Helv. Chim. Acta* **1979,** *62*, 1345. Although the observations made in the two studies are generally in good agreement, there are important differences between the interpretation of the observations.

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*Received July 16, 1979*

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# Novel *N*-Fluoroamines via the Chlorofluorination of Compounds with Carbon–Nitrogen Triple Bonds

*Sir:*

Studies in nitrogen–fluorine chemistry are extensive and a very large number of interesting compounds have been synthesized. Many of these syntheses are, however, very difficult and nonsystematic. During the preparation of some known *N*-fluoroperfluoroimines, an excellent method for the synthesis of *N*-chloro-*N*-fluoroamines has been found. This novel synthetic method, as well as some new reactions of these compounds, is reported here.

0002-7863/79/1501-7640$01.00/0