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.

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(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 (ϵ 3.55×10^3 M^{-1} cm^{-1}) and 520 nm in 25% ethanol–water. Here we find λ_{max} 516 nm at pH 9 with 2×10^{-2} M TEOA, 1×10^{-2} M Na_2SO_4; λ_{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 (λ_{max} 518 nm (ϵ 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 1×10^{-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).

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

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

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(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

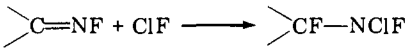
Novel *N*-Fluoroamines via the Chlorofluorination of Compounds with Carbon–Nitrogen Triple Bonds

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

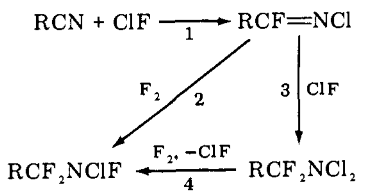
Five examples of *N*-chloro-*N*-fluorofluoroalkylamines are known, CF_3NClF,[1,2] $ClCF_2NClF$,[2] $(CF_3)_2CFNClF$,[2] $Cl_2CFNClF$,[2] and CH_3CF_2NClF.[3] These compounds were prepared by reactions of the corresponding *N*-fluoroimines with ClF, except for the last example which was obtained from CH_3CN and ClF_5.[2,3] The *N*-fluoroimines are very difficult to



$$CH_3CN + ClF_5 \longrightarrow CH_3CF_2NClF$$

prepare except for $(CF_3)_2C{=}NF$, which is available in good yield via the fluorination of $(CF_3)_2C{=}NH$ in the presence of CsF.[4] The reaction with ClF_5 has obvious potential dangers. As a result of these synthetic limitations, little is known about the chemistry of *N*-chloro-*N*-fluoroalkylamines.

By reaction of a mixture of ClF and F_2 with some halogenated nitriles, high yields of *N*-chloro-*N*-fluoroamines can be obtained. With RCN, the following reaction sequence is now reasonably well established (R = Cl, CF_3, C_2F_5). The reactions



are carried out by condensing 3 mmol of each reactant into a 75-mL stainless steel reactor at −195 °C. The mixture is then warmed to 22 °C over 1 h and allowed to stand at 22 °C for 4, 40, or 63 h for RCN (R = Cl, CF_3, and C_2F_5, respectively). The yields are >90% in each case. Under these conditions, ClF does not react with F_2 forming ClF_3, and F_2 does not react with RCN. Reactions 1 and 3 are known[5] and 2 and 4 were confirmed independently by reaction of $RCF{=}NCl$ and RCF_2NCl_2 with F_2. The mixture of F_2–ClF is more effective than ClF (reactions 1 and 3) followed by F_2 (4). Yields are considerably lower by this route. $ClCF_2NClF$ was identified by comparison of ^{19}F NMR and IR spectra and molecular weight with literature values.[2] The new compounds, CF_3CF_2NClF and $CF_3CF_2CF_2NClF$, exhibit the expected NMR and IR spectra and molecular weight. Attempts to extend the reaction to nonhalogenated nitriles using CH_3CN resulted in explosions at −195 °C.

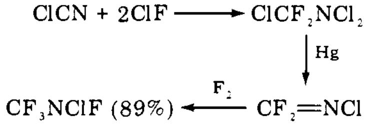
A special interest in synthesizing RCF_2NClF was to prepare $CF_2{=}NF$, the simplest fluorinated imine. This novel molecule has been nearly unavailable for chemical studies.[2,6,7a] The synthesis of $CF_2{=}NF$ can be carried out by reaction of $ClCF_2NClF$ with mercury.[2] On a 3-mmol scale CF_3Cl is a major byproduct, and it is very difficult to separate from $CF_2{=}NF$, even by efficient GLC. By carrying out the reaction of $ClCF_2NClF$ with Hg in the CF_3CO_2H (TFA) solvent, the CF_3Cl byproduct is eliminated forming $CF_2{=}NF$ in 90% yield.

Extension of this reaction to CF_3NClF, C_2F_5NClF, and n-C_3F_7NClF afforded surprisingly different results. The reactions give high yields of R_fNHF, 90–95%. The previously

$$R_fNClF + \xrightarrow[22\ ^\circ C]{TFA/Hg} R_fNHF$$

$$R_f = CF_3,\ C_2F_5,\ \text{or}\ n\text{-}C_3F_7$$

reported amine, CF_3NHF,[7] was identified by comparison of IR and NMR spectra and molecular weight with literature values. The new compounds, C_2F_5NHF and n-C_3F_7NHF, exhibit the expected IR and NMR spectra and molecular weight. They are the only other reported examples of a secondary fluoroperfluoroalkylamine. The earlier syntheses of CF_3NHF are difficult. Now by the sequence shown, combined with the above reaction, the compound is easily prepared.



Addition of F_2 to $CF_2{=}NCl$[5a] was not previously known and previous preparations of CF_3NClF are difficult.[1,2]

Caution! Some of the reactions involving mixture of ClF and F_2 are potentially explosive. R_fNClF and R_fNHF may also be explosive, although no explosive decompositions have been observed in this work.

Acknowledgment. The support of this research by the Army Research Office (Durham) (Grant No. GAAG29-77-G-0071) is gratefully acknowledged.

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Oxidation of μ-Oxo-Bridged Iron Porphyrin Dimers

Sir:

The existence of iron(IV) and its role as an intermediate in hemoproteins such as catalases, perioxidases, and cytochrome P-450 are topics of considerable current interest. Modern spectroscopic methods verify metal oxidation in peroxidases,[1] but adequate models for high oxidation state hemoproteins have yet to be reported. A major question concerning oxidation of isolated iron porphyrins is whether electron abstraction is formally from a metal or ligand based molecular orbital. Preparation of well-defined oxidized species is clearly prerequisite to answering this and other questions relevant to hemoprotein oxidation. Felton et al. reported preliminary electrochemical oxidation of monomeric and dimeric iron porphyrin species.[2] One-electron oxidation of μ-oxo-bis-5,10,15,20-tetraphenylporphyrinatoiron(III), $[FeTPP]_2O$, yielded a presumed mixed oxidation state dimer, $[Fe^{III}\text{-}O\text{-}Fe^{IV}]^+$. We have extended this work to isolation of the doubly oxidized dimeric species and further characterization of solution properties. Preliminary results reveal the doubly oxidized dimer as a desirable oxidizing agent or precursor for generation of model oxidized iron porphyrin compounds.

Electrochemical oxidation of $[FeTPP]_2O$ was carried out at 1.03 V (second cyclic voltammetry wave, reversible) vs. aqueous saturated calomel (SCE) in methylene chloride solvent using a tetraalkylammonium perchlorate salt as the supporting electrolyte.[3] Elemental analysis of the isolated solid was consistent with formulation as the bis perchlorate salt. The product was shown, by electron exchange with the parent iron(III) dimer, to possess two oxidation equivalents. Figure

0002-7863/79/1501-7641$01.00/0