

and 8.12 (bs, 2 H, *NH*), which in turn was dehydrated ( $P_2O_5$ ) to bis(nitrile) **2f**<sup>14</sup> [yellow needles, mp 205–216° (dec, sealed tube);  $\nu_{\max}^{KBr}$  2005, 2085, and 2225  $cm^{-1}$ ;  $\delta_{TMS}^{acetone-d_6}$  5.38 (s)]. In another sequence the acid chloride was treated with diazomethane followed by hydrogen chloride to give bis(chloromethyl ketone) **2g** [yellow needles, mp 115.5–117.5°;  $\nu_{\max}^{CHCl_3}$  1676, 2015, and 2075  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  4.26 (s, 4 H,  $CH_2Cl$ ) and 5.10 (s, 2 H, ring protons)]. The latter was readily converted to bis(iodomethyl ketone) **2h** (NaI–acetone) [orange microcrystals, mp 97–99°;  $\nu_{\max}^{CHCl_3}$  1667, 2010, and 2075  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  4.02 (AB quartet, 4 H,  $\Delta\nu_{AB} = 13.8$  cps,  $J_{AB} = 10.0$  cps,  $CH_2I$ ) and 5.02 (s, 2 H, ring protons)] or to bis(methyl ketone) **2i** (NaI–HOAc followed by  $Na_2S_2O_3$ ) [yellow microcrystals, mp 122.5–124.0°;  $\nu_{\max}^{KBr}$  1658, 1675, 1960, 1990, and 2060  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  2.25 (s, 6 H,  $COCH_3$ ) and 4.89 (s, 2 H, ring protons)]. In addition the acid chloride participated smoothly in Friedel–Crafts acylation ( $AlCl_3$ ) of benzene to give bis(benzoyl) derivative **2j** [yellow plates, mp 171–173°;  $\nu_{\max}^{KBr}$  1635, 1995, and 2062  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  5.00 (s, 2 H, cyclobutadiene ring protons), 7.23–7.65 (m, 6 H, *meta* and *para* protons), 7.65–8.00 (m, 4 H, *ortho* protons)] and esterification ( $C_6H_5CH_2OH-C_5H_5N$ ) to give bis(benzyl ester) **2k** [yellow needles, mp 70.0–71.5°;  $\nu_{\max}^{KBr}$  1730, 1977, 1998, and 2065  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  4.77 (s, 2 H, cyclobutadiene ring protons), 5.17 (s, 4 H,  $-OCH_2C_6H_5$ ), and 7.32 (s, 10 H,  $C_6H_5$ )].

Conclusive evidence that the aforementioned compounds are true cyclobutadiene complexes was obtained by chemical correlation. Treatment of bis(acid chloride) **2d** with sodium borohydride in dioxane afforded a somewhat unstable diol which was converted without characterization with concentrated hydrochloric acid to bis(chloromethyl) derivative **2l** [yellow solid, mp 73–77° (dec, HCl evolution);  $\nu_{\max}^{CHCl_3}$  1975 and 2045  $cm^{-1}$ ;  $\delta_{TMS}^{CDCl_3}$  4.09 (AB quartet, 4 H,  $\Delta\nu_{AB} = 6.0$  cps,  $J_{AB} = 13.1$  cps,  $-CH_2Cl$ ) and 4.37 (s, 2 H, ring protons)]. Reductive cleavage of the latter with lithium aluminum hydride in ether then produced the known 1,2-dimethylcyclobutadieneiron tricarbonyl (**2m**),<sup>15</sup> which was identified by comparison of the nmr spectrum with that reported and the infrared spectrum with that of an authentic sample. In addition, a great deal of the spectral data given above points toward or is consistent with the cyclobutadiene formulation. Especially indicative were the lack of observable spin–spin coupling between ring protons in half-ester **2c**, which is consonant with previous observations that such vicinal coupling is essentially zero,<sup>16</sup> and the nonequivalence of geminal protons which was evident in the nmr spectra of bis(iodomethyl ketone) **2h** and bis(chloromethyl) derivative **2l** and which is in accord with the expected  $m(C_s)$  molecular symmetry time averaged over rotational isomers.<sup>17</sup>

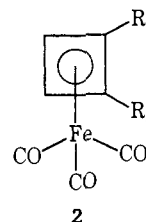
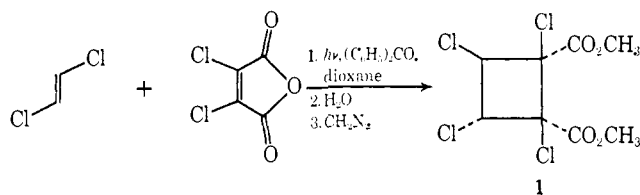
We are continuing to explore the potential for further development of the chemistry of cyclobutadiene now made possible by the availability of the series of complexes described herein.

(14) For a theoretical treatment of the cyclobutadienoid portion of this complex, see ref 5.

(15) H. A. Brune, W. Eberius, and H. P. Wolf, *J. Organometal. Chem.*, **12**, 485 (1968).

(16) (a) H. G. Preston, Jr., and J. C. Davis, Jr., *J. Amer. Chem. Soc.*, **88**, 1585 (1966); (b) H. A. Brune, H. P. Wolff, and H. Huther, *Chem. Ber.*, **101**, 1485 (1968).

(17) The same effect was not observed in bis(benzyl ester) **2k**, possibly because of a distance effect, and in bis(chloromethyl ketone) **2g**, possibly because of a smaller anisotropic effect of the chlorine.



a,  $R_1 = R_2 = CO_2CH_3$

b,  $R_1 = R_2 = CO_2H$

c,  $R_1 = CO_2CH_3$ ;  $R_2 = CO_2H$

d,  $R_1 = R_2 = COCl$

e,  $R_1 = R_2 = CONH_2$

f,  $R_1 = R_2 = CN$

g,  $R_1 = R_2 = COCH_2Cl$

h,  $R_1 = R_2 = COCH_2I$

i,  $R_1 = R_2 = COCH_3$

j,  $R_1 = R_2 = COC_6H_5$

k,  $R_1 = R_2 = CO_2CH_2C_6H_5$

l,  $R_1 = R_2 = CH_2Cl$

m,  $R_1 = R_2 = CH_3$

**Acknowledgment.** We gratefully acknowledge support from the Research Corporation during early stages of this work, and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also express our appreciation to Dr. H. A. Brune for graciously providing an infrared spectrum of authentic 1,2-dimethylcyclobutadieneiron tricarbonyl.

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(19) National Institutes of Health Predoctoral Fellow, 1966–1967.

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## Photochemical Reaction Pathways of Pentaammineruthenium(II) Complexes

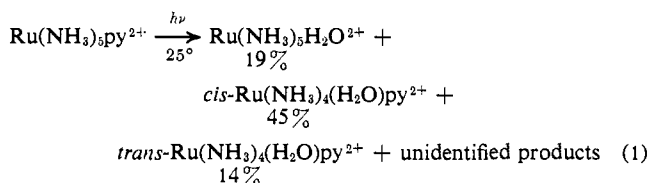
Sir:

Oxidation of ruthenium(II) has recently been reported<sup>1</sup> to be the principal photochemical reaction pathway for the Ru(II)–molecular nitrogen complexes,  $[Ru(NH_3)_5N_2]^{2+}$  and  $\{[Ru(NH_3)_3]_2N_2\}^{2+}$ . We have studied the photochemical reactions of several related pentaammineruthenium(II) complexes,  $Ru(NH_3)_5py^{2+}$ ,  $Ru(NH_3)_5(CH_3CN)^{2+}$ ,  $Ru(NH_3)_5H_2O^{2+}$ , and  $Ru(NH_3)_6^{2+}$ , and have found aquation of the complex as well as oxidation of Ru(II) to be a major photochemical reaction pathway in each case. Not surprisingly, preliminary studies show that the role played by the various pathways is dependent on the wavelength of the excitation radiation.

The spectrum of the pyridine complex,  $Ru(NH_3)_5py^{2+}$ , displays an intense metal-to-ligand charge-transfer (CT) band at 408 nm ( $\epsilon$  7800) and a ligand  $\pi$ – $\pi^*$  band

(1) C. Sigwart and J. Spence, *J. Am. Chem. Soc.*, **91**, 3991 (1969).

at 244 nm ( $\epsilon$  4570) as the only discernible features.<sup>2</sup> Irradiation of anaerobic aqueous  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  (0.001 *M* HCl) with 406-nm light (half-band width  $\sim 100$  Å) leads to photoaquation of this relatively substitution inert complex (eq 1). The reactions proceed with an



over-all quantum yield of  $0.35 \pm 0.1$ , determined by ferric oxalate actinometry. Since product ratios are somewhat dependent upon the extent of total reaction, the product yields in eq 1 and the quantum yield are reported for  $\sim 30\%$  disappearance of starting material to minimize complications derived from secondary photolysis. Products were identified by use of published procedures<sup>3,4</sup> which involve addition of sodium chloride or pyridine to separate aliquots of the product solution, oxidation to give the Ru(III) species, and independent elution of the two solutions from cation-exchange columns. The combination of these methods would not in all cases distinguish between a Ru(II) photoaquation product and a Ru(III) photooxidation product of the same coordination; however, when pyridine is added to the photolyzed solution ( $\sim 30\%$  reacted), the CT absorption in the 400-nm region is nearly completely regenerated. Although this absorption reflects the presence of several Ru(II)-pyridine species, its regeneration implies that photooxidation of the ruthenium(II) is at most a minor contributor to the reaction pathway at 406-nm excitation.

The 20–30% unaccounted for or unidentified ruthenium product (eq 1) is no doubt partly the result of analytical problems; however, secondary photolysis of the primary reaction products, *cis*- and *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{py}^{2+}$ , is probable since both ions have CT absorption maxima at  $\sim 400$  nm and of comparable intensity to that of the starting material. We have observed that the product ratio of free pyridine to  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$  is not constant but increases with increasing photolysis time, confirming this conclusion.

The spectrum of the acetonitrile complex ion,  $\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})^{2+}$ , displays a broad absorption band at 350 nm ( $\epsilon \sim 10^3$ ) and a more intense one at 229 nm ( $\epsilon \sim 15,500$ ).<sup>5</sup> Photolysis for long periods with 366-nm light does not affect the spectrum of a solution of this ion. However, 1-min irradiation of  $[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})][\text{BF}_4]_2$  ( $1.1 \times 10^{-4}$  *M*) in argon-deaerated sodium chloride solution (pH 3, 0.5 *M*) by the full ultraviolet-visible beam (infrared filtered) from a PEK 200-W high-pressure mercury lamp leads to complete disappearance of the 229-nm band. The spectrum of the product solution shows a new and well-defined absorption at 330 nm plus broad absorption centered about 280 nm. Further irradiation results in slow disappearance of the former band. Addition of acetonitrile to the product

solution does not affect the position or intensity of the 330-nm band but does partially regenerate absorption in the 220–230-nm region although not as a well-defined peak. Reduction of this solution results in the disappearance of the 330-nm band and in the appearance of a uv maximum at 226 nm of intensity comparable to that of the prephotolysis solution. These observations suggest that the 330-nm peak largely represents the photooxidation product  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  ( $\lambda_{\text{max}}$  328 nm ( $\epsilon$  1930))<sup>6</sup> which is the reported product of  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  photolysis under analogous conditions.<sup>1</sup> Four independent 1-min photolyses gave a  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  yield of  $73 \pm 2\%$ , determined spectrophotometrically. The remaining ruthenium products are apparently Ru(II) aquoammines since they react readily with acetonitrile. This conclusion was confirmed by adding pyridine to the product solution of a 1-min photolysis. A yellow color ( $\lambda_{\text{max}}$  402 nm, 370-nm shoulder) immediately developed, indicating the formation of Ru(II)-pyridine species. The spectrum shows that the new Ru(II)-pyridine complexes are not exclusively  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ ; however, if an extinction coefficient of 7800 is estimated for the maximum at 402 nm, a yield of about 30% is derived for the Ru(II) products. This value is surprisingly comparable to the percentage of ruthenium not accounted for as  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  ( $27 \pm 2\%$ ). The Ru(II) products are not the result of secondary photolysis of  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ , since direct photolysis of this ion under identical conditions gave only a 10% decrease of the 328-nm maximum after 2.6 min. Addition of pyridine to the resulting solution did not lead to the development of Ru(II)-pyridine CT absorption.

When deaerated aqueous solutions of  $[\text{Ru}(\text{NH}_3)_5\text{py}][\text{BF}_4]_2$ ,  $\text{Ru}(\text{NH}_3)_6^{2+}$ , or  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$  ( $\sim 1.3 \times 10^{-4}$  *M* complex, 0.5 *M* NaCl, pH 2) were irradiated with the PEK mercury lamp, photooxidation to form chloroammineruthenium(III) products ( $\lambda_{\text{max}}$   $331 \pm 1$  nm) occurs in each case. Addition of acetonitrile or pyridine results in some formation of Ru(II)- $\text{CH}_3\text{CN}$  or Ru(II)-pyridine species, respectively, indicating the presence also of aquoammine-ruthenium(II) complexes in the photolysis solution. This observation demonstrates that, at least in the first two cases, a photoaquation pathway is competitive with photooxidation. For each complex, the optimum photooxidation yield fell within the approximate range 60–80% based upon spectrophotometric identification of the Ru(III) product as  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ .

The similarity of the photolysis yields for the four different complexes and the existence of photoaquation pathways suggest the possibility of common intermediate(s), e.g.,  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ , in the oxidation pathway. Such a mechanism could also be operative in the analogous reactions of the  $\text{N}_2$  complexes. It is of interest to note that in every case, including that reported for the  $\text{N}_2$  complexes,<sup>1</sup> the spectrum of the photooxidation product(s) displays a  $\lambda_{\text{max}}$  several nanometers higher than  $\lambda_{\text{max}}$  for  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  which in the present work was checked on the same spectrophotometer. This small shift might reflect the presence of a small percentage of *trans*- $\text{Ru}(\text{NH}_3)_4\text{Cl}_2^+$  ( $\lambda_{\text{max}}$  332 nm ( $\epsilon$  4000)),<sup>7</sup> possibly generated by photoaquation followed by

(2) P. Ford, D. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

(3) P. Ford, J. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

(4) P. Ford and C. Sutton, *ibid.*, **8**, 1544 (1969).

(5) R. Clarke and P. Ford, submitted for publication.

(6) J. Broomhead, F. Basolo, and R. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(7) C. Sutton, unpublished results.

photooxidation. We are currently exploring this possibility by use of cation-exchange techniques.

Photooxidation of Ru(II) necessitates the corresponding reduction of some solution species. Sigwart and Spence<sup>1</sup> suggest the reduction of coordinated N<sub>2</sub> in the photolysis of Ru(II)-N<sub>2</sub> complexes since mass spectrometer experiments did not reveal H<sub>2</sub> as a reaction product. However, in photolysis of argon-deaerated Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>2+</sup> solutions, H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O appears to be the most likely oxidant. We have demonstrated in nonquantitative mass spectrometer experiments that the full-beam photolysis of Ru(NH<sub>3</sub>)<sub>5</sub>py<sup>2+</sup> (~4 × 10<sup>-3</sup> M, BF<sub>4</sub><sup>-</sup> salt) does produce H<sub>2</sub> in easily detectable quantities. Whether the formation of H<sub>2</sub> is a minor or major pathway in the photolysis of this ion and of the other Ru(II) ammines shall be elucidated by more quantitative experiments which are being initiated. Despite the care taken in deaerating the solution, we have not excluded the possibility of trace quantities of O<sub>2</sub> also acting as the electron acceptor. Nevertheless, the reproducibility of the photooxidation yields and the stability in the dark of Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>2+</sup> solutions (which are sensitive to O<sub>2</sub>) argue against this suggestion.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research. We thank Drs. C. Badcock, H. Offen, and G. Pritchard of this department for technical advice and for the loan of photolysis equipment.

(8) NSF Undergraduate Research Participant, Summer 1969.

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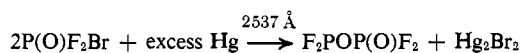
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Received August 15, 1969

### Difluorophosphoryl-μ-oxo-difluorophosphine. A Novel Mixed Valence Phosphorus Oxyfluoride

Sir:

The recent mention of compounds containing phosphorus in two valence states<sup>1</sup> prompts us to report our work on the preparation of F<sub>2</sub>POP(O)F<sub>2</sub>. We have prepared the compound in 40% yield by the photolysis of P(O)F<sub>2</sub>Br in the presence of mercury at 23°.



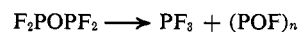
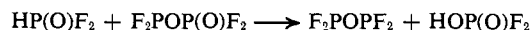
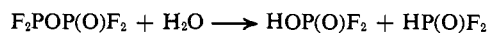
Other products formed include POF<sub>3</sub>, F<sub>2</sub>POPF<sub>2</sub>, P<sub>2</sub>O<sub>3</sub>F<sub>4</sub>, PF<sub>3</sub>, and unidentified colored solids. Purification of F<sub>2</sub>POP(O)F<sub>2</sub> was accomplished by fractionation through traps of -78 and -195°. The product and a small amount of P<sub>2</sub>O<sub>3</sub>F<sub>4</sub> were retained in the -78° trap.

Difluorophosphoryl-μ-oxo-difluorophosphine is a colorless liquid [mp -31°, bp 48°, vapor density molecular weight 174 (calcd for P<sub>2</sub>O<sub>3</sub>F<sub>4</sub>, 170.0)] which decomposes slowly at 23°. The <sup>19</sup>F nmr, infrared, and chemical reactivity are all consistent with the presence

(1) R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 434 (1969).

of both trivalent and pentavalent phosphorus atoms. The <sup>19</sup>F nmr spectrum obtained in 25% CFC<sub>3</sub> at 34.5° showed two doublets of equal area centered at φ 38.3 (F<sub>2</sub>PO) and 81.2 (OP(O)F<sub>2</sub>) with J<sub>PF</sub> = 1412 and 1033 Hz, respectively.<sup>2,3</sup> The resonance attributed to OP(O)F<sub>2</sub> was slightly broadened at 34.5°. On cooling to -26° (at lower temperatures the sample froze), a symmetrical complex multiplet of the type A<sub>2</sub>B<sub>2</sub>XX' was formed. The F<sub>2</sub>PO resonance, however, remained sharp at this temperature. The infrared spectrum of F<sub>2</sub>POP(O)F<sub>2</sub> contained absorptions at (cm<sup>-1</sup>): 1385 (s), P=O; 1024 (vs), P-O-P; 975 (s), P-F; 910 (w); 868 (s), P-F; 721 (m); 510 (m); 445 (w). The assignments are based on comparison with F<sub>2</sub>POPF<sub>2</sub><sup>4</sup> and F<sub>2</sub>P(O)OP(O)F<sub>2</sub>.<sup>5</sup> Further proof of the unsymmetrical structure of F<sub>2</sub>POP(O)F<sub>2</sub> was obtained by reaction with HCl. Stoichiometric amounts reacted nearly quantitatively at 23° forming HOP(O)F<sub>2</sub> and PF<sub>2</sub>Cl.

The decomposition of F<sub>2</sub>POP(O)F<sub>2</sub> appeared to be catalyzed by impurities, and considerable decomposition was often observed in the vacuum system. However, a 2-mmole sample was kept for 2 weeks in a sealed 100-ml Pyrex bulb without complete decomposition. The compound was extremely sensitive to traces of water and some HOP(O)F<sub>2</sub> was almost always observed along with PF<sub>3</sub> and F<sub>2</sub>POPF<sub>2</sub>. The effect of impurities and exact stoichiometry are not yet known, but our results to date are consistent with the following equations and previously reported instability of F<sub>2</sub>POPF<sub>2</sub><sup>4</sup> and HP(O)F<sub>2</sub>.<sup>6,7</sup>



Further studies of the decomposition and other chemical reactions of F<sub>2</sub>POP(O)F<sub>2</sub> are in progress along with a detailed analysis of the temperature-dependent nmr.

**Acknowledgment.** The author thanks D. T. Dix and R. G. Czerepinski of the Dow Chemical Co. for the nmr spectra. The partial support of this work by the National Science Foundation is gratefully acknowledged.

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(3) J. J. Burke and T. R. Krugh, "A Table of <sup>19</sup>F Chemical Shifts for a Variety of Compounds," Mellon Institute, Pittsburgh, Pa., 1964.

(4) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, 88, 3729 (1966).

(5) E. A. Robinson, *Can. J. Chem.*, 40, 1725 (1962).

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### A Molecular Orbital Correlation of the Rates of Formation of Arylmethyl Radicals

Sir:

In the past decade attempts to correlate the rates of formation of arylmethyl carbonium ions and carban-