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Synthetic Applications of Photosubstitution Reactions of Poly(pyridyl) Complexes of Ruthenium(II)

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Two new methods for the photochemical synthesis of complexes of the type Ru(bpy)$_2$LX$^+$ and Ru(bpy)$_2$X$_2$ (L = pyridine, CH$_3$CN, etc.; X = ClO$_4$, NO$_3$, NCS, Br, etc.) have been developed. The photochemistry is based on photosubstitution reactions of the parent complexes Ru(bpy)$_2$L$_2$$^{2+}$ most notably where L is pyridine in solvents of low polarity like dichloromethane. The photochemical methods are versatile and give products in good yield and purity. Mechanistically, the reactions appear to involve a dissociative step at the metal; a quantum yield of 0.18 is found for monosubstitution in Ru(bpy)$_2$(py)$_2$$^{2+}$, which is independent of the chemical identity and concentration of the entering ligand, X$^-$. Some deductions about the photochemical behavior of the related complex Ru(bpy)$_3$$^{2+}$ based on our observations with Ru(bpy)$_2$L$_2$$^{2+}$ are also presented, and the possibility of a special medium effect in low-polarity solvents like dichloromethane is discussed.

Introduction

In an early paper concerning the synthesis of complexes of the type [Ru^{II}(phen)$_2$L$_2$] and [Ru^{II}(bpy)$_2$L$_2$] (phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine), Bosnich and Dwyer[1] reported that some of their products were highly photosensitive in acetone solutions. The photochemical details of the reactions were not discussed, and apparently the work was not pursued further. Recently, Gleria and co-workers[2] reported that [Ru(bpy)$_3$]Cl$_2$ is photolabile in chlorinated solvents, giving Ru(bpy)$_2$Cl$_2$ as the major product. It was not clear from their report whether the origin of the chloride ligand was the Cl$^-$ counterion or solvent. Extensive photochemical studies based on Ru(bpy)$_3$$^{2+}$ have been carried out in potentially coordinating solvents such as H$_2$O[3] and CH$_3$CN[4] and the results obtained show that the complex is essentially photochemically inert at room temperature although Hoggard and Porter have reported the existence of a relatively inefficient photosubstitution reaction in DMF.[5] The photochemical stability of Ru(bpy)$_3$$^{2+}$ and related complexes is of more than passing interest since an increasingly serious case can be made for their role in possible solar energy conversion schemes.[6,7]

Because of our continuing interest in a variety of chemical problems based on 2,2′-bipyridyl complexes of ruthenium, we have begun to investigate their photochemical properties.[8] Among our interests are the development of a rationale to account for the remarkable differences in photochemical behavior which have already been observed. The main theme of this paper, however, is to describe our synthetic work based on the photolability of complexes of the type [Ru^{II}(bpy)$_2$L$_2$] in nonaqueous solvents.

Experimental Section

Materials. The complexes [Ru(bpy)$_3$](PF$_6$)$_2$,[9] [Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$,[10] [Ru(bpy)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$,[11] Ru(bpy)$_2$Cl$_2$·2H$_2$O,[12] [Ru(bpy)$_2$py(OH$_2$)](PF$_6$)$_2$,[13] and [Ru(bpy)$_3$](SCN)$_2$[5] were prepared according to literature procedures. All solvents were reagent grade and used without further purification (drying proved unnecessary). All other materials were obtained from commercial sources and used as received.

Equipment. UV–visible spectra were obtained by using a Bausch and Lomb Spectronic 210 UV spectrophotometer. Infrared spectra were obtained as KBr pellets or solutions in cells with NaCl windows on a Beckman Model IR4250 spectrometer. Cyclic voltammograms were obtained by using a Princeton Applied Research Model 175 universal programmer and Model 176 potentiostat. A platinum-bead working electrode, platinum-wire auxiliary electrode, and saturated NaCl calomel electrode (SSCE) were used in a cell of about 2-mL volume. Electrolyte solutions were either 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile or 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) in CH$_2$Cl$_2$.

Photochemical Procedures. Preparative photolyses were carried out with use of all-Pyrex glassware and a GE 275-W sunlamp at a distance of approximately 10 in. The glassware consisted of either round-bottom flasks fitted with condensers or cylindrical water-jacketed reaction vessels. The solutions were magnetically stirred and air saturated unless otherwise noted.

Quantum yield measurements and other investigative photolyses were carried out with use of radiation from a "Hanovia 97730010" 1000-W Hg–Xe arc lamp in a LH151N Schoeffel lamp housing, which was passed through a Bausch and Lomb monochromator (No. 33-66-79). An additional Corning 3-73 cutoff filter was placed in front of the 1-cm spectrophotometric cell which held the sample for irradiations at 436 nm and above. The bandwidth under the conditions of photolysis was calculated to be 20 nm. Actinometry was performed by using both Reinecke salt and ferrioxalate actinometers, according to Adamson and Parker and Hatchard, respectively.[14] Quantum yields were determined from initial slopes of plots of concentration of product vs. time. The concentrations were determined by solving simultaneous equations for the absorbances at two different wavelengths. The standard deviation in the quantum yield determinations was 0.02 on the basis of 10 measurements.

Preparations. [Ru(bpy)$_2$(py)$_2$](NO$_3$)$_2$. This salt was prepared in the manner described[5] for [Ru(bpy)$_3$](SCN)$_2$; however, a nitrate-saturated anion-exchange resin was used in place of a thiocyanate-saturated resin.

[Ru(bpy)$_2$(*t*-Bu(py))$_2$](PF$_6$)$_2$. The *tert*-butylpyridyl complex was prepared in an analogous manner to [Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ except that 4-*tert*-butylpyridine was used in place of pyridine. Anal. Calcd for C$_{38}$H$_{42}$N$_6$F$_{12}$P$_2$Ru: C, 46.87; H, 4.35; N, 8.63. Found: C, 48.13; H, 4.17; N, 8.48.

[Ru(bpy)$_2$(py)(NO$_2$)]PF$_6$. Ru(bpy)$_2$Cl$_2$·2H$_2$O (2.0 g) and pyridine (0.38 mL) were added to 200 mL of 50/50 water/ethanol. The

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solution was heated at reflux for 1 h. Sodium nitrite (0.33 g) was added, and the solution was heated at reflux for an additional 2 h. The solution was then evaporated under vacuum to half of the original volume and cooled in a refrigerator overnight. After filtration, about 1 mL of a concentrated aqueous solution of NH_4PF_6 was added. The product was collected by filtration, washed with water, and air-dried. The product was then dissolved in acetonitrile and the resulting solution added to diethyl ether, and the product was collected by filtration. Purification by chromatography with alumina was sometimes necessary; yield 2.0 g (76%). Anal. Calcd for $C_{25}H_{21}N_6O_2F_6PRu$: C, 43.93; H, 3.10; N, 12.30. Found: C, 44.14; H, 2.92; N, 12.28.

Photochemical Preparations. $[Ru(bpy)_2(py)(NO_3)](PF_6)$. $[Ru(bpy)_2(py)_2](PF_6)_2$ (200 mg) was partially dissolved in 800 mL of CH_2Cl_2, and 1 molar equiv of $[N(n\text{-}C_4H_9)_4](NO_3)$ (94 mg) was added. The solution was photolyzed for 3 h under reflux from the heat generated by the sunlamp. The complex dissolved almost completely during the photolysis, and the solution was filtered after completion to remove the remaining starting material. The solution volume was reduced by rotary evaporation, and diethyl ether was added. Appropriate blanks showed that thermal substitution is negligible under the same conditions. The resulting precipitate was collected by filtration and air-dried; yield 124 mg (76%). Before the final filtration, it was sometimes necessary to redissolve the product in acetone and reprecipitate with diethyl ether to avoid the oiling out of the product. Anal. Calcd for $C_{25}H_{21}N_6F_6O_3PRu$: C, 42.93; H, 3.03; N, 12.01. Found: C, 42.80; H, 2.81; N, 12.09. The nitrate complex can also be prepared as the NO_3^- salt by an analogous procedure using $[Ru(bpy)_2(py)_2](NO_3)_2$ as the starting material for the photolysis, but the product is extremely hygroscopic and therefore difficult to isolate as a solid.

$[Ru(bpy)_2(py)(ClO_4)](ClO_4)$. This salt was prepared as for the case of $[Ru(bpy)_2(py)(NO_3)](PF_6)$ except that $[Ru(bpy)_2(py)_2](ClO_4)_2$ was used as the starting material and as the source of ClO_4^-. Anal. Calcd for $C_{25}H_{21}N_5Cl_2O_8Ru$: C, 43.43; H, 3.06; N, 10.13. Found: C, 43.01; H, 3.78; N, 9.62.

$[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)](PF_6)\cdot H_2O$. The toluenesulfonate complex was prepared in the same manner as $[Ru(bpy)_2(py)(NO_3)](PF_6)$ except that *p*-toluenesulfonic acid was used as the source of the toluenesulfonate anion. The isolated product was purified by chromatography by washing with CH_2Cl_2 and eluting with CH_3CN. Anal. Calcd for $C_{32}H_{28}N_5F_6O_3PRuS$: C, 46.49; H, 3.65; N, 8.47. Found: C, 46.88; H, 3.13; N, 8.58.

$[Ru(bpy)_2(t\text{-}Bu(py))(CF_3CO_2)](PF_6)$. The trifluoroacetate complex was prepared and purified in a manner similar to that for $[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)](PF_6)$, but trifluoroacetic acid was used as the source of $CF_3CO_2^-$. Anal. Calcd for $C_{31}H_{29}N_5F_9O_2PRu$: C, 46.16; H, 3.52; N, 8.68. Found: C, 45.60; H, 3.65; N, 8.64.

$Ru(bpy)_2Cl(NCS)\cdot 2H_2O$. $[Ru(bpy)_2(py)(NCS)](PF_6)$ (45 mg) was dissolved in 70 mL of CH_2Cl_2, and 24 mg of $[N(n\text{-}C_4H_9)_4]Cl$ was added. The solution was photolyzed in a water-jacketed reactor for 3 h. The solution volume was reduced under vacuum, and diethyl ether was added. The product was collected by filtration and air-dried; yield 16 mg (50%). Anal. Calcd for $C_{21}H_{20}N_5ClORuS$: C, 46.44; H, 3.71; N, 12.89. Found: C, 46.43; H, 3.25; N, 12.68.

$[Ru(bpy)_2(py)(OH_2)](PF_6)_2\cdot H_2O$. $[Ru(bpy)_2(py)_2](PF_6)_2$ (80 mg) was dissolved in a minimum amount of acetone, and a saturated solution of $[N(n\text{-}C_4H_9)_4]Cl$ was added. The precipitate was filtered out, washed with diethyl ether, and air-dried. The solid was redissolved in 30 mL of 1 N H_2SO_4 and irradiated for $1^1/_2$ h. A saturated solution of NH_4PF_6 was added, and the precipitate was separated by filtration, washed with 2-propanol and then diethyl ether, and air-dried. Electrochemical, spectral, and elemental analysis data were to within experimental error identical with those obtained on a sample which was prepared by literature methods.[13]

$[Ru(bpy)_2(py)(NCS)](PF_6)$. $[Ru(bpy)_2(py)_2](PF_6)_2$ (210 mg) was dissolved in 300 mL of acetone, and the solution was photolyzed in a 500-mL round-bottom flask for 1 h. A slight excess of 1 molar equiv of NH_4SCN was added, and after the solution was allowed to stand for 1 h, the volume was reduced under vacuum. Diethyl ether was added and the resulting precipitate collected by filtration and air-dried. The product was purified by chromatography by washing with CH_2Cl_2 and eluting with acetone; yield 125 mg (76%). Anal. Calcd for $C_{26}H_{21}N_6SPF_6Ru$: C, 44.89; H, 3.04; N, 12.08. Found: C, 44.41; H, 2.80; N, 11.71.

$[Ru(bpy)_2(py)Cl](PF_6)\cdot H_2O$. $[Ru(bpy)_2(py)_2](PF_6)_2$ (100 mg) was dissolved in 100 mL of acetone, and the solution was photolyzed in a water-jacketed reactor for 1 h. The water in the outer jacket was not circulated but served to moderate the temperature increase to well below the boiling point of acetone. A slight excess of a 1 molar equiv of $[N(n\text{-}C_4H_9)_4]Cl$ and a procedure similar to that described for $[Ru(bpy)_2(py)NCS](PF_6)$ were used to recover and purify the product. Anal. Calcd for $C_{25}H_{21}ClPF_6Ru$: C, 43.46; H, 3.36; N, 10.14. Found: C, 43.85; H, 2.46; N, 9.92.

$[Ru(bpy)_2(py)(NO_2)](PF_6)$. A deaerated acetone solution of $[Ru(bpy)_2(py)_2](PF_6)$ was photolyzed for about 10 min or until spectral changes indicated that complete formation of $[Ru(bpy)_2(py)(solvent)]^{2+}$ had occurred. Excess $[N(n\text{-}C_4H_9)_4NO_2]$ was added, the solution volume was reduced under vacuum, and diethyl ether was added. The resulting precipitate was collected by filtration. The identity and purity of the product were shown by spectral (λ_{max} and ϵ values for the visible metal–ligand charge-transfer band) and electrochemical measurements (comparison of $E_{1/2}$ values for the irreversible oxidation of Ru(II) to Ru(III)).[15]

$Ru(bpy)_2(NCS)_2\cdot H_2O$. $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ (83 mg) and NH_4NCS (27 mg) were dissolved in 100 mL of acetone and irradiated for $1^1/_2$ h. The solution volume was reduced under vacuum to about 20 mL. The resulting precipitate was collected by filtration, washed several times with methanol, and air-dried. Anal. Calcd for $C_{22}H_{18}N_6OS_2Ru$: C, 48.25; H, 3.31; N, 15.34. Found: C, 48.32; H, 2.71; N, 15.34.

$Ru(bpy)_2Br_2\cdot 2H_2O$. $[Ru(bpy)_2(py)_2](PF_6)_2$ (150 mg) and $[N(n\text{-}C_4H_9)_4]Br$ (120 mg) were dissolved in 200 mL of CH_2Cl_2 in a round-bottom flask, and the solution was photolyzed for $3^1/_2$ h. Diethyl ether was added, and the resulting precipitate was collected by filtration. The product was redissolved in 100 mL of CH_2Cl_2/acetone (25/75), and then the mixture was evaporated under vacuum to about 30 mL. The solid product was collected by filtration, washed with diethyl ether, and air-dried; yield 85 mg (80%). Anal. Calcd for $C_{20}H_{20}N_4Br_2O_2Ru$: C, 39.44; H, 3.31; N, 9.20. Found: C, 40.26; H, 2.64; N, 9.27.

Chromatography. Where indicated, the products were purified by an abbreviated chromatographic technique. The complexes were placed on a column by dissolving them in a minimum of CH_2Cl_2 or a 1/1 mixture of CH_2Cl_2 and eluting solvent. Approximately 100 mL of additional CH_2Cl_2 was passed through the column, after which the product was quickly eluted with acetone or CH_3CN. The complexes are efficiently recovered by reducing the volume by evaporation under vacuum and precipitating with diethyl ether. The columns used were 2 cm in inner diameter; they were packed with 3 cm of alumina (Fisher A-540).

Results

Photolysis of $Ru(bpy)_2(py)_2^{2+}$ in dichloromethane or acetone solutions in the presence of coordinating anions results in efficient loss of pyridine from the complex and incorporation of the anion. The anions can be used at stoichiometric concentration levels and can be added as tetraalkylammonium salts to solutions of $[Ru(bpy)_2(py)_2](PF_6)_2$ or as the counterion in place of PF_6^-. In the presence of anions (X^-) such as NO_3^-, ClO_4^-, $p\text{-}CH_3C_6H_4SO_3^-$, or $CF_3CO_2^-$, only one pyridine ligand is lost from the complex, giving $Ru(bpy)_2(py)X^+$ even with excess X^- and extended photolyses. In the case of the organic acid anions, the source of the anions was simply the acid. All of the above products were formd quantitatively, on the basis of spectral measurements before isolation, and can be isolated in reasonable synthetic yields.

No systematic attempt was made to characterize fully the synthetic details of the reactions including the report of percent yields. Many of the compounds were prepared earlier by different procedures. The major scope of our effort was to test the generality of the photochemical syntheses.

In the presence of the more strongly coordinating anions ($Y^- = F^-, Cl^-, Br^-,$ or SCN^-), photolysis of $Ru(bpy)_2(py)_2^{2+}$ results in the displacement of both pyridine ligands to give $Ru(bpy)_2Y_2$. Spectrophotometric monitoring during the

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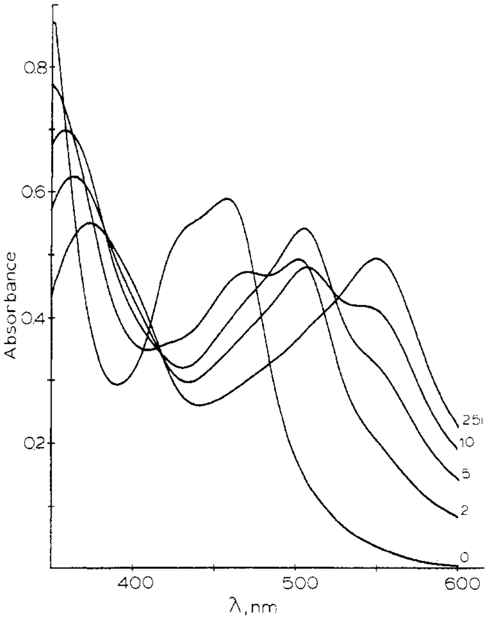


Figure 1. Visible spectra of a CH_2Cl_2 solution of $[Ru(bpy)_2(py)_2](PF_6)_2$ and excess $[N(C_4H_9)_4]Br$ taken at different times following irradiation at 436 nm. The data clearly show the sequential formation of $[Ru(bpy)_2(py)Br]^+$ (λ_{max} 504 nm) followed by $Ru(bpy)_2Br_2$ (λ_{max} 548, 378 nm).

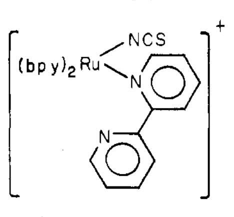
photolyses (Figure 1) shows that substitution reactions occur in a stepwise fashion (eq 1 and 2). For the reactions with

$$Ru(bpy)_2(py)_2^{2+} + Y^- \xrightarrow{h\nu} Ru(bpy)_2(py)Y^+ + py \quad (1)$$

$$Ru(bpy)(py)Y^+ + Y^- \rightarrow Ru(bpy)_2Y_2 + py \quad (2)$$

NCS^-, Cl^-, or NO_3^-, the quantum yield for loss of the first pyridine at 436 nm is 0.18 ± 0.02, independent of anion concentration. In most cases the second step appears to be less efficient by a factor of 2–4. Exact measurements are difficult because of the large number of species present, all of which absorb at nearly the same wavelengths.

The mixed-ligand complex $Ru(bpy)_2(NCS)Cl{\cdot}2H_2O$ was prepared by photolysis of $Ru(bpy)_2(py)(NCS)^+$ in CH_2Cl_2 with added Cl^-. The experiment demonstrates the synthetic potential of the photochemical reactions for preparing mixed-ligand complexes. The exclusive loss of pyridine suggests a selectivity with regard to the displacement of a neutral ligand by an anionic ligand. The reaction also supports the stepwise nature of the mechanism. Interestingly, the photochemical reaction of $Ru(bpy)_3^{2+}$ with added NCS^- is also stepwise (Figure 2), and the similarity in spectral properties between the intermediate and $Ru(bpy)_2(py)(NCS)^+$ strongly suggests that the intermediate is the singly bound bipyridyl complex,



We have not yet been able to isolate the monodentate bipyridyl species because it is thermally unstable and within minutes reacts further to give the disubstituted complex.

Where appropriate, the products of the photolyses were characterized by visible[16] and infrared spectroscopy, cyclic voltammetry,[17] elemental analyses, and comparison with known samples. The results of these measurements for many of the complexes investigated as well as for the starting materials are summarized in Tables I and II.

Especially noteworthy from the synthetic point of view is the ease of preparation of complexes containing anions that

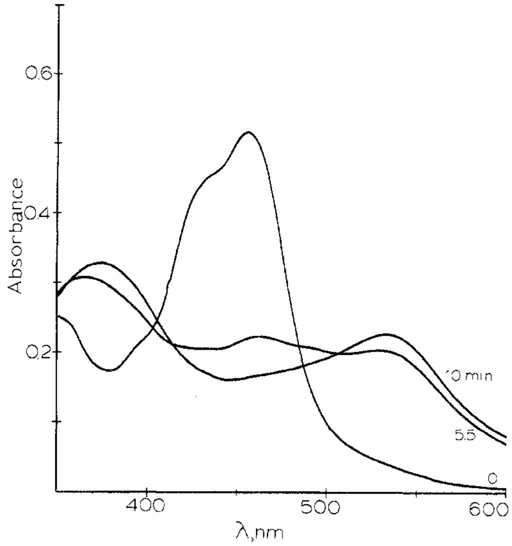


Figure 2. Visible spectra of a CH_2Cl_2 solution of $[Ru(bpy)_3](SCN)_2$ taken at different times following irradiation at 436 nm.

Table I. Visible Spectral and $E_{1/2}$ Values Determined by Cyclic Voltammetry

compd	λ_{max}, nm (ϵ)[a]	$E_{1/2}$, V[b]
$[Ru(bpy)_3](PF_6)_2$	452 (16 000)	+1.29
$[Ru(bpy)_2(py)_2](PF_6)_2$	460 (9200)	+1.29
$[Ru(bpy)_2(t\text{-}Bu(py))_2](PF_6)_2$	464 (8500), 338 (13 000)	+1.23
$[Ru(bpy)_2(py)CH_3CN](PF_6)_2$	440 (9700)	+1.35
$[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$	426 (8700)	+1.47
$Ru(bpy)_2Cl_2{\cdot}2H_2O$	556 (9400), 380 (9400)	+0.31
$Ru(bpy)_2Br_2{\cdot}2H_2O$	548 (9300), 378 (9500)	+0.37
$Ru(bpy)_2(NCS)_2{\cdot}H_2O$	520 (8300), 366 (9100)	+0.67
$Ru(bpy)_2(NCS)Cl{\cdot}2H_2O$	535 (8200), 372 (9000)	+0.50
$[Ru(bpy)_2(py)NCS]PF_6$	488 (8700)	+0.85
$[Ru(bpy)_2(py)Cl]PF_6$	505 (8200), 358 (10 000)	+0.76
$[Ru(bpy)_2(py)NO_3]PF_6$	488 (8100), 346 (10 500)	+0.91
$[Ru(bpy)_2(py)ClO_4]PF_6$	474 (8600), 339 (11 200)	+1.09
$[Ru(bpy)_2(py)NO_2]PF_6$	461 (7900), 340 (11 000)	+1.06[c]
$[Ru(bpy)_2(py)CF_3CO_2]PF_6$	499 (9200), 348 (11 600)	+0.89
$[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)]PF_6$	492 (9400), 345 (11 400)	+0.90
$[Ru(bpy)_2(t\text{-}Bu(py))H_2O](PF_6)_2$	466 (8900), 321 (12 600)	+1.18[d]
$[Ru(bpy)_2(py)H_2O](PF_6)_2$	470 (8400)	+0.90[e]
$[Ru(bpy)_2(t\text{-}Bu(py))NO_3]PF_6$	489 (9100), 343 (11 600)	+0.88

[a] In CH_2Cl_2 solution; ϵ values are molar extinction coefficients. [b] In 0.1 M $(NEt_4)(ClO_4)$–CH_3CN vs. the saturated sodium chloride calomel electrode. [c] Irreversible; potential cited is the potential at the peak current for a scan rate of 200 mV/s. [d] In a 0.2 M $[N(n\text{-}C_4H_9)_4]PF_6$–$CH_2Cl_2$ solution. [e] In H_2O (1.0 M $HClO_4$). From: Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978,** *100,* 3601.

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(17) Brown, G. M. Ph.D. Thesis, The University of North Carolina, 1974.

Table II. Infrared Spectral Data[a]

compd	characteristic IR bands,[a] cm^{-1}
$[Ru(bpy)_2(py)NO_3]PF_6$	~1460,[b] 1288, 1000
$[Ru(bpy)_2(py)ClO_4]ClO_4$	1150, 1015[c]
$[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)]PF_6$	1260, 1155, 1115, 1000
$[Ru(bpy)_2(py)(CF_3CO_2)]PF_6$	1710, 1690, 1410, 1195, 1132
$[Ru(bpy)_2(py)NCS]Cl$	2105, 802
$[Ru(bpy)_2(py)NO_2]PF_6$	1340, 1300
$Ru(bpy)_2(NCS)_2\cdot H_2O$	2105, 805
$Ru(bpy)_2(NCS)Cl\cdot 2H_2O$	2105, 800

[a] KBr pellet except as noted. [b] The exact band energy is somewhat uncertain because it appears as a shoulder on nearby bpy-ligand bands. [c] In CH_2Cl_2 solution.

are usually considered noncoordinating. For example, $[Ru(bpy)_2(py)NO_3]^+$ and $[Ru(bpy)_2(py)ClO_4]^+$ were easily prepared and isolated in high yield. The infrared spectra of the complexes suggest that the NO_3^- and ClO_4^- anions in the respective complexes are O-bound, unidentate ligands and that the thiocyanate complexes are N bound[18] (see Table II). The high yields and purities of the products are achieved because, once the products are formed, secondary photolysis and thermal back-reactions with the displaced pyridine are negligible. Continued photolysis past the initial reaction even for a few hours results in only minor spectral changes. The complexes however are not photoinert. Addition of anions such as Cl^- followed by photolysis results in the rapid incorporation of Cl^-, giving $Ru(bpy)_2Cl_2$. Preparation of mixed complexes such as $Ru(bpy)(NO_3)Cl$ is not possible under these conditions because fairly rapid thermal substitution also occurs, resulting in the loss of NO_3^-.

In order to study the generality of the photochemical reactions, we performed photolyses with other complexes and in a variety of solvents. Products were isolated in only a few cases, but the spectral evidence strongly supports the following conclusions. Photolysis of $Ru(bpy)_3^{2+}$, $Ru(bpy)_2(CH_3CH)_2^{2+}$, and $Ru(bpy)_2(t\text{-}Bu(py))_2^{2+}$ in CH_2Cl_2 in the presence of coordinating anions results in photosubstitution of the anion for bipyridine, CH_3CN, and *tert*-butylpyridine, respectively, similar to the case of $Ru(bpy)_2(py)_2^{2+}$. The only exception noted was that the photosubstitution of NO_3^- for bipyridine in $Ru(bpy)_3^{2+}$ did not occur, and presumably the other X^--type anions ClO_4^- etc. would behave similarly. The photochemical reactions of all the complexes tested except $Ru(bpy)_3^{2+}$ also occur in acetone with high efficiency. Acetone offers the advantage of greater complex solubility. In addition, photolysis of $Ru(bpy)_2(t\text{-}Bu(py))_2^{2+}$ with added NO_3^- or Br^- in $CHCl_3$, DME (1,2-dimethoxyethane), or THF results in rapid photosubstitution reactions identical in nature with the results described for $Ru(bpy)_2(py)_2^{2+}$ in CH_2Cl_2. These solvents, however, are less advantageous as reaction media because of such problems as reduced complex solubility or apparent side reactions. For example, photolysis of $Ru(bpy)_2(t\text{-}Bu(py))_2^{2+}$ in DME or THF in the presence of NO_3^- is complicated by a secondary reaction involving $Ru(bpy)_2(t\text{-}Bu(py))(NO_3)^+$ formed initially.

Surprisingly, $[Ru(bpy)_2(t\text{-}Bu(py))_2](PF_6)_2$ is photoactive in CH_2Cl_2 even in the absence of added anions, and our results indicate that $Ru(bpy)_2(t\text{-}Bu(py))(OH_2)^{2+}$ is the major photoproduct under these conditions. The concentration of water in reagent grade CH_2Cl_2 under the conditions of the photolyses was always in approximately 10-fold or greater excess compared to the concentration of complex used, and it appears difficult to reduce the water content to a level where photoaquation is no longer an interfering reaction. The aquo complex can be isolated from CH_2Cl_2 solutions.

Loss of a pyridyl group also occurs when acetone or DME solutions of $[Ru(bpy)_2(t\text{-}Bu(py))_2](PF_6)_2$ are photolyzed, but the products were not characterized and may be the aquo complex as in CH_2Cl_2 or the acetone or DME complexes, respectively. Acetone and DME have reasonable coordinating properties, and related complexes are known to exist.[12,19]

Once formed, the solvent complexes undergo thermal substitution very rapidly. Spectrophotometric studies indicate rapid displacement of the aquo ligand by Cl^-, NO_3^-, ClO_4^-, and NO_2^- in solvents such as CH_2Cl_2. We have used the thermal reactivity to advantage to produce monosubstituted complexes containing Y^--type anions by the reaction sequence presented in eq 3 and 4. In the procedure, the solvento

$$Ru(bpy)_2L_2^{2+} \xrightarrow[S]{h\nu} Ru(bpy)_2LS^{2+} + L \qquad (3)$$

$$Y^- + Ru(bpy)_2LS^{2+} \xrightarrow{dark} Ru(bpy)_2LY^+ + S \qquad (4)$$

complexes are produced photochemically and then allowed to react thermally with the anions. Neutral ligands such as CH_3CN and *tert*-butylpyridine will also displace the aquo ligand in $Ru(bpy)_2(t\text{-}Bu(py))(OH_2)^{2+}$; however, a large excess of the ligand is necessary for the reactions to go to completion at a reasonable rate.

Thermal substitution of anions and neutral ligands for water in $Ru(bpy)_2(t\text{-}Bu(py))(OH_2)^{2+}$ in CH_2Cl_2 proceeds through a distinct but short-lived intermediate. For example, a cyclic voltammogram of $Ru(bpy)_2(t\text{-}Bu(py))(OH_2)^{2+}$ in CH_2Cl_2 (0.2 M TBAH) exhibits a wave at +1.18 V ($E_{1/2}$ vs. SSCE). Addition of NO_3^- results in immediate loss of this wave and the appearance of a new wave at +0.90 V. Over a period of several minutes, the wave at +0.90 V disappears and a wave for the $Ru(bpy)_2(t\text{-}Bu(py))(NO_3)^{2+/+}$ couple appears at 1.08 V. Characteristic spectral changes occur in the solution on the same time scale.

Discussion

Our investigations into the photochemistry of complexes of the type $[Ru^{II}(bpy)L_2]$ have resulted in the development of two new and important synthetic techniques for the preparation of related complexes. The synthetic utility of the photochemical reactions has been illustrated in a dramatic fashion by our ability to prepare a variety of complexes containing what are usually considered to be noncoordinating anions. We have so far restricted our attention, for the most part, to complexes where L = pyridine or *tert*-butylpyridine; however, the reactions seem to be reasonably general. For example, $Ru(bpy)_2(CH_3CN)_2^{2+}$, which is very resistant to thermal substitution, can be readily converted photochemically into a large number of related complexes. The procedures described here probably represent only a small sample of the full scope of the photochemical reactions.

The first of the two techniques is based on the facile photochemical displacement of neutral ligands by negatively charged ligands in low dielectric solvents (eq 1 and 2). The choice of solvent does not appear to be critically important; solubility and a low dielectric constant were determining factors in the selection of a reaction medium. From our results, both CH_2Cl_2 and acetone are excellent choices as solvents for the bis(pyridyl) complexes, but reasonable efficiencies for photosubstitution in $Ru(bpy)_3^{2+}$ could only be obtained in CH_2Cl_2.

The reactions are surprisingly efficient even when a stoichiometric amount of entering ligand was used. In fact, for $Ru(bpy)_2(py)_2^{2+}$ the observed quantum efficiencies for the first

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step in CH_2Cl_2 are independent of the concentration of added anion. The source of the anion does not appear to be important. It can be added as the counterion of $Ru(bpy)_2(py)_2^{2+}$, or the tetraalkylammonium salts can be added to solutions containing $[Ru(bpy)_2(py)_2](PF_6)_2$. The alkylammonium salts have been used as the anion source most extensively because they are highly soluble in solvents used and because a wide variety of these salts are available commercially. Flash photolysis and rate studies show that the reactions involve direct reactions with the anions and not solvento-complex intermediates like $Ru(bpy)_2(py)(H_2O)^{2+}$, which do, in fact, provide the basis for the second synthetic route described below.

Perhaps the most appealing aspects of the reactions are their high efficiencies and their specificities. In general, the reactions require only a few hours of photolysis. The workup procedures are simple, and the products are obtained in high yield and purity. In the few cases where impure products were obtained, the impurities proved to be simple salts, e.g., pyridinium hexafluorophosphate or mixed counterions in the complex. The desired ruthenium complexes were almost always formed exclusively if the photolyses were carried out to completion. The reactions were easily monitored spectrophotometrically to ensure that the reactions were complete.

The preparation of the mixed-ligand complex $Ru(bpy)_2(NCS)Cl \cdot 2H_2O$ is worth noting since the photochemical reactions may be especially useful in this type of synthesis. Unfortunately, there are limitations associated with this approach. Weakly bound ligands such as NO_3^- or ClO_4^- are readily displaced, both thermally and photochemically, by anions such as Cl^-.

The second synthetic route makes use of photochemically generated solvento complexes such as $Ru(bpy)_2(py)(OH_2)^{2+}$. We have no rate data, but in solvents such as CH_2Cl_2 the rate of thermal substitution of the aquo ligand by anions is rapid and essentially complete on the time scale of minutes. Use of the solvento intermediates has the advantage that monosubstituted products can be prepared without complications arising from the appearance of disubstituted products.

Another advantage lies in the preparation and isolation of complexes which cannot be prepared by the direct photochemical route because of secondary photochemical reactions. Attempts to prepare $Ru(bpy)_2(py)(NO_2)^+$ by the direct method, for example, failed to produce the desired product, and a mixture of as yet unidentified products was obtained instead. The failure of the direct reaction has been traced to secondary photochemical reactions of $Ru(bpy)_2(py)NO_2^+$, which is produced initially.

As a last point, the indirect route can also be used with neutral entering groups although the ligand must be in large excess and the reactions are usually not as clean. Although other routes are available to the solvento complexes,[11-13,19] the photochemical preparations appear to be the most useful by a considerable degree.

The photochemical details of the reactions described here are clearly intriguing, and our observations provide some suggestions about the perplexing differences in the photochemical behavior of $Ru(bpy)_3^{2+}$ in CH_2Cl_2 as opposed to that observed in H_2O or CH_3CN and between $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$. Complexes like $[Ru(bpy)_2(py)CH_3CN]^{2+}$ and $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ or $[Ru(bpy)_2(OH_2)_2]^{2+}$ are stable, well-characterized species in acetonitrile or water, respectively. Upon visible irradiation, experiments in progress show that $[Ru(bpy)_2(py)_2]^{2+}$ undergoes a relatively efficient photosubstitution reaction in either solvent, yet $Ru(bpy)_3^{2+}$ is photoinert. Both undergo photosubstitution in CH_2Cl_2, but the net photochemistry of $Ru(bpy)_3^{2+}$ can be altered by competitive ring-closure steps as shown by the lack of reactivity with anions such as NO_3^-. In CH_2Cl_2 and other low-polarity solvents, solvation energies or solvation effects must play an important role in determining the photochemical behavior of $Ru(bpy)_3^{2+}$. In particular, with a solvent with as low a dielectric constant as dichloromethane ($D_s = 9$),[20] ion pairing is clearly of importance, and the incorporation of such weakly coordinating anions as ClO_4^- and NO_3^- suggests that the reduction in charge on the complex, e.g., $[Ru(bpy)_2(py)_2]^{2+} + ClO_4^- \xrightarrow{h\nu} [Ru(bpy)_2(py)ClO_4]^+ + py$, may be a strongly influencing factor in the net reactions.

We have investigated the photochemical details of the reactions in CH_2Cl_2. Our results will be fully described in a later paper, but in summary form they are as follows: the reactions involve ion pairs; they occur through an upper, probably d–d, excited state which is thermally populated from the emitting CT state much as proposed by Van Houten and Watts.[3] The lack of a significant entering-group dependence suggests that the substitution step is largely dissociative. In the photochemistry of $Ru(bpy)_2(py)_2^{2+}$ a reasonable picture then emerges where photoexcitation leads to a five-coordinate intermediate, $[Ru(bpy)_2(py)]^{2+}$, which in acetonitrile or water is captured by the solvent. The photochemical details for $Ru(bpy)_3^{2+}$ may be similar except for the complicating feature that reclosure of the chelate ring in the five-coordinate intermediate, $[Ru(bpy)_2(bpy)]^{2+}$, may be too rapid for capture by the solvent. In dichloromethane, where ion pairing is important, capture of the intermediate by the proximal counterion is relatively efficient. This is surprising at first glance, since it is not obvious why for $Ru(bpy)_3^{2+}$ in acetonitrile or water capture by the statistically more numerous solvent molecules in the outer coordination sphere should not be at least equally and probably more efficient. A possible explanation is that $Ru(bpy)_3^{2+}$ does undergo photosubstitution in water or acetonitrile but that the resulting intermediates like $[Ru(bpy)_2(bpy)H_2O]^{2+}$ undergo rapid rechelation. If so, and given the expected small but distinct spectral changes involved (note the data in Table I, for example), it is surprising that such intermediates are not observed routinely in flash-photolysis experiments, especially in acid solution where the protonated intermediate, $[Ru(bpy)_2(bpyH)H_2O]^{3+}$, would be the dominant form.

In fact, a special effect may be operative in relatively nonpolar solvents like dichloromethane. Van Meter and Neumann[21] have suggested that small molecules may actually penetrate into the cavities between the bipyridyl rings in poly(pyridyl) complexes. For anions like Cl^-, anion–solvent interactions are relatively weak as evidenced by lower solvation energies compared to those of polar solvents. The combination of polarization and especially electrostatic attraction for anions like Cl^- within the cavities close to the metal center may be appreciably larger than solvent–anion interactions. The role of the nonpolar solvent could then be viewed as driving the potential entering group into the intramolecular cavities close to the metal ion center. The same effect could lead to entrapment of small polar molecules like water within the cavities.

Further results from the study alluded to above show that only minor differences exist in the emission and absorption spectra and in the excited-state lifetime properties of $Ru(bpy)_3^{2+}$ under photochemical as compared to nonphotochemical conditions. It seems that the entrapped anions in CH_2Cl_2 do not exert a strongly perturbing electronic influence which changes the nature of the excited-state manifold. Rather, the effect that we observe may be a close-in proximal effect where a short-lived, photolabile excited state is captured by a tightly held, essentially intramolecular scavenger.

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Registry No. $[Ru(bpy)_2(t\text{-}Bu(py))_2](PF_6)_2$, 72525-66-7; $[Ru(bpy)_2(py)(NO_2)](PF_6)$, 36309-80-5; $Ru(bpy)_2Cl_2$, 19542-80-4; $[Ru(bpy)_2(py)(NO_3)](PF_6)$, 72378-65-5; $[Ru(bpy)_2(py)_2](PF_6)_2$, 72525-67-8; $[Ru(bpy)_2(py)_2](NO_3)_2$, 72525-68-9; $[Ru(bpy)_2(py)(ClO_4)](ClO_4)$, 72525-70-3; $[Ru(bpy)_2(py)_2](ClO_4)_2$, 63338-39-6; $[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)](PF_6)$, 72525-72-5; $[Ru(bpy)_2(t\text{-}Bu(py))(CF_3CO_2)](PF_6)$, 72525-74-7; $Ru(bpy)_2Cl(NCS)$, 72525-75-8; $[Ru(bpy)_2(py)(NCS)](PF_6)$, 72525-77-0; $[Ru(bpy)_2(py)(OH_2)](PF_6)_2$, 72525-78-1; $[Ru(bpy)_2(py)Cl](PF_6)$, 36413-31-7; $Ru(bpy)_2(NCS)_2$, 66238-39-9; $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$, 55124-54-4; $Ru(bpy)_2Br_2$, 23377-85-7; $[Ru(bpy)_3](PF_6)_2$, 60804-74-2; $[Ru(bpy)_2(py)CH_3CN](PF_6)_2$, 72525-79-2; $Ru(bpy)_2(NCS)Cl$, 72525-75-8; $[Ru(bpy)_2(py)ClO_4]PF_6$, 72525-80-5; $[Ru(bpy)_2(py)CF_3CO_2]PF_6$, 72525-82-7; $[Ru(bpy)_2(t\text{-}Bu(py))H_2O](PF_6)_2$, 72525-84-9; $[Ru(bpy)_2(py)H_2O](PF_6)_2$, 72525-78-1; $[Ru(bpy)_2(t\text{-}Bu(py))NO_3]PF_6$, 72525-86-1; $[Ru(bpy)_2(py)NCS]Cl$, 72525-87-2; $[Ru(bpy)_3](SCN)_2$, 72525-88-3; $[Ru(bpy)_2(py)Br]^+$, 72558-80-6.

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Alkyl Nitrite Complexes of Ruthenium Prepared by Acid–Base Chemistry at the Bound Nitrosyl Group

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The alkyl nitrite complexes $[Ru(bpy)_2(py)N(O)OR]^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine; R = methyl, ethyl, *n*-butyl, isopropyl) have been prepared by reactions involving attack of the corresponding alkoxide ions on the nitrosyl nitrogen in $[Ru(bpy)_2(py)NO]^{3+}$. In the products the alkyl nitrite groups appear to be N bound. From the properties of the complexes, it seems that $d\pi(Ru^{II}) \rightarrow \pi^*(N(O)OR)$ back-bonding is significant and that the alkyl nitrite group is a better π-electron acceptor than the nitro, pyridyl, or acetonitrile groups when bound to Ru(II). The complexes form in dry acetonitrile when both alcohol and base (collidine) are added, $Ru(bpy)_2(py)NO^{3+} + ROH + B \rightarrow Ru(bpy)_2(py)N(O)OR^{2+} + BH^+$, and the reversible nature of the chemistry is seen following the addition of excess acid, $Ru(bpy)_2(py)N(O)OR^{2+} + H^+ \rightarrow Ru(bpy)_2(py)NO^{3+} + ROH$. Once formed, the alkyl nitrite complexes undergo an irreversible, one-electron oxidation (at $\sim$+1.75 V vs. SSCE) and the major products are $[Ru(bpy)_2(py)NO]^{3+}$ and ROH. The chloro analogues $[Ru(bpy)_2(Cl)N(O)OR]^+$ (R = ethyl, isopropyl) have also been prepared, in this case by attack of RO^- on $[Ru(bpy)_2(Cl)NO]^{2+}$. It has proven difficult to characterize the complexes fully, but they appear to have properties similar to those found for the pyridyl complexes.

Introduction

Metal nitrosyl complexes with relatively high NO stretching frequencies (>1850 cm^{-1}) have a sufficiently high degree of NO^+-like ligand character that they undergo a series of reactions involving nucleophilic attack at the nitrosyl group.[1-5] The chemistry involved is often similar to reactions observed for relatively electron-deficient compounds containing the isoelectronic CO ligand.[6] Attack by OH^-, SH^-, N_3^-, and N_2H_4 has been found for metal nitrosyl complexes with appropriately high NO stretching frequencies.[2] Complexes of the type $[Ru(bpy)_2(L)NO]^{n+}$ (bpy = 2,2′-bipyridine; L = Cl^-, pyridine) (ν(NO) > 1930 cm^{-1}) fit well into this reactivity pattern in that their reactions with nucleophiles such as OH^-, N_3^-, aromatic amines, and phenoxide ion have been reported.[7-11] The reactions with OH^- are of interest in the present study because oxidation of the resulting nitro complexes, e.g., $[Ru^{II}(bpy)_2(py)NO_2]^+$, to Ru(III) gives short-lived intermediates which have been reported to act as net oxygen atom donors in the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide.[12,13]

Reed and Roper have reported[14] a series of acid–base reactions between alcohols and the nitrosyl complex $[IrCl_3(PPh_3)_2NO]^+$ which gave as products the complexes $IrCl_3(PPh_3)_2N(O)OR$, in which there are N-bound alkyl nitrite ligands. Similar reactivity for the ruthenium complex $[Ru(bpy)_2(py)NO]^{3+}$ was suggested by spectral changes observed when the complex was treated with alcohols under basic conditions. Isolation and characterization of the products seemed to be a worthwhile extension of the chemistry of the bound nitrosyl group. Of potentially more importance were the redox properties of the resulting complexes. As mentioned above, the analogous Ru(III) nitro complexes are known to

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