Separation of Positional Isomers of Oxidation Catalyst Precursors

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A series of polypyridyl ruthenium complexes of the general formula $[Ru(tpy)(bpy')Cl]^+$ where tpy is 2,2′:6′,2″-terpyridine and bpy′ is 4-carboxy-4′-methyl-2,2′-bipyridine (4-CO_2H-4′-Mebpy), a proline derivative (4-CO-Pra-(Boc)(OMe)-4′-Mebpy), or 4-((diethoxyphosphinyl)methyl)-4′-methyl-2,2′-bipyridine (4-$CH_2PO_3Et_2$-4′-Mebpy) are prepared. For each complex, two isomers exist, and these are separated chromatographically. The structure of the hexafluorophosphate salt of *cis*-$[Ru(tpy)(4\text{-}CO_2H\text{-}4'\text{-}Mebpy)Cl]^+$, *cis*-**1**, is determined by X-ray crystallography. The salt crystallizes in the monoclinic space group *Cc* with $a = 12.4778(6)$ Å, $b = 12.6086(6)$ Å, $c = 20.1215(9)$ Å, $\beta = 107.08200(1)°$, $Z = 4$, $R = 0.058$, and $R_w = 0.072$. The structures of the remaining complexes are assigned by ^{1}H NMR comparisons with *cis*-**1**. The complexes are potentially important precursors for the incorporation of $Ru^{IV}{=}O^{2+}$ oxidants into polymers or peptides or for their adsorption onto oxide surfaces. Preliminary electrochemical results for the isomers of $[Ru(tpy)(4\text{-}CH_2PO_3H_2\text{-}4'\text{-}Mebpy)(H_2O)]^{2+}$, **4**, adsorbed on ITO (In_2O_3:Sn) surfaces add support to a recently proposed electron-transfer mechanism involving cross-surface proton-coupled electron transfer.

Introduction

There is diverse redox chemistry of high oxidation state ruthenium−polypyridyl−oxo complexes such as *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru^{IV}(tpy)(bpy)(O)]^{2+}$ (where bpy = 2,2′-bipyridine, py = pyridine, and tpy = 2,2′:6′,2″-terpyridine),[1−12] which are accessible by sequential electron−proton loss from the corresponding aqua complexes.

We are interested in the evolution of this chemistry as related to the incorporation of oxo reagents and their precursors into new chemical environments. Recently we showed that $[Ru^{II}(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)]^{2+}$ could be adsorbed onto ITO (In_2O_3:Sn) electrodes and demonstrated that oxidation of $Ru^{III}{-}OH^{2+}$ to $Ru^{IV}{=}O^{2+}$ occurs vis proton-coupled electron transfer.[13] We have also developed procedures for derivatizing polystyrene polymers and oligoprolines with related polypyridyl complexes.[14−18] We are currently interested in incorporating oxo precursors as components of complex molecular assemblies based on these materials for possible applications in energy conversion or the creation of multiple-oxo reagents.

Much of this chemistry relies on coupling, either to a surface, typically through phosphonic or carboxylic acid substituted ligands, or through amide links to polymers or oligoprolines. The key precursors for amide coupling are complexes containing ligands with carboxylic acid substituents.[14−18]

Derivatives of $[Ru^{II}(tpy)(bpy)(H_2O)]^{2+}$ are particularly appealing for this work because of the stability of this complex and the reactivity of its $Ru^{IV}{=}O^{2+}$ form. While suitable monoderivatized versions of both tpy and bpy are known, the synthesis of tpy ligands is more complex than that of their bpy analogues. For example, the synthesis of 2,2′:6′,2″-terpyridine-4′-carboxaldehyde from commercially available starting materials involves several steps,[19] while that for 4′-methyl-2,2′-bipyridine-4-carboxaldehyde requires only one.[20] There is a disadvantage in using mono-CO_2H/PO_3H_2-bpy derivatives in that an isomerism arises between the isomers differing with regard to the relative dispositions of the $Ru^{II}{-}OH_2$ bond axis and the pyridyl ring bearing the acid substituent. The isomers for the aqua complex precursor $[Ru^{II}(tpy)(4\text{-}CO_2H\text{-}4'\text{-}Mebpy)Cl]^+$ are illustrated in Figure 1.

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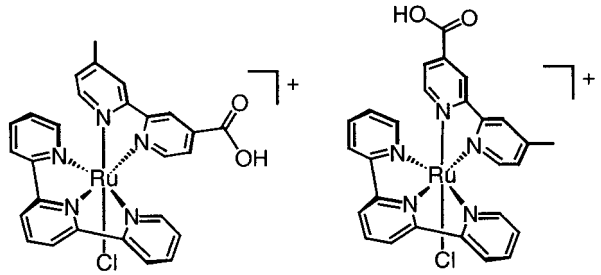

Figure 1. Cis and trans isomers of $[Ru^{II}(tpy)(4\text{-}CO_2H\text{-}4'\text{-}Mebpy)Cl]^+$.

We report here the preparation and separation of these isomers, their proline derivatives, and the corresponding isomers of the phosphonic diester derivatized complex $[Ru^{II}(tpy)(4\text{-}CH_2PO_3Et_2\text{-}4'\text{-}Mebpy)Cl]^+$. The electrochemical properties of the isomers of $[Ru^{II}(tpy)(4\text{-}CH_2PO_3H_2\text{-}4'\text{-}Mebpy)(H_2O)]^{2+}$ adsorbed on ITO electrodes are also reported.

Experimental Section

Materials. Solvents and reagents were obtained from commercial sources and used as received. Tetra-*n*-butylammonium hexafluorophosphate (TBAH; recrystallized three times from ethanol) and ferrocene (Fc; sublimed before use) were obtained from Aldrich. $Ru(tpy)Cl_3$, 4-carboxy-4′-methyl-2,2′-bipyridine (4-CO_2H-4′-Mebpy), (2*S*,4*S*)-4-amino-1-(*tert*-butoxycarbonyl)proline methyl ester hydrochloride (Boc-Pra−OCH_3), and 4-(bromomethyl)-4′-methyl-2,2′-bipyridine were synthesized according to published procedures.[20−23]

Instrumentation and Measurements. ^1H NMR spectra were recorded on a Bruker Aspect 3000, a Varian Gemini 300 MHz, or a Bruker AC/200 200 MHz spectrometer fitted with a 5 mm probe. Spectra were recorded in CD_3OD, DMSO-d_6, and CD_3CN and referenced to solvent resonances. The $^1H-^1H$ correlated 2D NMR spectrum was obtained on a Bruker AMX 300 MHz spectrometer. UV−visible spectra were recorded in 1 cm quartz cells on a Hewlett-Packard HP-8452A diode array spectrophotometer. Electrochemical measurements were conducted on an EG&G PAR model 273 potentiostat. Measurements on complexes **1**−**3** were made in DMF or CH_3CN, 0.1 M in $[N(n\text{-}C_4H_9)_4]PF_6$ (TBAH) as the electrolyte, in a three-compartment cell by using a platinum coil counter electrode, a platinum disk or glassy carbon working electrode (polished with 0.3 μm alumina), and a $Ag/AgNO_3$ (0.01 M in acetonitrile) reference electrode (+0.31 V vs SSCE; calibrated relative to the ferrocene$^{+/0}$ couple). Cyclic voltammograms were obtained at a sweep rate of 100 mV/s. For **4**, measurements were made in aqueous 0.1 M $NaClO_4$ in a two-compartment cell by using a platinum gauze counter electrode and an SSCE reference electrode with either a glassy carbon or a surface-modified ITO as the working electrode. Cyclic voltammograms were obtained at a sweep rate of 10 mV/s in experiments comparing isomers. Surface coverage, Γ (mol/cm^2), was measured by using a scan rate of 200 mV/s and electrodes of known surface area. The area under the voltammetric waves was integrated and divided by electron charge and the scan rate The $E_{1/2}$ values were calculated as averages of the oxidative and reductive peak potentials, $(E_{p,a} + E_{p,c})/2$. Microanalyses were performed by Oneida Research Services, Inc. (Whitesboro, NY).

Syntheses. 4-((Diethoxyphosphinyl)methyl)-4′-methyl-2,2′-bipyridine 4-$CH_2PO_3Et_2$-4′-Mebpy. This ligand was prepared by modifying a literature procedure.[24] 4-(Bromomethyl)-4′-methyl-2,2′-bipyridine was heated at reflux in freshly distilled diethyl phosphite for 7 h. Solvent was removed under vacuum, diethyl ether was added to the residue, and the mixture was refrigerated overnight. The resulting white solid that formed was collected and loaded onto an alumina column with a minimal amount of $CHCl_3$ as the solvent. Elution with ethyl acetate gave 4-$CH_2PO_3Et_2$-4′-Mebpy.

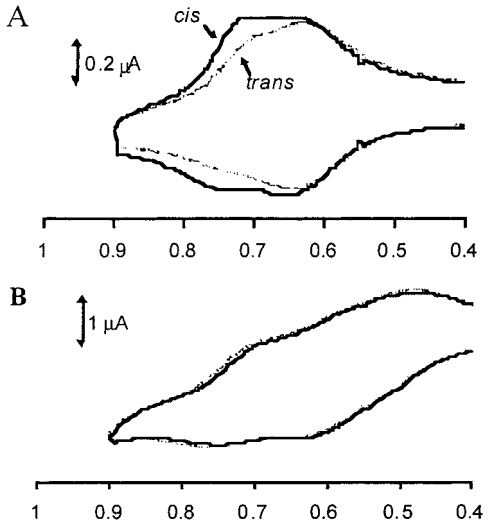

Figure 2. Cyclic voltammograms vs SSCE at a scan rate of 10 mV/s of *cis*- (—) and *trans*-$[Ru^{II}(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)]^{2+}$ (- - -): (A) sample fully loaded on ITO electrodes in 0.1 M $NaClO_4$, with $\Gamma = 0.7 \times 10^{-10}$ mol/cm^2; (B) 0.6 mmol solutions in 0.1 M $NaClO_4$ at glassy carbon working electrodes.

$[Ru^{II}(tpy)(4\text{-}CO_2H\text{-}4'\text{-}Mebpy)Cl]PF_6$ (1). This salt was prepared by modifying a literature procedure for $[Ru^{II}(tpy)(bpy)Cl]PF_6$.[5] Following formation of the complex, hot filtration, and solvent reduction, the chloride salt was precipitated by the addition of acetone (800 mL) and cooling (4 °C) for 2 h. The brown solution was decanted, and the solid was filtered off onto a fine-porosity frit and rinsed with acetone and diethyl ether. The product dissolved in a minimum amount of methanol was added to a solution of deionized water saturated with ammonium hexafluorophosphate. A few drops of dilute aqueous HCl were added to ensure protonation of the 4-CO_2H-4′-Mebpy ligand. Methanol was removed by rotary evaporation, and the mixture was cooled to 4 °C. The violet precipitate that appeared was filtered off and rinsed with dilute, acidic ammonium hexafluorophosphate in water and then with diethyl ether. The solid was used as a precursor in subsequent reactions. Gel filtration chromatography (Sephadex LH-20, methanol) was used to remove trace impurities from the complex. A yellow band (solvento complex) was eluted first, followed by an orange band of $[Ru^{II}(tpy)_2]^{2+}$. Violet bands, containing the two positional isomers, were collected together, and the solvent was removed by rotary evaporation.

Isolation of *cis*-$[Ru^{II}(tpy)(4\text{-}CO_2H\text{-}4'\text{-}Mebpy)Cl]PF_6$ (*cis*-1). Acetonitrile (∼15 mL) was added to ∼40 mg of the isomeric mixture. Insoluble particles were removed by filtration through a Kimwipes tissue plug in a pipet, and solvent was removed by rotary evaporation. This process was repeated twice, and the acetonitrile solution (∼3 mL) was chromatographed (Sephadex LH-20 gel; 95:5 (v:v) methanol/acetonitrile, 30 cm × 5 cm^2 column). The first band contained mainly the *cis* isomer; the second band contained a mixture of the two and was removed with 50:50 methanol/acetonitrile. This process was repeated with the first band three to five times to isolate the pure isomer, which precipitated following reduction of the solvent volume to ∼2−3 mL by rotary evaporation. Anal. Calcd for $C_{29}H_{24}ClF_6N_6O_2PRu$: C, 45.23; N, 10.91; H, 3.14. Found: C, 45.27; N, 10.84; H, 3.22. ^1H NMR (CD_3OD, δ) (corresponding carbon labels from the ORTEP drawing in Figure 2 are given in parentheses): 2.40, 3H, s, bpy-CH_3 (C47); 6.93, 1H, d, bpy-H5′ (C43); 7.20, 1H, d, bpy-H6′ (C42); 7.32, 2H, t, tpy-H5 (C13, C35); 7.70, 2H, d, tpy-H6 (C12, C36); 7.93, 2H, t, tpy-H4 (C14, C34); 8.17, 1H, t, tpy-H4′ (C24); 8.41, 1H, d, bpy-H5 (C55); 8.46, 1H, s, bpy-H3′ (C45); 8.52, 2H, m, tpy-H3 (C15, C33); 8.65, 2H, d, tpy-H3′ (C23, C25); 9.15, 1H, s, bpy-H3 (C53); 10.36, 1H, d, bpy-H6 (C56).

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Isolation of *trans*-[Ru^{II}(tpy)(4-CO$_2$H-4′-Mebpy)Cl]PF$_6$ (*trans*-1). Methanol was added to the isomeric mixture. Insoluble particles were removed by filtration through a Kimwipes tissue plug in a pipet, and the solution was reduced by rotary evaporation to ~3 mL and chromatographed (Sephadex LH-20 gel; methanol:acetonitrile gradient, 30 cm × 5 cm^2 column). Acetonitrile (100%) was first flashed through the column to quickly separate from the mixture the methanol used to add the complex to the column. After distinct separation of a broad band from a thin band, 95:5 (v:v) acetonitrile/methanol (200 mL) was flashed through the column, followed by 90:10 acetonitrile/methanol (100 mL). The broad band was allowed to travel without added pressure until it was nearly eluted, and the methanol content was increased (in the sequence 80:20, 70:30, 60:40 for acetonitrile:methanol). The trans isomer was eluted as a narrow band, and the solvent was removed by rotary evaporation. This procedure was repeated three to five times to achieve the pure isomer. ^{1}H NMR (CD$_3$OD, δ): 2.82, 3H, s, bpy-CH$_3$; 7.32, 2H, t, tpy-H5; 7.36, 2H, s, bpy-H5, bpy-H6; 7.69, 2H, d, tpy-H6; 7.85, 1H, d, bpy-H5′; 7.93, 2H, t, tpy-H4; 8.14, 1H, t, tpy-H4′; 8.51, 2H, m, tpy-H3; 8.61, 1H, s, bpy-H3′; 8.63, 2H, d, tpy-H3′; 8.74, 1H, s, bpy-H3; 9.97, 1H, d, bpy-H6′.

(2*S*,4*S*)-1-(*tert*-Butoxycarbonyl)-4-[1-(chloro(2,2′:6′,2″-terpyridine)-ruthenium(II)io)-4′-methyl-2,2′-bipyridine-4-carboxamido]-L-proline Methyl Ester Hexafluorophosphate, [Boc-Pra[Ru(tpy)(4-CO-4′-Mebpy)Cl]−OCH$_3$]PF$_6$ (2). [Ru^{II}(tpy)(4-CO$_2$H-4′-Mebpy)Cl]PF$_6$ (0.32 mmol), Boc-Pra−OCH$_3$ (0.32 mmol), (benzotriazolyl)oxy)tris-(dimethylamino)phosphonium hexafluorophosphate (BOP; 0.96 mmol), 1-hydroxybenzotriazole (HOBt; 0.96 mmol), *N*-methylmorpholine (NMM; 1.44 mmol), and 4-(dimethylamino)pyridine (DMAP; 0.08 mmol) were stirred in DMF (6 mL) for 47 h. The solvent was removed under vacuum to give a red/maroon oil. This residue was purified by alumina chromatography using toluene/acetonitrile (1:1) as the eluent. Anal. Calcd for $C_{38}H_{39}ClF_6N_7O_5PRu$: C, 47.78; N, 10.26; H, 4.12. Found: C, 47.78; N, 10.26; H, 4.12. The isomeric mixture was loaded onto a second alumina column and eluted with 1:1 toluene/acetonitrile with a slow eluent flow rate. *trans*-**2** eluted from the column first, followed by *cis*-**2**, the collection of which was completed by eluting with 1:3 toluene/acetonitrile. ^{1}H NMR for *trans*-**2** (CD$_3$CN, δ): 1.35/1.37, 6H/3H, s/s, Boc-CH$_3$; 2.00, 1H, m, β-CH$_2$; 2.52, 1H, m, β-CH$_2$; 2.76, 3H, s, bpy-CH$_3$; 3.40, 1H, m, δ-CH$_2$; 3.61, 1H, m, δ-CH$_2$; 3.67, 3H, s, OCH$_3$; 4.24, 1H, m, α-CH; 4.51, 1H, m, γ-CH; 7.14, 1H, d, bpy-H5; 7.25, 2H, t, tpy-H5; 7.45, 1H, d, bpy-H6; 7.62, 2H, d, tpy-H6; 7.82, 1H, d, bpy-H5′; 7.87, 2H, t, tpy-H4; 8.08, 1H, t, tpy-H4′; 8.36, 2H, d, tpy-H3; 8.48, 2H, d, tpy-H3′; 8.54, 1H, s, bpy-H3; 8.59, 1H, s, bpy-H3′; 9.99, 1H, d, bpy-H6′. ^{1}H NMR for *cis*-**2** (CD$_3$CN, δ): 1.40/1.45, 6H/3H, s/s, Boc-CH$_3$; 2.19, 1H, m, β-CH$_2$; 2.35, 3H, s, bpy-CH$_3$; 2.72, 1H, m, β-CH$_2$; 3.60, 1H, m, δ-CH$_2$; 3.79, 3H, s, OCH$_3$; 3.80, 1H, m, δ-CH$_2$; 4.37, 1H, m, α-CH; 4.74, 1H, m, γ-CH; 6.84, 1H, d, bpy-H5′; 7.15, 1H, d, bpy-H6′; 7.24, 2H, t, tpy-H5; 7.65, 2H, d, tpy-H6; 7.87, 2H, t, tpy-H4; 8.10, 1H, t, tpy-H4′; 8.17, 1H, d, bpy-H5; 8.31, 1H, s, bpy-H3′; 8.37, 2H, d, tpy-H3; 8.49, 2H, d, tpy-H3′; 8.85, 1H, s, bpy-H3; 10.32, 1H, d, bpy-H6.

[Ru^{II}(tpy)(4-CH$_2$PO$_3$Et$_2$-4′-Mebpy)Cl]PF$_6$ (3). This salt was prepared by a modification of a literature procedure for [Ru^{II}(tpy)(bpy)-Cl]PF$_6$. The synthesis was performed on $^1/_{20}$ the scale of the published procedure.[5] After hot filtration, saturated aqueous ammonium hexafluorophosphate (3 mL) was added and ethanol was removed under reduced pressure to give a red/brown precipitate. The crude isomeric mixture was loaded onto an alumina column and eluted with toluene/acetonitrile (1:1) by using a slow eluent flow rate. *trans*-**3** eluted first, followed by *cis*-**3**. Anal. Calcd for *trans*-**3**, $C_{31}H_{32}ClF_6N_5O_3P_2Ru$: C, 44.59; N, 8.39; H, 3.86. Found: C, 45.03; N, 8.02; H, 3.98. ^{1}H NMR for *trans*-**3** (CD$_3$CN, δ): 1.04, 6H, t, PO$_3$Et$_2$-CH$_3$; 2.74, 3H, s, bpy-CH$_3$; 3.14, 2H, d, bpy-CH$_2$; 3.87, 4H, m, PO$_3$Et$_2$-CH$_2$; 6.84, 1H, d, bpy-H5′; 7.17, 1H, d, bpy-H6′; 7.25, 2H, t, tpy-H5; 7.66, 2H, d, tpy-H6; 7.79, 1H, d, bpy-H5; 7.86, 2H, t, tpy-H4; 8.06, 1H, t, tpy-H4′; 8.18, 1H, s, bpy-H3′; 8.36, 2H, d, tpy-H3; 8.42, 1H, s, bpy-H3; 8.47, 2H, d, tpy-H3′; 9.99, 1H, d, bpy-H6. λ_{max}, nm (ϵ), for *trans*-**3**: 508 (15 000). ^{1}H NMR for *cis*-**3** (CD$_3$CN, δ): 1.31, 6H, t, PO$_3$Et$_2$-CH$_3$; 2.32, 3H, s, bpy-CH$_3$; 3.56, 2H, d, bpy-CH$_2$; 4.15, 4H, m, PO$_3$Et$_2$-CH$_2$; 6.78, 1H, d, bpy-H5; 7.09, 1H, d, bpy-H6; 7.25, 2H, t, tpy-H6; 7.66, 2H, d, tpy-H6; 7.87, 1H, d, bpy-H5′; 7.86, 2H, t, tpy-H4; 8.06, 1H, t, tpy-H4′; 8.14, 1H, s, bpy-H3; 8.36, 2H, d, tpy-H3; 8.49, 1H, s, bpy-H3′; 8.47, 2H, d, tpy-H3′; 10.08, 1H, d, bpy-H6′. λ_{max}, nm (ϵ), for *cis*-**3**: 508 (15 000).

Table 1. Summary of Crystal Data, Intensity Collection Details, and Structure Refinement Parameters for *cis*-[Ru^{II}(tpy)(4-CO$_2$H-4′-Mebpy)Cl]PF$_6$

empirical formula	$C_{29}H_{24}ClF_6N_6O_2PRu$	abs coeff μ (mm^{-1})	0.74
fw	770.03	F(000)	1541.03
a (Å)	12.4778(6)	$2\theta_{max}$ (deg)	50.00
b (Å)	12.6086(6)	no. of total reflns	11 384
c (Å)	20.1215(9)	no. of unique reflns	5177
β (deg)	107.08200(0)	no. of refined reflns[a]	4389
V (Å^3)	3026.01(25)	merging R value	0.083
Z	4	no. of atoms	70
crystal system	monoclinic	no. of parameters	413
space group	*Cc*	R (%)[b]	0.058
crystal size (mm)	0.20 × 0.20 × 0.20	R_w (%)[c]	0.072
ρ_{calcd} (Mg m^{-3})	1.690	goodness of fit[d]	1.73
radiation (λ (Å))	Mo Kα (0.710 73)	deepest hole (e/Å^3)	−1.040
collection temp (°C)	−100	highest peak (e/Å^3)	1.560

[a] $I_{net} > 3\sigma(I_{net})$. [b] $R = \sum(|F_o - F_c|)/\sum|F_o|$. [c] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [d] GoF $= [\sum w(F_o - F_c)^2/(n_{reflns} - n_{params})]^{1/2}$.

***cis*- and *trans*-[Ru^{II}(tpy)(4-CH$_2$PO$_3$H$_2$-4′-Mebpy)(H$_2$O)]$^{2+}$.** Both isomers of this complex were prepared by modification of a literature procedure for the synthesis of [Ru^{II}(tpy)(4,4′-(PO$_3$H$_2$)$_2$bpy)(H$_2$O)]$^{2+}$.[13] In each experiment, 20 mg of *cis*- (or *trans*-) [Ru^{II}(tpy)(4-CH$_2$PO$_3$Et$_2$-4′-Mebpy)Cl]PF$_6$ was heated at reflux in 15 mL of 4 M HCl for 14−18 h. Water and HCl were removed by rotary evaporation and then under vacuum for 24 h to ensure complete removal of HCl. The product was redissolved in acetone/water (15 mL, 1:1), and 1 equiv of AgClO$_4$ was added. The solution was heated at reflux for 1 h and filtered to remove AgCl. Solvent was then removed, the product was redissolved in 0.1 M HClO$_4$, and the solution was diluted to 25 mL in a volumetric flask. λ_{max} = 484 nm ($\epsilon \sim 9600$) for both isomers.

X-ray Crystallography. X-ray-quality crystals of *cis*-[Ru^{II}(tpy)(4-CO$_2$H-4′-Mebpy)Cl]PF$_6$ were obtained by slow diffusion of ether into a methanol/acetonitrile solution of the complex. A crystal of dimensions 0.20 mm × 0.20 mm × 0.20 mm was used for the structure determination. Cell dimensions were obtained from 8192 reflections, for 2θ angles in the range 3−50°, and intensity data were collected by using a Bruker SMART diffractometer in the ω-scan mode. A total of 11 384 reflections were obtained. Of the 5177 unique reflections, 4389 had $I > 3\sigma(I)$. Correction was made for absorption by using SADABS.

The structure was solved by direct methods with the NRCVAX system.[25−27] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalents of the carrier carbon atoms.

Crystallographic data are listed in Table 1.

Results

Reaction between Ru(tpy)Cl$_3$ and 4-CO$_2$H-4′-Mebpy in 1:3 ethanol/water gave a mixture of the two isomers of [Ru^{II}(tpy)-(4-CO$_2$H-4′-Mebpy)Cl]PF$_6$. This can be seen most clearly in the ^{1}H NMR spectrum in the 9.9−10.4 ppm region where two doublets are observed. These doublets, one for each isomer, arise from the bipyridine hydrogen atom in the 6-position of the pyridine group, cis to coordinated chloride. Similar low-field shifts were previously observed in the spectra of ruthenium polypyridyl complexes containing a coordinated chloride[14,28−30]

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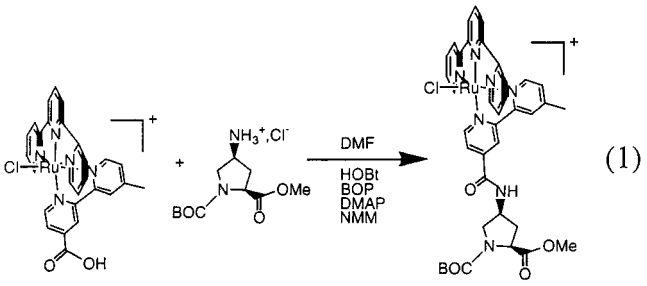
and are attributable to a proximal effect of the chlorine on this hydrogen atom. Isomeric ratios for this mixture were typically between 3:2 and 2:1, with the dominant isomer having the higher downfield resonances.

The separation of *cis*- and *trans*-**1** was based largely on solubility differences. The major isomer is more soluble in acetonitrile, and the minor isomer is more soluble in methanol. Their separation is difficult, possibly due to hydrogen bonding between the isomers. Evidence for this is the fact that the minor isomer is more soluble in acetonitrile in the presence of the major isomer.

The isomer separation procedure was monitored by ^{1}H NMR spectroscopy. The major isomer was tentatively assigned as *cis*-**1** on the basis of the different effects of the CH_3 and CO_2H substituents on the pyridyl resonances. Carboxylic acid groups typically induce larger downfield shifts than alkyl substituents. According to this criterion, the cis isomer, with the CO_2H-substituted ring closest to Cl, is the origin of the downfield resonance at 10.37 ppm. The X-ray crystal structure of the major isomer of **1** confirmed this assumption, showing the major isomer to be *cis*-**1**.

An isomeric mixture of **1** was used to couple it to Boc-protected aminoproline by using standard amide-coupling reagents. The reaction for the cis isomer is shown in eq 1. The



isomeric ratio in **1** was carried over to proline-coupled complex **2** as judged from the resonances in the 9.9−10.4 ppm region of its ^{1}H NMR spectrum. The isomers were separated by chromatography on alumina and structures assigned by comparison of the respective bpy-CH_3 and 9.9−10.4 ppm resonances (2.76, 9.95 ppm; 2.35, 10.32 ppm) with those of the corresponding isomers of **1** (*trans*-**1** 2.82, 9.97 ppm; *cis*-**1** 2.40, 10.36 ppm). As discussed above, the different downfield resonances for the isomers result from the different substituents on the pyridyl rings proximal to Cl. The variation in CH_3 resonances arises from a difference in tpy ring-current effects on these substituents in the two isomers.

Reaction of Ru(tpy)Cl_3 with 4-$CH_2PO_3Et_2$-4′-Mebpy in 1:3 ethanol/water gave an approximately 1:1 isomeric mixture of [Ru^{II}(tpy)(4-$CH_2PO_3Et_2$-4′-Mebpy)Cl]PF_6 (**3**). As for **2**, the isomers were separated by adsorption column chromatography on alumina. Despite the even abundances of the isomers in the crude product, the isolated yield of *trans*-**3** was significantly greater than that of *cis*-**3**. The cis isomer appears to have a greater propensity for irreversible adsorption during chromatography on alumina. In the ^{1}H NMR spectra, substituent effects on the downfield resonances are smaller in magnitude than those for **1** and **2**, but they do exist, allowing for assignment of the cis and trans isomers of **3**.

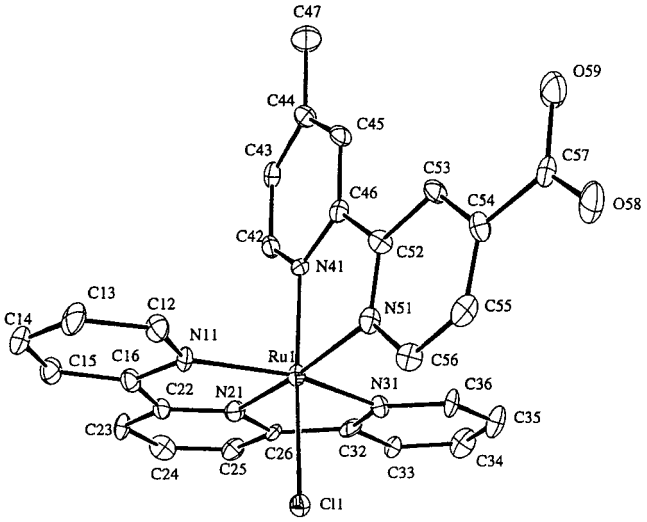


Figure 3. ORTEP drawing of the cationic unit *cis*-[Ru^{II}(tpy)(4-CO_2H-4′-Mebpy)Cl]$^+$ with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

UV/vis spectra and electrochemistry for both isomers of **1**−**3** are essentially the same. For example, for **1**, $\lambda_{max} = 510$ nm for the lowest energy, intense Ru → tpy band and $E_{1/2} = 0.74$ V vs SSCE for the Ru^{III}/Ru^{II} couple, for both isomers.

The two isomers of **3** were heated at reflux in 4 M HCl to hydrolyze the phosphonic diester groups, giving the respective phosphonic acid complexes. The aqua complexes, *cis*- and *trans*-**4**, were then formed by Ag^+-assisted removal of the chloro ligand. Solutions of known concentrations in 0.1 M $HClO_4$ were prepared from the resulting aqua complexes. ITO was exposed to these solutions for at least 24 h to form monolayer coatings for electrochemical studies.

Electrochemical experiments were performed on the two isomers of **4** both at pH 6.10 in solution and both adsorbed on ITO at monolayer coverages with $\Gamma = 0.7 \times 10^{-10}$ mol/cm^2 as determined by cyclic voltammetry. Figure 2A shows cyclic voltammograms of ITO electrodes which had been fully covered with *cis*- and *trans*-**4**. The peak currents for the Ru^{III}/Ru^{II} couples are consistent with approximately equal surface coverages of each isomer. By contrast, the current for the Ru^{IV}/Ru^{III} couple of the cis isomer is significantly greater than that for the trans isomer. Cyclic voltammograms of the two isomers in solution at the same concentration are superimposed, as shown in Figure 2B.

X-ray Crystallography. The major isomer of **1** crystallizes in the monoclinic space group *Cc* and contains one [Ru^{II}(tpy)-(4-CO_2H-4′-Mebpy)Cl]$^+$ cation and one PF_6^- anion in the asymmetric unit. A perspective view with the atom-labeling scheme for [Ru^{II}(tpy)(4-CO_2H-4′-Mebpy)Cl]$^+$ is shown in Figure 3, and a list of selected bond lengths and angles is given in Table 2.

Importantly, the structure confirms that the major isomer of **1** is the cis isomer, with the CO_2H-substituted pyridine ring cis to chloride. Other features of this structure are typical of other [Ru(tpy)(bpy)X]$^{n+}$ complexes.[31] The central Ru−N21 tpy bond length of 1.968(8) Å is significantly shorter than the other Ru−N distances, which range from 2.048(8) to 2.105(8) Å. The different Ru−N distances for the 4-CO_2H-4′-Mebpy ligand of 2.048(8) and 2.105(8) Å are consistent with the trans influence

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[Ru^{II}(tpy)(4-CO_2H-4′-Mebpy)Cl]PF_6 Based on the Labeling Scheme in Figure 3

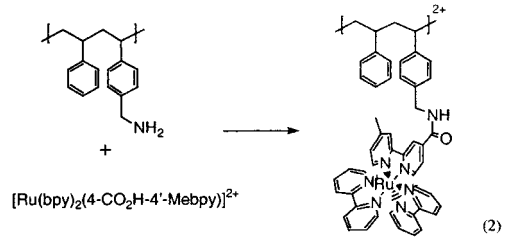
Ru1−Cl1	2.437(3)	C16−C22	1.469(15)	C46−C52	1.479(12)
Ru1−N11	2.069(7)	N21−C22	1.326(12)	N41−C46	1.404(13)
Ru1−N21	1.968(8)	N21−C26	1.406(13)	C44−C47	1.469(15)
Ru1−N31	2.088(7)	C26−C32	1.443(15)	C54−C57	1.507(13)
Ru1−N41	2.048(8)	N31−C32	1.360(12)	C57−O59	1.315(13)
Ru1−N51	2.105(8)	N51−C52	1.342(13)	C57−O58	1.175(12)
N11−C16	1.369(13)				

Cl1−Ru1−N11	89.49(22)	N11−Ru1−N51	101.4(3)
Cl1−Ru1−N21	92.93(23)	N21−Ru1−N31	80.7(3)
Cl1−Ru1−N31	90.51(22)	N21−Ru1−N41	93.6(3)
Cl1−Ru1−N41	173.4(3)	N21−Ru1−N51	173.4(3)
Cl1−Ru1−N51	93.62(24)	N31−Ru1−N41	91.8(3)
N11−Ru1−N21	78.8(3)	N31−Ru1−N51	91.1(3)
N11−Ru1−N31	159.4(3)	N41−Ru1−N51	79.9(3)
N11−Ru1−N41	90.5(3)		

of the short Ru−N21 tpy bond. There are no significant distortions from planarity in the aromatic rings of the 4-CO_2H-4′-Mebpy or tpy ligands.

Discussion

A useful procedure has been developed for derivatizing amine-containing polystyrene polymers by amide coupling to polypyridyl complexes, eq 2.[14−16] Typically, the acid group is



(2)

incorporated to form 4-carboxy-4′-methyl-2,2′-bipyridine (4-CO_2H-4′-Mebpy) as a ligand. The resulting derivatized polymers have proven to be very useful in the study of intrastrand electron and energy transfer.[14,32,33] This leads to the accomplishment of one of the goals of this work. Following incorporation of [Ru^{II}(tpy)(4-CO_2H-4′-Mebpy)Cl]$^+$ into these polymer arrays, replacement of Cl^- by H_2O and oxidation to Ru^{IV}═O^{2+} will provide access to a family of multioxo reagents in which orientational effects on reactivity can be studied by using the derivatized isomers of **1**.

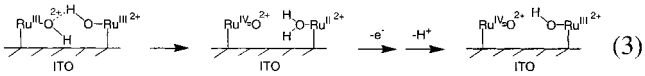
A second approach to the design of multifunctional assemblies is the use of peptide synthesis, in this case to give oligoproline arrays.[17,18] A major advantage of the oligopeptide approach is the spatial control of molecular design by using stepwise solid-phase peptide synthesis. The key precursors for the incorporation of ruthenium complexes are boc-protected prolines derivatized through amide coupling and having redox-active substituents.[22] While isomeric separation of carboxylic acid complexes is required for polymer synthesis, isomer mixtures can first be coupled to proline before isomer separation in the peptide precursors. This proved to be less time consuming than isomer separation for [Ru^{II}(tpy)(4-CO_2H-4′-Mebpy)Cl]$^+$.

The synthesis of **2** provides an important precursor for the investigation of oligoprolines containing Ru^{IV}═O^{2+}. Goals in this work are to use the helical structures of proline I and proline II to control the spatial separation between nearest-neighbor Ru^{IV}═O^{2+} groups (Figure 4) and to prepare a family of "super" oxidants containing three, four, or even more Ru^{IV}═O^{2+} groups.

A third application that we envisage is modification of oxide surfaces derivatized by adsorption of bpy−phosphonic acid complexes. Compared to bpy−carboxylic acid complexes, phosphonic acid derivatives offer the advantages of stronger surface adhesion, including stability in aqueous solutions, presumably due to phosphonate ester formation on the oxide surfaces.[34] While **1** and its related aqua complex could be used for surface-binding studies, we anticipate that the analogous aqua complex derived from **3** will form more robust monolayer structures.

Separation of the isomers of **3**, subsequent ester hydrolysis, and formation of the aqua complexes *cis*- and *trans*-**4** allowed for electrochemical studies of these complexes both in solution and on ITO surfaces. While the solution electrochemistries are similar for *cis*- and *trans*-**4**, significant differences are seen in the electrochemical responses of the two isomers when adsorbed on ITO surfaces, in particular, for the Ru^{IV}═O^{2+}/Ru^{III}−OH^{2+} couples (Figure 2).

For [Ru^{II}(tpy)(4,4′-$(PO_3H_2)_2$bpy)(H_2O)]$^{2+}$ on ITO, at less than complete surface coverage, oxidation to Ru^{IV}═O^{2+} is not observed, since direct Ru^{III}−OH^{2+} → Ru^{IV}═OH^{3+} oxidation occurs past the solvent limit. For the case of fully loaded surfaces, a Ru^{IV}═O^{2+}/Ru^{III}−OH^{2+} wave does appear due to disproportionation. It occurs by cross-surface proton-coupled electron transfer, eq 3, followed by Ru^{II}−$OH_2{}^{2+}$ → Ru^{III}−OH^{2+}



(3)

oxidation.[13] Proton-coupled electron transfer involves quantum mechanical tunneling and requires close contact to be facile.[35−40] While a related mechanism can be invoked to explain the surface voltammograms for *cis*- and *trans*-**4**, the difference in their voltammograms requires further explanation.

Invoking proton-coupled electron transfer as the key step in the formation of Ru^{IV}═O requires an understanding of the rate-controlling factors in disproportionation, eq 4. A recent report

$$2Ru^{III}-OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{IV}{=}O^{2+} + Ru^{II}-OH_2{}^{2+} \qquad (4)$$

on the reverse, comproportionation reaction, k_{-1} in eq 4, for a series derived from [Ru(tpy)(bpy)(H_2O)]$^{2+}$ emphasized the importance of the effect of driving force on the rate constant.[35] Further comparison with data for *cis*-[$Ru^{II}$$(bpy)_2(py)(H_2O)$]$^{2+}$ revealed the influence of steric crowding around the aqua/oxo ligands.

For the isomers of **4**, there is no change in driving force. Their $E_{1/2}$ values are within experimental error for the respective Ru^{III}−OH^{2+}/Ru^{II}−$OH_2{}^{2+}$ and Ru^{IV}═O^{2+}/Ru^{III}−OH^{2+} couples. Significant steric differences are unlikely, given the essentially superimposable cyclic voltammograms of *cis*- and *trans*-**4** in solution (Figure 2B).

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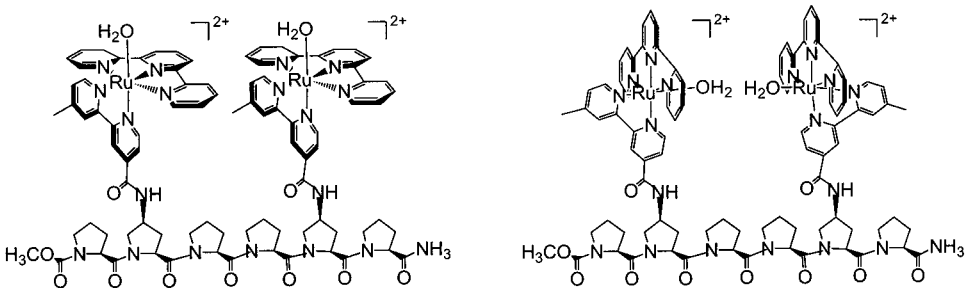

Figure 4. Proposed dispositions of the $Ru^{II}-OH_2^{2+}$ groups on a proline helix for cis and trans isomers of [Boc-Pra[Ru(tpy)(4-CO_2H-4′-Mebpy)]-OCH_3]$^{2+}$.

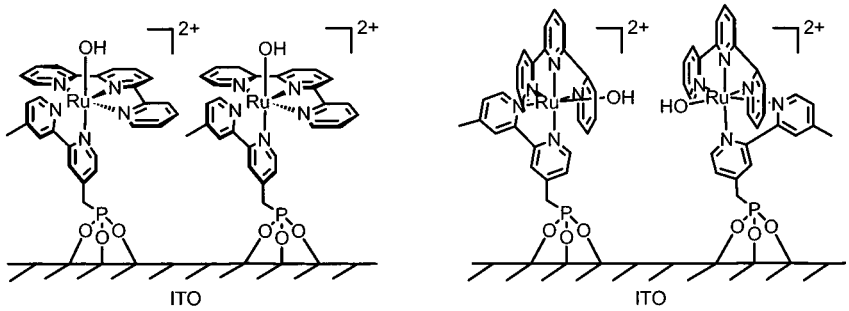

Figure 5. Illustration of the proposed surface structures for the isomers of $[Ru^{III}(tpy)(4\text{-}CH_2PO_3\text{-}4'\text{-}Mebpy)OH]^{2+}$ on ITO.

The different electrochemical responses of the two isomers on ITO can be rationalized by considering the predicted difference in local structures on the surface. As shown in Figure 5, a larger oxo/hydroxo/aqua separation distance is predicted for the surface-bound trans isomer. The resulting increase in tunneling distance for this isomer is most likely the explanation for the significant decrease in current relative to the cis isomer.

Conclusions

Three important precursors for the incorporation of $Ru^{IV}=O^{2+}$ oxidants into new molecular environments are reported. The cis and trans isomers of each have been isolated in good yields and isomeric structures assigned. The chemistry of these complexes and its dependence on isomeric structure are currently under investigation. Preliminary results have been presented demonstrating the influence of isomeric structure on the surface redox chemistry of the $Ru^{IV}=O^{2+}/Ru^{III}-OH^{2+}$ couples and its effect on proton-coupled electron transfer.

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Supporting Information Available: Listings of atomic coordinates and B_{iso} values, anisotropic displacement parameters, bond distances, bond angles, and torsional angles for *cis*-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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