Convenient Synthesis and Characterization of the Chiral Complexes *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$

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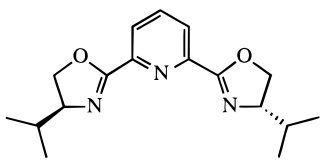
The chiral oxazoline complexes *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ were prepared from the common precursor *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$], and all three complexes were spectroscopically and structurally characterized. The complex *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ crystallized in $P2_12_12_1$ with $Z = 4$, $a = 8.396(2)$ Å, $b = 18.396(3)$ Å, $c = 20.954(3)$ Å, and $R = 0.039$ for 4131 reflections. The complex *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ crystallized in $P2_1$ with $Z = 2$, $a = 10.110(2)$ Å, $b = 13.566(2)$ Å, $c = 12.043(2)$ Å, $\beta = 106.10(2)°$, and $R = 0.039$ for 3869 reflections. The precursor *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] crystallized in $P2_12_12_1$ with $Z = 8$, $a = 15.856(2)$ Å, $b = 17.216(1)$ Å, $c = 17.768(1)$ Å, and $R = 0.030$ for 5826 reflections. A related reagent, [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$, was prepared by a more direct route and was also characterized. Aqua complexes were formed by hydrolysis of the chloride ligand in the bis(pyridine) complexes with retention of the stereochemistry. Electrochemical oxidation of the aqua complexes yielded oxo species which are formally ruthenium(IV). Reactions of the oxo complexes with the prochiral reductant, methyl *p*-tolyl sulfide led to stereoselective formation of the sulfoxide with enantiomeric excess of the *R* isomer ranging from 7% to 13%.

Introduction

The preparation of chiral complexes that undergo catalytic chemistry is of immense importance with potential applications in the preparation of chiral pharmaceuticals and other products.[1] One area that holds some promise involves the use of ruthenium complexes[2] which can be prepared in enantiomeric forms[3] and which perform a variety of stoichiometric and catalytic redox and atom transfer reactions for substrates such as alkanes,[4] alkenes,[5] alcohols,[6] phosphines,[7] and sulfides.[8] In addition, ruthenium centers have been practically applied to the recognition and cleavage of DNA[9] and in the construction of molecular nanostructures.[10] In an earlier report, the complex [Ru(bpy)$_2$(py)O]$^{2+}$ was employed in the stereoselective oxidation of sulfides to sulfoxides.[11] The stereoselectivity observed is disappointing but is comparable to that found with the complex [Ru((*S*)-bpop)(trpy)O]$^{2+}$ where (*S*)-bpop is the chiral ligand 2,2-bis[2-[4(*S*)-phenyl-1,3-oxazolinyl]]propane.[12] Chiral pyrazole derivatives have also been exploited in atom transfer reactions with some success.[13]

The chiral terdentate ligand 2,6-bis[4(*S*)-isopropyl-2-oxazolin-2-yl]pyridine ((*SS*)-Pr^{i}pybox) has found a number of useful



(SS)-Pr^{i}pybox

applications and provides a chiral environment for reactions where additional coordination sites are available.[14] The chemistry of complexes of this ligand with ruthenium is of interest and has been only partially exploited.[15] One problem in dealing

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with complexes of this sort with a combination of the tridentate ligand and monodentate ligands is the ubiquitous formation of both cis and trans isomers.[16] Stereochemically controlled synthesis is important in achieving the well-defined inorganic architecture essential for high stereoselectivity. In this paper, the isomerically controlled syntheses and characterization of *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ from *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] and the synthesis of [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$ are reported. In addition, the preparation of the corresponding aqua and oxo complexes and the reactions of the latter reagents with the prochiral probe methyl *p*-tolyl sulfide ((4-methylthio)toluene) are presented.

Experimental Details

Measurements. ^{1}H NMR spectra were obtained on a Varian 300-MHz instrument. Studies in D$_2$O were referenced to the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid, DSS, while tetramethylsilane, TMS, was used in other solvents. UV−visible spectra were run on a Varian Cary 3 spectrometer, and circular dichroism was measured on an Aviv 62DS spectrophotometer. MS/FAB analyses were performed on a JEOL JMS-AX505HX instrument. Cyclic voltammograms were generated with a Princeton Applied Research Corp. Model 173 potentiostat in conjunction with a Model 175 universal programmer and a Model 179 digital coulometer. A single-compartment cell with a three-electrode configuration consisting of a Ag/AgCl reference, a platinum wire auxiliary electrode, and a glassy carbon working electrode was employed for measurements in aqueous solution. In nonaqueous media, a similar setup was used and the potentials were referenced to the ferrocene/ferrocenium couple (Fc/Fc$^+$). The solutions were thoroughly purged with argon and all voltammetric experiments recorded under a positive pressure of this gas at 20 °C. The pH of aqueous solutions was determined by use of a Corning pH meter and combination pH electrode with a saturated calomel (NaCl) reference. Buffer solutions for the electrochemical measurements were prepared from HClO$_4$ with NaH$_2$PO$_4$·H$_2$O, Na$_2$HPO$_4$·7H$_2$O and Na$_3$PO$_4$·12H$_2$O (pH 2−12). Controlled-potential oxidations were performed with a flow system consisting of a graphite powder working electrode packed in a porous-glass column and wrapped externally with a platinum wire auxiliary electrode.[17] In general, solutions of *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$OH$_2$]$^{2+}$ or [Ru((*SS*)-Pr^{i}pybox)(bpy)OH$_2$]$^{2+}$, prepared at pH 7, were oxidized at 0.85 V relative to a Ag/AgCl electrode. Elemental analyses were performed by MHW Laboratories.

Materials. [Ru(4-isopropyltoluene)(py)Cl$_2$][18] and (*SS*)-Pr^{i}pybox[19] were prepared by literature procedures. In general, the nonaqueous solvents used were HPLC or spectroscopic grade, stored in a dry argon atmosphere, and were used without further purification. The methyl *p*-tolyl sulfide was >99% pure, and other reagents were of analytical reagent grade.

Preparation of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$]. The ligand (*SS*)-Pr^{i}pybox, 30 mg (0.1 mmol), was added to a solution of 35 mg (0.09 mmol) of [Ru(4-isopropyltoluene)(py)Cl$_2$] in 15 mL of methylene chloride. The mixture was heated at reflux for 6 h; then the volume of reaction mixture was reduced, and a violet solid was precipitated by adding hexane. The product was recrystallized from CH$_2$Cl$_2$/hexane to yield 45 mg (90%). Anal. Found (calcd) for *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$]: C, 47.84 (47.84); H, 5.05 (5.07); N, 10.20 (10.14). ^{1}H NMR (300 MHz, CD$_3$Cl, TMS): 9.81 (d, J = 5.07, 2H); 7.87 (t, J = 7.6, 1H); 7.63 (m, 2H); 7.54−7.45 (m, 3H); 4.91−4.72 (m, 4H); 4.24 (m, 2H); 1.67 (m, 2H); 0.76 (d, J = 7.17, 6H); 0.70 (d, J = 6.75, 6H). Chemical shifts are reported in ppm and J values are given in hertz throughout.

Preparation of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$. Pyridine (5 mL) was added to a solution of 200 mg (0.36 mmol) of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] in 5 mL of DMSO. The mixture was heated at 110 °C for 4 h and then cooled to room temperature; a brown powder was precipitated by the addition of hexane. The complex was dissolved in a small amount of ethanol and was purified by silica gel column chromatography; an ethanol:H$_2$O:NaCl = 10:10:1 mixture was used as the eluent. The product was isolated as the [PF$_6$]$^-$ salt. It was further recrystallized from 1,2-dichloroethane/isopropyl ether; yield 60%. Anal. Found (calcd) for *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$: C, 43.67 (43.72); H, 4.70 (4.45); N, 9.09 (9.45). FAB-MS: *m*/*z* 596 (M − PF$_6$)$^+$. ^{1}H NMR (300 MHz, CD$_3$Cl, TMS): 8.31 (d × d, J = 6.54, 1.48, 4H); 8.04−7.92 (m, 3H); 7.59 (d × d × d, J = 7.6, 6.54, 1.48, 2H); 7.17 (d × d), J = 7.6, 6.54, 4H); 4.71 (m, 4H); 3.98 (m, 2H); 2.57 (m, 2H); 0.88 (d, J = 7.18, 6H); 0.24 (d, J = 6.76, 6H). The reduction potential for the ruthenium(III/II) couple is 0.440 V (vs Fc/Fc$^+$) in acetonitrile solution (0.1 M TBAP).

Preparation of *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$. To a solution of 200 mg (0.36 mmol) of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] in 5 mL of ethylene glycol was added 5 mL of pyridine; the mixture was heated at 60 °C for 3 h and then cooled to room temperature, and a brown powder was precipitated by adding hexane. The complex was dissolved in a small amount of ethanol and was purified by silica gel column chromatography; an ethanol:H$_2$O:NaCl = 10:10:1 mixture was used as the eluent. The product was isolated as the [PF$_6$]$^-$ salt. It was further recrystallized from 1,2-dichloroethane/isopropyl ether; yield 65%. Anal. Found (calcd) for *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$: C, 43.33 (43.72); H, 4.70 (4.45); N, 9.22 (9.45). FAB-MS: *m*/*z* 596 (M − PF$_6$)$^+$. ^{1}H NMR (300 MHz, CD$_3$Cl, TMS): 9.14 (d, J = 4.85, 2H); 8.02−7.96 (m, 2H); 7.85−7.79 (m, 2H); 7.63−7.55 (m, 5H); 7.15 (d × d, 6.75, 6.65, 2H); 5.05−4.68 (m, 4H); 4.43 (m, 1H); 4.31 (m, 1H); 1.91 (m, 1H); 1.44 (m, 1H); 0.95 (d, J = 6.96, 3H); 0.73 (d, J = 6.96, 3H); 0.69 (d, J = 6.54, 3H); 0.38 (d, J = 6.76, 3H). The reduction potential for the ruthenium(III/II) couple is 0.348 V (vs Fc/Fc$^+$) in acetonitrile solution in 0.1 M TBAP.

Preparation of [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$. To a solution of 100 mg (0.16 mmol) of [Ru(4-isopropyltoluene)Cl$_2$]$_2$ (Aldrich) in 15 mL of methylene chloride was added 100 mg (0.33 mmol) of (*SS*)-Pr^{i}pybox. After the mixture was stirred at room temperature for 1 h, the solvent methylene chloride was removed under reduced pressure and 54 mg (0.33 mmol) of 2,2′-bipyridine in 20 mL of absolute ethanol was added. The resulting mixture was heated at reflux for 12 h, after which the volume was reduced and the complex was purified by silical gel column chromatography; an ethanol:H$_2$O:NaCl = 10:10:1 mixture was used as the eluent. The product was isolated as the [PF$_6$]$^-$ salt. It was further recrystallized from 1,2-dichloroethane/isopropyl ether; yield 90%. Anal. Found (calcd) for [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$: C, 43.81 (43.88); H, 4.40 (4.23); N, 9.44 (9.44). FAB-MS: *m*/*z* 594 (M − PF$_6$)$^+$. ^{1}H NMR (300 MHz, CD$_3$Cl, TMS): 10.3 (d, J = 5.7, 1H); 8.47 (d, J = 7.9 1H); 8.28 (d, J = 7.6 1H); 8.12 (d × d × d, J = 7.9, 7.6, 1.5, 1H); 8.02−7.91 (m, 3H); 7.82−7.70 (m, 2H); 7.28 (m, 2H); 4.75−4.49 (m, 4H); 3.98 (m, 1H); 3.27 (m, 1H); 1.47 (m, 1H); 0.824 (d, J = 6.9, 3H); 0.626 (d, J = 7.2, 3H); 0.59 (m, 1H); 0.512 (d, J = 6.6, 3H); −0.288 (d, J = 6.6, 3H). The reduction potential for the ruthenium(III/(II) couple is 0.348 V (vs Fc/Fc$^+$) in acetonitrile solution in 0.1 M TBAP.

Preparation of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(H$_2$O)](PF$_6$)$_2$·2H$_2$O. Silver trifluoromethanesulfonate (35 mg 0.134 mmol) and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ (50 mg, 0.067 mmol) were refluxed for 1 h in 15 mL of 25% ethanol/75% H$_2$O; the mixture was then cooled to room temperature and filtered. A few drops of saturated NH$_4$PF$_6$ were added to the filtrate, and the volume was slowly reduced to ≈5 mL by rotary evaporation at 30 °C. The yellow precipitate was collected, washed with cold water, air-dried, and recrystallized from warm water; yield 50 mg, 85%. Anal. Found (calcd) for *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(H$_2$O)](PF$_6$)$_2$·2H$_2$O: C, 35.69 (35.80); H, 4.37 (4.34);

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N, 7.94 (7.74). ^{1}H NMR (300 MHz, D_2O, DSS): 0.69 (d, J = 6.60, 6H); 0.19 (d, J = 6.90, 6H).

Preparation of *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(H$_2$O)](PF$_6$)$_2$·H$_2$O. Silver trifluoromethanesulfonate (35 mg 0.134 mmol) and *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]PF$_6$ (50 mg, 0.067 mmol) were heated for 4 h in 15 mL of 25% ethanol/75% H_2O at 60 °C, and the mixture was then cooled to room temperature and filtered. A few drops of saturated NH_4PF_6 were added to the filtrate, and the volume was slowly reduced to ≈5 mL by rotary evaporation at 30 °C. The yellow-brown precipitate was collected, washed with cold water, air-dried, and recrystallized from warm water; yield 48 mg, 80%. Anal. Found (calcd) for *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(H$_2$O)](PF$_6$)$_2$·H$_2$O: C, 36.51 (36.58); H, 4.39 (4.21); N, 7.61 (7.90). ^{1}H NMR (300 MHz, D_2O, DSS): 0.70 (d, J = 6.90, 3H); 0.60 (d, J = 6.90, 3H); 0.37 (d, J = 6.90, 3H); −0.02 (d, J = 6.60, 3H).

Preparation of [Ru((*SS*)-Pr^{i}pybox)(bpy)(H$_2$O)](PF$_6$)$_2$. Silver trifluoromethanesulfonate (35 mg 0.134 mmol) and [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF$_6$ (50 mg, 0.067 mmol) were refluxed for 1 h in 15 mL of 25% ethanol/75% H_2O, and the mixture was then cooled to room temperature, and filtered. A few drops of saturated NH_4PF_6 were added to the filtrate, and the volume was slowly reduced to ≈5 mL under reduced pressure at 30 °C. The yellow-brown precipitate was collected, washed with cold water, air-dried, and recrystallized from warm water; yield 50 mg, 85%. Anal. Found (calcd) for [Ru((*SS*)-Pr^{i}pybox)(bpy)(H$_2$O)](PF$_6$)$_2$: C, 36.51 (36.58); H, 4.39 (4.21); N, 7.61 (7.90). ^{1}H NMR (300 MHz, D_2O, DSS): 0.51 (d, J = 6.90, 3H); 0.42 (d, J = 7.20, 3H); 0.30 (d, J = 6.60, 3H); −0.46 (d, J = 6.30, 3H).

Suitable crystals of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)(Cl)$_2$], *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(Cl)](PF$_6$), and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(Cl)](PF$_6$) were examined at 20 °C on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-crystal, incident-beam monochromator using Mo Kα radiation (λ = 0.710 73 Å). A summary of the crystal data collection conditions and structure solutions is available as Supporting Information.

The species formulated as *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$(O)]$^{2+}$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)(O)]$^{2+}$ were generated electrochemically in aqueous solution. Typically, a solution containing 15 mg of the corresponding aqua salt in 10 mL of H_2O (0.01 M $NaClO_4$) at pH 7 was oxidized at 20 °C. In the case of [Ru((*SS*)-Pr^{i}pybox)(bpy)(OH$_2$)]$^{2+}$, attempts were made to determine the oxidizing stoichiometry by quenching a known volume of oxidized solution (≈5 × 10^{-4} M) in a small excess of 4 × 10^{-4} M iron(II) at pH 2. The iron(II) remaining was determined as [Fe(phen)$_3$]$^{2+}$ in the presence of citrate at pH 7. In an average of three determinations, 1.7(2) equiv of iron(II) was consumed by each equivalent of oxidized ruthenium. The instability of the oxidant leads to an underestimation of the oxidation state, and consequently, the complex is formulated as a ruthenium(IV) species. The complex is also capable of oxo-transfer reactions. In experiments to determine the selectivity in the oxidation of methyl *p*-tolyl sulfide, 10 mL of the electrolyzed solution was added dropwise to a solution of 10−50-fold excess of (4-methylthio)toluene in 25 mL of acetonitrile under argon. After 3 h of stirring at room temperature, solvent was removed and the residue was extracted twice with 5 mL of ether. Ether and unreacted sulfide were removed under vacuum. The product methyl *p*-tolyl sulfoxide was identified by ^{1}H NMR, and the enantiomeric enrichment was determined, again by ^{1}H NMR, in the presence of (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)(α-methylbenzyl)amine.[20]

Results

Reaction of [Ru(4-isopropyltoluene)(py)Cl$_2$] with (*SS*)-Pr^{i}pybox in methylene chloride yields *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] in high yield. Furthermore, the stereochemistry of further addition of pyridine to form [Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ is controlled by reaction solvent and temperature. When *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] is refluxed in absolute ethanol with an excess of pyridine, the product is greater than 80% *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$, while the same reaction in methanol yields 85% *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$. Further optimization of reaction conditions showed that, in ethylene glycol at 60 °C, the reaction product is solely the cis form, while, in DMSO at 110 °C, it is solely the trans form.

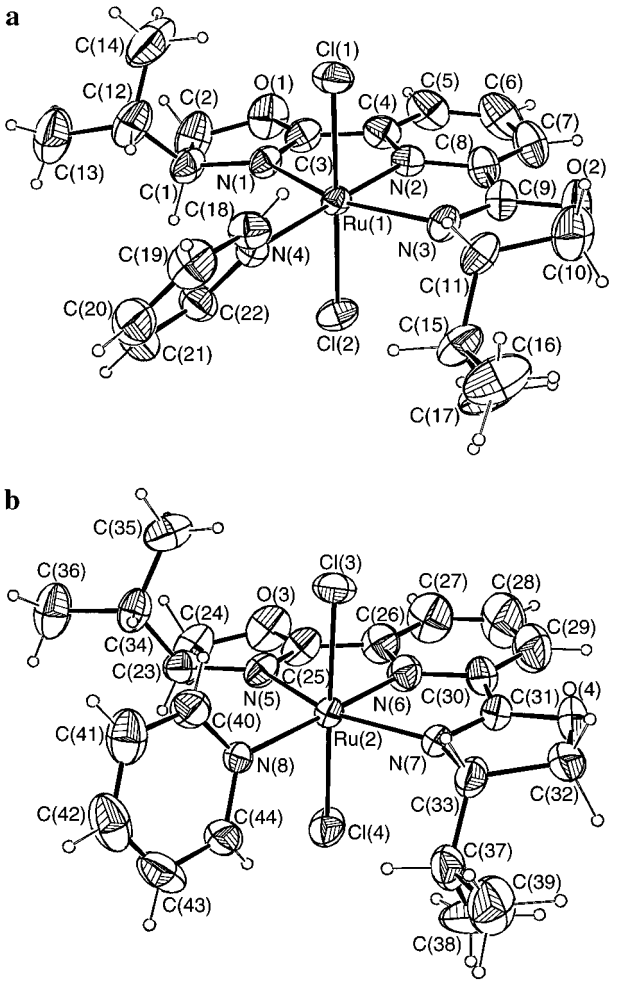

Figure 1. ORTEP diagram of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% level for non-hydrogen atoms, and arbitrarily small radii are used for the hydrogen atoms. (a) Important bond lengths (Å) and angles (deg): Ru(1)−Cl(1) = 2.3903(9), Ru(1)−Cl(2) = 2.3942(9), Ru(1)−N(1) = 2.076(3), Ru(1)−N(2) = 1.945(2), Ru(1)−N(3) = 2.066(3), Ru(1)−N(4) = 2.128(2), Cl(1)−Ru(1)−Cl(2) = 179.14(3). The pyridine ligand plane deviates 33.14(8)° from the vertical plane defined by N(2), N(4), Cl(1), and Cl(2). (b) Important bond lengths (Å) and angles (deg): Ru(2)−Cl(3) = 2.3909(9), Ru(2)−Cl(4) = 2.402(1), Ru(2)−N(5) = 2.085(3), Ru(2)−N(6) = 1.938(3), Ru(2)−N(7) = 2.090(3), Ru(2)−N(8) = 2.155(2), Cl(3)−Ru(2)−Cl(4) = 178.41(3). The pyridine ligand plane deviates 19.38(9)° from the vertical plane defined by N(6), N(8), Cl(3), and Cl(4).

The stereochemistry of these complexes is readily determined by ^{1}H NMR where the isopropyl groups on the chiral center are particularly useful. The spectrum of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$] shows only two methyl environments as expected for a complex with C_2 symmetry. The trans form of [Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ also has C_2 symmetry with both pyridines in the same magnetic environment and two magnetically different methyl groups, while the lower symmetry cis form has two sets of pyridine peaks and four sets of methyl peaks. The spectrum is very similar to that for [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]$^+$, where a cis geometry is required for the bidentate chelating ligand.

The structures of all three chloro−pyridine complexes were confirmed by X-ray crystallography. None of the structures, shown in Figures 1−3, are particularly remarkable. Bond lengths range from 2.38 to 2.43 Å for Ru−Cl, while, with one exception, the Ru−N(oxazoline) bond lengths are grouped closely around 2.08 Å. The exception, in *cis*-[Ru((*SS*)-Pr^i-

(20) Desmukh, M. N.; Dunach, E.; Juge, S.; Kagan, H. B. *Tetrahedron Lett.* **1984**, *25*, 3467−3470.

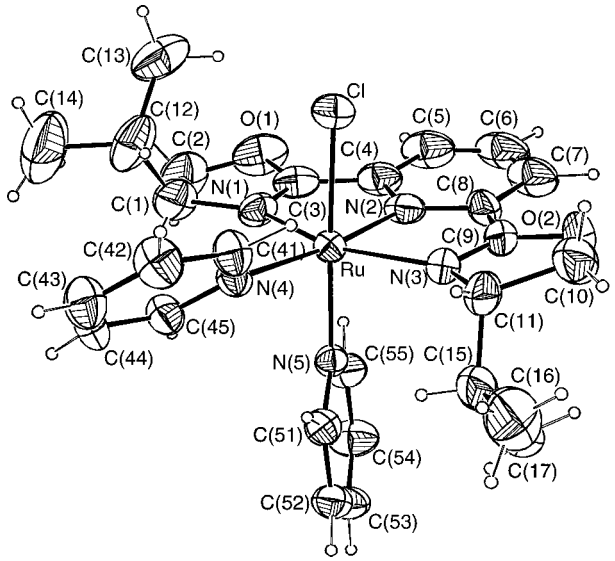

Figure 2. ORTEP diagram of *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% level for non-hydrogen atoms, and arbitrarily small radii are used for the hydrogen atoms. Important bond lengths (Å) and angles (deg): Ru−Cl = 2.381(1), Ru−N(1) = 2.078(3), Ru−N(2) = 1.955(4), Ru−N(3) = 2.118(3), Ru−N(4) = 2.119(3), Ru−N(5) = 2.093(3), Cl−Ru−N(4) = 89.86(9), Cl−Ru−N(5) = 177.81(9), N(4)−Ru−N(5) = 90.7(1). The equatorial pyridine ligand plane deviates 47.24(10)° from the vertical plane defined by N(2), N(4), N(5), and Cl. The axial pyridine ligand plane deviates 34.49(17)° from the same vertical plane.

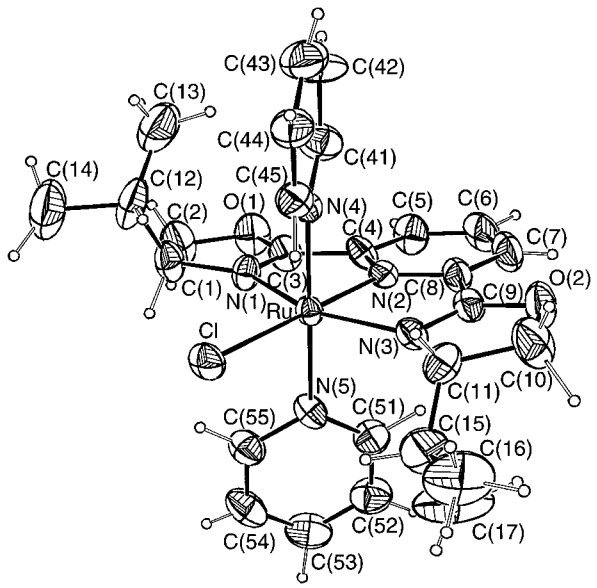

Figure 3. ORTEP diagram of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% level for non-hydrogen atoms, and arbitrarily small radii are used for the hydrogen atoms. Important bond lengths (Å) and angles (deg): Ru−Cl = 2.427(1), Ru−N(1) = 2.067(2), Ru−N(2) = 1.933(3), Ru−N(3) = 2.088(3), Ru−N(4) = 2.083(4), Ru−N(5) = 2.107(4), Cl−Ru−N(4) = 89.7(1), Cl−Ru−N(5) = 89.5(1), N(4)−Ru−N(5) = 179.1(1). The axial pyridine ligand planes deviate 34.14(11)° (N(4)) and 35.87(19)° (N(5)) from the vertical plane defined by N(2), N(4), N(5), and Cl.

pybox)(py)$_2$Cl]$^+$, appears to be a lengthening to 2.118 Å as a result of an unfavorable steric interaction with one of the pyridine ligands. The pyridine Ru−N bond length within the tridentate ligand is shorter, 1.93−1.96 Å, than the free pyridine Ru−N, 2.08−2.13 Å and noticeably shorter than the corresponding bond lengths in organometallic derivatives[15] where π-back-bonding from trans ligands has an effect. The (*SS*)-Pr^i-

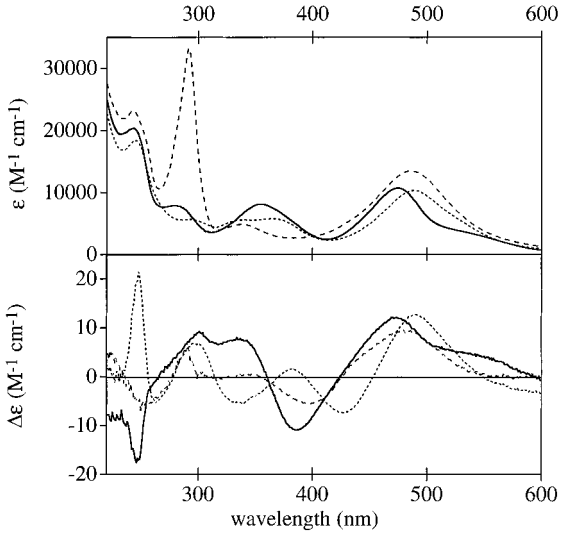

Figure 4. Uv−visible and circular dichroism spectra of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ (—), *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ (···), and [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]$^+$ (- - -).

pybox ligand is substantially planar in all three complexes, with puckering of the five-membered rings the most significant distortion.

A further feature of interest was noted in the unit cell of *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)Cl$_2$]. There are two independent molecules which differ in the orientation of the pyridine plane to the plane of the chiral ligand, Figure 1. This creates a further chiral element in the structure, a feature noted recently in other systems,[21] but the solution ^{1}H NMR indicates only one form and no attempt was made to isolate the isomeric forms.

Absorption spectra of the complexes show characteristics similar to those of spectra for other ruthenium polypyridyl species, and spectra for the monochloro species are presented in Figure 4. As for ruthenium(II) complexes with polypyridyl ligands, the spectra are dominated by intense metal-to-ligand charge-transfer bands in the visible region and intraligand bands in the ultraviolet region. The complexes are chiral due to the presence of the asymmetric isopropyl groups and exhibit circular dichroism signals. Data for all complexes are summarized in Table 1, and some points are worthy of note. The intense absorption in the visible spectrum of [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]$^+$ at 292 nm resulting from the bpy ligand shows only weak circular dichroism. The most intense feature in the circular dichroism spectra is for that of *cis*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$, where there appears to be a strong couplet presumably associated with an intraligand band of the *cis* pyridine ligands around 260 nm. No comparable feature is noted for the bpy complex.

All three complexes, *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]$^+$, are readily aquated, eq 1, in a reaction with Ag$^+$, and the resulting aqua complexes

$$[\text{Ru}((SS)\text{-Pr}^i\text{pybox})(\text{bpy})\text{Cl}]^+ + \text{Ag}^+ \rightarrow [\text{Ru}((SS)\text{-Pr}^i\text{pybox})(\text{bpy})\text{OH}_2]^{2+} + \text{AgCl} \quad (1)$$

were isolated and identified by ^{1}H NMR spectroscopy. For *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)(py)$_2$Cl]$^+$, the aquation reaction occurs with retention of stereochemistry below 60 °C, but above 80 °C partial isomerization of the cis form to the more thermodynamically stable trans form is detected. Both ^{1}H NMR and microanalytical data are consistent with the substitution of the single chloride ion by a water molecule to give the dicationic

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Table 1. Circular Dichroism and UV−Vis Spectroscopic Data

complex	λ, nm	ϵ, M^{-1} cm^{-1}	λ, nm	$\Delta\epsilon$, M^{-1} cm^{-1}
trans-[Ru((*SS*)-Pr^{i}pybox)(py)Cl_2][a]	515	10500	530	+10.6
	355	4200	480	−8.71
	294	5400	352	+5.81
	248	17200	304	+6.84
			268	−7.20
			244	+8.06
cis-[Ru((*SS*)-Pr^{i}pybox)$(py)_2$Cl]PF_6[b]	488	10300	492	+12.6
	365	5700	427	−7.42
	340	5600	381	+1.58
	293	5700	334	−5.19
	245	18400	297	+6.79
			263	−5.41
			248	+21.5
trans-[Ru((*SS*)-Pr^{i}pybox)$(py)_2$Cl]PF_6[b]	475	10700	476	+12.0
	354	8100	383	−10.8
	279	7900	334	+8.03
	243	20000	301	+9.20
			246	−17.6
[Ru((*SS*)-Pr^{i}pybox)(bpy)Cl]PF_6[b]	486	13500	482	+9.40
	337	4900	399	−5.52
	292	33000	348	+0.96
	242	23000	291	+5.84
			252	−6.10
cis-[Ru((*SS*)-Pr^{i}pybox)$(py)_2H_2O$]$(PF_6)_2$[c]	460	10700	463	+15.1
	348	5950	406	−9.43
	281	8000	367	+2.98
	236	19900	330	−5.93
			286	+11.5
			248	+10.7
trans-[Ru((*SS*)-Pr^{i}pybox)$(py)_2H_2O$]$(PF_6)_2$[c]	451	7100	458	+6.89
	348	5800	373	−5.17
	278 (sh)	8500	330	+4.04
	234	18200	297	+7.02
			254	−2.83
[Ru((*SS*)-Pr^{i}pybox)(bpy)H_2O]$(PF_6)_2$[c]	462	14600	460	+10.5
	343 (sh)	3120	377	−6.54
	287	34700	283	+9.87
	235	24700	240	−10.1
cis-[Ru((*SS*)-Pr^{i}pybox)$(py)_2O$]$(PF_6)_2$[c]	430 (sh)	1300	398	+2.61
	390 (sh)	2200	350	−3.38
	340 (sh)	3300	294	+1.65
	254	15000	268	−4.6
trans-[Ru((*SS*)-Pr^{i}pybox)$(py)_2O$]$(PF_6)_2$[c]	440 (sh)	1300	390	2.39
	360 (sh)	2100	346	−0.91
	280	6800	292	+0.94
	252	11000		
[Ru((*SS*)-Pr^{i}pybox)(bpy)O]$(PF_6)_2$[c]	450 (sh)	1300	390	+1.60
	380 (sh)	4000	350	−1.02
	300	12000	296	+2.76
	240	17000	250	−1.82

[a] $CHCl_3$ solution. [b] CH_3CN solution. [c] Aqueous solution, pH 7.0.

aqua complexes. The absorption and circular dichroism spectral data for the complexes are included in Table 1. The UV−visible spectra are independent of pH over the range pH 1−8 but at higher pH show changes consistent with hydrolysis. Good isosbestic behavior is maintained up to pH 11.5, and analysis gives pK_a values of 9.89 for the cis, 9.55 for the trans, and 10.05 for the bpy complex, eq 2.

$$[\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)OH}_2]^{2+} \rightleftharpoons [\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)OH}]^{+} + \text{H}^{+} \quad (2)$$

Cyclic voltammetry studies in aqueous solution reveal that both *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2OH_2$]$^{2+}$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)OH_2]$^{2+}$ undergo a single, reversible oxidation which is strongly dependent on pH. The process involves the loss of two electrons. The potential decreases linearly with pH over the range pH 2−9 with a slope of 57(2) mV, as shown in Figure 5 for [Ru((*SS*)-Pr^{i}pybox)(bpy)OH_2]$^{2+}$, and indicates that a two-proton process is coupled to the two-electron transfer, consistent with eq 3. The reduction potentials (NHE) are 1.045, 1.070, and 1.090 V for *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2OH_2$]$^{2+}$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)OH_2]$^{2+}$, respectively. Between pH 9 and 10 the slopes diminish, consistent with the deprotonation of the reduced form of the complex and a two-electron oxidation in which a single proton is transferred, eq 4.

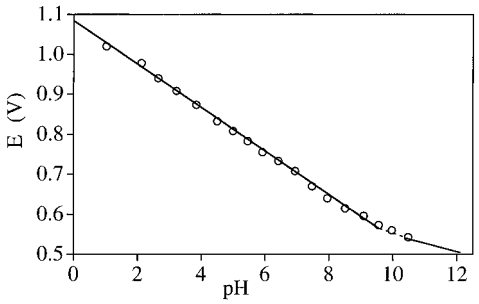

Figure 5. Reduction potential of [Ru((*SS*)-Pr^{i}pybox)(bpy)(O)]$^{2+}$ as a function of pH.

$$[\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)O}]^{2+} + 2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons [\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)OH}_2]^{2+} \quad (3)$$

$$[\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)O}]^{2+} + \text{H}^{+} + 2\text{e}^{-} \rightleftharpoons [\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)OH}]^{2+} \quad (4)$$

The ruthenium(IV)−oxo complexes derived from *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2OH_2$]$^{2+}$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)OH_2]$^{2+}$ are relatively short lived ($t_{1/2} \approx 0.5$ h) and could not be isolated. Spectroscopic studies were carried out by a combination of spectroelectrochemical techniques and flow electrolysis, and the results are summarized in Table 1. The UV−visible spectra are not unlike those of other ruthenium(IV) complexes with polypyridine ligands, and the circular dichroism is weak, comparable to that of [Ru$(bpy)_2$pyO]$^{2+}$. After a cycle of electrochemical oxidation of *cis*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2OH_2$]$^{2+}$ followed by reduction with methyl *p*-tolyl sulfide, the cis complex is quantitatively recovered and identified by ^{1}H NMR. A similar observation is made with recovery of *trans*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2OH_2$]$^{2+}$ when the trans complex is used as the starting material. Thus, the stereochemistry of these complexes is retained on oxidation and reduction at ambient temperatures.

The oxidation of methyl *p*-tolyl sulfide to the corresponding sulfoxide has been used as a primary indicator of stereoselective behavior in chiral complexes of this type.[11,12] Studies of the reactions of *cis*- and *trans*-[Ru((*SS*)-Pr^{i}pybox)$(py)_2O$]$^{2+}$ and [Ru((*SS*)-Pr^{i}pybox)(bpy)O]$^{2+}$, prepared electrolytically, with an excess of methyl *p*-tolyl sulfide show that the reactants are discriminating with exclusive production of the sulfoxide, eq 5. The sulfoxide is readily identified by the two methyl signals

$$[\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)O}]^{2+} + \text{CH}_3\text{SC}_6\text{H}_4\text{CH}_3 + \text{H}_2\text{O} \rightarrow [\text{Ru((}SS\text{)-Pr}^i\text{pybox)(bpy)OH}_2]^{2+} + \text{CH}_3\text{SOC}_6\text{H}_4\text{CH}_3 \quad (5)$$

at 2.42 and 2.70 ppm corresponding to the S-bound and aromatic methyl groups, respectively. In the presence of the chiral amine (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)(α-methylbenzyl)amine, the resonance for the S-bound signal is split and the enantiomeric purity of the sulfoxide can be determined. Chiral induction is modest in all three reactions studied with an excess of the *R* isomer produced. The enantiomeric excess in the different reactions is given in Table 2. In a few experiments with *cis*-[Ru((*SS*)-

Table 2. Chiral Induction in the Oxidation of Methyl *p*-Tolyl Sulfide

oxidant	enantiomeric excess	ref
Δ-$[Ru(bpy)_2(py)O]^{2+}$	15 ± 2% *R*	11
$[Ru((S)\text{-bpop})(trpy)O]^{2+}$	12 ± 2% *R*	12
trans-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$	7 ± 2% *R*	this work
cis-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$	11 ± 1% *R*	this work
cis-$[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)O]^{2+}$	13 ± 2% *R*	this work

Pr^ipybox)$(py)_2O]^{2+}$, the sulfide was held as limiting reagent and production of the sulfone was detected in addition to the sulfoxide. Interestingly, under such conditions, the chiral induction in the sulfoxide is diminished, indicating that the (*R*)-sulfoxide is more reactive for the formation of the sulfone. Observations of this sort have been made previously in related reactions.[12]

Discussion

The preparation of cis and trans isomers of $[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2Cl]^+$ from a common starting material is relatively unusual. Although preparations of both trans and cis isomers of $[Ru(terpy)(py)_2Cl]PF_6$ have been reported,[22] the methods require substantially different starting materials and reaction conditions. In that case, the trans isomer is formed from reaction of pyridine with *trans*-$[Ru(terpy)(PPh_3)Cl_2]$ and the cis isomer by photolysis of $[Ru(terpy)(py)_3](PF_6)_2$. Other species show similar limitations.[23,24] Attempts were made to obtain *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2Cl]^+$ by a number of different routes, but ultimately, the convenient strategy involving *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)Cl_2]$ as a common precursor was discovered and employed.

The oxazole complexes described in this work show chemistry which is comparable to that of ruthenium(II) polypyridyl species. Thus the $Ru^{III/II}Cl$ potentials for *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2Cl]^{2+/+}$ in acetonitrile solution are similar to those for $[Ru(trpy)(bpy)Cl]^{2+/+}$ under the same conditions. The trans isomer is a better oxidant than the cis isomer by almost 0.1 V, a difference comparable to that found in other systems.[16,24]

The aqua complexes are formed readily in a reaction of the chloro complexes with Ag^+ and also show spectroscopic properties comparable to those for corresponding ruthenium(II) polypyridyl species. The circular dichroism spectra are most intense in the ligand-to-metal charge-transfer region in the visible part of the spectrum, contrasting with the strong ligand−ligand signals in species such as $[Ru(bpy)_2(py)_2]^{2+}$, where there is a chiral center at the metal.[3,11] It is interesting to note that the *cis* form has more intense circular dichroism in the ligand−ligand region. In the spectrum of the bpy complex, there is no strong signal in this region, which suggests that it is the interaction of the two pyridine ligands that gives rise to this signal.

The oxidation of the ruthenium(II) aqua complexes appears to take place in a single two-electron step. Normally, with the polypyridine species and with $[Ru((S)\text{-bpop})(trpy)OH_2]^{2+}$, two single-electron processes are noted and an intermediate ruthenium(III) species is thermodynamically accessible.[2,12] The complexes *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2OH_2]^{2+}$ and $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)OH_2]^{2+}$ show only a single cyclic voltammetry response. Peak−peak separations for these quasi-reversible processes are unhelpful in distinguishing between one- and two-electron changes, but single-step two-electron oxidation has been shown for related complexes.[25] Coulometric experiments could not be carried out in the present case due to the instability of the oxidation product; however, chemical analysis results are consistent with a two-electron oxidation.

The reduction potentials for the oxo-aqua couple reveal that, as expected, the trans isomer is a moderately better oxidant than the cis and that $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)O]^{2+}$ has a similar reduction potential. Data for all three complexes show the effects of hydrolysis of the reduced form at higher pH where the dependence of the potential on pH shows a slope decrease from 57(2) mV, supporting evidence that this is a two-electron process. It should be noted that the pK_a for the cis complex is greater than that for the trans, indicating that the chelated pyridine group is a stronger donor in the trans position.

The reactions of all three oxidants with methyl *p*-tolyl sulfide yield cleanly the methyl *p*-tolyl sulfoxide under conditions of excess reductant. The sulfide is prochiral, and the resulting sulfoxide has a new chiral center created in the oxidation process. As with Δ-$[Ru(bpy)_2(py)O]^{2+}$ and$[Ru((S)\text{-bpop})(trpy)O]^{2+}$,[11,12] the induction of chirality is modest and shows a dependence on the structure of the oxidant though, in all cases, the *R* isomer is favored. Thus, *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$, where the oxo group is bracketed by the two oxazoline ligand chiral centers, shows the lowest selectivity, while *cis*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$ and $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)O]^{2+}$ show larger values, comparable to those for $[Ru((S)\text{-bpop})(trpy)O]^{2+}$. It is noteworthy that the more rigid $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)O]^{2+}$ shows a higher selectivity than *cis*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$, and it may be that ligand flexibility plays a key role in the discrimination. It is also noteworthy that in none of the studies involving the use of chiral ligand systems does the selectivity eclipse that for the more rigid Δ-$[Ru(bpy)_2(py)O]^{2+}$, where the chirality is derived from the metal center.

It is difficult to draw strong mechanistic conclusions from these observations on the asymmetric oxygen transfer from these chiral ruthenium(IV) complexes. The chiral induction is modest, much smaller than that observed with catalytic systems involving chiral complexes of titanium, vanadium, and manganese.[26] It may be that the Lewis acid property of the chiral complexes plays an important role in the catalytic process, unavailable in the stoichiometric reaction. The detailed work of Takeuchi[8,12] suggests that the stoichiometric oxidation of sulfides by ruthenium(IV) takes place by a mechanism involving single electron transfer and that the less intimate interactions involved explain the low stereoselectivity. The present work is consistent with this proposed mechanism.

Supporting Information Available: Text describing the structure solutions, tables giving crystal data and details of structure determinations, fractional atom coordinates and *B* values, bond lengths, bond angles, and anisotropic thermal parameters, and figures showing UV−visible and circular dichroism spectra of *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)Cl_2]$, *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2OH_2]^{2+}$, $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)OH_2]^{2+}$, *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(py)_2O]^{2+}$, and $[Ru((SS)\text{-Pr}^i\text{pybox})(bpy)O]^{2+}$ and cyclic voltammograms for *cis*- and *trans*-$[Ru((SS)\text{-Pr}^i\text{pybox})(by)_2(H_2O)](PF_6)_2$ (49 pages). Ordering information is given on any current masthead page.

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