for the exceptional entropic driving force of the Q_p equilibrium. Unfortunately, there is no obvious explanation of the apparent attenuation of Q_p values for the $L^- = NCO^-$ and CN^- dimers, which presumably underlies their failures to exhibit saturation base hydrolysis kinetics. As a point for further examination, we note that increases in b_{1u} MO energy (and antibonding character) should destabilize a b_{1u}–OH^- interaction by forcing the ΔH° term to become even more endothermic.

According to the proposed mechanism, k_{OH} in rate expression 6 is equivalent to the product $k_2 Q_p$. In order to facilitate a comparison of overall base hydrolysis reactivities among the three CrOCr dimers, k_2 values calculated in this fashion for $L^- = NCS^-$ are included in Table III. On this basis, 40 °C k_{OH}/k_0 ratios may be ranked according to NCS^- (300) $\gg$ NCO^- (26) > CN^- (6). The substantial variation in this ratio throughout the series supports our hypothesis of rate-limiting Cr–L dissociation induced by oxo-bridge migration. In this respect, the CrOCr dimer base hydrolyses are typical of chromium(III) complexes as a whole, for which kinetic leaving group sensitivities are larger in base hydrolysis processes than in related acid hydrolysis or simple aquation reactions.[10] Indeed, composite k_{OH} ($L^- = NCS^-$) activation parameters calculated from the temperature dependences of k_2 and Q_p ($\Delta H^\ddagger = 27.3$ kcal mol^{-1}; $\Delta S^\ddagger = +21$ eu) are strongly reminiscent of those reported for a variety of Cr(III) and Co(III) species.[10] It should also be noted that the trend in CrOCr dimer k_{OH}/k_0 ratios results almost entirely from variations in k_{OH}. Thus,

the k_0(40 °C) values characteristic of $L^- = NCS^-$, NCO^-, and CN^- are essentially identical at $(5 \pm 2) \times 10^{-5}$ s^{-1}, suggesting that Cr–O rather than Cr–L bond-breaking dominates the activation process corresponding to the minor hydroxide-independent term.

Finally, a comparison of rate parameters for $[Cr(tmpa)L]_2O^{2+}$ and $[Cr(tmpa)(O)]_2^{2+}$ base hydrolysis reactions is instructive. Most noteworthy are the small k_{OH}/k_0 ratios that characterize both fast (1.9) and slow (0.6) phases of dioxo dimer base hydrolysis.[6] The importance of OH^- as an attacking nucleophile therefore is dramatically muted in $Cr(O)_2Cr$ dimer cleavage, for which the second bridging oxo function occupies the position thought to be filled by the incoming OH^- ligand in the analogous LCrOCrL reactions. Nevertheless, there is an unexpectedly close resemblance between the $[Cr(tmpa)(NCS)]_2O^{2+}$ k_{OH} activation parameters and those reported previously for $[Cr(tmpa)(OH)]_2O^{2+}$ ($\Delta H^\ddagger = 28$ kcal mol^{-1}; $\Delta S^\ddagger = +14$ eu)[6] cleavage. The overall base hydrolysis reactivities of the two families are not greatly different at 40 °C, considering the k_{OH} (M^{-1} s^{-1}) ranking: $[Cr(tmpa)(NCS)]_2O^{2+}$ (1.6×10^{-2}) > $[Cr(tmpa)(O)]_2^{2+}$ (4.6×10^{-3})[6] > $[Cr(tmpa)(NCO)]_2O^{2+}$ (1.1×10^{-3}) > $[Cr(tmpa)(CN)]_2O^{2+}$ (4.2×10^{-4}) > $[Cr(tmpa)(OH)]_2O^{2+}$ (1.5×10^{-4}).[6]

Synthesis and Electrochemistry of 2,2'-Bipyridyl Complexes of Dioxorhenium(V)

M. S. Ram, Christopher S. Johnson, Robert L. Blackbourn, and Joseph T. Hupp*

The rhenium(V) bipyridyl (bpy) complexes $[(bpy)(py)_2Re(O)_2](ClO_4)$ and $[(bpy)(3-pySO_3)_2Re(O)_2](Na)\cdot 2H_2O$ have been prepared by reaction of 2,2'-bipyridine with *trans*-$[(py)_4Re(O)_2](Cl)$ and *trans*-$[(3-pySO_3)_4Re(O)_2](Na)_3$ in methanol or methanol/water solutions (py = pyridine, 3-pySO$_3$ = 3-pyridinesulfonate). Despite the seemingly trivial change in coordination environment, the bpy-containing complexes were found to behave very differently from the corresponding tetrapyridyl complexes. For example, the pH-independent formal potential for reduction of Re(VI) to Re(V) was lowered by some 600 mV. On the other hand, the pH-dependent potential for the Re(V/III) couple increased by ca. 200 mV upon bpy coordination. The V/III couple also became considerably more reversible (kinetically) in its electrochemical response. The Re(III/II) potential was also shifted in the positive direction. At high pH's, the V/III and III/II couples coalesced to yield the first example of three-electron redox behavior in rhenium chemistry. By analogy with known dioxoosmium complexes, both the thermodynamic and kinetic electrochemical effects were attributed to a relative stabilization of the inaccessible Re(IV) oxidation state following bpy coordination. It was proposed that the destabilization is induced by trans to cis isomerization. The *cis*-dioxo configuration has only rarely been seen in d^2 coordination chemistry, and never for hexacoordinate rhenium. Nevertheless, circumstantial evidence from IR, NMR, and Raman experiments supported the assignment. Unfortunately, proof was not possible by these methods since both cis- and *trans*-$(bpy)(py)_2Re(O)_2^+$ would possess C_{2v} symmetry. Very recent X-ray investigations (to be reported elsewhere) have now confirmed the cis assignment.

Introduction

We and many others have had a long-standing interest in the kinetics and dynamics of single-electron-transfer (ET) reactions involving metal complexes.[1] Recently that interest has turned toward multielectron processes. In particular, we have been interested in multi-ET kinetics at electrochemical interfaces. Among the most prominent multielectron reagents are the many oxo and dioxo complexes of transition metals.[2] Typically these feature a very rich, yet chemically reversible, redox chemistry.[3]

Furthermore, they often figure importantly in both artificial and naturally occurring catalytic systems.[2]

For our purposes the *trans*-dioxo complexes of rhenium(V) were deemed nearly ideal for initial studies.[4–6] While not yet par-

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ticularly noteworthy as redox catalysts, these species do display a pH-dependent, two-electron reduction that is evidently kinetically hindered at electrochemical interfaces.[6] Furthermore the complexes are known to possess interesting *photo*redox properties.[5] Nevertheless, before initiating kinetic studies, we felt that two minor difficulties—poor aqueous solubility (millimolar or less) and poor stability in lower oxidation states (typically a few hours)—ought to be corrected. We reasoned that both could be accomplished with minimal synthetic effort. As it turns out, the synthetic remedies have been only partially successful. For $(py)_4Re(O)_2^+$ (py = pyridine), aqueous solubility was readily induced by adding sulfonate substituents. On the other hand, chemical stability was actually worsened by replacement of two monodentate ligands by the chelate 2,2'-bipyridine.

These observations, while useful, would not generally be of sufficient interest to justify separate publication. Much more compelling and surprising, however, are the rather large redox thermodynamic and kinetic effects induced by the seemingly trivial substitution of 2,2'-bipyridine for a pair of monopyridyl ligands in each of two tetrapyridyl complexes. Specifically, we find that introduction of a single ancillary carbon–carbon bond leads to (1) very substantial thermodynamic destabilization of Re(V) versus both Re(VI) and Re(III) and (2) significant kinetic enhancement of the Re(V) → Re(III) process at the electrode/solution interface. In this report, the first issue and the associated experimental data are examined in some detail; the second is the focus of ongoing experimental work and will eventually be described elsewhere. From the results contained herein, the most probable explanation for both observations is that trans to cis isomerization occurs upon ligand substitution, with resultant destabilization of Re(V).

One other aspect of the investigation which initially surprised us was the comparative difficulty in synthesizing various bipyridyl complexes of dioxorhenium. In fact we were never able to obtain an authentic bis(bipyridyl) complex. In view of this difficulty, we suggest that the single literature report[4,8] on the preparation of *trans*-$(bpy)_2Re^V(O)_2^+$ may possibly be mistaken.

Experimental Section

Materials. Triflic acid, CF_3SO_3H, was obtained from Alfa Chemicals. Bio-Gel P2 was obtained from Bio-Rad Laboratories. All other chemicals were obtained from Aldrich or Mallinckrodt Chemicals and were used as received. Aqueous solutions were prepared with water purified by a Millipore system.

Metal Complexes. $ReO(Cl)_3(PPh_3)_2$ (isomer a; PPh_3 = triphenylphosphine) was prepared according to the method of Wilkinson and co-workers.[10]

***trans*-[$(py)_4Re(O)_2$](ClO_4).** This compound was also prepared according to Wilkinson's method, but we found it necessary to add 1% water to the ethanol (or better yet, acetone) reaction mixture. (Water hydrolyzes the dimeric oxo-bridged intermediate species.) The perchlorate salt was obtained (always in small quantities) from the chloride by following the procedure of Pipes and Meyer.[6]

***trans*-[$(3-pySO_3)_4Re(O)_2$](Na)_3·3H_2O.** A 50-g sample of 3-pyridinesulfonic acid ($3-pySO_3H$) was added slowly with stirring to a suspension of 24 g of $NaHCO_3$ in 200 mL of water. (More complete neutralization was found to be a complication in the next step; unneutralized $3-pySO_3H$ did not react with the triphenylphosphine complex.) The solution was rotary-evaporated to near dryness at 60 °C and, after cooling to room temperature, precipitated further by addition of ethanol. The precipitate was collected by filtration and dried. The salt proved to be completely insoluble in ethanol or acetone but was very highly soluble in water. About 2 g of $ReOCl_3(PPh_3)_2$ and 6 g of $3-pySO_3Na$ were then refluxed in 95% ethanol for 1.5 h, and the mixture was cooled in ice. The precipitated complex was washed thoroughly with acetone. For further reaction with 2,2'-bipyridine, the complex was used in crude form; otherwise, the complex was dissolved in 10 mL of water and the solution was passed through a Bio-Gel P2 column (150-mL volume). The central

portion of the yellow band was collected into 100 mL of ethanol cooled in ice. The purified product was filtered out, washed with ethanol, and dried in a vacuum oven at 45 °C. Anal. Calcd: C, 24.64; H, 2.25; N, 5.75. Found: C, 24.44; H, 2.11; N, 5.54.

[$(bpy)(py)_2Re(O)_2$](ClO_4). A 1-g amount of [$(py)_4Re(O)_2$](Cl) was stirred at room temperature for 24 h with 4 g of 2,2'-bipyridine in methanol (70 mL). About 700 mL of ether and 50 mL of CH_2Cl_2 were added to the solution, which was stirred and then allowed to settle for 30 min. The precipitated complex was separated by decantation. It was then dissolved in 100 mL of water (kept chilled in ice), and the solution was filtered and loaded onto a Sephadex C-25 cation-exchange column (Aldrich). The unreacted yellow tetrapyridyl complex was first eluted with 0.1 M $NaNO_3$. The ionic strength was then raised to 0.3 M in $NaNO_3$; the red bipyridyl complex was eluted into a beaker containing 4 mL of saturated $NaClO_4$, and the mixture was kept chilled. The precipitated complex was filtered out and washed with two 1-mL portions of water and two 20-mL portions of ether containing 10% acetone. The complex was dried in a vacuum oven at 40 °C. Solutions of this complex were always kept cold. Even so, significant decomposition was often evident within 2 h. It is also worth mentioning that the reaction is reversible: $(py)_4Re(O)_2^+$ is obtained in good yield following 10 min of heating in CH_3CN with excess pyridine. Anal. Calcd: C, 38.0; H, 2.85; N, 8.86; Cl, 5.13. Found: C, 36.68; H, 2.77; N, 8.59; Cl, 5.60.

[$(bpy)(3-pySO_3)_2Re(O)_2$](Na)·2H_2O. A 1-g sample of [$(3-pySO_3)_4Re(O)_2$](Na)_3 and 4 g of 2,2'-bipyridine were stirred in 100 mL of CH_3OH and 40 mL of water. The solution was filtered and stirred for 24 h. The complex was precipitated by repeated ether/CH_2Cl_2 addition. The complex was finally dissolved in 100 mL of water, and the mixture was filtered (while cold) and loaded onto a Sephadex A-25 column, which was washed thoroughly with ice-cold water. The complex was eluted with an ice-cold 0.3 M $NaNO_3$ solution. The red band was eluted and rapidly rotary-evaporated at 35 °C to near dryness. The complex, contaminated heavily with $NaNO_3$, was precipitated further with an ethanol/ether mixture, filtered out, and dried. From the crude solid, about 90% of the complex was extracted with CH_3OH and precipitated with ether. The complex was still contaminated significantly with $NaNO_3$. It was redissolved, therefore, in a minimal amount of water, and the mixture was passed through a Bio-Gel P2 column, with cold water as the eluent. The middle fraction of the red band was collected and rapidly rotary-evaporated to near dryness at 35 °C. The complex was precipitated with the addition of an ethanol/ether mixture, filtered out, and dried in a vacuum oven at 40 °C. Solutions of the complex were kept cold; otherwise they decomposed significantly in solution within 2 h. Anal. Calcd: C, 32.0; H, 2.66; N, 7.42. Found: C, 31.86; H, 2.42; N, 7.55.

Attempted Preparation of $(bpy)_2Re(O)_2^+$. The reaction of $ReOCl_3$-$(PPh_3)_2$ with 2,2'-bipyridine gave a purple-black material, in wet or dry ethanol or acetonitrile in the presence or absence of oxygen. On the basis of NMR and IR spectroscopy, cyclic voltammetry, and elemental analysis, the identity of the product could not be established. Clearly, however, it was not [$(bpy)_2Re(O)_2$](X). The reaction of the same starting materials in either CH_2Cl_2 or DMSO gave red solutions. Workup yielded only an ether-soluble neutral compound, possibly $(bpy)ReOCl_3$. Reactions of 5-chlorophenanthroline, 5-sulfonato-2,2'-bipyridine (sodium salt),[11] and 4,4'-dichloro-2,2'-bipyridine with $ReOCl_3(PPh_3)_2$ in refluxing ethanol gave only unidentifiable blue, purple, and green products. The reaction of $(py)_4Re^V(O)_2^+$ and $(3-pySO_3)_4Re^V(O)_2^{3-}$ with 2,2'-bipyridine at >40 °C appeared to give the same products as with the phosphine reaction. Finally, the reaction of 2,2':6',2''-terpyridyl with $(py)_4Re^V(O)_2$ gave a purple material that could not be identified.

Measurements. Background-corrected ultraviolet and visible spectra were obtained in a single quartz cell (path length = 0.5 cm) with a Cary 14 spectrophotometer that had been rebuilt by On-Line Instruments Service. Spectroelectrochemical experiments were carried out, under argon, by using a thin-layer cell. The cell contained a gold-minigrid working electrode, a platinum-wire counter electrode, and a saturated (sodium) calomel reference.[7] The potential was controlled with a PAR 273 potentiostat. The concentration of the rhenium complex typically was 1 to 2 mM. In acidic solutions, attempts to reduce Re(V) to Re(III) or Re(II) were initially frustrated by concurrent proton reduction. We found, however, that this difficulty could be suppressed by addition of 2.5×10^{-4} M $Pb(NO_3)_2$. (Under- as well as overpotentially deposited lead is a well-known inhibitor of molecular hydrogen evolution on electrocatalytic surfaces.[8]) In a few instances problems still remained due to *homogeneous* proton (or water) reduction by electrogenerated Re(II).[6] Cyclic as well as rotating-disk voltammograms were obtained by using

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Table 1. Infrared and Raman Data (750–950 cm⁻¹) for Dioxorhenium (V) Complexes

complex	IR[a]	Raman[b]
[(bpy)(py)₂Re(O)₂](ClO₄)	767, 845, 904	770, 845, 905
[(bpy)(3-pySO₃)₂Re(O)₂](Na)	767, 845, 904	
[(3-pySO₃)₄Re(O)₂](Na)₃	769, 828	
[(py)₄Re(O)₂](ClO₄)	820	916[c]

[a] KBr pellet. (The first complex was also examined in CH₃CN and gave identical results.) [b] Aqueous solution. [c] Reference 5c.

a well-polished, ultrasonicated glassy-carbon electrode in the usual three-electrode arrangement. Potentials were applied by using a Pine Instruments RDE 4 potentiostat. Except as noted, solutions were prepared by dissolving the complexes in appropriate aqueous buffer solutions at $\mu = 0.1$ M. (The buffers or electrolytes were trifluoromethanesulfonic acid and its sodium salt for pH 1–2, chloroacetic acid/chloroacetate for pH 3, acetic acid/acetate for pH 4 and 5, phosphate for pH 7, Tris for pH 8, sodium borate for pH 9, bicarbonate/carbonate for pH 10, diethylamine for pH 11, and sodium hydroxide for pH 12 and above. Most solutions contained ~0.02 M buffer plus ~0.08 M sodium trifluoromethanesulfonate.) These were degassed by purging with nitrogen. IR spectra were obtained as KBr pellets in a Mattson FTIR instrument. NMR spectra were obtained in acetone-d_6 or D₂O with a Varian XLA-400 spectrometer. In the spectra the solvent itself was taken as a reference. Elemental analyses were obtained from the Analytical Services Laboratory of Northwestern University or from Galbaith Laboratories. Fast atom bombardment (FAB) measurements were likewise made in NU's Analytical Services Laboratory. Raman measurements were obtained in aqueous solution (Na₂SO₄ reference) by using a windowless flow cell. The excitation sources and other instrumentation have been described previously.[9]

Results

Vibrational Spectra. Table I lists selected IR spectral data for the dioxorhenium(V) complexes. Only the bands in the metal–oxo stretching region (750–950 cm⁻¹) are given. We note that in (py)₄Re(O)₂⁺ an intense band at 820 cm⁻¹ has previously been assigned to an asymmetric O=Re=O stretch.[4i] This band shifts to 828 cm⁻¹ in (3-pySO₃)₄Reⱽ(O)₂³⁻ and 845 cm⁻¹ in each of the bipyridyl complexes. (Note that each of these bands is far removed from the Re–O–Re stretch found in μ-oxo rhenium dimeric complexes.[13,14]) Also seen for the bipyridyl complexes are intense transitions near 904 and 767 cm⁻¹. The higher energy band is

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(18) A dissociative mechanism, as sketched below, might provide a kinetic basis for favoring the cis geometry. Presumably, the second step in the mechanism would be driven by the need to relieve steric crowding in the vicinity of the pyridine α protons. On the basis of this speculation, the eventual synthesis of a *trans*-dioxorhenium bipyridyl complex would probably require a much more reactive starting material or intermediate species than employed here (so that substitution could outrun isomerization).
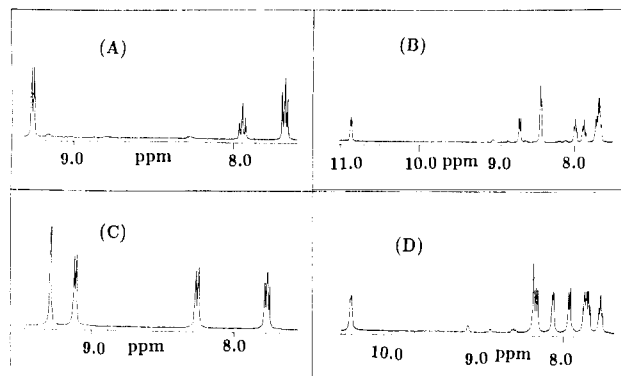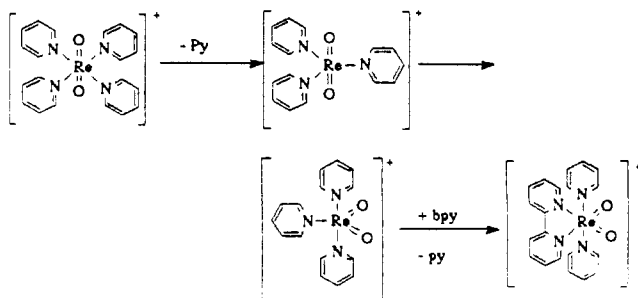
Figure 1. ¹H NMR spectra of dioxorhenium complexes (reference solvent). (A) (py)₄Re(O)₂⁻ complex in acetone-d_6: δ 9.25 (d, 8 H), 7.94 (t, 4 H), 7.68 (t, 8 H). (B) (bpy)(py)₂Re(O)₂⁺ complex in acetone-d_6: δ 10.87 (d, 2 H), 8.70 (d, 2 H), 8.44 (d, 4 H), 7.99 (t, 2 H), 7.88 (t, 2 H), 7.69 (m, 6 H). (C) (3-pySO₃)₄Re(O)₂³⁻ complex in D₂O: δ 9.28 (s, 4 H), 9.11 (d, 4 H), 8.26 (d, 4 H), 7.77 (t, 4 H). (D) (bpy)(3-pySO₃)₂Re(O)₂⁻ complex in D₂O: δ 10.36 (d, 2 H), 8.31 (m, 4 H), 8.12 (d, 2 H), 7.4 (d, 2 H), 7.74 (m, 4 H), 7.59 (t, 2 H).

most reasonably assigned as the symmetric O=Re=O stretch. The lower presumably is an additional asymmetric stretch, although an assignment as a low-frequency bpy mode cannot be ruled out. (Actually, two overlapping bands appear in the 770–775-cm⁻¹ region.) Interestingly, the same set of bands appears in Raman spectra of the bpy complexes (Table I). The appearance of all three bands in both spectra clearly indicates a lack of inversion symmetry. (In contrast, in the higher symmetry tetrapyridyl complexes the IR/Raman exclusion principle is followed.) We further observed that of the oxo modes in the bpy complexes only the lowest energy (possibly bpy) and highest energy ones were resonantly enhanced. Finally, we note that the IR spectrum of (bpy)(py)₂Re(O)₂⁺ in CH₃CN was identical with that obtained in a KBr pellet.

Mass Spectra. A positive-ion FAB spectrum of (bpy)(py)₂Re(O)₂⁺ contained the expected parent peak at $m/e = 533$. Other large peaks exist at $m/e = 454$ and 375. These can reasonably be assigned as the one and two pyridyl loss fragments. No peaks are observed below the cluster at $m/e = 375$. Also, none are found from $m/e = 535$ up to $m/e = 1200$; consequently, dimer formation can be ruled out. Negative-ion FAB on (bpy)(3-pySO₃)₂Re(O)₂⁻ gave peaks at $m/e = 691$ and below, as expected. (No peaks above $m/e = 691$ were observed). Finally, a total mass determination by osmometry (Galbraith Laboratories) for [(bpy)(py)₂Re(O)₂](ClO₄) yielded 607 g/molecular formula in acetone (633 g/molecular formula expected), further reinforcing the assignment of the bpy complexes as monomers.

¹H NMR Spectra. The proton NMR spectra of the complexes are given in Figure 1. The spectra can be rationalized on the basis of simple AB coupling, although there is one non-first-order coupled multiplet in the (bpy)(3-pySO₃)₂Reⱽ(O)₂⁻ spectrum. For (bpy)(py)₂Re(O)₂⁺ (Figure 1B) the spectrum integrates as 2 H (doublet, 10.87 ppm), 2 H (doublet, 8.70 ppm), 4 H (doublet, 8.44 ppm), 2 H (triplet, 7.99 ppm), 2 H (triplet, 7.88 ppm), and 6 H (multiplet, 7.69 ppm). Note that the α protons (pyridine ring) in the bpy complexes are shifted upfield compared to those in the tetrapyridyl species. On the other hand, the α protons of the bipyridyl ligand itself are found relatively far downfield (δ > 10 ppm). Finally, we note that the NMR measurements (Figure 1B,D) are very sensitive to trace impurities of the starting tetrapyridyl complexes, as these have 2–4 times the number of equivalent protons at any given resonance. From the extraneous peaks, the purities for both bpy complexes appear to be greater than 96%, at least with respect to starting materials.

UV–Vis Spectra of Rhenium(V). The UV–vis spectral data for five Re(V) complexes in water (and other solvents) are summarized in Table II. The bipyridyl complexes display a visible band at about 490 nm with an extinction coefficient of 4.2–4.6 × 10³ M⁻¹ cm⁻¹. Both spectra are completely independent of pH in the range from 0.5 to 10. (Decomposition occurs below pH

Table II. UV–Vis Data for Dioxorhenium(V) Complexes

Re(V) complex	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})			
$(py)_4Re(O)_2^+$	water	445 (1.2×10^3)	331 (1.94×10^4)		245 (1.53×10^4)
	CH_3OH	429	344		
	CH_3CH_2OH	416	347		
	CH_3CN	422	352		
	DMSO	423	356		
$(4\text{-picoline})_4Re(O)_2^+$	water	453 (1.24×10^3)	331 (2.2×10^4)		245 (1.37×10^4)
$(bpy)(py)_2Re(O)_2^+$	water	498 (4.2×10^3)	383 (8.3×10^3)	300 (1.64×10^4)	245 (1.45×10^4)
	CH_3OH	521	400		
	CH_3CH_2OH	523	402		
	CH_3CN	525	406		
	DMSO	527	413		
$(3\text{-pySO}_3)_4Re(O)_2^{3-}$	water	433 (1.4×10^3)	346 (2.1×10^4)		253 (1.9×10^4)
	CH_3OH	419	354		
	DMSO	434	361		
$(bpy)(3\text{-pySO}_3)_2Re(O)_2^-$	water	490 (4.6×10^3)	411 (9.7×10^3)	300 (1.64×10^4)	254 (1.4×10^4)
	CH_3OH	516	418		
	CH_3CH_2OH	519	417		
	CH_3CN	521	413		
	DMSO	526	421		

Table III. Visible Data for Rhenium(III) and Rhenium(II) at pH 10

	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	
Re(V) complex	Re(III)	Re(II)
$(py)_4Re(O)_2^+$	409 (1.1×10^4)	466
$(bpy)(py)_2Re(O)_2^+$	454 (1.0×10^4)	501 (1.3×10^4)
$(3\text{-pySO}_3)_4Re(O)_2^{3-}$	494	not measd
$(bpy)(3\text{-pySO}_3)_2Re(O)_2^-$	506 (9×10^3)	546 (1.3×10^4)

0.5.) The visible spectra of the bipyridyl complexes display a solvent dependence that differs from that of the tetrapyridyl species. Most notably, the band near 490 nm in the former moves toward longer wavelength (ca. 525 nm) upon replacement of water by methanol, ethanol, acetonitrile, or DMSO. The band near 400 nm also moves to longer wavelength (see Table II). In the tetrapyridyl complexes, the band at ~445 nm moves to 420 nm, and the band at 331 nm moves to 400 nm, in the same series of solvents (Table II). Apart from an extra band near 300 nm for the bipyridyl species, the UV spectra for all five complexes are similar.

Visible Spectra of Re(III) and Re(II). Generation of both Re(III) and Re(II) initially proved difficult. For example, chemical reductions with dithionite, hydrazine, or Zn(Hg) in acidic aqueous solutions gave color changes, but reoxidation with Ru-$(NH_3)_6^{3+}$ led to only about 10% recovery of Re(V). Furthermore, at pH >5, turbidity resulted upon reduction. Bulk electrolysis over a mercury pool also appeared to induce decomposition. In addition, there were difficulties in transferring the reduced solutions to spectral cells. Initial attempts at direct electrolysis (acidic solutions) within a spectral cell proved unsuccessful due to hydrogen and heat evolution at the gold or platinum working electrode and because of the excessive time required for electrolysis. Eventually we found, however, that a gold-minigrid electrode in an optically transparent thin-layer cell was suitable for obtaining spectra of the reduced bipyridyl complexes. At pH 10, the hydrogen evolution problem was not serious. Because of the extremely slow reduction of Re(V) to Re(III), however, a sufficient potential to generate Re(II) was employed. This species was then reoxidized to Re(III) at –0.9 V. More than 90% of the original Re(V) spectrum could be restored upon applying 0 V. The primary spectral features of the reduced species at pH 10 are given in Table III, and the full spectrum is shown in Figure 2.

The attempted reduction of the bipyridyl complexes below pH 7 with the gold minigrid was initially unsuccessful. Upon addition of 2.5×10^{-4} M $Pb(NO_3)_2$ (see Experimental Section), the Re(V) $\rightarrow$ Re(III) reduction was possible, but the spectrum of Re(II) could not be obtained. The reversibility of the two-electron transformation was greater than 80% when implemented within 1 h of applying the initial reduction potential. The maximum absorption for $(bpy)(py\text{-}X)_2Re^{III}(OH)(OH_2)^{n+}$ was at 383 nm (X = H) or 450 nm (X = SO_3^-) (pH 2). For $(bpy)(py\text{-}X)_2Re^{III}\text{-}(OH)_2^{n+}$ λ_{max} is found at 450 nm (X = H) or 506 nm (X = SO_3^-) (pH 5 and 10). We are unable to give precise extinction coef-
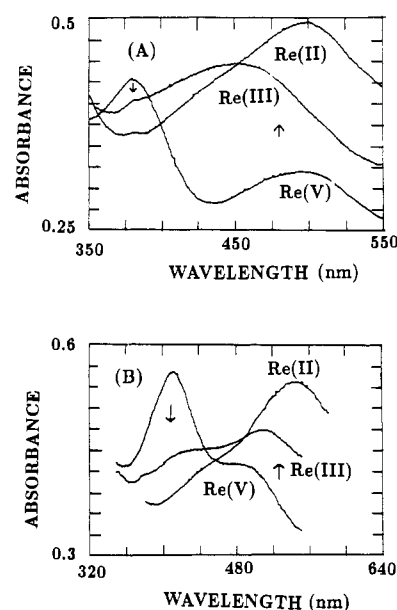

Figure 2. Spectral changes accompanying the reduction of (A) (bpy)-$(py)_2Re(O)_2^+$ and (B) $(bpy)(3\text{-pySO}_3)_2Re(O)_2^-$ complexes to Re(III) and Re(II) at pH 10 in a thin-layer cell with a gold-minigrid working electrode.

ficients, but generally they were in the vicinity of 1×10^4 M^{-1} cm^{-1}.

Oxidation of Re(V). The dioxorhenium(V) bipyridyl complexes could be oxidized essentially instantaneously in acidic aqueous solution with Ce(IV), HNO_3, or Br_2. Unfortunately, the oxidation product (Re(VI)) was stable for only a few seconds. In neutral solution, rhenium(V) could be oxidized slowly by persulfate, but the product was still unstable. Similarly, Re(VI) instability was observed in spectroelectrochemical experiments. We had hoped that the rhenium(VI) bipyridyl complexes would be chemically stable because of the large thermodynamic stabilization of Re(VI) relative to Re(V). We note, however, that rhenium(VI) (like Os(VII)) is generally regarded as structurally unstable.[19,20] Nevertheless, in acetonitrile as solvent, Re(VI) *was* found to be resonably robust as shown by a successful (slow) bulk electrolysis to Re(VI) and back to Re(V).

Pourbaix Diagrams of Bipyridyl Complexes. Cyclic voltammograms for both the $(py)_4Re^V(O)_2^+$ and $(bpy)(py)_2Re^V(O)_2^+$

(19) (a) Cotton, F. A.; Oldham, C.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 214. (b) Jaecker, J. A.; Murtha, D. P.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *13*, 21.

(20) Johnson, N. P.; Taha, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2614.

(21) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1971**, *49*, 603.
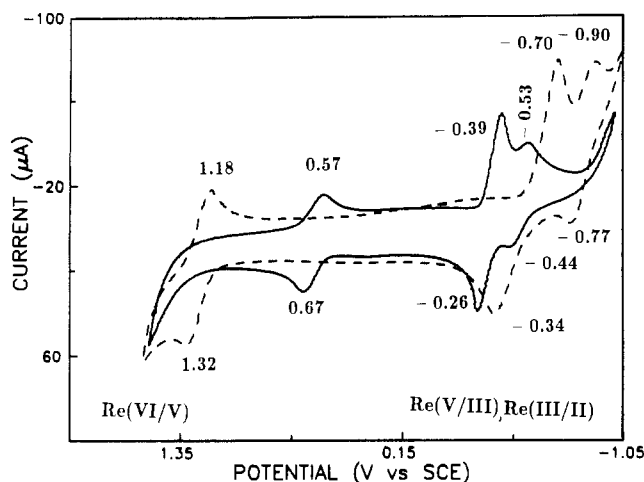
Figure 3. Cyclic voltammograms of the $(bpy)(py)_2Re(O)_2^+$ (solid line) and $(py)_4Re(O)_2^+$ (dashed line) complexes at pH 2, with a glassy-carbon working electrode.
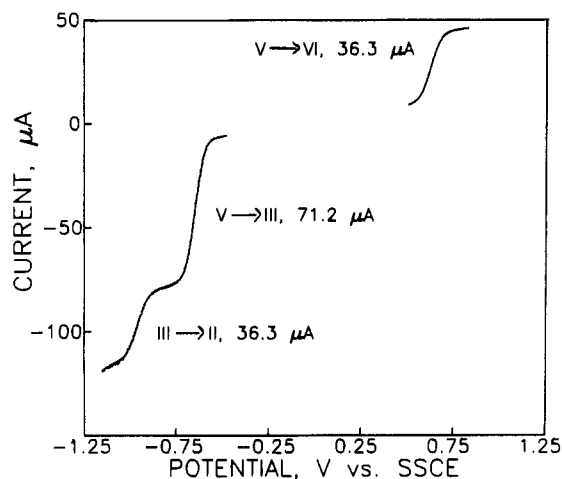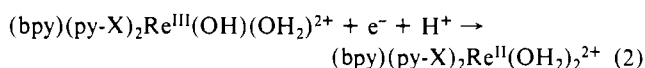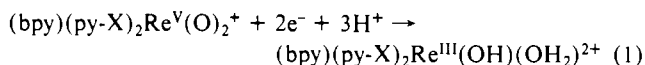

Figure 4. RDE limiting currents for the various redox processes involving $(bpy)(py)_2Re(O)_2^+$ at pH 6.8. Rotation rate = 1000 rpm; scan rate = 5 mV/s; $[Re^V]$ = 1.67 mM.

species at pH 2 are shown in Figure 3. The overall cyclic voltammetric patterns for all the complexes are similar in that the VI/V, V/III, and III/II couples are observed. The limiting currents for these couples in rotating-disk experiments, are in the ratio 1:2:1 (Figure 4). Note, however, that the VI/V couple in the bpy complex is shifted negative by about 600 mV in comparison to that of the tetrapyridyl complex. Furthermore, the V/III couple is appreciably more reversible (kinetically) in the bpy case. Latimer diagrams for the various complexes at pH 2 are offered in Figure 5. The pH dependence of the potentials for the various redox couples (Pourbaix diagrams) associated with the bipyridyl complexes are shown in Figures 6 and 7.

The reduction potentials of the rhenium(V) bipyridyl complexes are markedly pH dependent, just as for the $(py)_4Re^V(O)_2^+$ complex.[6] The slopes of $E_{1/2}$ vs pH for the various redox couples are also similar. The potential for the VI/V couple (which is chemically reversible on a CV time scale despite the problems noted above) is independent of pH in the range from 1 to 11. The potentials for the V/III and III/II couples are as follows: In the region 1 < pH < 3.15, the V/III couple shows a 90 mV/pH slope, while the III/II couple shows a 60 mV/pH slope. These can be represented by eq 1 and 2 (X = H or SO_3^-; for X = SO_3^- the

$(bpy)(py-X)_2Re^V(O)_2^+ + 2e^- + 3H^+ \rightarrow$
$$(bpy)(py-X)_2Re^{III}(OH)(OH_2)^{2+} \quad (1)$$

$(bpy)(py-X)_2Re^{III}(OH)(OH_2)^{2+} + e^- + H^+ \rightarrow$
$$(bpy)(py-X)_2Re^{II}(OH_2)_2^{2+} \quad (2)$$

overall charge is 2 units less than indicated). At pH 3.15, the
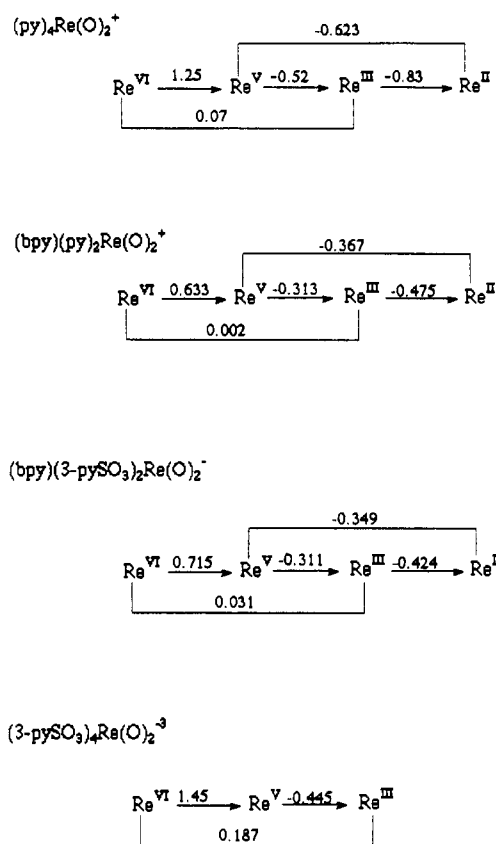

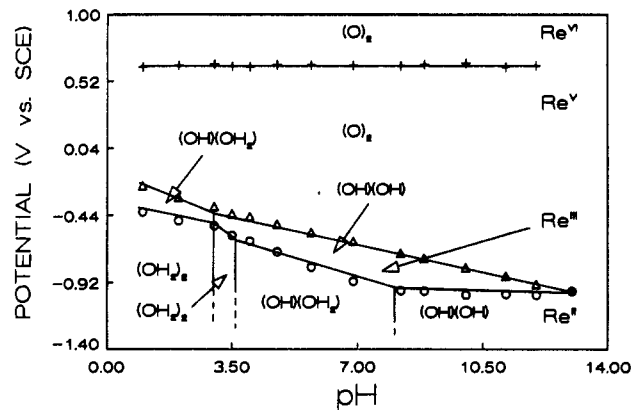**Figure 5.** Latimer diagrams for dioxorhenium complexes at pH 2.

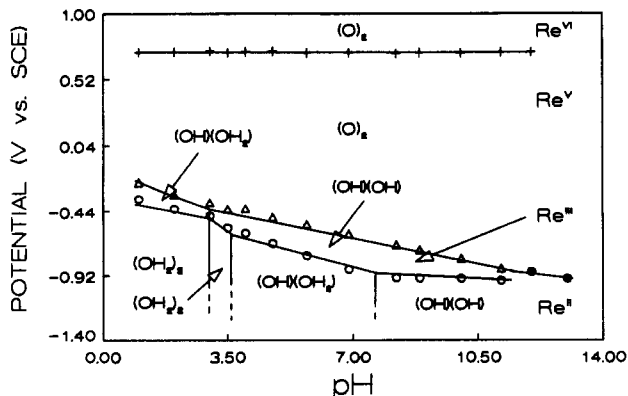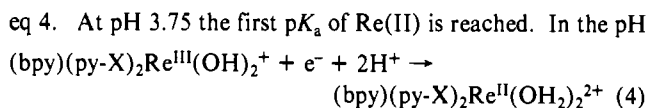**Figure 6.** Pourbaix diagram for the $(bpy)(py)_2Re(O)_2^+$ complex.
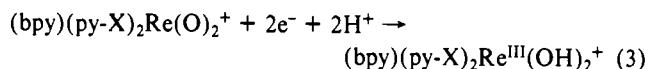

**Figure 7.** Pourbaix diagram for the $(bpy)(3-pySO_3)_2Re(O)_2^-$ complex.

pK_a of Re(III) is reached. From pH 3.15 to 12 (or higher, depending on X) the Pourbaix diagram for rhenium(V/III) has a 60 mV/slope. In this region the reaction can be represented by eq 3. In the pH region 3.15–3.75, the rhenium(III/II) couple has a slope of 120 mV. The reaction here can be represented by

$(bpy)(py\text{-}X)_2Re(O)_2{}^+ + 2e^- + 2H^+ \rightarrow$

$\qquad\qquad (bpy)(py\text{-}X)_2Re^{III}(OH)_2{}^+ \quad (3)$

eq 4. At pH 3.75 the first pK_a of Re(II) is reached. In the pH

$(bpy)(py\text{-}X)_2Re^{III}(OH)_2{}^+ + e^- + 2H^+ \rightarrow$

$\qquad\qquad (bpy)(py\text{-}X)_2Re^{II}(OH_2)_2{}^{2+} \quad (4)$

region 3.75–8.0, the rhenium(III/II) potential varies by 60 mV/pH unit. The reaction here can be described by eq 5. At

$(bpy)(py\text{-}X)_2Re^{III}(OH)_2{}^+ + e^- + H^+ \rightarrow$

$\qquad\qquad (bpy)(py\text{-}X)_2Re^{II}(OH)(OH_2)^+ \quad (5)$
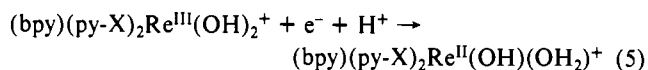
pH 8.0, the second pK_a of Re(II) is reached. Consequently, in the pH range 8.0–13.0 the Re(III/II) potential is independent of pH. This can be represented by eq 6.

$(bpy)(py\text{-}X)_2Re^{III}(OH)_2{}^+ + e^- \rightarrow (bpy)(py\text{-}X)_2Re^{II}(OH)_2$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (6)$
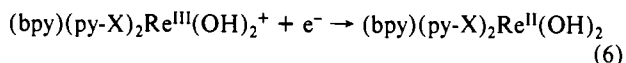
Finally, for X = $SO_3{}^-$, in the pH range 12–13 the V/III and III/II lines merge and the slope becomes 40 mV/pH unit. Furthermore, slow sweep voltammograms within this pH region yield peak separations of less than 28 mV. It follows that the reaction can best be described as

$(bpy)(3\text{-pySO}_3)_2Re^V(O)_2{}^- + 3e^- + 2H^+ \rightarrow$

$\qquad\qquad (bpy)(3\text{-pySO}_3)_2Re^{II}(OH)_2{}^{2-} \quad (7)$
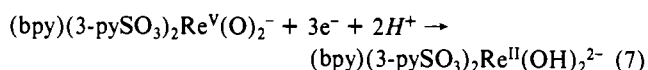
For the corresponding complex with X = H, the V/III and III/II couples coalesce near pH 13 (see Figure 6). An extrapolation of the V/III and the III/II lines for the related tetrapyridyl system indicates that a similar three-electron couple will likely exist only at unattainably high pH values.

Discussion

Synthesis. Given the rather striking effects accompanying bipyridyl substitution, one must ask what species have actually been synthesized. The sum of NMR, Raman, IR, FAB, and elemental analysis studies clearly indicates that the new chelate complexes have the formulas $[(bpy)(py)_2Re(O)_2](ClO_4)$ and $[(bpy)(3\text{-pySO}_3)_2Re(O)_2](Na)$. The isomeric form these take, however, is less clear. There are three possibilities:

1   2

3
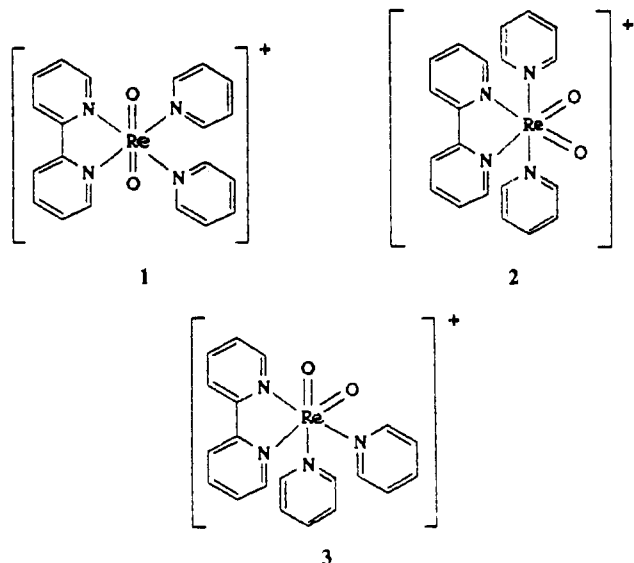
The very low symmetry cis isomer (**3**) can be ruled out on the basis of NMR spectra.[15] The distinction between the trans isomer (**1**) and the alternate cis isomer (**2**) is more problematic. Both possess C_{2v} symmetry, but lack inversion symmetry. Consequently the selection rules for vibrational spectroscopy within the pair are, strictly speaking, identical. For **1** and **2**, symmetric as well as asymmetric IR and Raman stretches (O=Re=O) are permitted. Indeed both types are found in both sets of spectra.

Despite these theoretical considerations, the strictly empirical studies by Griffith on related low-symmetry dioxoosmium com-

plexes suggest that a spectral distinction between **1** and **2** may still be possible.[13e,f] Griffith finds for structures like **1** that the pattern of IR and Raman behavior is well explained by approximate D_{4h} symmetry. In other words, intense asymmetric metal–oxo stretches are found in the IR and intense symmetric stretches in Raman spectra, but not vice versa. On that basis we are inclined to designate the bpy-containing species as cis-dioxo complexes (isomer **2**). Additional circumstantial evidence comes from UV–vis and especially electrochemical data (described below). If the assignments are correct, the two rhenium(V) bipyridyl complexes would apparently represent the first examples of solution-stable cis-dioxo species (hexacoordinate) with d^2 electronic configuration. (Three additional examples are known: $[(bpy)_2Os^{VI}(O)_2](ClO_4)$,[16] which is stable in the solid state, $[(bpy)_2Ru^{VI}(O)_2](ClO_4)$, which has a transient solution existence,[17] and potassium tris(acetato)dioxoosmate, which may or may not be solution stable.[22]) Given the rarity of d^2 cis complexes, however, it is somewhat surprising that the corresponding trans-dioxorhenium(V) complexes (with bpy) have proven elusive.[18]

Turning to the last synthesis (or attempted synthesis), we believe that we have obtained the same material described in the literature as $[(bpy)_2Re^V(O)_2](ClO_4)$, although by a different route.[4h] It is difficult to know for certain because the literature reference lacks UV–vis, IR, Raman, and NMR characterization and analysis for carbon. The blue-purple compound we obtained [λ_{max} = 600 nm (ϵ = 9 × 10^3 M^{-1} cm^{-1}), 571 nm (sh), and 282 nm (ϵ = 3 × 10^4 M^{-1} cm^{-1})] changes to purple in 1 M H_2SO_4 (λ_{max} = 516 nm). The compound has a band in the IR spectrum at 873 cm^{-1}, a very poor NMR spectrum, and a cyclic voltammogram featuring only two anodic peaks. Upon reduction with zinc amalgam, the compound decomposes. We do not believe that this is the cis-dioxo complex, as the cis configuration would likely be unstable for a d^2 species (but note preceding discussion). Furthermore, the IR frequency would probably be lower.[13,14] It is worth noting that Cotton and co-workers have isolated only $ReCl_3(bpy)$ from their reactions of chlororhenium complexes[19] and that Johnson, Taha, and Wilkinson have reported only an oxo-bridged rhenium dimer.[20] Lock has pointed out that, unlike $ReOCl_3(py)_2$ (the first intermediate in the formation of $(py)_4Re(O)_2{}^+$ from $ReOCl_3(PPh_3)_2$), the $ReOCl_3(bpy)$ species does not hydrolyze the chloride trans to the oxo ligand; instead it forms an oxo-bridged dimer.[21] The above reactivites all imply that our complex is not trans-bis(bipyridyl)dioxorhenium(1+). A plausible partial explanation for the apparent inaccessibility of the latter can be found in the probable synthetic intermediacy of cis-$(bpy)(py)_2Re^V(O)_2{}^+$ (**2**).

Electronic Spectra. Even though there is only a slight difference in the gross structure of $(bpy)(py)_2Re^V(O)_2{}^+$ versus $(py)_4Re^V(O)_2{}^+$, tremendous differences exist in both the UV–vis spectra and the electrochemistry. The UV spectrum of either $(bpy)(py)_2Re^V(O)_2{}^+$ or $(bpy)(3\text{-pySO}_3)_2Re^V(O)_2{}^-$ (or, for that matter, $(py)_4Re^V(O)_2{}^+$ or $(3\text{-pySO}_3)_4Re^V(O)_2{}^{3-}$) can easily be understood as a ligand-based ($\pi \rightarrow \pi^*$) transition. $(3\text{-pySO}_3)_4Re^V(O)_2{}^{3-}$ and $(py)_4Re^V(O)_2{}^+$ each display additional bands at 331 and 445 nm. In the bpy complexes these are replaced by bands at 383 and 498 nm. We note, however, that the solvent dependence of the 498-nm band in the bipyridyl complexes differs from that of the tetrapyridyl complexes (Table II). This suggests that the transitions have different electronic origins. In the bipyridyl complexes the bands at 383 and 498 nm are tentatively assigned as metal-to-ligand charge-transfer transitions. On the other hand, Thorp, Van Houten, and Gray have recently assigned the shorter wavelength transition in $(py)_4Re^V(O)_2{}^+$ as the MLCT, $d_{xy} \rightarrow \pi^*(py)$ transition and the longer wavelength (solvent independent) transition as a d–d transition with intensity stealing from the adjacent MLCT band.[5c] These differences imply a fundamental difference in electronic structure for the bpy vs tetrapyridyl complexes. One further indication of substantial structural differences is the complete absence of room-temperature luminescence from excited

(22) Behling, T.; Capparelli, M. V.; Skapski, A. C.; Wilkinson, G. *Polyhedron* **1982**, *1*, 840.

(bpy)(py)$_2$Re(O)$_2^+$ in a variety of nonaqueous solvents. ((py)$_4$Re(O)$_2^+$ is highly luminescent.[5]) Evidently in the bpy complex the usually luminescent ^3E_g state no longer represents the lowest lying, excited electronic configuration.

For Re(III) and Re(II) Pipes and Meyer have assigned the visible region absorption of the tetrapyridyl complex to d$\pi \rightarrow \pi^*$(py).[6] They have pointed out that contributions from other MLCT or LMCT transitions (p*(OH) → dπ(Re)) are also likely. These arguments may well be appropriate for bipyridyl and pyridinesulfonate complexes also.

Electrochemistry. One of the interesting features of the dioxorhenium in comparison to, e.g., osmium[16] or ruthenium[17] is the tremendous stabilization of the often inaccessible d^1 configuration. For example, in *trans*-(py)$_4$Re(O)$_2^{n+}$ the d^1 state (Re^{VI}) is attainable at +1.25 V, but in analogous Ru and Os species the M^{VII} states are unknown.[2,16,17] In the rhenium case, the apparent isomerization to the cis form enhances that stabilization, lowering the d^1/d^2 potential to +0.62 V. This suggests that the corresponding Re^{VII} and Os^{VII} might also be observable from *cis*-(bpy)$_2$M(O)$_2^+$, on the basis of oxidation in conventional nonaqueous solvents (i.e., the M(VII/VI) couple might well be accessible at potentials below +2.0 V).

For the Re(V/III) couple, bpy substitution and (apparent) trans → cis isomerization have the opposite effect: E_f is shifted positive in comparison to that of the tetrapyridylrhenium couple. The effect can perhaps be partially understood in terms of a relative destabilization of Re^V, as suggested by the shift in VI/V potential (assuming no other states are highly stabilized, or destabilized). A more informative analysis, however, is in terms of d^3 stabilization (relative to d^2) upon trans → cis isomerization. The key oxidation state is then the "invisible state" Re^{IV}. Dobson et al. have noted that, in the corresponding (bpy)$_2$Os^V(O)$_2^+$ species, isomerization should lead to a significant change in filled-orbital energetics.[16] In *trans*-dioxoosmium the proposed orbital-ordering scheme is d$_{xy}$ < d$_{xz}$ < d$_{yz}$, where the z axis runs along the O=Os=O molecular axis. The ground-state configuration for Os^V (or Re^{IV}) will then be (d$_{xy}$)^2(d$_{xz}$)^1.

For *cis*-dioxorhenium (or -osmium) the d$_{xz}$ and d$_{yz}$ orbitals are expected to be nearly equivalent.[16] Exact equivalence apparently is absent, judging by the lack of paramagnetic effects in the NMR spectrum of Re^V (Figure 1); a probable explanation for the ground-state Re^V diamagnetism can be found in spin–orbit coupling energetics. Under these conditions, Dobson et al.[16] suggest that d$_{xz}$ and d$_{yz}$ are mixed and then slightly split to give dπ_1 <dπ_2 ≪ d$_{xy}$. This leads to a (dπ_1)^2(dπ_2)^1 configuration for either Re^{IV} or Os^V. The important point is that electronic destabilization will be relatively slight in adding one electron to the initially unfilled dπ_2 orbital in the *cis*-dioxometal complex; for one-electron addition to the *trans*-dioxometal complex the destabilization should be greater.

In the (bpy)$_2$Os(O)$_2^{n+}$ case, Dobson's arguments are amply illustrated by the 370-mV positive shift in the VI/V potential (pH 10; proton decoupled) upon trans → cis isomerization.[16] In the rhenium case, the corresponding V/IV couple is buried within the overall two-electron, proton-coupled V/III transformation. In

other words, at all accessible pH's Re^{IV} will disproportionate into Re^V and Re^{III} (or Re^{II}). Nevertheless, the fate of the V/IV couple can still be inferred by noting that E_f(V/III) = $^1/_2 E_f$(V/IV) + $^1/_2 E_f$(IV/III). If it is assumed for the moment that the redox transition, d^3 + e$^-$ + nH$^+$ → d^4, is subject to no *extra* electronic stabilization (or destabilization) upon isomerization, then E_f-(IV/III)(cis) − E_f(IV/III)(trans) will simply equal E_f(V/IV)(cis) − E_f(V/IV)(trans). The observed trans → cis shift to roughly +200 mV for Re(V/III) could then be ascribed to an identical shift for the thermodynamically inaccessible V/IV couple. Alternatively, if the change in V/III potential is attributed entirely to the first reduction, then E_f(V/IV) would shift by roughly +400 mV, in close agreement with the known Os(VI/V) behavior.[16] In either case, the shift in Re(V/IV) potential should also lead to greater Re(IV) *kinetic* accessibility (cis isomer) and, therefore, faster 2e reduction kinetics. Faster kinetics indeed are observed for cis vs trans (see Figure 3), but the details are not yet fully established.

An overview of the complementary VI/V and V/III potential shifts is provided by the Latimer diagram in Figure 5. From the diagram it can be seen that the hypothetical VI/III reduction potentially is largely *unaffected* by trans → cis isomerization (i.e. by substitution). There is a caveat, however. Over much of the available pH range, the trans isomer reportedly undergoes only a one-proton change.[6] Reduction of the cis isomer, however, always requires at least two protons. Thus the comparison may not be fully appropriate. On the other hand, the observation of a one-proton change in the tetrapyridyl reaction is surprising since it leads to an apparent violation of the general (empirical) rule against low-valent metal–oxo formation.[2b,14] Inasmuch as the assignment of Re^{III}–oxo and Re^{II}–oxo species is predicated upon only slight spectral ($\Delta\lambda_{max}$ = 4 nm) and electrochemical changes,[6] this particular (minor) point might deserve reexamination.

One other interesting aspect of the *cis*-Re^V(O)$_2^+$ chemistry[23] is the appearance of a simultaneous three-electron reduction at pH ≥12. This is an obvious consequence of (1) the compression of all the Re-based redox potentials and (2) the extended pH depencence of the V/III potential over the range where the III/II couple is pH independent. The only other examples of three-electron behavior for monomeric species are apparently those involving reduction of *trans*-(bpy)$_2$Os^{VI}(O)$_2^{2+}$ (low pH's),[16] (terpyridine)Os^{VI}(O)$_2$(OH)$_2^{2+}$ (low and intermediate pH's),[3a] and (phenanthroline)Os^{VI}(O)$_2$(OH)$_2$ (high pH's).[3a] One of the striking aspects of the Re(V/II) electrochemical reaction, in comparison to the osmium examples, is just how facile the rhenium reaction is kinetically.

(23) On the basis of an X-ray crystallographic investigation, we have now confirmed (some months after the original manuscript submission) that the (bpy)(py)$_2$Re(O)$_2^+$ complex indeed does possess a cis configuration. The complete details of this study will be reported elsewhere.