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(acac)<sub>2</sub>Cl(H<sub>2</sub>O)].

**Supplementary Material Available:** For the Ru-acac complex, Tables SI-SIII and SV, listing assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and full crystal and intensity data (4 pages); Table SIV, listing observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
Northwestern University, Evanston, Illinois 60208-3113

## Ligand Tuning Effects upon the Multielectron Reduction and Single-Electron Oxidation of (Bi)pyridyl Complexes of *cis*- and *trans*-Dioxorhenium(V): Redox Thermodynamics, Preliminary Electrochemical Kinetics, and Charge-Transfer Absorption Spectroscopy

M. S. Ram, Lisa M. Jones, Howard J. Ward, Ying-Hsiow Wong, Christopher S. Johnson, P. Subramanian, and Joseph T. Hupp\*

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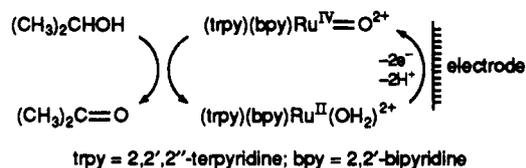
The effects of ligand substituents upon the electrochemistry and charge-transfer absorption spectroscopy of complexes of the type *trans*-(O)<sub>2</sub>Re<sup>V</sup>(py-X)<sub>4</sub><sup>+</sup> (py-X is a substituted pyridine) and *cis*-(O)<sub>2</sub>Re<sup>V</sup>(bpy-Y<sub>2</sub>)(py-X)<sub>2</sub><sup>+</sup> (bpy-Y<sub>2</sub> is a doubly substituted 2,2'-bipyridine ligand) have been examined. Both series of complexes undergo a simple one-electron oxidation, but the Re(VI/V) potentials (*E*<sub>r</sub>) are roughly 600 mV higher for the *trans* series compared with the *cis*. For both series, (bi)pyridyl substituents exert large effects: *E*<sub>r</sub>(VI/V) increases by as much as several hundred millivolts upon replacement of electron-withdrawing substituents by electron-donating groups. Reduction of Re(V) is more complex. For the *cis* series, and a portion of the *trans*, it occurs by a two-electron process followed by a one-electron step. For some of the *trans* species, however, a three-electron reduction (to Re(II)) is seen. Furthermore the reductive reactions are pH dependent, indicating the uptake of protons (and oxo to hydroxo or aqua ligand conversion) upon Re(III) or Re(II) formation. A surprising finding in view of the Re(VI/V) results is that *E*<sub>r</sub>(V/III) is essentially independent of ligand composition for both the *trans* and *cis* series. A careful consideration of substituent effects for *cis*-(OH)<sub>2</sub>Re<sup>III</sup>(bpy-Y<sub>2</sub>)(py-X)<sub>2</sub><sup>+</sup> reduction, which displays both pH-dependent (low and intermediate pH's) and pH-independent (high pH) behavior, suggests an explanation: electron-donating substituents evidently function simultaneously to decrease the affinity of the lower oxidation state for electrons (thereby making *E*<sub>r</sub> more negative) while increasing the affinity for protons (thereby making *E*<sub>r</sub> more positive), resulting in only a small net substituent effect. The electron/proton compensation effect appears also to be operative in the electrochemical kinetics of reduction of *trans*-(O)<sub>2</sub>Re(py-X)<sub>4</sub><sup>+</sup>. Preliminary experiments show that, at *E*<sub>r</sub>, the two-electron reduction is controlled by the rate of the Re(IV) to Re(III) step and that this step is preceded by a single protonation step. Qualitative rate comparisons, based on cyclic voltammetry peak separation measurements, reveal significant ligand substituent effects. There is no systematic dependence, however, of rate upon ligand electron-withdrawing or -donating character. The lack of correlation is interpreted in terms of compensating "electron demand" and "proton demand" effects in the overall two-electron, two-proton kinetic process. Studies of electronic absorption reveal complex correlations between metal-to-ligand charge transfer (MLCT) energies and *E*<sub>r</sub>(VI/V) for both the *cis* and the *trans* series. For the *cis* series, the charge-transfer absorptions are assigned as Re(V)-to-pyridine (higher energy) and Re(V)-to-bipyridine (lower energy) on the basis of resonance Raman enhancement effects. The effects of solvent on MLCT energies and Re(VI/V) potentials are described in the Appendix. An empirical correlation between both quantities and the so-called solvent acceptor number is found. The correlations are tentatively interpreted in terms of the metal oxidation-state dependence of specific interactions between comparatively electron-rich oxo ligands and electron-deficient solvent functionalities.

### Introduction

The growing interest among both inorganic and organic chemists in selective, redox-mediated electrocatalysis has led to a proliferation of mechanistic and synthetic studies of oxo and dioxo transition-metal complexes.<sup>1-5</sup> Oxo-containing species can

- (1) Representative work: (a) Thompson, M. S.; De Giovanni, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *49*, 4972. (b) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. (c) Dobson, J. C.; Seok, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513. (d) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855. (e) Collin, J. P.; Sauvage, J. P. *Inorg. Chem.* **1986**, *25*, 135. (f) Che, C. M.; Wong, K. Y.; Poon, C. K. *Inorg. Chem.* **1986**, *25*, 1809. (g) Che, C. M.; Ho, C.; Lee, W. O.; Lau, T. C. *Preprints: Symposium on Selective Catalytic Oxidation of Hydrocarbons, ACS Division of Petroleum Chemistry*; American Chemical Society: Washington, DC, 1990; pp 179-186. (h) Yam, V. W. W.; Che, C. M.; Tang, W. T. *J. Chem. Soc., Chem. Commun.* **1988**, 100. (i) Leising, R. A.; Takeuchi, K. *J. Inorg. Chem.* **1987**, *26*, 4391. (j) Marmion, M. E.; Takeuchi, K. *J. Am. Chem. Soc.* **1988**, *110*, 1472. (k) Charney, L. M.; Finklea, H. O.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 549.
- (2) For a review, see: Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221c.
- (3) For general reviews of transition-metal oxo chemistry, see: (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

### Scheme I



be quite potent as redox catalysts on account of (1) their ability to stabilize extremely high oxidation states, (2) their ability to

- (4) (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373. (b) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346. (c) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (d) Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334. (e) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364. (f) Newsham, M. D.; Giannelis, E. P.; Pinnavia, T. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 3885. (g) Brewer, J. C.; Gray, H. B. *Preprints: Symposium on Selective Catalytic Oxidation of Hydrocarbons, ACS Division of Petroleum Chemistry*; American Chemical Society: Washington, DC, 1990; pp 187-191. (h) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

undergo chemically reversible multielectron transformations, and (3) their tendency to abstract protons from substrates or solvent, concurrent with metal-centered reduction. Typically the oxo species are used to oxidize some substrate to product (e.g. water to oxygen, olefins to epoxides, alcohols to ketones or aldehydes, etc.) with the reduced catalyst then being regenerated at an electrode, as in Scheme I.<sup>2</sup>

Although interesting and impressive "solution side" catalytic chemistry has begun to emerge from such studies, a common complication is the occurrence of slow-electron-transfer kinetics on the "electrode side" of the catalytic scheme. Sluggish electrochemical kinetics require the introduction of an overpotential and therefore the expenditure of excess energy (beyond that required thermodynamically) to drive reactions at an acceptable rate. In view of this particular problem, and as part of a more general effort to understand multielectron transfer kinetics, we have initiated systematic studies of redox reactivity of high-valent oxo species. The systems chosen for initial study were dioxo complexes of rhenium(V), containing pyridyl (and bipyridyl) species as the ancillary ligands.<sup>4-6</sup> The rhenium complexes are actually very poor oxidants and so are not viable candidates for catalytic sequences like that in Scheme I.<sup>7</sup> Nevertheless, they do exhibit a number of properties that make them attractive for fundamental studies. These include (1) a fairly expansive display of proton-coupled one-, two-, and/or three-electron redox chemistry,<sup>4b,5a</sup> (2) good chemical stability in multiple oxidation states,<sup>4c,e,h,5a</sup> (3) measurably slow interfacial electron-transfer kinetics,<sup>4h,5a,c</sup> and (4) an expanding, and now quite general, synthetic chemistry.<sup>4d,5a,c,6</sup>

In an earlier report the synthesis of *cis*-dioxorhenium(V) complexes was described.<sup>5a,b</sup> Comparative electrochemical studies of related *cis* and *trans* complexes revealed surprisingly large thermodynamic differences (e.g. shifts of up to 600 mV in formal potential) as well as substantial multielectron kinetic effects. The latter were explained qualitatively on the basis of relative kinetic accessibilities to a thermodynamically "invisible" intermediate oxidation state (Re(IV)). In this paper we report the effects of a more subtle perturbation due to changes in ligand substituents. The redox thermodynamics of a total of 20 *cis*- and *trans*-dioxorhenium(V) complexes are surveyed; 5 of these have been subjected to more extensive pH dependent studies in order to elucidate how electron transfer is coupled to proton release and uptake. Also reported is a brief study of substituent effects upon electronic absorption spectra for the *cis*-dioxo series. These measurements (along with resonance Raman and electrochemical studies) have been used to show that the *cis* spectra, in contrast to the *trans*, are dominated by charge-transfer transitions. Other significant findings are (1) that the one-electron Re(VI) reduction potentials are influenced in a predictable fashion by substituent electronic effects, (2) that the two-electron Re(V) reduction potentials, surprisingly, are not affected appreciably by ligand-substituent-based electron withdrawal or donation effects, and (3) that the two-electron reduction kinetics, however, are influenced detectably by remote ligand substituents. The second and third observations are perhaps the most intriguing; they are tentatively interpreted in terms of proton demand and in terms of "invisible oxidation state" effects.

- (5) (a) Ram, M. S.; Johnson, C. S.; Blackburn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238. (b) Blackburn, R. L.; Jones, L. M.; Ram, M. S.; Sabat, M.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 1791. (c) Ram, M. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 130. (d) Jones, L. M. Unpublished data.
- (6) (a) Beard, J. H.; Calhoun, C.; Casey, J.; Murmann, R. K. *J. Am. Chem. Soc.* **1968**, *90*, 3389. (b) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1978**, *B34*, 923. (c) Beard, J. H.; Murmann, R. K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2467. (d) Murmann, R. K. *Inorg. Synth.* **1968**, *8*, 173. (e) Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1971**, *10*, 2352. (f) Fenn, R. H.; Graham, A. J.; Johnson, N. P. *J. Chem. Soc. A* **1971**, 2880. (g) Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem.* **1965**, *4*, 797.
- (7) *trans*-(O)<sub>2</sub>Re<sup>VI</sup>(py)<sub>4</sub><sup>2+</sup>, however, has been shown to catalyze the oxidation of secondary alcohols to ketones.<sup>4c</sup> Re(II), on the other hand, has been shown to catalyze the reduction of NO<sub>2</sub><sup>-</sup> to NH<sub>3</sub> and N<sub>2</sub>O, H<sup>+</sup> to H<sub>2</sub>, and SO<sub>3</sub><sup>2-</sup> to H<sub>2</sub>S.<sup>4b</sup>

## Experimental Section

**Materials.** All starting materials were reagent grade chemicals from Aldrich or Mallinckrodt and were used without further purification. Aqueous solutions were prepared with water purified by a Millipore system.

**Metal Complexes.** The majority of complexes were prepared as described in a recent paper.<sup>5c</sup> The complexes *trans*-(py)<sub>4</sub>Re(O)<sub>2</sub><sup>+</sup>, *trans*-(3-SO<sub>3</sub>py)<sub>4</sub>Re(O)<sub>2</sub><sup>2+</sup>, *trans*-(4-MeOpy)<sub>4</sub>Re(O)<sub>2</sub><sup>+</sup>, *cis*-(bpy)(py)<sub>2</sub>Re(O)<sub>2</sub><sup>+</sup>, and *cis*-(bpy)(3-SO<sub>3</sub>py)<sub>2</sub>Re(O)<sub>2</sub><sup>+</sup>, however, were prepared by alternative literature methods.<sup>4d,5a</sup> (py is pyridine; 3-SO<sub>3</sub>py is 3-sulfonatopyridine; 4-MeOpy is 4-methoxypyridine; bpy is 2,2'-bipyridine.)

**Measurements.** UV-visible absorption spectra were obtained with a Cary 14 spectrophotometer that had been rebuilt by On-Line Instruments Service. Raman measurements involved continuous excitation (50–60 mW) with either a Coherent Innova 100 Krypton ion laser (406.7 nm) or a Spectra Physics Series 2000 argon ion laser (514.5 nm). Samples were dissolved in 52:48 (v/v) methanol/water, and the solutions were placed in spinning NMR tubes as sample holders and probed in a 180° backscattering geometry. The experiments involving Krypton ion laser excitation were performed at Marquette University in the laboratory of Prof. Jim Kincaid.

Formal potentials were estimated by cyclic voltammetry. Voltammograms typically were collected with a PAR 273 potentiostat or with a computer-interfaced RDE4 potentiostat from Pine Instruments. A three-electrode arrangement was employed with a glassy-carbon working electrode (Tokai GC-20s), a saturated (aqueous) NaCl (SSCE) or KCl calomel reference electrode, and a platinum counter electrode. In the voltammetric experiments significant kinetic irreversibility was often observed (especially for the *trans* systems; see below). In order to ensure that reasonably accurate *E*<sub>f</sub> values were being obtained, we checked selected *trans* systems by recording CV's at several sweep rates and extrapolating to zero sweep rate. The resulting "true" formal potentials typically differed from the apparent potentials (obtained at ca. 100 mV s<sup>-1</sup>) by 20–40 mV. We deemed this amount to be insignificant in the context of Pourbaix studies where pH-dependent shifts in *E*<sub>f</sub> spanned a range as large as 600 mV. Also, because the errors tend to be similar for similar chemical systems, some cancellation can be expected when intercomparisons of potentials are made. Nevertheless, it should be kept in mind that larger than usual uncertainties exist in the *E*<sub>f</sub>(V/III) values for the *trans* series.

Solutions were prepared by dissolving complexes in appropriate aqueous or mixed aqueous/nonaqueous buffer solutions at μ = 0.1 M (or occasionally 0.05 M). Mixed solvents were an unavoidable necessity in several instances on account of solubility problems in pure aqueous solutions. The buffers and electrolytes employed were trifluoromethanesulfonic acid and its sodium salt (pH\* ≈ 1–2), citric acid/acetate (pH\* ≈ 3), acetic acid/acetate (pH\* ≈ 4–5), citrate/dibasic citrate (pH\* ≈ 6), monobasic phosphate/dibasic phosphate (pH\* ≈ 7), tris (pH\* ≈ 8), ammonia/ammonium (pH\* ≈ 9–10), bicarbonate/carbonate (pH\* ≈ 10), ethylenediamine (pH\* ≈ 10), dibasic phosphate/phosphate (pH\* ≈ 12), and hydroxide (pH\* ≈ 12–13).<sup>8</sup>

Apparent pH's (designated pH\*) were determined with a Beckman 31 pH meter and a Beckman Model 39386 combination electrode (or calculated as -log [H<sup>+</sup>] for pH\*'s below 1.0). Although there are difficulties in placing pH\* values on a common scale with purely aqueous pH measurements, the observed differences in pH\* for different buffers do appear to be meaningful and can be used, therefore, to derive information about relative pK<sub>a</sub>'s, coupled proton/electron-transfer stoichiometries, and so on, from electrochemical measurements.

## Results

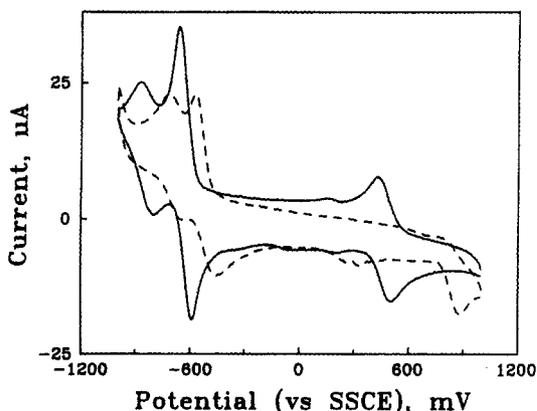
**Solvent Systems.** From previous work both the *cis*- and *trans*-dioxorhenium complexes were expected to display redox chemistry over a wide range of electrochemical potential.<sup>4h,5a</sup> Unfortunately, because of complex solubility problems, the solvent of choice in earlier experiments (water) was not universally acceptable here. Instead the reductive voltammetry of the rhenium(V) species was examined in 52:48 (v/v) methanol/water, buffered at pH\* = 5.7 with acetic acid/acetate (0.1 M total). A buffer aqueous solution is required because two- and three-electron rhenium(V) reductions are generally accompanied by oxo ligand protonation. One-electron rhenium(V) oxidations, on the other hand, are most often pH independent. Consequently, acetonitrile was acceptable here as solvent. (Unfortunately, the solvent ox-

(8) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; John Wiley: New York, 1974.

**Table I.** Redox Potentials for *cis*-(O)<sub>2</sub>Re(bpy-X<sub>2</sub>)(py-Y)<sub>2</sub><sup>2+</sup> Species as a Function of Ligand Composition

| ligands                     |                      | $E_f(\text{VI/V})^{a,c}$ | $E_f(\text{V/III})^{b,c}$ | $E_f(\text{III/II})^{b,c}$ |
|-----------------------------|----------------------|--------------------------|---------------------------|----------------------------|
| 4,4'-Cl <sub>2</sub> bpy    | py                   | 0.84                     | -0.57                     | -0.76                      |
| bpy                         | 3-Cl-py              | 0.77 <sup>b</sup>        | -0.57                     | -0.76                      |
|                             |                      | 0.80 <sup>b</sup>        |                           |                            |
| bpy                         | 3-SO <sub>3</sub> py | 0.85                     | -0.57                     | -0.76                      |
|                             |                      | 0.95                     |                           |                            |
| 4,4'-Cl <sub>2</sub> bpy    | 3-Cl-py              | 0.84 <sup>b</sup>        | -0.52                     | -0.70                      |
| bpy                         | 4-MeOpy              | 0.67                     | -0.59                     | -0.79                      |
|                             |                      | 0.38 <sup>b,d</sup>      |                           |                            |
|                             |                      | 0.60 <sup>b</sup>        |                           |                            |
| 4,4'-(OMe) <sub>2</sub> bpy | py                   | 0.65                     | -0.60                     | -0.82                      |
| 4,4'-(OMe) <sub>2</sub> bpy | 4-MeOpy              | 0.58 <sup>b</sup>        | -0.63                     | -0.83                      |
|                             |                      | 0.54                     |                           |                            |
| 4,4'-Cl <sub>2</sub> bpy    | 4-MeOpy              | 0.46 <sup>b</sup>        | -0.58                     | -0.71                      |
|                             |                      | 0.73                     |                           |                            |
|                             |                      | 0.65 <sup>b</sup>        |                           |                            |

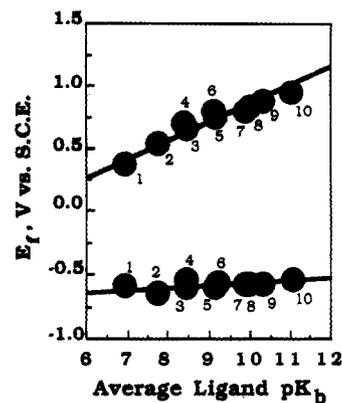
<sup>a</sup> Re(VI/V) potentials in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) electrolyte, except as noted. <sup>b</sup> Reduction potentials in 52:48 (v/v) methanol/water, buffered at pH\* = 5.7 with acetic acid/acetate (0.1 M total). <sup>c</sup> In V vs SSCE. Reference and working electrodes in separate compartments but in contact with the same solvent. <sup>d</sup> After subtraction of voltammetric signal due to *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup> (impurity).



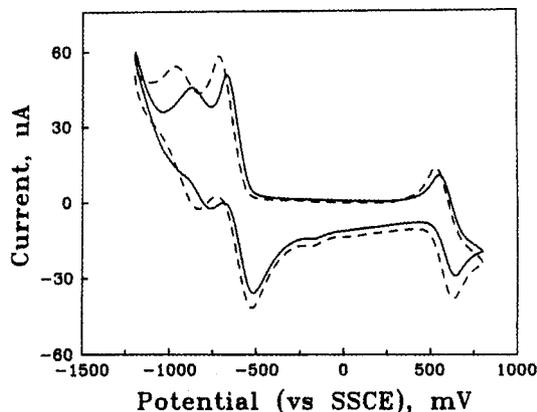
**Figure 1.** Cyclic voltammetry of *cis*-Re(O)<sub>2</sub>(4,4'-(MeO)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> (solid line) and *cis*-Re(O)<sub>2</sub>(4,4'-Cl<sub>2</sub>bpy)(3-Clpy)<sub>2</sub><sup>+</sup> (dashed line) at a 3-mm glassy-carbon disk in 52:48 (v/v) methanol/water at pH\* = 5.7. Sweep rate = 100 mV/s. (Note that the missing peak for reduction of the chloro-derivatized Re(VI) complex is seen at higher sweep rates and that  $\Delta E_p$  is close to 60 mV.)

idation limit for aqueous methanol (ca. +1.4 V vs SSCE) was too low to permit direct evaluation of the oxidative electrochemistry of *trans* complexes containing electron-deficient pyridines as ligands.) For detailed pH-dependent electrochemical studies it seemed desirable to examine all of the redox processes for a given complex in a common solvent system. Aqueous (50%) acetonitrile was eventually found to be an acceptable solvent system.

**Nonaqueous and Fixed-pH Aqueous Electrochemistry.** Perhaps the simplest electrochemical behavior was that found for the Re(VI/V) couple. Tables I and II list  $E_f$  values for all 20 systems, grouped according to *cis* or *trans* geometry. Comparisons between the tables show that the ligand geometry can indeed exert a very strong influence upon the Re(VI) reduction potential (i.e. much more positive potentials for the *trans* geometry). We note that for d<sup>2</sup> species the *trans*-dioxo configuration is generally stabilized greatly with respect to the *cis* (largely because the *trans* geometry minimizes interactions between d<sup>2</sup><sub>xy</sub> and the filled p orbitals of the oxygens).<sup>3</sup> On the other hand, for d<sup>0</sup> species the *cis* configuration is strongly favored (because of the ability of the filled oxygen p orbitals to achieve overlap with all three dπ(Re) orbitals).<sup>3</sup> For d<sup>1</sup> species the geometric preference is less clear-cut.<sup>3</sup> Given these general trends, reduction of a d<sup>1</sup> metal center to d<sup>2</sup>



**Figure 2.** Formal potentials for reduction of *cis*-(O)<sub>2</sub>Re(bpy-X<sub>2</sub>)(py-Y)<sub>2</sub><sup>2+</sup> (half-filled circles) and *cis*-(O)<sub>2</sub>Re(bpy-X<sub>2</sub>)(py-Y)<sub>2</sub><sup>+</sup> (filled circles) versus average ligand pK<sub>b</sub> (<sup>1</sup>/<sub>2</sub>pK<sub>b</sub>(bpy-X<sub>2</sub>) + <sup>1</sup>/<sub>2</sub>pK<sub>b</sub>(py-Y)). Solvent is 52:48 (v/v) CH<sub>3</sub>OH/water. Pyridine pK<sub>b</sub> values were taken from Sawada et al.<sup>43</sup> Bipyridine pK<sub>b</sub> values were assumed to be one pK unit higher than the corresponding py values. Key to complexes: (1) *cis*-(O)<sub>2</sub>Re(bpy)(4-NMe<sub>2</sub>py)<sub>2</sub><sup>+</sup>; (2) *cis*-(O)<sub>2</sub>Re(4,4'-(OMe)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup>; (3) *cis*-(O)<sub>2</sub>Re(4,4'-(OMe)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup>; (4) *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup>; (5) *cis*-(O)<sub>2</sub>Re(4,4'-(Cl<sub>2</sub>bpy))(4-MeOpy)<sub>2</sub><sup>+</sup>; (6) *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup>; (7) *cis*-(O)<sub>2</sub>Re(4,4'-(Cl<sub>2</sub>bpy))(py)<sub>2</sub><sup>+</sup>; (8) *cis*-(O)<sub>2</sub>Re(bpy)(3-pySO<sub>3</sub>)<sub>2</sub><sup>+</sup>; (9) *cis*-(O)<sub>2</sub>Re(bpy)(3-Cl-py)<sub>2</sub><sup>+</sup>; (10) *cis*-(O)<sub>2</sub>Re(4,4'-Cl<sub>2</sub>bpy)(3-Cl-py)<sub>2</sub><sup>+</sup>.



**Figure 3.** Cyclic voltammetry for *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup> (dashed line) and *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> (solid line) at a 3-mm glassy-carbon disk in 52:48 (v/v) methanol/water at pH\* = 5.7. Sweep rate = 100 mV/s.

ought to be appreciably easier with the *trans*-dioxo geometry than the *cis*.<sup>9</sup> Indeed, for rhenium, this is the experimental result. Figure 1, which shows voltammograms for *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> and *cis*-Re(O)<sub>2</sub>(4,4'-Cl<sub>2</sub>bpy)(3-Cl-py)<sub>2</sub><sup>+</sup> (4,4'-Cl<sub>2</sub>bpy is 4,4'-dichloro-2,2'-bipyridine; 3-Cl-py is 3-chloropyridine), illustrates (or at least implies) three additional points: (1) The Re(VI/V) voltammetry is reversible in an electrochemical kinetic sense. (2) In a chemical sense, however, the voltammetry can sometimes be irreversible—especially at low sweep rates and with *cis* complexes containing electron-deficient pyridyl and bipyridyl ligands. (All entries in Table II were obtained in the chemically reversible limit.) (3) For both the *cis* and *trans* series there is a strong dependence of  $E_f$  upon the electron-donating or electron-withdrawing characteristics of the ligand substituents themselves. Figure 2, which shows a plot of  $E_f$  versus the average ligand pK<sub>b</sub>, illustrates the ligand basicity effect for the *cis* series. It should be noted that a pK<sub>a</sub>/ $E_f$  correlation has previously been presented for *trans* complexes.<sup>48</sup> Figure 3, which shows voltammograms for *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup> and *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup>, serves to demonstrate that the ligand

(9) Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357.

Table II. Redox Potentials for *trans*-(O)<sub>2</sub>Re(py-X)<sub>2</sub>(py-Y)<sub>2</sub><sup>+</sup> Species as a Function of Ligand Composition

| ligands                          |                                  | $E_f(\text{VI/V})^{a,c}$ | $E_f(\text{V/III})^{b,c}$ | $E_f(\text{V/III})^{c,e}$ | $E_f(\text{III/II})^{b,e}$ | $E_f(\text{III/II})^{d,e}$ |
|----------------------------------|----------------------------------|--------------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| py                               | py                               | 1.37                     | -0.80                     | -0.86                     |                            | -1.43                      |
| 3-Cl-py                          | py                               | 1.47                     | -0.80                     |                           | -1.33                      |                            |
| 3-Cl-py                          | 3-Cl-py                          | 1.57                     | -0.77                     | -0.85                     | -1.24                      | -1.49                      |
| 3-SO <sub>3</sub> py             | 3-SO <sub>3</sub> py             | 1.45 <sup>f</sup>        | -0.74                     | -0.75                     | -1.29                      |                            |
| 4-CONH <sub>2</sub> <sup>g</sup> | 4-CONH <sub>2</sub> <sup>g</sup> | 1.43 <sup>f</sup>        | -0.74                     | -0.80                     | -1.02                      | -1.44                      |
| 4-Mepy                           | 4-Mepy                           | 1.23                     | -0.84                     |                           |                            |                            |
| 4-NMe <sub>2</sub> py            | 4-NMe <sub>2</sub> py            | 0.53 <sup>h</sup>        | -0.88                     | -1.06                     |                            |                            |
| py                               | 4-NMe <sub>2</sub> py            | 0.86                     | -0.87                     | -0.92                     |                            | -1.55                      |
| 4-MeOpy                          | 4-MeOpy                          | 1.04                     | -0.87                     | -0.95                     |                            | -1.66                      |
|                                  |                                  | 0.96 <sup>f</sup>        |                           |                           |                            |                            |
| py                               | 4-Cl-py <sup>i</sup>             | 1.41                     | -0.79                     |                           |                            |                            |

<sup>a</sup> Re(VI/V) potentials in acetonitrile with 0.1 M TBAH electrolyte, except as noted. <sup>b</sup> Reduction potentials in 52:48 (v/v) methanol/water buffer at pH\* = 5.7 with acetic acid/acetate (0.1 M total). <sup>c</sup> Reduction potentials in 50:50 (v/v) acetonitrile/water, buffered at pH\* = 7.6. <sup>d</sup> Reduction potentials in 50:50 (v/v) methanol/water in the pH\* independent range 10–13. <sup>e</sup> In V vs SSCE. Reference and working electrodes in separate compartments but in contact with the same solvent. <sup>f</sup> Re(VI/V) potential recorded in pure aqueous solvent, due to insolubility of complexes in acetonitrile. <sup>g</sup> 4-CONH<sub>2</sub> is isonicotinamide. <sup>h</sup> Ionic strength = 0.01 M. <sup>i</sup> 4-Cl-py = 4-chloropyridine.

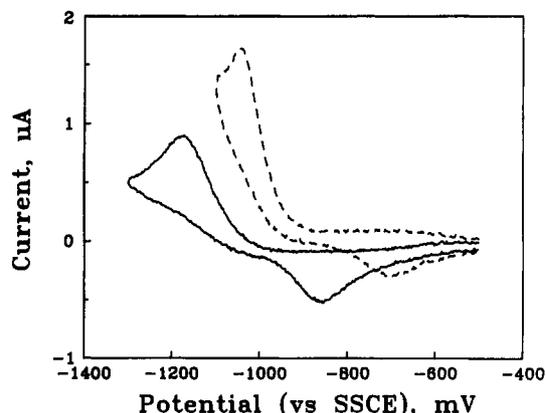


Figure 4. Cyclic voltammetry of *trans*-(O)<sub>2</sub>Re(3-Cl-py)<sub>4</sub><sup>+</sup> (dashed line) and *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup> (solid line) at a 3-mm glassy-carbon disk in 52:48 (v/v) methanol/water. Sweep rate = 100 mV/s.

substituent effect in the *cis* case is transmitted with equal efficacy by pyridine and 2,2'-bpy.

Data for the pH-dependent Re(V/III) couple at pH\* = 5.7 are presented in Tables I and II. Again there is a significant geometric effect but now with the *cis* species showing the higher potentials. Somewhat surprisingly, however, there is almost no substituent effect upon  $E_f$  for either series of complexes (see, for example, Figure 1).

Closer examination of Figure 1 and also Figure 4 (CV's of *trans*-(O)<sub>2</sub>Re(3-Cl-py)<sub>4</sub><sup>+</sup> and *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup>) shows that there are detectable ligand-based kinetic effects—manifest here as variable anodic/cathodic peak separations. Furthermore, the figures seem to indicate a systematic dependence of redox kinetics upon ligand electronic characteristics (i.e. slower rates with electron-withdrawing substituents and faster rates with electron-donating substituents).<sup>10</sup> A more complete consideration of peak separation effects ( $\Delta E_p$ ; Table III) implies more complex behavior. Thus, if only like-charged complexes are considered (i.e. pyridinesulfonate complexes are ignored), no obvious reactivity pattern is discerned. (Note, in particular, that the one available mixed-ligand complex displays a  $\Delta E_p$  value that does not fall between the values for the two related pure-ligand complexes.)

(10) A reviewer has argued that just the opposite effect would have been expected on the basis of the increased inner-shell activation barriers for more strongly electron-donating ligands, as reported for example by Saveant et al. (*J. Electroanal. Chem. Interfacial Electrochem.* 1982, 140, 285). It should be noted, first, that counter examples exist (Constant and Davis, *J. Electroanal. Chem. Interfacial Electrochem.* 1976, 74, 85) and, second, that important chemical differences exist between the Re(V/III) systems and the cobalt-based redox couples studied by Saveant. Most notably, the latter involve cleavage of metal–ligand bonds during electrochemical reduction whereas the dioxo systems do not.

Table III. Cyclic Voltammetry Peak Separations for Two-Electron Reduction and Reoxidation of *trans*-Dioxorhenium(V) Pyridyl Complexes

| complex <sup>a</sup>   | py pK <sub>b</sub> <sup>b</sup> | $\Delta E_p$ , V <sup>c</sup> |
|--|---------------------------------|-------------------------------|
| <i>t</i> -(O) <sub>2</sub> Re(3-Cl-py) <sub>4</sub> <sup>+</sup>                                 | 11.0                            | 0.408                         |
| <i>t</i> -(O) <sub>2</sub> Re(4-CONH <sub>2</sub> ) <sub>4</sub> <sup>+</sup>                    | 10.1                            | 0.360                         |
| <i>t</i> -(O) <sub>2</sub> Re(3-SO <sub>3</sub> py) <sub>4</sub> <sup>3-</sup>                   | 10.2                            | 1.035 <sup>d</sup>            |
| <i>t</i> -(O) <sub>2</sub> Re(py) <sub>4</sub> <sup>+</sup>                                      | 8.6                             | 0.432                         |
| <i>t</i> -(O) <sub>2</sub> Re(4-MeOpy) <sub>4</sub> <sup>+</sup>                                 | 7.2                             | 0.404                         |
| <i>t</i> -(O) <sub>2</sub> Re(py) <sub>2</sub> (4-NMe <sub>2</sub> py) <sub>4</sub> <sup>+</sup> | 6.4 <sup>b</sup>                | 0.504                         |
| <i>t</i> -(O) <sub>2</sub> Re(4-NMe <sub>2</sub> py) <sub>4</sub> <sup>+</sup>                   | 4.2                             | 0.276                         |

<sup>a</sup> Concentration = 0.8 mM. <sup>b</sup> Average value (see caption to Figure 2 for source of pK<sub>b</sub> data). <sup>c</sup> Electrochemical measurements made at 20 mV/s in 50:50 (v/v) acetonitrile/water, buffered at pH\* = 7.6. <sup>d</sup> Extrapolated ( $E_p$  vs log sweep rate) from measurements made at higher sweep rate.

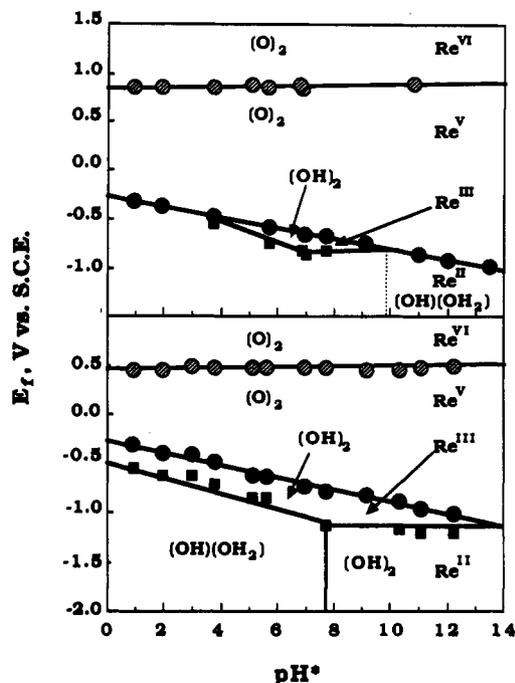
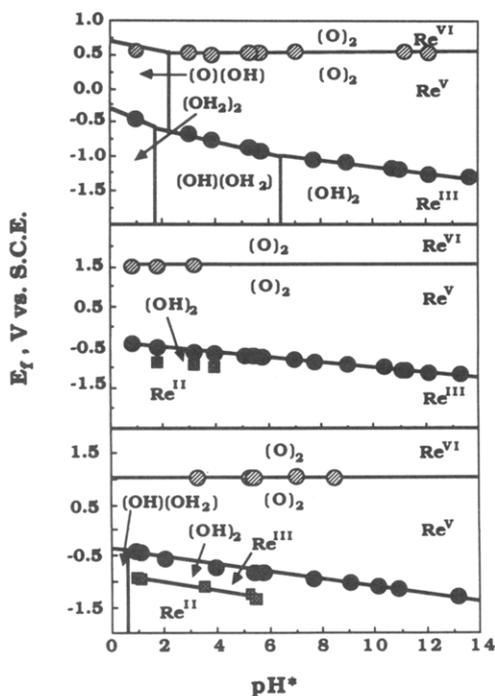


Figure 5. Pourbaix diagrams for *cis*-(O)<sub>2</sub>Re(4,4'-Cl<sub>2</sub>bpy)(3-Clpy)<sub>2</sub><sup>+</sup> (top) and *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> (bottom) in 50:50 (v/v) CH<sub>3</sub>CN/water.

It may well be that a simple reactivity pattern does exist but that electrostatic work terms and/or specific adsorption conspire to obscure the trend.<sup>11,12</sup>

(11) Complementary studies of homogeneous outer-sphere reactivity would probably answer this question.

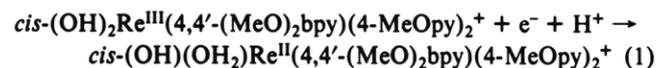


**Figure 6.** Pourbaix diagrams for  $trans\text{-}(\text{O})_2\text{Re}(4\text{-NMe}_2\text{py})_4^+$  (top),  $trans\text{-}(\text{O})_2\text{Re}(3\text{-Cl-py})_4^+$  (middle), and  $trans\text{-}(\text{O})_2\text{Re}(4\text{-MeOpy})_4^+$  (bottom) in 50:50 (v/v)  $\text{CH}_3\text{CN}/\text{water}$ . (Note that solvent oxidation interferes with  $trans\text{-}(\text{O})_2\text{Re}(3\text{-Cl-py})_4^+$  oxidation at  $\text{pH}^* > 3$ .) (Note additionally that the species  $t\text{-}(\text{O})(\text{OH})\text{Re}(4\text{-NMe}_2\text{py})_4^{2+}$  was identified spectrochemically; see Table IV.)

Further reduction of the parent complexes leads to  $\text{Re}(\text{II})$ .<sup>4h,5a</sup> The potentials for the  $\text{Re}(\text{III}/\text{II})$  couple (at  $\text{pH}^* = 5.7$ ) are listed in Tables I and II. In a few cases the potentials have been omitted—either because of interferences due to catalytic hydrogen evolution<sup>4h</sup> or because the redox couple was simply not observed within the available solvent-limited potential window. For the  $\text{Re}(\text{III}/\text{II})$  couple, the  $E_f$  values exhibit a small but detectable dependence on ligand basicity; they also display a dependence on  $\text{Re}(\text{O})_2$  geometry. At  $\text{pH}^* = 5.7$ , for example, the *cis* potentials are  $\sim 0.5\text{--}0.6$  V more positive than the *trans*.

**Variable pH Electrochemistry.** Figures 5 and 6 show pH vs  $E_f$  plots (Pourbaix plots) for two *cis*- and three *trans*-dioxo complexes. Figure 5 contains data for  $cis\text{-}(\text{O})_2\text{Re}(\text{Cl}_2\text{bpy})(3\text{-Cl-py})_2^+$  and  $cis\text{-}(\text{O})_2\text{Re}(4,4'\text{-(MeO)}_2\text{bpy})(4\text{-MeOpy})_2^+$ . Figure 6 shows data for  $trans\text{-}(\text{O})_2\text{Re}(4\text{-NMe}_2\text{py})_4^+$ ,  $trans\text{-}(\text{O})_2\text{Re}(3\text{-Cl-py})_4^+$ , and  $trans\text{-}(\text{O})_2\text{Re}(4\text{-MeOpy})_4^+$ . These five complexes were chosen so as to encompass the expected extremes of ligand electronic inductive effects.

The Pourbaix diagrams are particularly useful in that they provide an indication of how electron transfer is coupled to proton transfer, at least in a thermodynamic sense. The slopes of the plots (in mV per  $\text{pH}^*$  unit) are expected to equal  $-59p/n$ , where  $p$  is the integral number of protons acquired upon reduction and  $n$  is the number of electrons. For example, between  $\text{pH}^* 1$  and  $7.8$  the one-electron reduction of  $(\text{OH})_2\text{Re}^{\text{III}}(4,4'\text{-(MeO)}_2\text{bpy})(4\text{-MeOpy})_2^+$  (Figure 5) yields a  $-60\text{-mV}$  slope, indicating the reversible formation of a *cis*-aqua-hydroxorhenium(II) species:



At  $\text{pH}^* = 7.8$  the slope changes to 0 mV, indicating a zero-proton,

**Table IV.** Hydroxyl Ligand  $\text{pK}_a$ 's for  $trans\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(\text{py-X})_4^{2+}$  Complexes in 50:50 (v/v) Acetonitrile/Water

| complex   | $\text{pK}_a$    |
|---|------------------|
| $t\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(\text{dmap})_4^{2+}$                          | 2.3 <sup>a</sup> |
| $t\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(\text{py})_2(4\text{-NMe}_2\text{py})_2^{2+}$ | 0.8 <sup>b</sup> |
| $t\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(4\text{-MeOpy})_4^{2+}$                       | 0.5 <sup>b</sup> |
| $t\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(\text{py})_4^{2+}$                            | $-0.3^b$         |
| $t\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(3\text{-Cl-py})_4^{2+}$                       | $-0.5^b$         |

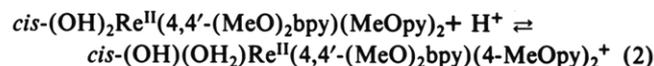
<sup>a</sup> Determined by spectrophotometric titration of the dioxo complex with trifluoromethanesulfonic acid. <sup>b</sup> Determined by spectrophotometric titration of the dioxo complex with sulfuric acid.

**Table V.** Electronic Absorption Spectra for  $trans\text{-}(\text{O})_2\text{Re}(\text{py-X})_2(\text{py-Y})_2^{2+}$  Species<sup>a</sup>

| ligands               |                       | abs max, nm (extn coeff, $\text{M}^{-1}\text{cm}^{-1}$ ) |                            |                           |  |
|-----------------------|-----------------------|--|----------------------------|---------------------------|--|
| 3-Cl-py               | 3-Cl-py               | 428 ( $1.33 \times 10^3$ )                               | 346 ( $2.0 \times 10^4$ )  | 258 ( $1.6 \times 10^4$ ) |  |
| 3-Cl-py               | py                    | 434 ( $1.4 \times 10^3$ )                                | 338 ( $1.9 \times 10^4$ )  | 253 ( $1.3 \times 10^4$ ) |  |
| 4-NMe <sub>2</sub> py | py                    | 471 ( $1.6 \times 10^3$ )                                | 363 ( $1.0 \times 10^4$ )  | 253 ( $1.7 \times 10^4$ ) |  |
|                       |                       |  | 316 ( $2.8 \times 10^4$ )  |                           |  |
| 4-CONH <sub>2</sub>   | 4-CONH <sub>2</sub>   | 436 (sh) ( $4.3 \times 10^3$ )                           | 370 ( $2.6 \times 10^4$ )  | 253 ( $1.9 \times 10^4$ ) |  |
| 3-SO <sub>3</sub> py  | 3-SO <sub>3</sub> py  | 431 ( $1.4 \times 10^3$ )                                | 349 ( $2.1 \times 10^4$ )  | 254 ( $1.8 \times 10^4$ ) |  |
| 4-MeOpy               | 4-MeOpy               | 448 ( $1.3 \times 10^3$ )                                | 337 ( $2.5 \times 10^4$ )  | 246 ( $1.4 \times 10^4$ ) |  |
| py                    | py                    | 440 ( $1.4 \times 10^3$ )                                | 337 ( $2.8 \times 10^4$ )  | 247 ( $2.0 \times 10^4$ ) |  |
| 4-NMe <sub>2</sub> py | 4-NMe <sub>2</sub> py | 493 ( $1.6 \times 10^3$ )                                | 330 ( $3.9 \times 10^4$ )  | 281 ( $4.0 \times 10^4$ ) |  |
| py                    | 4-Cl-py               | 437 ( $1.27 \times 10^3$ )                               | 342 ( $1.54 \times 10^4$ ) | 248 ( $1.2 \times 10^4$ ) |  |

<sup>a</sup> Solvent is 52:48 (v/v) methanol/water.

one-electron change. The break point defines the  $\text{pK}_a$  for dihydroxorhenium(II) (or possibly aqua-hydroxorhenium(II)) protonation:



Further analysis has permitted us to identify the dominant species at each pH in each oxidation state for each of the five complexes (see Figures 5 and 6). The only significant ambiguity (apart from the dihydroxo vs aqua, oxo possibility mentioned above) comes in the case of  $trans\text{-}(\text{O})_2\text{Re}(4\text{-NMe}_2\text{py})_4^+$  (4-NMe<sub>2</sub>py = 4-(dimethylamino)pyridine). Here we have assumed that only the oxo ligands are protonated. We have not been able to rule out completely, however, the possibility of tertiary amine protonation, especially in the lowest rhenium oxidation states.

The data presented in Figures 5 and 6 (and Table IV) resemble qualitatively those reported elsewhere for  $cis\text{-}(\text{O})_2\text{Re}(\text{bpy})(\text{py})_2^+$  and  $trans\text{-}(\text{O})_2\text{Re}(\text{py})_4^+$ .<sup>4h,5a</sup> There are, however, several new features worth noting. First, below  $\text{pH}^* = 2.3$  we find clear evidence for protonation of  $trans\text{-}(\text{O})_2\text{Re}^{\text{V}}(4\text{-NMe}_2\text{py})_4^+$ , presumably to give  $trans\text{-}(\text{O})(\text{OH})\text{Re}^{\text{V}}(4\text{-NMe}_2\text{py})_4^{2+}$ . (See Table IV; evidently the  $\text{pH}^*$  range in the electrochemical studies was too narrow to permit the protonation to be easily observed in Pourbaix plots.) For  $trans\text{-}(\text{O})_2\text{Re}^{\text{V}}(3\text{-Cl-py})_4^+$ , on the other hand, protonation occurs only below  $\text{pH}^* = -0.5$ , consistent with the electron-withdrawing nature of the chloro substituents and their anticipated effect upon the electron density at  $\text{Re}(\text{V})$  and ultimately at the oxo ligand sites. For the *cis* complexes protonation is absent in oxidation state V, even when the ancillary ligands carry electron-donating substituents.<sup>13</sup> For oxidation state VI, protonation is absent at all accessible  $\text{pH}$ 's for all complexes.

For the lower oxidation states, the most interesting observation is the appearance of a three-electron reaction ( $\text{V} \rightarrow \text{II}$ ) for  $cis\text{-}(\text{O})_2\text{Re}(\text{Cl}_2\text{bpy})(3\text{-Cl-py})_2^+$  at  $\text{pH}^* = 11$  and above and also below  $\text{pH}^* = 4$ . (A three-electron conversion was previously noted for  $cis\text{-}(\text{O})_2\text{Re}(\text{bpy})(\text{py})_2^+$  at  $\text{pH} > 13$ .<sup>5a,14</sup>) Confirmation of the three-electron nature of the reaction was obtained by cyclic

(12) One factor we have not considered in these preliminary kinetics studies is the role of  $\text{Re}^{\text{IV}}$  disproportionation ( $2\text{Re}^{\text{IV}} \rightarrow \text{Re}^{\text{V}} + \text{Re}^{\text{III}}$ ) and its possible effect upon apparent electrochemical rate parameters (and its possible dependence upon ligand composition). Variable concentration studies (and further digital simulation studies) should yield additional experimental insight. For a theoretical discussion of disproportionation effects in cyclic voltammetry, see: Hinkleman, K.; Heinze, J. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 243.

(13) Lack of protonation of the *cis* complex, in contrast to the *trans*, can likely be attributed to the enhanced  $\pi$ -bonding in the *cis* complex, which would lead to less electron density on the oxo ligands in the *cis* complex. We thank a reviewer for suggesting this explanation.

(14) Other examples of three-electron transfer reactions: (a) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 4042. (b) Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357.

Table VI. Electronic Absorption Spectra for *cis*-(O)<sub>2</sub>Re(bpy-X<sub>2</sub>)(py-Y)<sub>2</sub><sup>+</sup> Species<sup>a</sup>

| ligands                     |                          | abs max, nm (extn coeff, M <sup>-1</sup> cm <sup>-1</sup> ) |                              |                                   |                                   |
|-----------------------------|--------------------------|---|------------------------------|-----------------------------------|-----------------------------------|
| 4,4'-Cl <sub>2</sub> bpy    | py                       | 534 (6 × 10 <sup>3</sup> )                                  | 385 (1.1 × 10 <sup>4</sup> ) | 305 (2.1 × 10 <sup>4</sup> )      | 241 (1.8 × 10 <sup>4</sup> )      |
| bpy                         | 4,4'-Cl <sub>2</sub> bpy | 502 (4 × 10 <sup>3</sup> )                                  | 410 (8 × 10 <sup>3</sup> )   | 302 (1.4 × 10 <sup>4</sup> )      | 250 (1.3 × 10 <sup>4</sup> )      |
| bpy                         | 3-SO <sub>3</sub> py     | 498 (4 × 10 <sup>3</sup> )                                  | 410 (8 × 10 <sup>3</sup> )   | 300 (1.4 × 10 <sup>4</sup> )      | 254 (1.4 × 10 <sup>4</sup> )      |
| 4,4'-Cl <sub>2</sub> bpy    | 4,4'-Cl <sub>2</sub> bpy | 523 (5.5 × 10 <sup>3</sup> )                                | 404 (1.1 × 10 <sup>4</sup> ) | 305 (1.7 × 10 <sup>4</sup> )      | 248 (sh) (1.6 × 10 <sup>4</sup> ) |
| bpy                         | py                       | 506 (1 × 10 <sup>4</sup> )                                  | 385 (2 × 10 <sup>4</sup> )   | 302 (2 × 10 <sup>4</sup> )        | 244 (3.2 × 10 <sup>4</sup> )      |
| bpy                         | 4-NMe <sub>2</sub> py    | 540 <sup>b</sup>  | <i>b</i>                     | <i>b</i>                          | <i>b</i>                          |
| bpy                         | 4-MeOpy                  | 522 (5.1 × 10 <sup>3</sup> )                                | 360 (1.0 × 10 <sup>4</sup> ) | 305 (1.2 × 10 <sup>4</sup> )      | 227 (1.8 × 10 <sup>4</sup> )      |
| 4,4'-(OMe) <sub>2</sub> bpy | py                       | 496 (5.1 × 10 <sup>3</sup> )                                | 401 (1.0 × 10 <sup>4</sup> ) | 299 (d) (1.2 × 10 <sup>4</sup> )  | 227 (3.6 × 10 <sup>4</sup> )      |
| 4,4'-(OMe) <sub>2</sub> bpy | 4-MeOpy                  | 522 (4.6 × 10 <sup>3</sup> )                                | 372 (1.1 × 10 <sup>4</sup> ) | 292 (d) (1.5 × 10 <sup>4</sup> )  | 228 (5.8 × 10 <sup>4</sup> )      |
| 4,4'-Cl <sub>2</sub> bpy    | 4-MeOpy                  | 546 (5.5 × 10 <sup>3</sup> )                                | 355 (9.7 × 10 <sup>3</sup> ) | 306 (2.1 × 10 <sup>4</sup> )      | 222 (4.2 × 10 <sup>4</sup> )      |
|                             |                          |   |                              | 299 (sh) (1.7 × 10 <sup>4</sup> ) |                                   |

<sup>a</sup>Solvent is 52:48 (v/v) methanol/water. <sup>b</sup>Absorption maximum and/or extinction coefficient omitted due to contamination of sample by *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup> (see ref 5c).

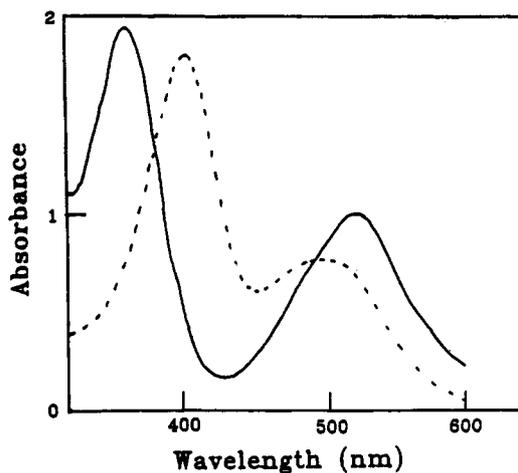


Figure 7. Electronic absorption spectra for *cis*-(O)<sub>2</sub>Re(4,4'-(OMe)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup> (dashed line) and *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> (solid line) in 52:48 (v/v) methanol/water as solvent.

voltammetry and by rotating-disk voltammetry (limiting current measurements). The V → II reaction also exists for *cis*-(O)<sub>2</sub>Re(4,4'-(OMe)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> but only at pH\* ≥ 13. Other noteworthy observations: (1) For the *cis* complexes, at least, the pK<sub>a</sub> of (OH)(OH<sub>2</sub>)Re<sup>III</sup>L<sub>x</sub>L<sub>y</sub><sup>+</sup> increases as the pyridyl (or bipyridyl) ligand basicity increases. (2) Likewise for the *trans* species the pK<sub>a</sub>'s of (OH)(OH<sub>2</sub>)Re<sup>III</sup>L<sub>x</sub>L<sub>y</sub><sup>2+</sup> and/or (OH)<sub>2</sub>Re<sup>III</sup>L<sub>x</sub>L<sub>y</sub><sup>+</sup> clearly increase as the ancillary ligand basicity increases. Evidently, pyridyl and bipyridyl ligand substituents have a substantial and general effect upon the affinity of oxo and hydroxo ligands for protons.

**Electronic Absorption Spectra.** The absorption spectra for the *trans* complexes are characterized in all cases by a relatively weak band near 430 nm and a much stronger band at ~340 nm (see Table V). The low-energy transition has been unambiguously assigned to a d-d absorption with intensity stealing from a higher energy charge-transfer transition.<sup>4b</sup> The stronger band has been ascribed to both metal-to-pyridine and oxo-to-metal transitions,<sup>4f</sup> although the most recent work by Brewer and Gray clearly favors the former.<sup>4g</sup> Curiously the d-d band energy responds strongly to substituent changes, while the charge-transfer band is relatively unaffected.<sup>15</sup>

In the *cis*-dioxo complexes two visible region bands are observed. Both are solvent dependent (see Appendix) and both have high intensities, suggesting that both may be charge-transfer transitions.<sup>5a</sup> From Table VI, the transition energies are also clearly dependent upon the nature of the substituents, again supporting

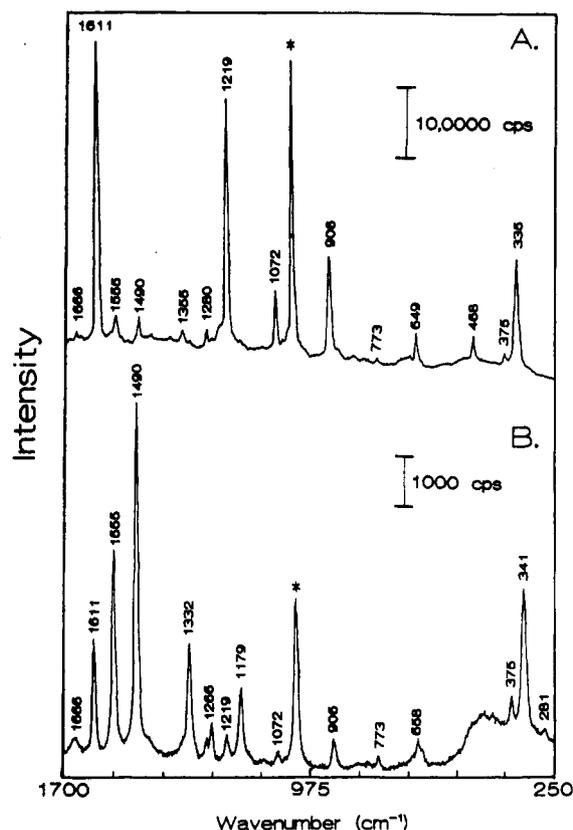


Figure 8. Resonance Raman spectra of *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup> based on 406.7 nm (spectrum A) and 514.5 nm (spectrum B) excitation. The asterisk denotes the solvent band in the 52% aqueous methanol solution. Spectrum A is dominated by resonantly enhanced coordinated pyridyl modes at 1611, 1219, and 1072 cm<sup>-1</sup>. In contrast, spectrum B shows resonant enhancement of coordinated bipyridyl modes at 1555, 1490, and 1332 cm<sup>-1</sup>. The dominant peaks in the spectra are summarized and tentatively assigned in Table VIII. Note that the absolute intensities differ for the two spectra in part because of different detector responses and power densities at the two excitation wavelengths.

the charge-transfer assignment. The assignment can be further specified by noting that the isoelectronic complex *cis*-(O)<sub>2</sub>Os(bpy)<sub>2</sub><sup>2+</sup>, which is much less readily oxidized, is transparent in the visible region.<sup>9</sup> This supports a metal-to-ligand, rather than ligand-to-metal, charge-transfer description for the lowest energy transitions in the *cis*-dioxorhenium(V) spectrum.

On the basis of the charge-transfer description, one might expect to see correlations between E<sup>MLCT</sup> and the ease of Re(VI) reduction. At first glance (Tables I, II, V, and VI) such correlations are absent. For example, pairs of species like *cis*-(O)<sub>2</sub>Re(4,4'-(OMe)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup> and *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> exhibit essentially identical redox potentials (Figure 3) but quite distinct absorption spectra (Figure 7). Further consideration suggests that the spectra differ because the lower energy band in each case

(15) Similar observations have been made previously by Brewer and Gray.<sup>4d</sup> In the charge-transfer case, the cumulative influence of four pyridyl substituents upon the Re(d<sub>xy</sub>) orbital energy evidently is equivalent to the influence of any one substituent upon the pyridyl (π\*) energy, leading to no net energy effect upon the d<sub>xy</sub>-π\* transition. Note, however, that when only two pyridyl ligands are derivatized (mixed-ligand complexes; Table V), significant transition-energy shifts are seen.

**Table VII.** Preliminary Peak Assignments from Resonance Raman Spectra of *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup>

| 514.5-nm excitation <sup>a</sup> | 406.7-nm excitation <sup>a</sup> | assgmt <sup>b,c</sup>   |
|----------------------------------|----------------------------------|-------------------------|
| 1611 m                           | 1611 vs                          | ip ring (py)            |
| 1555 s                           | 1555 w                           | ip ring (bpy)           |
| 1490 vs                          | 1490 w                           | C-H def (bpy)           |
| 1332 m                           |                                  | ip ring (bpy)           |
|                                  | 1219 vs                          | ip ring (py)            |
| 1072 w                           | 1072 m                           | ring breathing (py)     |
| 906 w                            | 906 m                            | asym O=Re=O stretch     |
| 773 w                            | 773 w                            | H wag                   |
| 655 w                            | 649 w                            | ring breathing (bpy,py) |
| 341 m                            | 341 m                            | M-N                     |

<sup>a</sup> m = medium, s = strong, v = very, and w = weak; energies in cm<sup>-1</sup>.

<sup>b</sup> ip = in plane, def = deformation, and asym = asymmetric.

<sup>c</sup> Pertinent references: Castellucci, E.; Angeloni, L.; Neto, N.; Sbrana, G. *Chem. Phys.* **1975**, *43*, 365-373. Chambers, J. P.; Buck, R. P. *J. Electroanal. Chem.* **1984**, *163*, 297-314. Mallick, P. K.; Danzer, G. D.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1988**, *92*, 5628-5634.

involves charge transfer to bipyridine, while the higher band involves charge transfer to pyridine. Note that these assignments are consistent with the relative ordering of π\*-orbital energies for the two ligand types.<sup>16</sup>

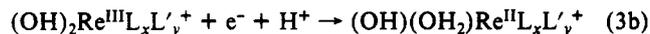
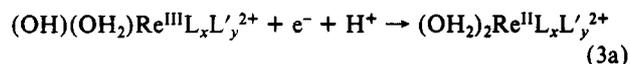
To confirm the assignments, we resorted to resonance Raman spectroscopy. Resonant excitation is expected to lead to selective enhancement of scattering modes associated with the ligand accepting the transferred electron. Figure 8 shows Raman scattering spectra for *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup> based on excitation at 406.7 nm (higher band) and 514.5 nm (lower band). Selected modes are labeled in the caption (see also Table VII). The key point is that the enhanced portions of the spectrum differ in the two experiments. Excitation at 406 nm leads to pyridyl mode enhancement, while excitation at 514 nm leads to enhanced scattering from coordinated bipyridine. (Interestingly, both experiments lead also to enhancement of rhenium-oxygen stretches, implying significant displacement of these modes upon oxidation from Re(V) to Re(VI).) The assignment of ligand modes in Figure 8 was made by comparing scattering spectra for (1) *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup> and *cis*-(O)<sub>2</sub>Re(bpy)(py-d<sub>5</sub>)<sub>2</sub><sup>+</sup>,<sup>17</sup> (2) free pyridine and its perdeuterated analogue,<sup>18</sup> and (3) various other *cis*-dioxorhenium(V) complexes for which either bpy or pyridine (and, in one case, both) had been modified with electron-withdrawing or -donating substituents.<sup>19</sup> The resonance Raman experiments clearly establish the MLCT (bpy) and MLCT (py) assignments as the correct electronic descriptions.

## Discussion

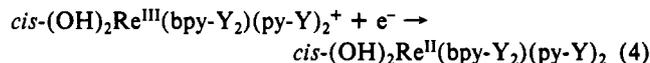
**Thermodynamics.** Figure 2 and Tables I and II reveal a very large but readily interpretable effect of ligand basicity upon *E*<sub>f</sub> for Re(VI/V). If the pyridyl basicity is viewed in terms of electron density at the nitrogen coordination site, then greater basicity (smaller p*K*<sub>b</sub>) should lead to preferential stabilization of Re(VI)

(versus Re(V)) and the observed negative shifts in *E*<sub>f</sub>. Increasing the electron density at the metal center (via pyridyl substituents) should also lead indirectly to an increase in electron density on the oxo ligands and ultimately to an enhanced affinity of these ligands for protons. This effect appears to be operative in Table IV, where the hydroxo p*K*<sub>a</sub>'s for *trans*-(O)(OH)Re<sup>V</sup>(py-X)<sub>4</sub> increase in the order 3-Clpy < 4-MeOpy < 4-NMe<sub>2</sub>py. It is worth noting that the corresponding *cis* complexes are appreciably more acidic and that protonation of *cis*-dioxorhenium(V) is never seen.

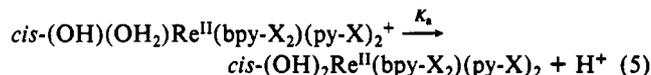
The thermodynamics of the V/III couples obviously are more complex; it may be useful then to consider first the Re(III/II) reactions. The III/II couples differ most strikingly from their VI/V counterparts in their lack of substantial response to ligand substituent changes and in their linkage to proton uptake, e.g.:



We wish to suggest that the two observations are closely interrelated. For example, from Figure 3 the reduction potentials for *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> and *cis*-(O)<sub>2</sub>Re(Cl<sub>2</sub>bpy)(3-Cl-py)<sub>2</sub><sup>+</sup> at pH\* = 5 differ by 175 mV. At this pH the reductions involve uptake of one proton (eq 3b). At pH\* = 8 the potentials differ by 350 mV and the redox reaction is decoupled from proton transfer:



It is important to note further that the p*K*<sub>a</sub>'s for the two possible hydroxo-aqua-rhenium(II) complexes (eq 5) differ by 1-2 pH\*



units. This, of course, shifts the "break point" in the Pourbaix diagrams (Figure 5) for Re(III/II). When formal potentials are compared at pH\*'s above the break point, eq 4 is followed and the inductive electronic influence of the ligand substituents upon *E*<sub>f</sub>(III/II) can clearly be seen. Below the break point, the difference in formal potentials is less because the effects of hydroxo ligand protonation (eq 5) act to counterbalance to some extent (via a shift in p*K*<sub>a</sub>) the simple inductive electronic effect. In other words, electron-donating substituents function simultaneously to decrease the affinity of (OH)<sub>2</sub>Re<sup>II</sup>(bpy-X<sub>2</sub>)(py-X)<sub>2</sub><sup>0</sup> for electrons while increasing the affinity for protons; electron-withdrawing substituents exert the opposite effect. The net result is a smaller than expected change in *E*<sub>f</sub> with changes in the nature of the substituent, X.

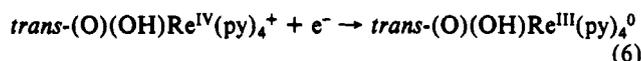
The Re(V/III) reaction is more complex in that two electrons and two protons are transferred at most pH's. Although direct evidence is lacking at present, we suggest that the V/III reaction is also subject to electron/proton compensation effects; this would account nicely for the observed immunity of *E*<sub>f</sub>(V/III) to substituent effects (Figure 2). Proof of this hypothesis will require further information about (1) the isolated V/IV and IV/III thermodynamics and/or (2) potentials for the V/III reactions when these are effectively decoupled from proton-transfer steps. Studies currently under way with closely related oxo, alkoxide complexes seem to provide an entry into both the proton-decoupled V/IV redox process and the following proton-dependent IV/III reaction.

**Electrode Kinetics.** Preliminary studies of both *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup> and *trans*-(O)<sub>2</sub>Re(py)<sub>4</sub><sup>+</sup> show that the rates of two-electron transfer (at *E*<sub>f</sub>) are limited by the Re(IV) to Re(III) step.<sup>20</sup> Further studies with the *trans* complex indicate that the rate-limiting electron transfer is preceded by a single protonation step, at least in the pH\* range from 4 to 10.<sup>20</sup> Thus, the rate-

- (16) The signs of the substituent-induced shifts in spectral energy—when the two charge-transfer bands and two ligand types are considered separately—are consistent with MLCT (rather than LMCT) assignments. In other words, introduction of electron-withdrawing substituents leads to a red shift, while electron-donating substituents cause a blue shift, as expected from the simplest energetic considerations.
- (17) For example, the A<sub>1</sub>, A<sub>1</sub>', and B<sub>2</sub> modes of coordinated pyridine (1611, 1219, and 649 cm<sup>-1</sup>) shift to 1569, 897, and 623 cm<sup>-1</sup> for coordinated pyridine-d<sub>5</sub>.
- (18) See, for example: (a) Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; John Wiley and Sons: New York, 1974; p 522. (b) DiLella, D. P.; Stidham, H. D. *J. Raman Spectrosc.* **1980**, *9*, 90. (c) Stidham, H. D.; DiLella, D. P. *J. Raman Spectrosc.* **1980**, *9*, 247.
- (19) The complexes investigated were *cis*-(O)<sub>2</sub>Re(4,4-(MeO)<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup>, *cis*-(O)<sub>2</sub>Re(4,4'-Cl<sub>2</sub>bpy)(py)<sub>2</sub><sup>+</sup>, *cis*-(O)<sub>2</sub>Re(4,4'-Cl<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup>, *cis*-(O)<sub>2</sub>Re(bpy)(4-MeOpy)<sub>2</sub><sup>+</sup>, and *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup>. It was assumed that derivatization would cause shifts in frequency only for modes associated with the ligand to which the substituent was directly attached.

- (20) Jones, L. M.; Lyons, L. Unpublished work (see supplementary material Figure S1).

determining event, at least in the *trans* case, is



These findings, while very preliminary and incomplete, do provide a basis for speculation regarding the overall patterns of V/III interfacial reactivity. In the simplest sense, the electrochemical kinetics can be viewed as depending on just two parameters or effects: (1) the intrinsic rate<sup>21</sup> of reaction 6 and (2) the degree of thermodynamic (in)accessibility of the inherently unstable species, (O)(OH)Re<sup>IV</sup>L<sub>x</sub>L'<sub>y</sub><sup>+</sup> and (O)(OH)Re<sup>III</sup>L<sub>x</sub>L'<sub>y</sub><sup>0</sup>. If, for simplicity,<sup>22</sup> we focus only on the second effect, a further breakdown into two elements can be suggested. These would be (1) the formal potential for the isolated one-electron reduction (eq 6) in comparison to  $E_f$  for the overall two-electron, two-proton reaction and (2) the magnitude of the unfavorable equilibrium constant for intermediate protonation (or deprotonation, depending on the direction of the reaction), which precedes the rate-determining step.

It is important to note that both elements should be influenced by pyridyl (or bpy) substituents. From the results above for Re(VI/V) and -(III/II) under pH-independent conditions, the formal potential for the isolated, pH-independent Re(IV/III) couple (eq 6) should become significantly more negative if electron-donating substituents are added (or less negative if electron-withdrawing substituents are introduced). Recall that the overall two-electron, two-proton  $E_f$  is *not* significantly influenced by substituents (Figure 2). This implies, then, that the isolated IV/III step (eq 6) will become progressively more favorable in a thermodynamic sense as ligand basicity (or electron-donating character) is decreased (assuming that the overall reaction is evaluated at the formal potential for Re(V/III)). This in turn suggests that the electrochemical kinetics should accelerate as the basicity of the ancillary ligands is decreased.

Countering this effect is the need to protonate one of the two oxo sites prior to the rate-determining electron-transfer step. Again from the preceding studies there are predictable effects. Most notably, as the pyridyl (or bipyridyl) ligand basicity is decreased, the affinity of Re=O for protons will decrease (see Table IV). Since oxo protonation is a preequilibrium process (as indicated by preliminary studies of the pH dependence of electrochemical kinetics), one would expect the overall two-electron reduction rate to *decrease* as the ancillary ligand basicity is decreased. Experimentally, however, there is no clear dependence of interfacial ET rate (or equivalently,  $\Delta E_p$ ; see Table III) upon ligand basicity. Evidently in this case the effects of ligand substituents upon proton demand are completely compensated by their effect upon Re(IV) accessibility (i.e.  $E_f(\text{IV/III})$ ; eq 6) in the overall redox kinetics. It is interesting to note that efficient proton/electron energy compensation also exists in a thermodynamic sense (as discussed above) but that in the thermodynamics (Figure 2; Tables I and II) the electronic inductive effect is slightly more important than the protonation (oxo pK<sub>a</sub>) effect.

In view of this analysis, it is worth asking what steps might be taken to bring about faster two-electron transfer kinetics. Clearly the electron/proton energy compensation phenomenon (and the results in Table III) argue against any *large* effects due to (bi)pyridyl ligand substituents. On the other hand, geometric effects (*trans* to *cis* isomerization) have been shown to accelerate the electrode kinetics<sup>5a</sup>—evidently because of preferential stabilization of the Re(IV) oxidation state. An alternative approach would be to attempt somehow to eliminate or bypass the kinetically deleterious preequilibrium protonation step. Our current studies with oxo(alkoxide)rhenium(V/III) suggest that this may be a fairly effective approach. Preliminary experiments indicate that moderately fast two-electron reduction rates are seen in the oxo, alkoxide case and that the fast kinetics arise because the double

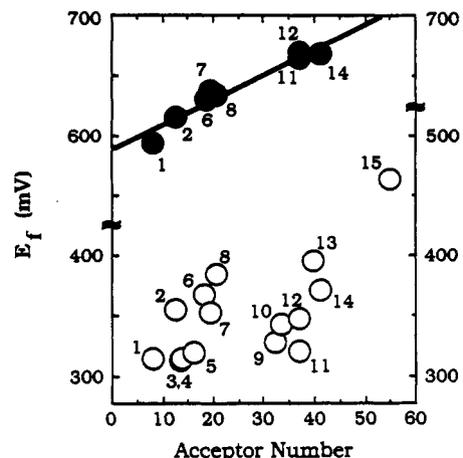


Figure 9. Formal potentials for *trans*-(O)<sub>2</sub>Re(4-MeOpy)<sub>4</sub><sup>2+/+</sup> (closed circles) and *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>2+/+</sup> (open circles) versus solvent acceptor number. Key to solvents: (1) tetrahydrofuran; (2) acetone; (3) *N*-methyl-2-pyrrolidone; (4) dimethylacetamide; (5) dimethylformamide; (6) propylene carbonate; (7) acetonitrile; (8) nitromethane; (9) *N*-methylformamide; (10) 2-propanol; (11) 1-propanol; (12) ethanol; (13) formamide; (14) methanol; (15) water. The line shown is a best fit (least-squares) line, omitting water. Missing from the plot is  $E_f(\text{trans})$  in water (765 mV).

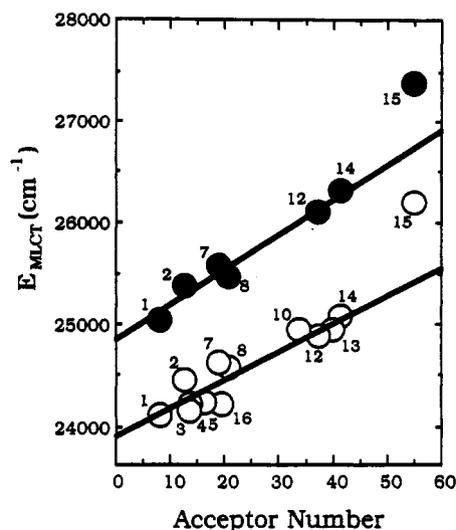


Figure 10. Metal-to-pyridine charge-transfer energies for *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup> (open circles) and *cis*-(O)<sub>2</sub>Re(4,4'-(MeO)<sub>2</sub>bpy)(4-MeOpy)<sub>2</sub><sup>+</sup> (closed circles) versus solvent acceptor number. The key to solvents is given in the caption to Figure 9, except point 16 is dimethyl sulfoxide. Lines drawn are best fit (least-squares) lines, omitting water. The slope for the lower line is 27 cm<sup>-1</sup>/AN unit ( $r = 0.93$ ). The slope for the upper line is 35 cm<sup>-1</sup>/AN unit ( $r = 0.99$ ).

redox step is linked to only a single (rather than double) proton transfer step. A related approach would be to combine proton transfer with electron transfer in an elementary H-atom or hydride transfer step.<sup>23</sup> There exist precedents for such steps in the homogeneous redox chemistry of ruthenium(IV) oxo complexes.<sup>24</sup> An obvious difficulty in implementing this strategy at an electrode surface is the tendency for conventional electrodes (metal or carbon) to function only as electron sources or sinks. With appropriate redox-active metal-oxide electrode surfaces, however, it might be possible to observe interfacial H-atom or hydride

(21) In other words, the rate when the thermodynamic driving force for the elementary reaction (eq 6, in isolation) is zero.

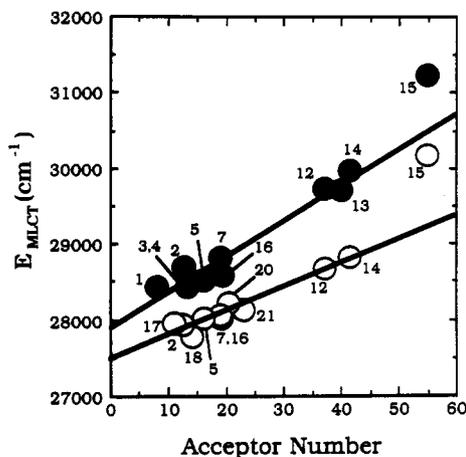
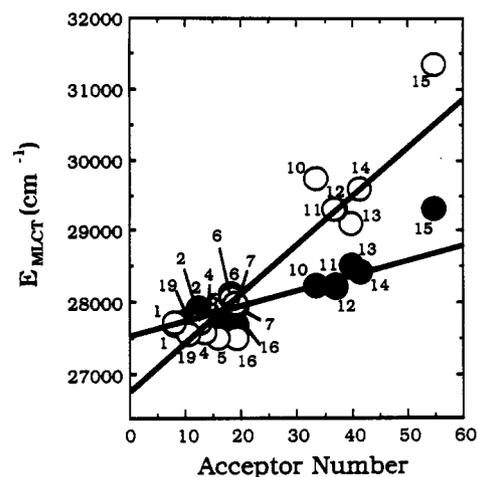
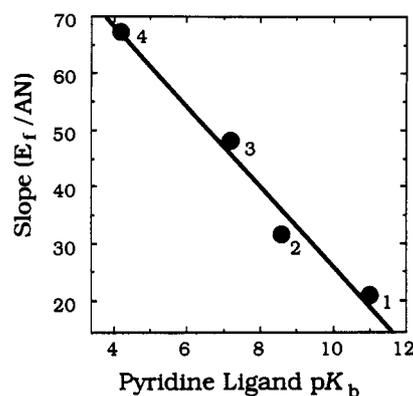
(22) And for lack of detailed information concerning the first effect.

(23) Note that we are *not* implying that such effects exist for the present experiments.

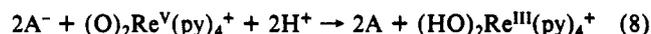
(24) (a) Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3287. (b) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897. (c) Gilbert, J. A.; Gersten, S. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6872.

**Table VIII.** Solvent Dependence of Formal Potentials for *trans*-(O)<sub>2</sub>Re(MeOpy)<sub>4</sub><sup>2+/+</sup> and *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>2+/+</sup> versus SSCE

| solvent (AN) <sup>a</sup>             | E <sub>f</sub> ( <i>trans</i> ), mV | E <sub>f</sub> ( <i>cis</i> ), mV |
|---------------------------------------|-------------------------------------|-----------------------------------|
| tetrahydrofuran (8)                   | 1025                                | 712                               |
| acetone (12.5)                        | 1020                                | 724                               |
| <i>N</i> -methyl-2-pyrrolidone (13.3) |                                     | 674                               |
| dimethylacetamide (13.3)              |                                     | 653                               |
| dimethylformamide (16)                |                                     | 668                               |
| propylene carbonate (18.3)            | 928                                 | 703                               |
| acetonitrile (19.3)                   | 1003                                | 729                               |
| nitromethane (20.5)                   | 938                                 | 743                               |
| <i>N</i> -methylformamide (32.1)      |                                     | 695                               |
| 2-propanol (33.5)                     |                                     | 766                               |
| 1-propanol (37)                       | 1090                                | 755                               |
| ethanol (37.1)                        | 1072                                | 791                               |
| formamide (39.8)                      |                                     | 649                               |
| methanol (41.3)                       | 1065                                | 781                               |
| water (54.8)                          | 915                                 | 581                               |

<sup>a</sup>AN = solvent acceptor number.**Figure 11.** Metal-to-pyridine charge-transfer energies for *trans*-(O)<sub>2</sub>Re(py)<sub>4</sub><sup>+</sup> (open circles) (data taken from ref 35) and *trans*-(O)<sub>2</sub>Re(4-MeOpy)<sub>4</sub><sup>+</sup> (closed circles) versus solvent acceptor number. The key to solvents is given in the captions to Figures 9 and 10, except points 17–21 are respectively hexamethylphosphoramide, dioxane, pyridine, dichloromethane, and chloroform. Lines drawn are best fit (least-squares) lines, omitting water. The slope for the lower line is 31 cm<sup>-1</sup>/AN unit (*r* = 0.97). The slope for the upper line is 47 cm<sup>-1</sup>/AN unit (*r* = 0.97).transfer events.<sup>25,26</sup> Finally, one might be able to carry out efficient two-electron, two-proton transfer reactions at electro-(25) For an early example from the organic electrochemical literature, see: Fleischman, M.; Korinek, K.; Pletcher, D. *J. Electroanal. Chem. Interfacial Electrochem.* 1971, 31, 39.(26) In a very recent report (*Inorg. Chem.* 1991, 30, 494) Thorp and co-workers have asserted that such a pathway exists for oxidation of an oxomanganese(III) dimer at a glassy-carbon surface. It should be noted that the assertion is based on a somewhat disingenuous claim of an H/D kinetic isotope effect of ~4; the actual measured electrochemical isotope effect (*k<sub>H</sub>/k<sub>D</sub>* = 2) is well within the range that has been reported elsewhere for known single-electron, proton-decoupled outer-sphere reactions at clean metal surfaces (see, for example: Weaver, M. J.; et al. *J. Phys. Chem.* 1983, 87, 1153; *J. Electroanal. Chem. Interfacial Electrochem.* 1980, 114, 53). For the known outer-sphere reactions the kinetic isotope effects seem to be associated with either hydrogen bonding or inner-shell quantum effects. Thus, the observed small isotope effects in the recent manganese study do *not* prove that an H-atom transfer pathway exists (on the other hand they do not necessarily rule it out). It should further be noted that detectable kinetic isotope effects would *generally* be expected for sequential electron/proton (or proton/electron) transfer reactions whenever the p*K<sub>b</sub>*'s associated with the reactions display a significant isotope effect. (It is unclear whether the p*K<sub>b</sub>* for manganese(III) oxo protonation in the Thorp study differs for H<sub>2</sub>O vs D<sub>2</sub>O as solvent.) For a general (elementary) discussion of the electrochemical kinetic consequences of sequentially coupling chemical steps (such as proton transfer) to interfacial electron-transfer events, see: Alberty, W. J. *Electrode Kinetics*; Clarendon Press, Oxford, England, 1980; Chapter 5.**Figure 12.** Metal-to-pyridine charge-transfer energies for *trans*-(O)<sub>2</sub>Re(3-Cl-py)<sub>4</sub><sup>+</sup> (closed circles) and *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup> (open circles) versus solvent acceptor number (open circles). The key to solvents is given in the captions to Figures 9 and 10. Lines drawn are best fit (least-squares) lines, omitting water. The slope for the lower line is 21 cm<sup>-1</sup>/AN unit (*r* = 0.90). The slope for the upper line is 67 cm<sup>-1</sup>/AN unit (*r* = 0.93).**Figure 13.** Plots of slopes of  $E^{MLCT}/AN$  from Figures 10–12 versus free pyridine ligand p*K<sub>b</sub>* for various *trans*-dioxorhenium(V) pyridyl species. Key to complexes: (1) *t*-(O)<sub>2</sub>Re(3-Cl-py)<sub>4</sub><sup>+</sup>; (2) *t*-(O)<sub>2</sub>Re(py)<sub>4</sub><sup>+</sup>; (3) *t*-(O)<sub>2</sub>Re(4-MeOpy)<sub>4</sub><sup>+</sup>; (4) *t*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup>.

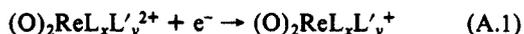
chemical interfaces simply by relying upon mediators or “redox catalysts”, e.g.

Saveant has discussed the necessary mechanistic and energetic criteria for efficient redox catalysis.<sup>27</sup> For the dioxo complexes, appropriate mediator species (based on energetics) might include methylpyridinium ions and/or osmium-ammine complexes.**Acknowledgment.** Professor Jim Kincaid and Dr. Krystaf Bahjidor of Marquette University kindly provided equipment and expertise for the near-UV Raman studies. This work was supported by a grant from the Office of Naval Research. The OLIS-modified Cary 14 spectrophotometer was acquired with funds from the National Science Foundation (Grants CHE-8552627 and CHE-8722985). The Raman facilities at Northwestern are part of the Materials Research Center (Grant NSF-DMR-8821571). J.T.H. acknowledges a fellowship from the Alfred P. Sloan Foundation.(27) See, for example: Andrieux, C. P.; Saveant, J.-M. *Investigation of Rates and Mechanisms of Reactions. Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; Vol. 6, Part 2.

## Appendix: Solvent Effects

The preceding sections describe systematic thermodynamic studies of two- and three-electron reductive and one-electron oxidative reactivity for some 20 dioxorhenium(V) complexes. Unfortunately, due to limitations imposed by reactant solubility and/or solvent electrochemistry, it has been necessary to collect data in not only aqueous media but also mixed aqueous/nonaqueous solvents and completely nonaqueous solvents. While this approach leads to an expansion of the available collection of data, it also leads to questions regarding quantitative data intercomparisons. Of particular concern are the possible effects of *specific* interactions between formally dinegative oxo ligands and electron-deficient solvent functionalities.<sup>28</sup> Such interactions are known, for example, to exert a strong influence upon the redox energetics of cyanide-containing metal complexes,<sup>29</sup> and it has been suggested that they may also play a role in chloro complexes.<sup>30</sup>

To address these concerns, we undertook a survey of dioxorhenium(VI/V) formal potentials ( $E_f$ ) as a function of solvent composition:

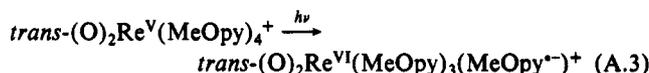
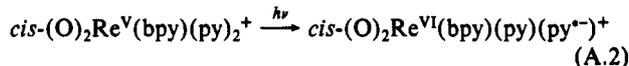


Two redox couples were examined: *trans*-(O)<sub>2</sub>Re(4-MeOpy)<sub>4</sub><sup>2+/+</sup> and *sym,cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>2+/+</sup>. These were chosen so as to provide access to the maximum number of solvents. (The pertinent factors were solubility and, more importantly, the anticipated location of  $E_f$  in comparison to the onset potential for solvent oxidation.) Table VIII lists the "raw" experimental data, i.e. values of  $E_f$  for both complexes in several solvents versus a sodium chloride SCE reference immersed in the listed solvent. The primary conclusion to be drawn from the tabulation is that the *apparent*  $E_f$  values are relatively invariant with solvent.

While the tabulated results provide an immediate positive answer to the pragmatic question of direct solvent-to-solvent data comparisons, they shed little light on the more fundamental question of "real" or true variations of  $E_f$  with solvent. It is possible, for example, that real variations exist but that they are obscured by solvent-dependent liquid junction effects or related phenomena. In order to avoid or minimize these effects, we have also chosen to evaluate formal potentials versus ferrocenium/ferrocene (Fc<sup>+/0</sup>),<sup>31</sup> where the absolute value of  $E_f$ (Fc<sup>+/0</sup>) has been taken to be approximately independent of solvent.<sup>31a</sup> Figure 9 shows plots of ferrocene-scale  $E_f$  values for *cis*- and *trans*-dioxorhenium(VI/V) versus the so-called solvent acceptor number (AN).<sup>32</sup> The acceptor number has been variously interpreted as a measure of solvent "polarity",<sup>33</sup> Lewis acidity,<sup>32</sup> or simply electrostatic interaction capability.<sup>34,35</sup> (Very similar plots are obtained when the acceptor number is replaced by Reichardt's  $E_T$  parameter<sup>36</sup>—another purported measure of solvent polarity<sup>36</sup> or perhaps acidity.<sup>32</sup>) From the plots, a statistically significant

correlation exists for the *trans* complex (correlation coefficient,  $r = 0.97$ ) such that  $E_f$ (*trans*) increases with increasing  $E_T$  or AN (slope =  $2.1 \pm 0.8$  mV/acceptor number unit). For the *cis* complex the variation of  $E_f$  with AN is much weaker (slope =  $1.0 \pm 0.6$  mV (one standard deviation)) and the existence of a physically meaningful correlation is less certain ( $r = 0.45$ ). Excluded from both correlations is water, which, in both cases, lies well above the best fit line.

The electrochemical experiments in Figure 9 clearly point to a greater solvent dependence for  $E_f$ (*trans*) than  $E_f$ (*cis*), at least for the pair of species studied. An independent experiment is needed, however, to ascertain whether the statistically weak correlation observed for the *cis* complex is chemically meaningful and whether substituent differences might also contribute to the apparent *cis/trans* disparity. Optical experiments (metal-to-ligand charge transfer) provide an alternative means for assessing the solvent dependence of Re(V) oxidation:



In the experiments, shifts in  $E^{MLCT}$  (the metal-to-ligand charge-transfer energy) will yield a direct measure of solvent effects upon the (O)<sub>2</sub>Re<sup>V</sup>/(O)<sub>2</sub>Re<sup>VI</sup> couple, provided that specific solvation effects are absent for the coordinated py/py<sup>+</sup> couple.<sup>37</sup> Figures 10 and 11 present plots of  $E^{MLCT}(\text{cis})$  (two complexes) and  $E^{MLCT}(\text{trans})$  (two complexes)<sup>38</sup> versus AN.<sup>39</sup> For clarity, Figure 12 presents separately  $E^{MLCT}$  data for two additional complexes, *trans*-(O)<sub>2</sub>Re(4-NMe<sub>2</sub>py)<sub>4</sub><sup>+</sup> and *trans*-(O)<sub>2</sub>Re(3-Cl-py)<sub>4</sub><sup>+</sup>. From the three figures, charge-transfer energies for all six species clearly increase with increasing solvent acceptor number, implying that the weak electrochemical effects in Figure 9 indeed are physically significant. We observe further that the solvatochromic effect for *trans*-(O)<sub>2</sub>Re(MeOpy)<sub>4</sub><sup>+</sup> is greater than for *cis*-(O)<sub>2</sub>Re(bpy)(py)<sub>2</sub><sup>+</sup>, again consistent with the electrochemical findings. Consideration of substituent effects for a given isomer indicates, however, that these effects (substituents), rather than geometric effects, are responsible for the differing solvent sensitivities in Figure 9. (Thus, when substituents are made identical, the *cis/trans* difference disappears in solvatochromic plots.) To elaborate, for a given isomer type the solvatochromic effects are greater for those complexes featuring strongly electron-donating substituents and weakest for those possessing electron-withdrawing groups. The trend is more clearly illustrated in Figure 13, where slopes of  $E^{MLCT}/AN$  for the *trans* series (Figures 11 and 12) have been plotted versus free py basicity (or py electron-donating ability; see Results).

The gross solvent dependencies of both  $E_f$  and  $E^{MLCT}$  are readily interpretable—at least at a qualitative or intuitive level—by donor-acceptor, acid-base, or simple electrostatic arguments. Inasmuch as the rhenium/oxo bonds are believed to be somewhat polarized,<sup>3a</sup> it is reasonable to expect the comparatively electron-rich oxo ligands on Re(V) to interact specifically with electron-deficient (acidic) or partially positively charged solvent functionalities. Electrochemical or optical oxidation of the rhenium metal center, however, should lead to electron withdrawal from the oxo sites and a decreased affinity of these ligands for acidic (Lewis) solvents. Obviously, it is the difference in solvent affinity between dioxorhenium(V) and dioxorhenium(VI) that gives rise to the energy or formal potential shifts. Highly acidic solvents

(28) For a very recent report, see the ESR study by Bramley et al. of oxochromium(V) species (*Inorg. Chem.* 1990, 29, 3089).

(29) (a) Fung, E. Y.; Chua, A. C. M.; Curtis, J. C. *Inorg. Chem.* 1988, 27, 1294. (b) Kitamura, N.; Sato, M.; Kim, H.-B.; Obata, R.; Tazuke, S. *Inorg. Chem.* 1988, 27, 651. (c) Toma, H. E. *J. Solution Chem.* 1989, 18, 575. (d) Gutmann, V.; Gritzner, G.; Danksagmüller, K. *Inorg. Chim. Acta* 1976, 17, 81.

(30) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* 1983, 22, 224.

(31) (a) Koepp, H. M.; Wendt, H.; Streblow, H. Z. *Elektrochem.* 1960, 64, 483. (b) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* 1980, 19, 2854.

(32) Gutmann, V. *Electrochem. Acta* 1976, 21, 661.

(33) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* 1981, 46, 661.

(34) Kober, E. M. *Abstracts (Inorganic Division) of Papers, 199th National Meeting of the American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 1990.*

(35) Obviously polarity, acidity, and electrostatic binding capability represent distinctly different concepts and properties and we do not regard them as physically or chemically equivalent; neither do we propose a favor one over another in the interpretation of purely empirical parameters (i.e. acceptor numbers). We note simply that the topic is controversial and that all three interpretations have been invoked in the existing literature.<sup>32-34</sup>

(36) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 98.

(37) Evidence in support of this contention exists from MLCT absorption studies of polypyridyl complexes. See, for example: Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* 1984, 23, 2098.

(38) Data for *t*-(O)<sub>2</sub>Re(py)<sub>4</sub><sup>+</sup> were taken from ref 39.

(39) Mention should be made of a much earlier study by Beard and Murmann (*J. Inorg. Nucl. Chem.* 1968, 30, 2467). They observed that  $E^{MLCT}$  for *trans*-(O)<sub>2</sub>Re(py)<sub>4</sub><sup>+</sup> could be correlated reasonably well with solvent dielectric constant, provided that one was willing to accept two distinct sets of correlations (depending on solvent) for one electronic transition.

should stabilize the lower oxidation state ( $\text{Re}^{\text{V}}$ ) to a greater extent than the higher one, thereby causing a net positive shift in  $E_T$  (or, alternatively, an increase in charge-transfer transition energy). If the solvent acceptor number is an appropriate measure of solvent acidity (or some closely related quantity), then the observed correlations (Figures 9-12) can be rationalized.

Water evidently is an exception to the general pattern of solvent effects; both  $E_T$  and  $E^{\text{MLCT}}$  show "anomalously" high values in this solvent. It may simply be that the acceptor number scale does not accurately represent the acidity or polarity of  $\text{H}_2\text{O}$  relative to other solvents.<sup>40</sup> Alternatively, the nature of the solute/solvent interactions may differ in a qualitative way for water versus other solvents. For example, there is independent evidence to suggest that stable molecular adducts (as opposed to weakly hydrogen-bond "complexes") are formed between *trans*-( $\text{O}$ )<sub>2</sub> $\text{Re}(\text{py})_4^+$  and water.<sup>4b,c,41</sup> In any case, the current experiments clearly imply that an exceptionally large degree of oxidation-state tuning of ligand/solvent interactions occurs in water, in comparison to other solvents.

(40) It should be mentioned that in the "restricted" solvatochromic correlation proposed by Beard and Murmann (so called "protic" solvents only) water is not anomalous.<sup>39</sup>

(41) From previous studies,<sup>1b</sup> one manifestation of specific oxo/water interactions is a large solvent isotope effect upon ( $\text{O}$ )<sub>2</sub> $\text{Re}(\text{py})_4^+$  excited-state lifetimes. We searched for solvent isotope effects in the  $E_T$  studies but did not observe any (despite their known importance in transition-metal *aqua* redox thermodynamics; see: Nettles, S. M.; Weaver, M. J. *Inorg. Chem.* 1980, 19, 1641).

Finally, returning to the substituent effects, those ligands that impart the greatest Brønsted basicity to the dioxorhenium(V) complex (see Table IV) also appear (from Figure 13) to induce the greatest Lewis basicity at the oxo sites—a result that certainly makes intuitive sense (assuming that the acceptor number can be taken as an approximate measure of solvent Lewis acidity characteristics). More precisely, the most basic pyridyl ligands seem to induce the greatest *differential* in basicity between dioxorhenium(V) and -(VI). If we assume that at least the relative Lewis basicity of dioxorhenium is indicated by the corresponding Brønsted measurement and if we note further that for ( $\text{O}$ )<sub>2</sub> $\text{Re}^{\text{V}}$  the basicity is ligand variant, we are lead to the additional conclusion that the basicity of ( $\text{O}$ )<sub>2</sub> $\text{Re}^{\text{VI}}$  must be ligand independent (or at least less dependent than in the lower oxidation state). In work to be reported elsewhere<sup>42</sup> for tetrapyrrolyl oxo alkoxide species, we have been able to confirm (indirectly, through appropriate thermochemical cycles) the very weak dependence of dioxorhenium(VI) basicity on ancillary ligand composition (as well, of course, as the exceedingly weak absolute basicity ( $\text{p}K_a \approx -13$ ) in this oxidation state).

**Supplementary Material Available:** Figure S1, showing experimental and digitally simulated cyclic voltammograms for reduction of *trans*-( $\text{O}$ )<sub>2</sub> $\text{Re}(\text{py})_4^+$  (1 page). Ordering information is given on any current masthead page.

(42) Ram, M. S.; Jones, L. M.; Wong, Y. H.; Johnson, C. S.; Hupp, J. T. Unpublished work.

(43) Sawada; et al. *Bull. Chem. Soc. Jpn.* 1984, 106, 5145.

Contribution from the Department of Chemistry, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

## Synthesis and Voltammetry of Two Series of Isonitrile/Halide Complexes of Ruthenium: $\text{RuX}_{6-n}(\text{CNBu}^t)_n$ ( $X = \text{Cl}, \text{Br}$ )

Colleen M. Duff\* and Roy A. Schmid

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Two new  $\text{Ru}^{\text{III}}$  isonitrile/halide complexes,  $(\text{Bu}_4\text{N})[\text{RuX}_4(\text{CNBu}^t)_2]$  ( $X = \text{Cl}, \text{Br}$ ), have been prepared by reaction of *tert*-butyl isocyanide ( $\text{CNBu}^t$ ) with  $(\text{Bu}_4\text{N})_2[\text{RuCl}_6]$  and  $\text{K}_3\text{Ru}_2\text{Br}_9$ , respectively. The  $\text{Ru}^{\text{II}}$  bromide complex  $\text{RuBr}_2(\text{CNBu}^t)_4$  has been prepared by reduction of  $[\text{RuBr}_4(\text{CNBu}^t)_2]^-$  in the presence of the isonitrile. The halide-to-metal charge-transfer spectra and the mid- and far-infrared spectra are reported as are the voltammetric data for the two series  $\text{RuCl}_{6-n}(\text{CNBu}^t)_n$  and  $\text{RuBr}_{6-n}(\text{CNBu}^t)_n$  ( $n = 0, 2, 4, 6$ ) measured in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ , and liquid  $\text{SO}_2$ . Electrode potentials and redox-linked ligand substitution are discussed relative to ligand additivity.

We have been studying the electrochemistry and optical spectroscopy of several series of simple binary complexes of ruthenium as part of a broader interest in ligand effects and the additive effect of these on physical characteristics.<sup>1</sup> The initial investigation into mixed nitrile/halide systems has expanded to include ligands that exhibit more varied bonding behavior. In particular, we are interested in systems employing ligands that are good  $\pi$ -acceptors and contrast these to simple  $\sigma$ -donors.

Isonitrile ligands are intriguing because they are among the few ligands that can exhibit both strong  $\sigma$ -donating and  $\pi$ -accepting character. In addition, it has been noted that metal complexes with isonitrile ligands do not always follow a simple electrochemical ligand additivity relationship.<sup>2</sup> We feel it is the deviations from typical linear ligand additivity theory such as these that will ultimately yield the most information about bonding in coordination complexes and have chosen to investigate simple isonitrile/halide complexes.

The majority of reports on isonitrile complexes found in the literature concentrate on metals in low oxidation states; many of

these are in combination with other  $\pi$ -accepting ligands such as carbonyl and alkylphosphines. In particular, there are few  $\text{Ru}^{\text{III}}$  ( $d^5$ ) isonitrile complexes known, these being the oxidized forms of  $\text{RuCl}_2(\text{isonitrile})_4$ . This paper reports the synthesis of two new  $\text{Ru}^{\text{III}}$  complexes,  $[\text{RuCl}_4(\text{CNBu}^t)_2]^-$  and  $[\text{RuBr}_4(\text{CNBu}^t)_2]^-$ , where  $\text{CNBu}^t$  is *tert*-butyl isocyanide, and the voltammetry of two series  $\text{RuX}_{6-n}(\text{CNBu}^t)_n$  ( $X = \text{Br}, \text{Cl}; n = 0, 2, 4, 6$ ). The electrode potentials of the present series are related to ligand additivity and Lever's electrochemical ligand parameter ( $E_L$ ).<sup>2</sup>

### Experimental Section

All solvents were distilled under  $\text{N}_2$  from appropriate drying agents;  $\text{RuCl}_2 \cdot x\text{H}_2\text{O}$  and  $\text{CNBu}^t$  were purchased from Aldrich. Microanalyses were performed by the Research School of Chemistry Microanalytical Laboratory, Australian National University. The complexes  $(\text{Bu}_4\text{N})_2[\text{RuCl}_6]$ ,<sup>3</sup>  $(\text{Bu}_4\text{N})_2[\text{RuBr}_6]$ ,<sup>4</sup>  $\text{K}_3[\text{Ru}_2\text{Br}_9]$ ,<sup>5</sup>  $[(\text{CNBu}^t)_6\text{Ru}](\text{PF}_6)_2$ ,<sup>6</sup> and *trans*- $\text{RuCl}_2(\text{CNBu}^t)_4$ <sup>7</sup> were prepared as reported.

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