or a slight decrease in metal–metal separation. By way of contrast, the SCF–Xα–SW method predicts the σ ionizations should occur at least 2 eV to higher energy than the π ionizations for systems with quadruple bonds.[7,10,17,23] We and others have found the latter result to be extremely dependent on the sphere radii selected.[16,24] The use of the atomic spheres within which only a spherically symmetric potential is felt[25] apparently dilutes the very directional nd_{z^2}–ns,np_z interaction so that the SW approach is inappropriate for this particular problem.

This work clearly demonstrates the narrow width of the σ ionization in systems with metal–metal triple bonds. This is experimental support for the calculational results of Ziegler[22] and by analogy indicates that the "extra" sharp ionization band of $W_2(O_2CCF_3)_4$ is due to ionization of the valence σ orbital.[5] Additionally, the relative shifts of the π and σ ionizations in going from W_2 to Mo_2 observed here suggest that these ionizations are coincident in quadruply bonded Mo_2 species as suggested by others.[21] These relative shifts are supported by related work on the mixed-metal systems $MM'(O_2CR)_4$ and $MM'Cl_4(PMe_3)_4$ (M, M' = Mo, W).[8,26]

(23) (a) Reference 1a, pp 356–389.
(24) Sattelberger, A. P., unpublished results.
(25) (a) Case, D. A. *Annu. Rev. Phys. Chem.* **1982**, *33*, 151–171. (b) Slater, J. C. "The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1963; Vol. 4.
(26) Lichtenberger, D. L.; Kober, E. M.; Blevins, C. H., II; McCarley, R. E.; Carlin, R. T.; Sattelberger, A. P., manuscript in preparation.

Aqueous Electrochemistry of *trans*-(py)$_4$Re^V(O)$_2^+$. Electrocatalytic Reductions Based on Rhenium(II)

David W. Pipes and Thomas J. Meyer*

*Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514*

Received May 29, 1985

We have previously reported that for polypyridyl aqua complexes of Ru and Os, five oxidation states (M^{II}–M^{VI}) are accessible in the same coordination environment over a relatively narrow potential range ($\sim$0.7 V).[1] The higher oxidation states are stabilized by proton loss and metal–oxo formation, e.g., $(bpy)_2Os^{VI}(O)_2^{2+}$ (bpy is 2,2'-bipyridine), and have an extensive stoichiometric and catalytic chemistry as oxidants.[2] We report here that an equally diverse redox chemistry exists for Re in a closely related coordination environment, however, Re(V) is the stable oxidation state as *trans*-(py)$_4$Re^V(O)$_2^+$ [3] (py is pyridine) and reduction leads to strongly reducing aqua complexes, which

(1) (a) Pipes, D. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7653. (b) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407.
(2) (a) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310. (b) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106; (c) *Ibid.* **1982**, *104*, 5070. (d) Ellis, C. D.; Gilbert, J. A.; Murphy, W. R., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4842.
(3) (a) The complex *trans*-(py)$_4$Re^V(O)$_2^+$ was prepared by the method of Wilkinson et al. (Wilkinson, G.; Johnson, N. P.; Lock, C. J. K. *J. Chem. Soc.* **1964**, 1054–1066) except that the Cl$^-$ salt obtained was converted to the ClO$_4^-$ salt by dissolution in H$_2$O and addition of a saturated NaClO$_4$ solution to cause precipitation. (b) The UV–vis and IR spectra of the sample used in our study agreed with literature values. Anal. Calcd for [(C$_5$H$_5$N)$_4$Re(O)$_2$](ClO$_4$): %C = 37.88; %H = 3.19; %Cl = 8.84; %Cl = 5.59. Found, %C = 38.06; %H = 3.70; %N = 8.87; %Cl = 5.08. (c) The X-ray crystal structure of the Cl$^-$ salt verifies the trans dioxo structure at Re with average Re–O bond lengths of 1.76 (3) Å: Calvo, C.; Krishnamachori, N.; Lock, C. J. K. *J. Cryst. Mol. Struct.* **1971**, *1*, 161.
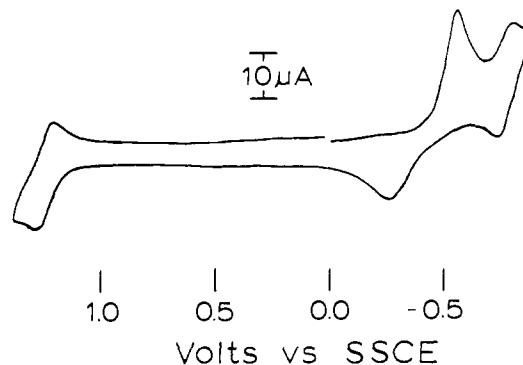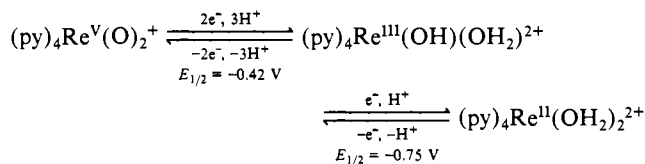

Figure 1. Cyclic voltammogram of 0.1 mM *trans*-[(py)$_4$Re^V(O)$_2$](ClO$_4$) in 0.1 M triflic acid (pH 1.0) using an unactivated Tokai glassy carbon working electrode vs. the SSCE reference electrode at a sweep rate of 100 mV/s.

behave in the reverse fashion, as potentially useful electrocatalytic reductants.
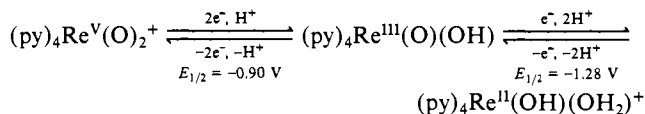
A cyclic voltammogram of *trans*-(py)$_4$Re^V(O)$_2^+$ in 0.1 M triflic acid (CF$_3$SO$_3$H) (pH 1.0) using a Tokai glassy carbon electrode as the working electrode vs. the saturated sodium chloride calomel (SSCE) reference electrode is shown in Figure 1. The reversible wave at $E_{1/2}$ = 1.25 V is independent of pH from pH 0.5 to 11 and is an oxidation of Re(V) to (py)$_4$Re^{VI}(O)$_2^{2+}$. By coulometry, n = 1.0 $\pm$ 0.2 but the Re(VI) complex is unstable on time scales longer than the coulometry experiment.

The first wave in the reductive direction is multielectron in nature (n = 2.0 $\pm$ 0.2 by coulometry) and at pH 1 gives (py)$_4$Re^{III}(OH)(OH$_2$)$^{2+}$ from pH-dependent potential measurements. As shown in Figure 1, at a normal Tokai glassy carbon electrode, the wave is chemically reversible but electrochemically irreversible. The same result was obtained if the reverse, oxidative scan was initiated past the Re(V)/(III) wave or past the following Re(III)/(II) wave. However, at pH 1 the wave at $E_{1/2}$ = –0.42 V is quasi-reversible at an oxidatively activated glassy carbon electrode.[1a,4] As a function of scan rate ΔE_p varies from 0.14 (200 mV/s) to 0.04 V (20 mV/s). A second one-electron wave (n = 1.0 $\pm$ 0.4) occurs at $E_{1/2}$ = –0.75 V for the reduction of Re(III) to (py)$_4$Re^{II}(OH$_2$)$_2^{2+}$, but the acquisition of accurate coulometric data is difficult because, as noted below, the Re(II) complex is a catalyst for the reduction of H$_2$O to H$_2$.
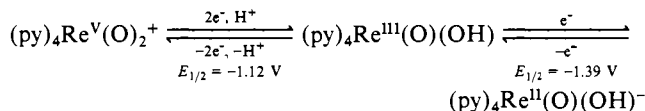
The potentials for the Re(V/III) and Re(III/II) couples are pH dependent because of the acidic character of the aqua ligands in the three oxidation states. Reduction potentials and dominant proton compositions at pH 1.0, 7.0, and 13.0 are as follows:
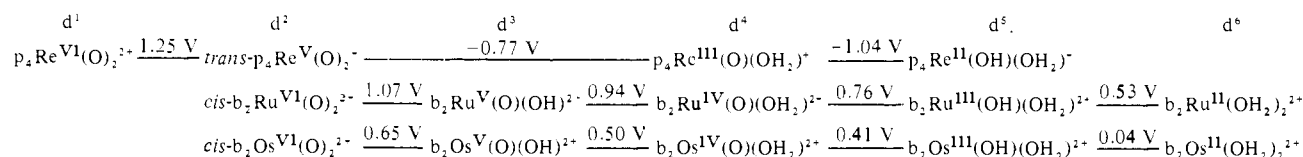
pH 1.0

$$(py)_4Re^V(O)_2^+ \underset{\underset{E_{1/2}\,=\,-0.42\text{ V}}{-2e^-,\,-3H^+}}{\overset{2e^-,\,3H^+}{\rightleftharpoons}} (py)_4Re^{III}(OH)(OH_2)^{2+}$$

$$\underset{\underset{E_{1/2}\,=\,-0.75\text{ V}}{-e^-,\,-H^+}}{\overset{e^-,\,H^+}{\rightleftharpoons}} (py)_4Re^{II}(OH_2)_2^{2+}$$

pH 7.0

$$(py)_4Re^V(O)_2^+ \underset{\underset{E_{1/2}\,=\,-0.90\text{ V}}{-2e^-,\,-H^+}}{\overset{2e^-,\,H^+}{\rightleftharpoons}} (py)_4Re^{III}(O)(OH) \underset{\underset{E_{1/2}\,=\,-1.28\text{ V}}{-e^-,\,-2H^+}}{\overset{e^-,\,2H^+}{\rightleftharpoons}}$$

$$(py)_4Re^{II}(OH)(OH_2)^+$$

pH 13.0

$$(py)_4Re^V(O)_2^+ \underset{\underset{E_{1/2}\,=\,-1.12\text{ V}}{-2e^-,\,-H^+}}{\overset{2e^-,\,H^+}{\rightleftharpoons}} (py)_4Re^{III}(O)(OH) \underset{\underset{E_{1/2}\,=\,-1.39\text{ V}}{-e^-}}{\overset{e^-}{\rightleftharpoons}}$$
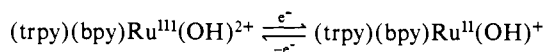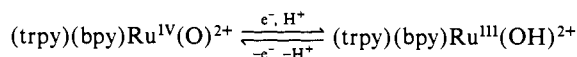
$$(py)_4Re^{II}(O)(OH)^-$$

(4) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *7*, 1845–1853.
(5) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *2*, 1037–1042.

Scheme I[a]

d¹	d²	d³	d⁴	d⁵	d⁶

$p_4Re^{VI}(O)_2^{2+}$ ──1.25 V──→ *trans*-$p_4Re^V(O)_2^-$ ────────−0.77 V──────── $p_4Re^{III}(O)(OH_2)^+$ ──−1.04 V──→ $p_4Re^{II}(OH)(OH_2)^-$

cis-$b_2Ru^{VI}(O)_2^{2-}$ ──1.07 V──→ $b_2Ru^V(O)(OH)^{2-}$ ──0.94 V──→ $b_2Ru^{IV}(O)(OH_2)^{2-}$ ──0.76 V──→ $b_2Ru^{III}(OH)(OH_2)^{2+}$ ──0.53 V──→ $b_2Ru^{II}(OH_2)_2^{2+}$

cis-$b_2Os^{VI}(O)_2^{2-}$ ──0.65 V──→ $b_2Os^V(O)(OH)^{2+}$ ──0.50 V──→ $b_2Os^{IV}(O)(OH_2)^{2+}$ ──0.41 V──→ $b_2Os^{III}(OH)(OH_2)^{2+}$ ──0.04 V──→ $b_2Os^{II}(OH_2)_2^{2+}$

[a] $\mu = 0.1$ M at pH 4.0, volts vs. SSCE; p is pyridine and b is bipyridine.

With the data on the Re system available, it is possible to compare redox characteristics for coordinately closely related complexes of Ru, Os, and Re as shown in Scheme I, where the classification is based on the d-electron configuration at the metal. The compilation of data is revealing in illustrating the sometimes remarkable differences in redox potentials that can exist for closely related metal complexes.[5] These differences play an important role in the underlying descriptive chemistry as evidenced by the appearance of the d¹ Re(VI) case and the nonappearance of the d⁶ Re(I) case within the potential limits imposed by oxidation or reduction of the solvent.[6] The "disappearance" of oxidation states like Re(IV) has been observed in related monomeric[1] and dimeric[7] systems of Ru and Os. An important role in such cases is played by differences in pH dependences for adjacent couples, e.g.,

$$(trpy)(bpy)Ru^{IV}(O)^{2+} \underset{-e^-, -H^+}{\overset{e^-, H^+}{\rightleftharpoons}} (trpy)(bpy)Ru^{III}(OH)^{2+}$$

$$(trpy)(bpy)Ru^{III}(OH)^{2+} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (trpy)(bpy)Ru^{II}(OH)^+$$

trpy is 2,2′:6,2″-terpyridine

which can lead to an instability toward disproportionation,

$$OH^- + 2(trpy)(bpy)Ru^{III}(OH)^{2+} \rightarrow$$
$$(trpy)(bpy)Ru^{IV}(O)^{2+} + (trpy)(bpy)Ru^{II}(OH)^+ + H_2O$$
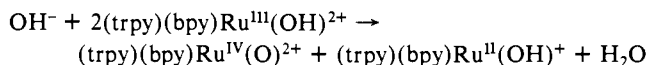
for the intermediate oxidation state as the pH is increased.

In terms of implied reactivity the strongly reducing potentials for the Re(V/III) and Re(III/II) couples are notable. In fact, reduction at potentials more negative than the potential of the Re(III/II) couple gives Re(II), which is an electrocatalyst for the reduction of H_2O to H_2 over the pH range 0.5–13. For example, electrolysis at a mercury pool electrode of $(py)_4Re^V(O)_2^+$ (5.2 × 10^{-4} M, 0.1 M triflic acid) at $E_{app} = -0.87$ V and pH 1.0 in a gas-tight electrochemical cell gave a sustained (26 cycles based on reduction of Re(III) to Re(II)) catalytic current and in approximately 40 min. H_2 was produced at >90% efficiency as shown by GC analysis. Electrochemical generation of Re(II) (λ_{max} = 458 nm, ϵ_{max} 8600 M^{-1} cm^{-1}) in a spectroelectrochemical cell at pH 1.0 was followed by the appearance of Re(III) (λ_{max} = 387 nm, ϵ_{max} = 6300 M^{-1} cm^{-1}) with an isosbestic point maintained at 398 nm during the course of the reaction. From the electrochemical, spectral, and GC results, the stoichiometry of the *net* reaction in acidic solution is

$$2(py)_4Re^{II}(OH_2)_2^{2+} \rightarrow 2(py)_4Re^{III}(OH)(OH_2)^{2+} + H_2$$
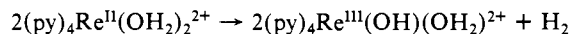
The H_2 evolution reaction followed first-order kinetics in Re(II) with k = 2.4 (±1.5) × 10^{-3} s^{-1} at pH 1.0.

At pH 6.8, where the rate of H_2 evolution is actually enhanced compared to pH 1.0, added NO_2^- (0.1 M) suppresses catalytic H_2 production at −1.39 V because of competitive catalytic reduction of NO_2^-. The electrocatalytic reduction of NO_2^- is currently under investigation. We have identified NH_3 as a major reduction product by GC under conditions where the direct electroreduction of NO_2^- to NH_3 is negligible. The reactivity that we find for the Re system appears to parallel that found earlier for (catecholato)$_2$Mo^{VI}(O)$_2^{2-}$ by Schultz and Finklea,[8] for Ni(CN)$_3^-$ by Vincente-Perez et al.,[9] for polypyridine–nitrosyl complexes of Ru(II) and Os(II),[10] and for a tetrasulfonated, water-soluble iron porphyrin.[11]

(8) Lahr, S. K.; Finklea, H. O.; Schultz, F. A. *J. Electroanal. Chem.* **1984**, *163*, 237.

(9) Vicente-Perez, S.; Cabrera-Martin, A.; Gonzalez-Martin, C. *Quim. Anal.* **1976**, *30*, 149.

(10) Murphy, W. R., Jr.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5817–5819.

(11) Barley, M. H.; Takeuchi, K. J.; Murphy, W. R. Jr.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 507–508.

Time-Resolved Resonance Raman Studies of the $\delta\delta^*$ Excited State of $Re_2Cl_8^{2-}$

Richard F. Dallinger

Department of Chemistry, Wabash College
Crawfordsville, Indiana 47933

The characterization of excited electronic states continues to be an important problem in inorganic photochemistry. Recent work has demonstrated that the technique of time-resolved resonance Raman (TR³) spectroscopy has been extremely useful in elucidating excited-state molecular structure.[1–10] The TR³ method provides specific structural information, from the vibrational frequencies, on excited-state transients at submillimolar concentrations in room temperature fluid solution. A class of molecules whose excited-state structure has been the subject of intense experimental and theoretical effort are the multiply metal–metal bonded dimers.[11–15] In this paper, we wish to report the results of a TR³ study of the prototypical molecule of this group, the quadruply bonded octachlorodirhenate dianion ($Re_2Cl_8^{2-}$).

The photochemically important excited state of $Re_2Cl_8^{2-}$ has

(1) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.

(2) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(3) McClanahan, S.; Hayes, T.; Kincaid, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 4486.

(4) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.

(5) Dallinger, R. F.; Guanci, J. J.; Woodruff, W. H.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1355.

(6) Dallinger, R. F.; Woodruff, W. H.; Rodgers, M. A. J. *Photochem. Photobiol.* **1981**, *33*, 275.

(7) Dallinger, R. F.; Farquharson, S.; Woodruff, W. H.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 7433.

(8) Wilbrandt, R.; Jensen, N. H. *J. Am. Chem. Soc.* **1981**, *103*, 1036.

(9) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595.

(10) Che, C. H.; Butler, L. G.; Gray, H. B.; Crooks, R. M.; Woodruff, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 5492.

(11) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982.

(12) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

(13) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232.

(14) Templeton, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 210.

(15) Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007.

(6) At high pH, evidence from cyclic voltammetry exists for a further reduction (pH 13. $E_{p,c}$ = −1.72 V), which shows current enhancement due to H_2O reduction.

(7) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R. Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855–3864.