3, R = H
4, R = NO₂
5, R = NH₂

6, R = NH—N=C—COOEt (with CH₃ substituent)

could be separated by recrystallization from acetone–ethanol, mp >230 °C sublimes (37%). Hydrogenation of **4** in ethanol over 10% Pd/C followed by filtration into 1 N HCl and evaporation afforded the amine hydrochloride[11] **5** (93%). Treatment of **5** with 1 equiv of aqueous HCl and sodium nitrite (5 °C for 10 min) yielded the diazonium salt which was added to a stirred ethanolic solution of 1.2 equiv of ethyl α-methylacetoacetate and potassium hydroxide at 0 °C. After 18 h at 4 °C **6**[11] was isolated by ether extraction (18%). Cyclization and transformation of the nitrile function to an ester function (Pinner synthesis) to yield the indole[11] **7** was carried out in one step by stirring a solution of **6** in saturated

7   8   9ox
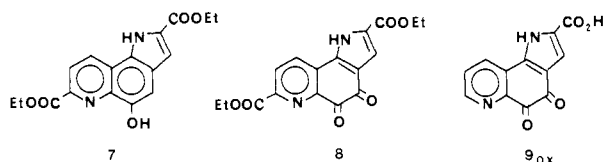
ethanolic HCl for 3 days followed by evaporation and addition of water (77%). Oxidation of the *o*-quinone **8** was accomplished by adding an aqueous solution of ceric ammonium nitrate (5.5 equiv) to a suspension of **7** in acetonitrile at 5 °C. Evaporation to low volume and addition of water yielded the crude *o*-quinone (51%). Recrystallization from acetonitrile afforded **8**[12] as bright-orange flakes mp 314–316 °C (darkens >300 °C). TLC (silica gel with methylene chloride–ethanol 9:1) shows single spot R_f 0.74; UV_{max} (CH_3CN) 220 (ϵ 13 000), 242 (ϵ 15 500), 275 (ϵ 25 200), 308 sh (ϵ 15 800), 318 sh (ϵ 16 700) 329 nm (ϵ 17 600). Hydrolysis of **8** was accomplished by stirring in concentrated hydrochloric acid at 100 °C for 20 h to precipitate 9-decarboxymethoxatin[13] (**2ox**) as an orange-brown solid after filtration, washing with water and acetone, and drying (86%). TLC (reverse phase with water–ethanol–triethylamine 70:30:1) shows single spot R_f 0.9; UV_{max} (H_2O) 243 (ϵ 20 900), 275 (ϵ 30 600), 315 nm (ϵ 17 700).

The macroscopic pK_a values of **2ox** (eq 1) were determined by

(1)
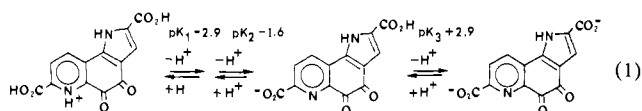
spectral titration between $H_0 = -4.4$ (315 nm) and pH 4.29 (315 and 275 nm).

Equilibrium complexing of Cd^{2+} with **2ox** and **9ox** was studied at pH 4.0 ($\mu = 1.0$ with $NaClO_4$) by the procedure of Walker.[14] A plot of ln $(A_0 - A_t)/(A_t - A_\infty)$ vs. ln $[Cd^{2+}]$ provided stoichiometry of 1/1 as slope and $K = 1.9 \times 10^4$ M⁻¹ (330 and 315 nm) as intercept. This may be compared to $K = 3.5 \times 10^7$ M⁻¹ for 1:1 complexing of Cd^{2+} by α-picolinic acid.[5] No complexation of Cd^{2+} by **9ox** could be detected. Thus, although the pyridine

nitrogen and C(7) carboxyl functions of **2ox** are only very weakly basic, **2ox** is a reasonable metal-complexing agent. By using the same plotting technique to determine the binding of Cu^{2+} to **2ox**, there was obtained a slope of 1.5/1, interpretable as the formation of a (**2ox**)₂(Cu^{2+})₃ complex ($K = 4 \times 10^7$ M⁻⁴).

Examination of Stuart–Briegleb molecular models and considerations of functional group basicity assures us that **1red** and **2red** will behave as strong tridentate metal-complexing agents. Since metal ion binding to **1red** and **2red** should be much greater than to **1ox** and **2ox**, metal ions may well play a catalytic role in the reduction of these quinones (eq 2). Availability of **2ox** in

(2)
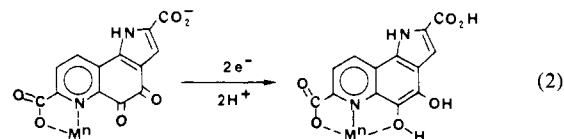
reagent quantity has made it possible to undertake our current studies to determine: (i) the complexing constants of various metal ions with **2ox** and **2red**; (ii) modes of interaction of metal ions with the radical **2rad**; (iii) the influence of metal ion binding upon the electrochemical potentials and rates of stepwise 1e⁻ reduction of **2ox** to **2rad** and **2red**. The results of these studies will be reported as full papers.

The Valence σ Ionization in Systems with Multiple Metal–Metal Bonds

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Chemical systems containing multiple bonds between metal atoms have provided many theoretical and synthetic challenges.[1] Photoelectron spectroscopy (PES) has played an important role in the experimental investigation of their electronic structure,[2] particularly for the π- and δ-type bonds.[3–8] However, an ionization associated with a σ bond has not been firmly identified, although a sharp "extra" ionization (fwhm 0.3 eV) in the PES of W₂-

(11) ¹H NMR, IR, and mass spectral data were obtained for each intermediate and were in full agreement with the postulated structure.

(12) Additional data for **8** are as follows: ¹H NMR (Me₂SO-*d*₆) δ 1.34 (3 H, t, CH₃), 1.36 (3 H, t, CH₃), 4.33 (2 H, q, CH₂), 4.42 (2 H, q, CH₂), 7.19 (1 H, s, H₃), 8.27 (1 H, d, H₈), 8.85 (1 H, d, H₉), 13.42 (1 H, s, NH) exchangeable. Anal. Calcd for C₁₇H₁₄N₂O₆: C, 59.65; H, 4.09; N, 8.19. Found: C, 59.80; H, 4.15; N, 8.45; IR_max 1660, 1720, 3500 cm⁻¹.

(13) Additional data for **2** are as follows: ¹H NMR (Me₂SO-*d*₆) δ 7.15 (1 H, s, H₃), 8.24 (1 H, d, H₈), 8.22 (1 H, d, H₉), 13.35 (1 H, s, NH) exchangeable. Anal. Calcd for C₁₃H₆N₂O₆·¹/₂H₂O: C, 52.88; H, 2.37; N, 9.49. Found: C, 53.03; H, 2.55; N, 9.38. IR_max 1600, 1700 cm⁻¹.

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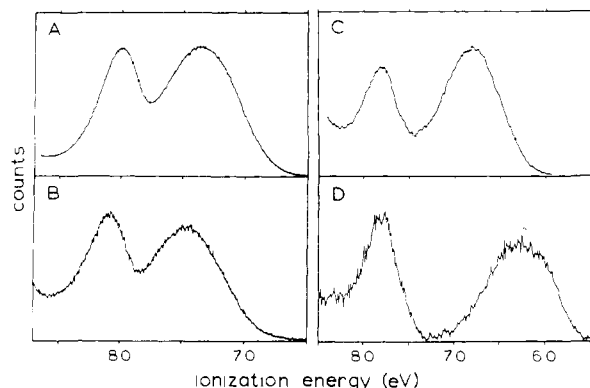(8) Blevins, C. H., II *Diss. Abstr. Intl., B* **1984**, *45*, 1186. (See Chapters 5 and 6.)

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Communications to the Editor

Figure 1. Close-up HeI PES showing metal-based ionizations of (A) $Mo_2(OCHMe_2)_6$, (B) $Mo_2(OCH_2CMe_3)_6$, (C) $Mo_2(OCMe_3)_6$, and (D) $W_2(OCMe_3)_6$.

Table I. Peak Maxima, Widths, and Relative Areas of the Metal Ionizations

compound	maxima (fwhm), eV		π/σ^b
$Mo_2(OCHMe_2)_6$	7.33 (0.69)	7.99 (0.35)	2.4
$Mo_2(OCH_2CMe_3)_6$	7.46 (0.69)	8.08 (0.36)	2.1
$Mo_2(OCMe_3)_6$	6.79 (0.74)	7.80 (0.43)	2.0
$W_2(OCMe_3)_6$	6.27 (0.82)	7.79 (0.40)	2.0

^{a} Determined by best-fit least-squares analysis with asymmetric Gaussian peaks.[14] ^{b} Relative area of the π and σ ionizations.

$(O_2CCF_3)_4$ has been put forward as a possibility.[5] We have observed a similar ionization feature in the spectra of other $W_2(\sigma^2\pi^4\delta^2)$ dimers.[7-9] Two arguments against assignment of this feature to the σ ionization have been that (1) the band is too narrow to represent the ionization of a supposedly strongly σ-bonding electron[8-10] and (2) SCF-Xα-SW calculations predict that the σ-based ionization should occur at a much higher energy.[7,11] Other assignments for this sharp ionization feature have been suggested.[6-10] Herein we report evidence supporting the assignment of this ionization to the ^2A_g (σ) state and briefly discuss the implications of this assessment.

Molecules of the type $M_2(OR)_6$ contain a triple bond ($\sigma^2\pi^4$) and the PES of one complex (M = Mo, R = CH_2CMe_3) clearly identified the σ and π ionizations.[12] The spectra of this and three similar complexes (M = Mo, R = $CHMe_2$, CMe_3; M = W, R = CMe_3)[13] obtained under conditions of higher resolution and signal to noise[14,15] are shown in Figure 1. The spectra are all similar to the one reported previously,[12] showing oxygen lone pair ionizations between 8.5 and 11.0 eV and metal-based ionizations at less than 8.5 eV. The band characteristics of the metal-based ionizations are summarized in Table I.

The broad lower energy component of the metal-based ionizations is assigned to the π ionization, while the higher energy, sharper band is assigned to the σ ionization. Both SCF-Xα-SW[12] and Fenske-Hall[16] MO calculations cleanly place the σ and π ionizations at lowest energy for these complexes, with the π occurring at about 1 eV lower energy than the σ. These ionizations are well removed from the oxygen lone pair ionizations and less than 20% metal–ligand mixing is calculated to be present. The relative areas of the π/σ ionizations are found to be approximately 2:1 in agreement with a calculated prediction.[12]

The half-widths of the π ionizations (fwhm ca. 0.7 eV) are similar to those observed for species with quadruple bonds[3-8] and are consistent with the orbital being strongly bonding. This ionization gives rise to a ^2E_u state (D_{3d} symmetry) which will split through spin–orbit interaction into $E_{1/2}$ and $E_{3/2}$ components.[6-10,17] Without further interactions the splitting would equal λ, the metal's spin–orbit coupling constant. The increase in half-width of the π ionization in going from Mo to W is approximately 0.1 eV, and can be largely accounted for by the increase in spin–orbit coupling constant from Mo to W (λ_{Mo} = 0.1 eV, λ_W = 0.2–0.3 eV).[18] The possibility that the second, sharp band might be a spin–orbit component of the π ionization (as has been suggested in other systems)[7-9,17] is untenable in the present case. The assignments of the σ and π ionizations are thus strongly supported.

The significant observation is the narrow width of the σ-based ionization (fwhm 0.4 eV). This ionization is much narrower than the π ionization and is about the same width as the ionization of the weakly bonding δ orbital of species with metal–metal quadruple bonds.[3-8] This narrow width shows that the bond distance changes occurring with removal of the σ-orbital electron are relatively small, as though this orbital is weakly bonding at best. The origin of this unexpected result lies in the close contact of the two atoms, which causes a substantial overlap and consequent repulsive interaction between the valence nd_{z^2} orbital of one metal with the outer core ns and np_z orbitals of the other metal (n = 4 for Mo and n = 5 for W). To help appreciate the significance of this interaction, we have calculated the overlap integrals between the outer core and valence atomic orbitals of two metals separated by 2.22 Å.[19] The nd_{z^2} overlaps with ns and np_z orbitals on the neighboring metal atom are about 0.12 and are essentially the same as the $nd_{z^2} - nd_{z^2}$ overlap. The ionization of a valence σ electron reduces this valence repulsion with the outer core, and as a result the metal–metal distance does not increase as one would normally expect for removal of an electron from a σ bonding orbital. This valence σ interaction with the outer core also serves to destabilize the valence σ level such that its ionization occurs in close proximity to the π ionization.

Calculations based on the LCAO approach predict[20,21] the close proximity of the σ and π ionizations for both triple and quadruple metal–metal bond complexes. In addition, recent calculational results of Ziegler[22] on the equilibrium geometries of the ground and ionized states of various systems with triple or quadruple metal–metal bonds are consistent with the sharpness of the σ ionization band we observe. These calculations indicate that ionization from the valence σ orbital results in either no change

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(15) The spectra were collected by heating the compounds to their sublimation temperatures: $Mo_2(OCHMe_2)_6$ 80 °C, $Mo_2(OCH_2CMe_3)_6$ 110 °C, $Mo_2(OCMe_3)_6$ 90 °C, $W_2(OCMe_3)_6$ 100 °C. The latter two compounds exhibited slight and extensive decomposition, respectively, at these temperatures as evidenced by the appearance of ionization bands characteristic of isobutylene. This did not interfere with the metal-based ionizations that occur at lower energies. The resolution as measured by the fwhm of the reference Ar 3p ionization was typically 0.025–0.035 eV.

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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]

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Aqueous Electrochemistry of *trans*-(py)₄Re^V(O)₂⁺. Electrocatalytic Reductions Based on Rhenium(II)

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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 (~ 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)₄Re^V(O)₂⁺[3] (py is pyridine) and reduction leads to strongly reducing aqua complexes, which

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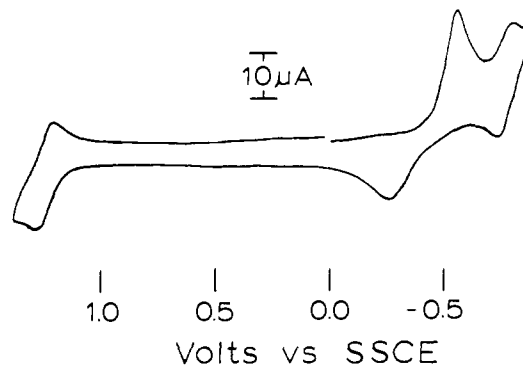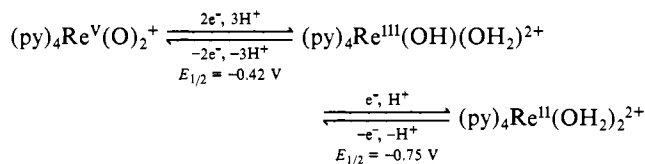

Figure 1. Cyclic voltammogram of 0.1 mM *trans*-[(py)₄Re^V(O)₂](ClO₄) in 0.1 M triflic acid (pH 1.0) using an unactivated Tokai glassy carbon working electrode vs. the SSCE reference electrode at a sweep rate of 100 mV/s.

behave in the reverse fashion, as potentially useful electrocatalytic reductants.
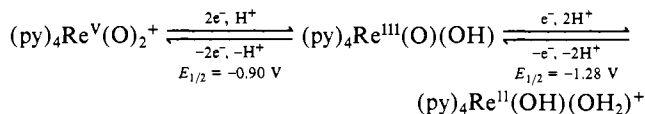
A cyclic voltammogram of *trans*-(py)₄Re^V(O)₂⁺ in 0.1 M triflic acid (CF_3SO_3H) (pH 1.0) using a Tokai glassy carbon electrode as the working electrode vs. the saturated sodium chloride calomel (SSCE) reference electrode is shown in Figure 1. The reversible wave at $E_{1/2} = 1.25$ V is independent of pH from pH 0.5 to 11 and is an oxidation of Re(V) to (py)₄Re^VI(O)₂²⁺. 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)₄Re^III(OH)(OH₂)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)₄Re^II(OH₂)₂²⁺, but the acquisition of accurate coulometric data is difficult because, as noted below, the Re(II) complex is a catalyst for the reduction of H₂O to H₂.
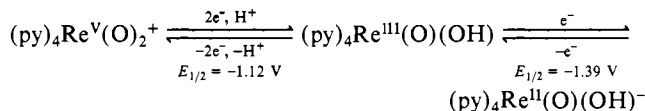
The potentials for the Re(V/III) and Re(III/II) couples are pH dependent because of the acidic character of the aqua ligands in the three oxidation states. Reduction potentials and dominant proton compositions at pH 1.0, 7.0, and 13.0 are as follows:

pH 1.0

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

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

pH 7.0

$$(py)_4Re^V(O)_2^+ \underset{-2e^-, -H^+}{\overset{2e^-, H^+}{\rightleftarrows}} (py)_4Re^{III}(O)(OH) \underset{-e^-, -2H^+}{\overset{e^-, 2H^+}{\rightleftarrows}}$$
$$E_{1/2} = -0.90 \text{ V} \qquad E_{1/2} = -1.28 \text{ V}$$
$$(py)_4Re^{II}(OH)(OH_2)^+$$

pH 13.0

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

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