

Redox tuning of binuclear rhenium(V) complexes: the influence of pyridine substituents on the voltammetry of μ -oxobis[*cis*-dichloro-*cis*-dipyridyloxorhenium(V)]

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Abstract

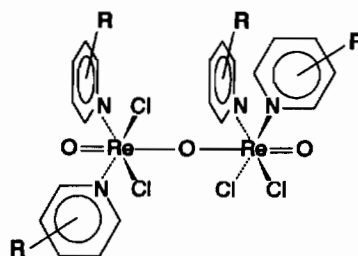
The recent interest in the voltammetry of the dioxorhenium(V) complexes of pyridine prompted us to investigate the voltammetry of μ -oxo-bis[*cis*-dichloro-*cis*-dipyridyloxorhenium(V)] complexes. Seven compounds containing pyridines with electron-withdrawing or electron-donating substituents were synthesized and their redox behavior characterized by variable potential sweep rate cyclic voltammetry and variable pulse height differential pulse voltammetry. Four one-electron redox couples are observed within the accessible potential range of CH_2Cl_2 containing 0.10 M $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte. The dimeric structure remains intact for the two oxidation and first reduction processes. The complex undergoes a reversible heterolytic cleavage of the μ -oxo linkage following the second reduction process. The redox potential for each process correlates with the inductive effect of the pyridyl substituent.

Introduction

A large number of very stable oxo and dioxo complexes of rhenium(V) possessing either $\text{Re}=\text{O}$, $\text{O}=\text{Re}=\text{O}$ or $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ moieties have been reported [1]. These were prepared by (i) reduction of perrhenate in the presence of the desired ligand in strongly acid solution; (ii) ligand substitution of $\text{ReOCl}_3(\text{PPh}_3)_2$ or $\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2$; (iii) solvolysis of ReCl_5 , or (iv) aerial oxidation of $\text{Re}(\text{III})$ or $\text{Re}(\text{IV})$ [2]. The oxygen atoms in the $\text{O}=\text{Re}=\text{O}$ complexes are typically *trans*, however *cis* conformations have been recently reported [3]. These compounds have been well studied because of their unusual electrochemical, photochemical and photophysical behavior as well as their utility as one-electron oxidants [4].

Several examples of μ -oxo bridged rhenium(V) complexes of general formula $\text{Re}_2\text{O}_3\text{X}_4(\text{L})_4$ are known [5]. The most popular synthon for preparing these $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ complexes is *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$ [6]. Pyridine containing μ -oxo complexes were first synthesized in 1964, yet there is no published information concerning the voltammetric behavior of complexes of this type [5c]. The recent interest [3, 4] in the voltammetry of the dioxorhenium(V) complexes of pyridine

prompted us to investigate the voltammetry of the corresponding μ -oxorhenium(V) complexes of general formula $\text{Re}_2\text{O}_3\text{Cl}_4(\text{R-py})_4$ whose generalized structure is shown below.



The crystallographic structure of $\text{Re}_2\text{O}_3\text{Cl}_4(\text{py})_4$ has been determined by Lock and Turner [7]. In the solid state, the pyridine rings are *cis* on each rhenium. Two of the rings are rotated out of the rhenium–chlorine plane by 45° ; the other two lie in the same plane as the rhenium–chloride bonds, but rotated by 180° from each other. No rotation around the $\text{Re}-\text{N}$ bond is possible due to van der Waals forces between the rings. Steric interactions do not allow rotations about the $\text{Re}-\text{O}-\text{Re}$ vector. In this report, we present a detailed study of the electrochemical reactivity of these complexes and compare this reactivity to that of $[\text{Re}(\text{O})_2(\text{R-py})_4]^+$.

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Experimental

trans-ReOCl₃(Ph₃P)₂ was synthesized from potassium perrhenate (Aldrich Chemicals) by the method of Chatt and Rowe [8]. The various Re₂O₃Cl₄(R-Py)₄ complexes investigated herein were prepared from *trans*-ReOCl₃(PPh₃)₂ according to Johnson's method [5c]. The various substituted pyridines were purchased from Aldrich Chemicals and used as received. Each of the Re₂O₃Cl₄(R-Py)₄ complexes exhibited a broad, low intensity electronic absorption band with maximum over the range 692–706 nm and an intense absorption over the range 276–280 nm. The absorbance maxima depended upon the identity of R. IR spectra of samples (pressed into KBr pellets) were acquired on either a Beckman model 4240 IR spectrometer or a Nicolet 5DXB FT-IR spectrometer. The IR spectrum exhibited the characteristic pattern of the substituted pyridine vibrations. However, the peaks were slightly shifted to higher frequencies. In addition, the symmetric Re=O stretch and the antisymmetric Re–O–Re stretch were observed over the ranges 969–973 and 670–686 cm⁻¹, respectively.

¹H NMR spectra were acquired in CDCl₃ on a Bruker WM-300 NMR spectrometer or a Varian Gemini 300 NMR spectrometer. Chemical shifts were internally referenced to Me₄Si. The spin multiplicities and the proton designations are given in brackets. Abbreviations used for spin multiplicities are: s=singlet; d=doublet; t=triplet; 2d=doublet of doublets; 3t=triplet of triplets; 2t=doublet of triplets; 3d=triplet of doublets. Re₂O₃Cl₄(3,4-Me₂Py)₄: 8.29 (s, H₂), 6.98 (d, H₅, *J*=5.8 Hz), 7.98 (d, H₆, *J*=5.8 Hz), 2.16 (s, 3-Me resonance), 2.53 (s, 4-Me resonance); Re₂O₃Cl₄(4-MePy)₄: 8.71 (2d, H_{2,6}, *J*=6.6 Hz), 7.06 (2d, H_{3,5}, *J*=1.5 Hz), 2.63 (s, 4-Me resonance); Re₂O₃Cl₄(3,5-Me₂Py)₄: 8.10 (s, H_{2,6}), 7.26 (d, H₄, *J*=2.0 Hz), 2.17 (s, 3,5-Me₂ resonance); Re₂O₃Cl₄(3-MePy)₄: 8.48 (s, H₂), 7.32 (t, H₄, *J*=7.6 Hz), 7.16 (2d, H₅, *J*=5.8 Hz), 8.12 (d, H₆, *J*=1.7 Hz), 2.26 (s, 3-Me resonance); Re₂O₃Cl₄(Py)₄: 8.86 (2d, H_{2,6}, *J*=5.4 and 1.5 Hz), 7.24 (3d, H_{3,5}, *J*=6.2 and 1.5 Hz), 7.44 (3t, H₄, *J*=6.2 and 1.2 Hz); Re₂O₃Cl₄(3-ClPy)₄: 8.44 (d, H₂, *J*=1.9 Hz), 7.58 (2t, H₄, *J*=8.3 and 1.5 Hz), 7.65 (2d, H₅, *J*=5.9 and 8.3 Hz), 8.43 (d, H₆, *J*=5.9 Hz); Re₂O₃Cl₄(3-BrPy)₄: 8.50 (d, H₂, *J*=1.9 Hz), 7.72 (2t, H₄, *J*=8.3, 1.2 and 1.9 Hz), 7.33 (2d, H₅, *J*=5.3 and 8.3 Hz), 8.4 (d, H₆, *J*=5.3 and 1.2 Hz). Interestingly, the ¹H resonance multiplicities and coupling constants were relatively unchanged upon complexation. The chemical shifts display significant deshielding by the electropositive rhenium(V) centers. The deshielding effect is modulated by the location and identity of the pyridine substituent.

The supporting electrolyte for all electrochemical experiments was n-Bu₄NPF₆ which was 0.10 M in

CH₂Cl₂. CH₂Cl₂ (Fisher) was purified in the usual fashion [9]. n-Bu₄NPF₆ was prepared by metathesis from concentrated solutions of n-Bu₄NBr and KPF₆. The precipitate was washed with H₂O and dried *in vacuo* for 8 h at 110 °C. Voltammetric and coulometric experiments were carried out at ambient temperature using the equipment and procedures previously described [10]. All potentials reported herein were referenced to SCE. Day-to-day drift of the reference electrode were corrected with the ferrocene/ferricinium ion couple as an internal standard.

Results and discussion

Four one-electron-transfer processes (two oxidations and two reductions) were observed at a Pt button electrode for each of the Re₂O₃Cl₄(R-py)₄ complexes investigated within the accessible potential window of CH₂Cl₂/n-Bu₄NPF₆. A cyclic voltammogram typical of those obtained for the entire series is depicted in Fig. 1. Variable potential sweep rate (cyclic voltammetry) and variable pulse amplitude (differential pulse voltammetry) studies were carried out on each electron transfer process for every Re₂O₃Cl₄(R-py)₄ complex. For both redox couples at positive potentials (labelled 1, 1', 2 and 2' in Fig. 1) and the first redox couple at negative potentials (labelled 3 and 3' in Fig. 1), the peak potential and peak magnitude dependences on potential sweep rate and pulse amplitude were consistent with the theory for a reversible electron transfer process [11]. The potentials were invariant over the range of added [R-py] or [n-Bu₄NCl] from 0 to 1.0 M indicating that all three redox processes were outer sphere reactions. The number of electrons transferred in each of these steps was verified by coulometry. The half-wave potentials for the two oxidations and the first reduction process are listed in Table 1. Based on these

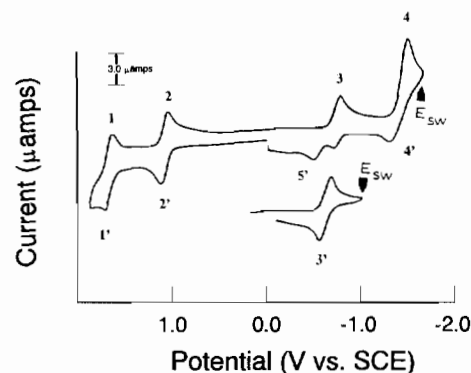


Fig. 1. Cyclic voltammogram obtained for Re₂O₃Cl₄(3,4-Me₂Py)₄ at a Pt button electrode at a potential sweep rate of 200 mV s⁻¹. This voltammogram is typical of those obtained for each of the complexes investigated.

TABLE 1. Half-wave potentials^a for the electrode reactions of the Re₂O₃Cl₄(R-Py)₄ complexes

Complex	pK _a	σ ^b	Reaction number			
			1	2	3	4
Re ₂ O ₃ Cl ₄ (3,4-Me ₂ Py) ₄	6.46	-0.239	1.60	0.99	-0.90	-1.65 ^c
Re ₂ O ₃ Cl ₄ (3,5-Me ₂ Py) ₄	6.15	-0.138	1.64	1.02	-0.92	-1.64 ^c
Re ₂ O ₃ Cl ₄ (4-MePy) ₄	5.98	-0.170	1.65	1.06	-0.84	-1.64 ^c
Re ₂ O ₃ Cl ₄ (3-MePy) ₄	5.79	-0.069	1.68	1.06	-0.84	-1.60 ^c
Re ₂ O ₃ Cl ₄ (Py) ₄	5.28	0.000	1.72	1.11	-0.77	-1.58 ^c
Re ₂ O ₃ Cl ₄ (3-ClPy) ₄	2.81	0.373	1.83	1.23	-0.67	-1.39 ^c
Re ₂ O ₃ Cl ₄ (3-BrPy) ₄	2.84	0.391	1.84	1.24	-0.64	-1.42 ^c

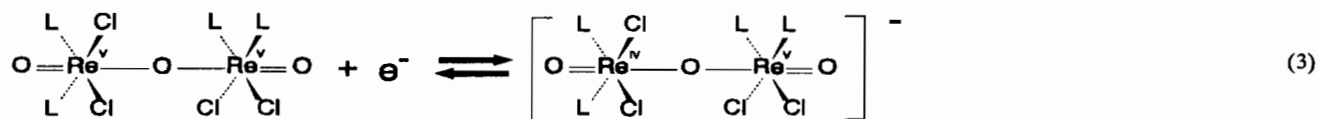
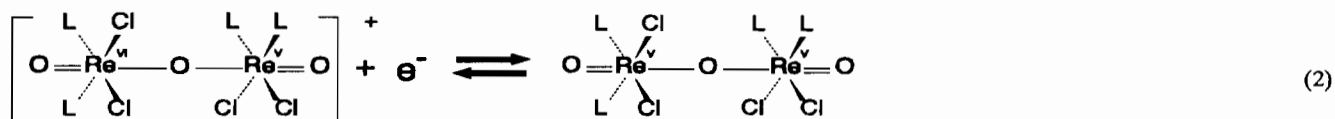
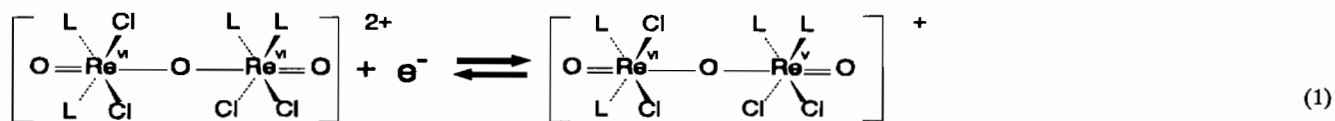
^aMeasured in CH₂Cl₂/0.1 M n-Bu₄NPF₆ at a Pt button electrode. ^bHammett-Taft substituent constant for the pyridine substituent. ^cE_{p,c} measured at a potential sweep rate of 0.10 V s⁻¹.

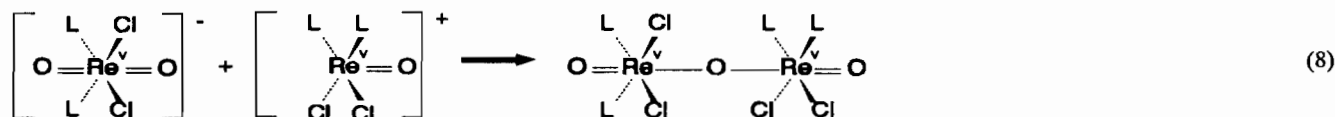
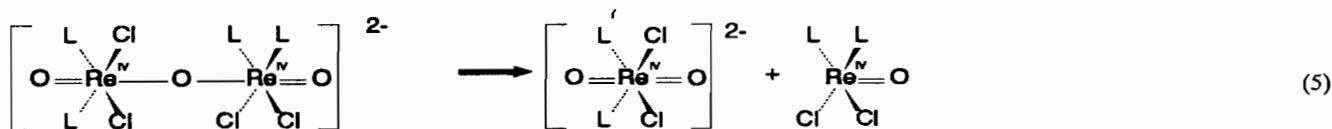
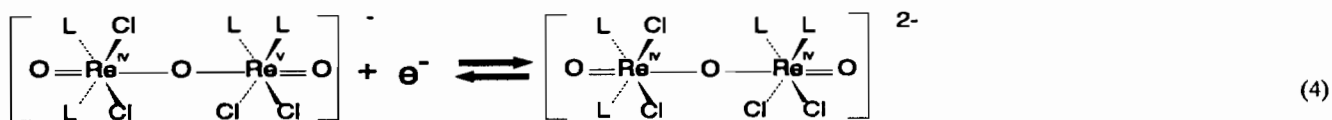
results, we propose the following sequence of reactions, eqns. (1)–(3), for the electrooxidations and first electroreduction of Re₂O₃Cl₄(R-py)₄ where L denotes the substituted pyridyl ligands.

The second process at negative potential (labelled 4 and 4' in Fig. 1) is complicated by a following chemical reaction. The trends observed from the results of a variable potential sweep rate study are: i_b/i_f was less than unity and increased slightly with ν , $i_{p,c}/\nu^{1/2}$ dropped slightly with increasing ν ; $E_{p,c}$ shifted cathodically by up to 60 mV with increasing ν ; the cathodic and anodic peak separation increased from 160 to 200 mV with increasing ν over the range 0.02 to 10 V s⁻¹ (compared to the 70 mV peak separation observed for the first reduction process); the apparent midpoint potential for this process depended upon the identity of the pyridyl substituent and ranged from -1.30 to -1.57 V. Cathodic peak potentials for this reduction are given in Table 1. In addition, a variable pulse amplitude study showed that $W_{1/2}$ increased from a low of 142 at 30 mV pulse amplitude to 163 at 110 mV pulse amplitude. The background corrected $i_{p,c}$ for the second reduction was equal in magnitude to the values of $i_{p,c}$ observed for the other redox processes. Coupled to the second

reduction was a small oxidative process (labelled 5' in Fig. 1 and observed in the range -0.39 to -0.65 V) which was 250 mV anodic of the first reduction for all complexes investigated. This process is only observed when the direction of the scan is switched after the second reduction. On repetitive sweeps through the potential region containing the processes, 4, 4' and 5', a coupled reduction process to 5' was not observed at potential sweep rates up to 1 V s⁻¹. The peak potentials ($E_{p,c}$ and $E_{p,a}$) for the second reduction process as well as that of the coupled oxidation process were invariant with the concentration of added R-py or n-Bu₄NCl (over the range 0 to 1.0 M) indicating that this redox process does not involve the exchange of either the substituted pyridine or chloride ligands. Isolation and chemical characterization of the products of the second electroreduction process has proven elusive. Based on the results obtained to date, we postulate the following sequence of reactions, eqns. (1)–(3), for the second electroreduction of Re₂O₃Cl₄(R-py)₄ on the voltammetric time scale.

The initial product is the rhenium(IV)–rhenium(IV) dianion (eqn. (4)). This species is unstable and rapidly decomposes into a dianionic *trans*-dioxorhenium(IV)





species and a neutrally charged oxorhenium(IV) complex (eqn. (5)). Both products are electrooxidized to an anionic *trans*-dioxorhenium(V) species and a positively charged oxorhenium(V) complex (eqns. (6) and (7)) which recombine to form the parent complex $\text{Re}_2\text{O}_3\text{Cl}_4(\text{R-py})_4$ (eqn. (8)). We have tentatively assigned the process labelled 5' (Fig. 1) to the oxidation of the neutral oxorhenium(IV) species and process 4' (Fig. 1) as the oxidation of the dianionic *trans*-dioxorhenium(IV) species. The latter assignment is supported by the unusually large potential separation between processes 4 and 4' and the observed increase in $E_{p,a} - E_{p,c}$ values with increasing potential sweep rate. In addition, voltammograms recorded at -10°C showed diminished peak separations and increased peak current ratios compared to the separations and ratios determined from voltammograms recorded at ambient temperature.

Analysis of the potential data shows several interesting trends. First, the half-wave potentials for each redox process correlated with the Hammett-Taft substituent constant for the pyridine substituent. The potential data was best fit by the models: $E_{1/2}$, eqn. (1) = $0.361(\sigma_p) + 1.70$; $E_{1/2}$, eqn. (2) = $0.376(\sigma_p) + 1.09$; $E_{1/2}$, eqn. (3) = $0.403(\sigma_p) - 0.80$; $E_{p,c}$, eqn. (4) = $0.419(\sigma_p) - 1.57$. Since each redox reaction involves only one of the two rhenium centers each coordinated to two substituted pyridines, the electrochemically determined ρ values correspond to chemical ρ values of 3.05, 3.18, 3.41 and 3.55, respectively [12]. Thus, the ρ values

increase with decreasing charge on the μ -oxo dimer. Interestingly, $E_{p,c}$ for process 5' also correlated with σ_p and gave a chemical ρ value of 3.64. This value compares favorably with the chemical ρ value of 3.52 computed from the data published by Ram *et al.* for the Re(VI)/Re(V) couple of *cis*-(O)₂Re(bpy)(R-py)₂⁺ [3d].

Second, the potential data correlated with the Bronsted-Lowry basicity of the pyridyl ligand. Since the $\text{p}K_a$ of each substituted pyridine is an indirect measure of the sigma donor strength of the pyridine N atom. The best fitting models were: $E_{1/2}$, eqn. (1) = $-0.059 \text{p}K_a + 2.01$; $E_{1/2}$, eqn. (2) = $-0.062 \text{p}K_a + 1.42$; $E_{1/2}$, eqn. (3) = $-0.067 \text{p}K_a - 1.21$, respectively. Third, the potential separation between each pair of redox processes were consistently 0.61, 1.90 and 0.76 V, respectively. Thus, the substituent dependences delineated herein indicate that variation in the pyridyl substituent provides a straightforward means for tuning the redox potential to a desired value without diminishing the chemical stability of the complex. This finding has application in redox catalysis [13]. We are currently exploring this possibility.

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