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Technetium Electrochemistry. 4.[1] Electrochemical and Spectroelectrochemical Studies on the Bis(tertiary phosphine or arsine (D))rhenium(III) Complexes *trans*-$[ReD_2X_2]^+$ (X = Cl, Br). Comparison with the Technetium(III) Analogues

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The redox properties of a series of rhenium(III) complexes with the general formula *trans*-$[ReD_2X_2]^+$ (where D is one of the chelating phosphine or arsine ligands 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diethylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane, or 1,2-bis(dimethylarsino)benzene and X is Cl or Br) were investigated in 0.5 M TEAP/DMF by cyclic voltammetry, thin-layer electrochemistry, and thin-layer spectroelectrochemistry. The cationic *trans*-$[ReD_2X_2]^+$ complexes exhibit a diffusion-controlled, reversible one-electron reduction to the neutral *trans*-$[ReD_2X_2]^0$ complexes at a platinum-disk electrode. The formal reduction potential, $E^{\circ\prime}$, of the Re(III/II) redox couple ranges from −0.205 to −0.450 V vs. Ag/AgCl (3 M NaCl). Further reduction to the rhenium(I) anion, *trans*-$[ReD_2X_2]^-$, is possible; however, the reversibility of this process depends on the nature of the coordinating ligands and the experimental conditions. The Re(II/I) redox couple occurs at an $E^{\circ\prime}$ value ca. 1.11 V more negative than that of the corresponding Re(III/II) couple. Thin-layer spectroelectrochemistry has been used to study the halogen-to-metal charge-transfer (HTMCT) band(s) of the Re(III) and Re(II) complexes. Comparisons of the resulting electrochemical and spectroscopic properties are made to those of analogous *trans*-$[TcD_2X_2]^{+/0}$ complexes. For nine M(III/II) and M(II/I) couples ranging over 1.5 V, a plot of $E^{\circ\prime}$(Tc) vs. $E^{\circ\prime}$(Re) is linear with a slope of 1.04 ± 0.01 and an intercept of 219 ± 15 mV. Thus, for complexes of the type *trans*-$[MD_2X_2]^{+/0/-}$ the rhenium complex is on the average 219 ± 15 mV more difficult to reduce than the technetium analogue, and this potential difference is largely independent of metal oxidation state, trans-halide ligand, and equatorially coordinated D ligand. Correspondingly, the HTMCT transition in the M(III) complexes occurs at an energy 260 ± 30 mV ($n = 5$) lower for the technetium center than for the rhenium analogue.

Introduction

The chemistry and biochemistry of coordination complexes of technetium have attracted much attention due to the utility of the metastable isotope, ^{99m}Tc, in diagnostic nuclear medicine.[2–7] Particularly, cationic complexes of technetium that incorporate tertiary phosphine or arsine ligands have been studied for their use as myocardial imaging agents.[8,9] However, due to the radioactivity and low concentrations of the ^{99m}Tc complexes used as radiopharmaceuticals, characterization of these species by conventional physical methods is quite difficult or impossible. In order to study the chemical and physical properties of these complexes, synthetic methods have been developed for their preparation with macroscopic amounts of the long-lived technetium isotope, ^{99}Tc.[2,3,9–12] Thus, characterization of technetium complexes by single-crystal X-ray structure analysis,[12–16] EXAFS,[15] IR and UV–vis spectroscopy,[11,12,15] and electrochemistry[1,12,16–18] has been possible.

More recently, analogous complexes of a radioactive isotope of rhenium, ^{186}Re, have been investigated with regard to their potential use in nuclear medicine.[19,20] Although analogous technetium and rhenium complexes exhibit similar physical properties because of the periodic relationship of these elements, subtle chemical differences between complexes can result in distinctly different biological behavior. Paramount among these chemical differences is the redox behavior of the central metal; complexes of rhenium are more difficult to reduce than the corresponding technetium complexes.[17,19] This difference in redox potentials can be large enough to shift one complex or the other out of the range of potentials readily accessible to biological systems. This phenomenon has recently been established by a comparative biodistribution study of $[^{99m}Tc(dmpe)_2Cl_2]^+$ and $[^{186}Re(dmpe)_2Cl_2]^+$.[19,20] The biodistribution data reveal that in vivo reduction occurs for the technetium complex but not for the rhenium analogue. In vivo reduction of the Tc(III) cation converts it to the more lipophilic Tc(II) neutral complex, $[^{99m}Tc(dmpe)_2Cl_2]^0$, which causes myocardial washout and unfavorable imaging characteristics.

In light of the importance that the reduction potential of a complex has in determining its biological activity, we have continued our investigations into the electrochemistry of analogous technetium and rhenium complexes. Previous publications have described the electrochemistry and thin-layer spectroelectrochemistry of mixed-ligand cationic complexes of Tc(III) with the general formula *trans*-$[TcD_2X_2]^+$, where D represents a chelating bis(tertiary phosphine or arsine) ligand and X represents a halogen or a pseudohalogen.[16–18] Here we report complementary elec-

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Table I. Formal Redox Potentials and *n* Values for *trans*-$[ReD_2X_2]^{+/0/-}$ Couples in 0.5 M TEAP/DMF[a]

	Re(III/II)				Re(II/I)
	$E^{\circ\prime b}$	$E^{\circ\prime c}$	$E^{\circ\prime d}$	n^d	$E^{\circ\prime b}$
$Re(depe)_2Cl_2^+$	−0.450	−0.451	−0.456	0.99	−1.61[e]
$Re(dmpe)_2Cl_2^+$	−0.423	−0.423	−0.433	0.93	−1.56
$Re(diars)_2Cl_2^+$	−0.319	−0.321	−0.324	0.95	−1.45
$Re(dppe)_2Cl_2^+$	−0.205	−0.205	−0.210	0.97	−1.20[e]
$Re(dmpe)_2Br_2^+$	−0.297	−0.297	−0.305	0.97	−1.42

[a] $E^{\circ\prime}$ is in volts vs. Ag/AgCl (3 M NaCl). [b] $E^{\circ\prime} = (E_{p,c} + E_{p,a})/2$ from cyclic voltammetry at a PDE with a scan rate of 100 mV/s. [c] $E^{\circ\prime} = (E_{p,c} + E_{p,a})/2$ from thin-layer cyclic voltammetry at an OTTLE with a scan rate of 2 mV/s. [d] Spectropotentiostatic determination at an OTTLE. [e] At −40 °C; see text.

Table II. Spectroscopic Data for *trans*-$[ReD_2X_2]^{+/0}$ Complexes[a]

	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)		
	Re(III)	Re(II)	λ_{iso}, nm
$Re(depe)_2Cl_2^+$	439 (1480)	385 (2410)	398
	409 (1740)	344 (1360)	
$Re(dmpe)_2Cl_2^+$	438 (2340)	383 (3680)	396
	408 (2520)	345 (2120)	
$Re(diars)_2Cl_2^+$	418 (2390)	446 (1780)	434, 377
	388 (3750)	363 (5180)	
$Re(dppe)_2Cl_2^+$	426 (3100[b])	398 (6600[b])	422
	454 (sh) (2500)		
$Re(dmpe)_2Br_2^+$	467 (3380)	408 (4300)	421, 334
	434 (sh) (2370)	343 (1210)	

[a] Determined spectroelectrochemically in 0.5 M TEAP/DMF by using an OTTLE. sh = shoulder. [b] See ref 27.

trochemical and spectroelectrochemical studies of the Re(III) complexes *trans*-$[ReD_2X_2]^+$ and discuss the relationships between these results and those previously obtained for the *trans*-$[^{99}TcD_2X_2]^+$ analogues.

Experimental Section

Materials. The ligands 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,2-bis(dimethylarsino)benzene (diars) were purchased from Strem. Ammonium perrhenate was obtained from Johnson Matthey. These chemicals were of adequate purity for synthetic purposes and were used without further purification. All other chemicals were of reagent grade quality. *trans*-$[Re(dmpe)_2Cl_2]PF_6$,[19] *trans*-$[Re(dmpe)_2Br_2]CF_3SO_3$,[19] *trans*-$[Re(depe)_2Cl_2]PF_6$,[19] *trans*-$[Re(dppe)_2Cl_2]PF_6$,[21] and *trans*-$[Re(diars)_2Cl_2]CF_3SO_3$[22] were prepared by literature procedures.

N,N-Dimethylformamide, DMF (Burdick and Jackson), and polarographic grade tetraethylammonium perchlorate, TEAP (G. F. Smith), were used in the electrochemical experiments. Prior to use, the TEAP was dried at 60 °C in vacuo over P_2O_5. No significant electroactive impurities were detected in either the solvent or supporting electrolyte.

Methods. In general, experiments were conducted as previously described.[1,17,18,23] Each spectrum in the spectropotentiostatic experiments was recorded 5 min after potential application. This time was sufficient to attain equilibrium values of [O]/[R].

Instrumentation. Electrochemical measurements were made with either a Bioanalytical Systems Inc. (BAS) CV-1B voltammograph or a BAS-100 electrochemical analyzer. Potentials were monitored with a Keithley 178 digital multimeter when the CV-1B was used. Voltammograms were recorded on a Hewlett Packard 7015B X-Y recorder or a Houston Instruments DMP-2 digital plotter. Visible spectra were recorded on a Cary 210 spectrophotometer; the cell compartment was modified to accommodate electrical leads and an inert-gas inlet. The working electrode for conventional cyclic voltammetry was a platinum-disk electrode, PDE (BAS), with a surface area of 0.0223 cm² as determined by chronocoulometry of a standard potassium ferricyanide solution. Optically transparent thin-layer electrodes, OTTLE's, were constructed as previously described with a 100 wires/in. gold minigrid.[24] The cell volume and optical thickness were calibrated by coulometry and spectrophotometry[24] and were 46 μL and 0.024 cm, respectively. An aqueous Ag/AgCl (3 M NaCl) electrode (BAS) and a platinum wire were used as reference and auxiliary electrodes, respectively. The reference electrode was isolated from the solution by a porous Vycor plug. All potentials are reported vs. the Ag/AgCl (3 M NaCl) electrode.

Results and Discussion

Electrochemistry and Spectroelectrochemistry of *trans*-$[ReD_2X_2]^+$ Complexes. The electrochemical and spectroelectrochemical studies were performed in 0.5 M TEAP/DMF. DMF is a suitable solvent for the investigation of these complexes because it (i) exhibits a good negative potential range for cathodic electrochemistry, (ii) provides solubility for the Re(III), Re(II), and Re(I) species, and (iii) allows a facile comparison to be made to the results of previous studies on the analogous Tc(III) complexes conducted in the same medium. In the following discussion of electrochemical properties, $[Re(dmpe)_2Cl_2]^+$ is taken as the representative complex and described in the greatest detail. Summaries of the electrochemical and spectroscopic results for all complexes are given in Tables I and II.

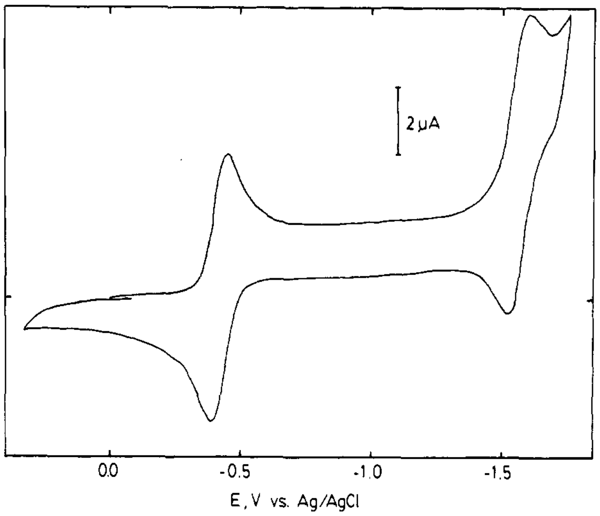

Figure 1. Cyclic voltammogram of 1.08 mM $[Re(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF at a PDE. Scan rate is 100 mV/s.

(i) $[Re(dmpe)_2Cl_2]^+$. A typical bulk-solution cyclic voltammogram of $[Re(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF at a PDE is shown in Figure 1. A negative potential scan initiated at 0.0 V yields two reduction waves with peak potentials of −0.455 and −1.60 V. Upon reversal of the scan at −1.85 V, the corresponding reoxidation waves are observed at −1.52 and −0.391 V. On the basis that (i) the peak currents are proportional to the square root of the scan rate in the range from 25 to 300 mV/s, (ii) the peak-to-peak separation is typical for one-electron redox processes of inorganic complexes in nonaqueous solvents, and (iii) the ratio of peak currents is approximately unity, both redox couples are attributed to diffusion-controlled, reversible one-electron processes that are schematically depicted by eq 1 and 2. The peak separations for the Re(III/II) and Re(II/I) redox couples are 64 and 76 mV, respectively. The formal reduction potentials, $E^{\circ\prime}$, for eq 1 and 2 are −0.423 and −1.56 V, as determined by averaging the anodic and cathodic peak potentials. These values are somewhat more negative than those previously reported (−0.398 and −1.548 V) in a less detailed study.[19] A positive potential scan yields an anodic peak at +1.2 V, which represents the irreversible oxidation of Re(III) to Re(IV). This is in accord with cyclic voltammetry data reported for other *trans*-$[ReD_2X_2]^+$ complexes

$$[Re^{III}D_2X_2]^+ + e^- \rightleftharpoons [Re^{II}D_2X_2]^0 \tag{1}$$

$$[Re^{II}D_2X_2]^0 + e^- \rightleftharpoons [Re^{I}D_2X_2]^- \tag{2}$$

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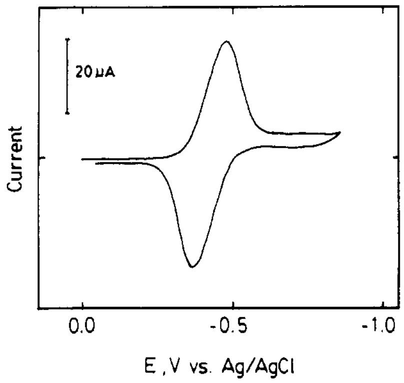

Figure 2. Thin-layer cyclic voltammogram of 0.80 mM $[Re(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF at an OTTLE. Scan rate is 2 mV/s.

where both reversible[26] (when D is 1,2-bis(diphenylphosphino)ethylene (dppee)) and irreversible[22] (when D is diars) oxidations to Re(IV) have been observed.

Figure 2 illustrates the thin-layer cyclic voltammogram of the Re(III/II) couple. The scan is initiated at 0.0 V and proceeds in the negative direction with a scan rate of 2 mV/s. The reduction of $[Re(dmpe)_2Cl_2]^+$ to $[Re(dmpe)_2Cl_2]^0$ occurs with a peak potential of −0.480 V. After complete electrolysis in the OTTLE cell, the scan is reversed at −0.82 V and the wave for reoxidation to $[Re(dmpe)_2Cl_2]^+$ is observed at −0.365 V. Identical cyclic voltammograms are observed during repetitive cycles between the Re(III) and Re(II) oxidation states, which establishes the chemical stability of the cationic and neutral forms of the complex on the time scale of this experiment. $E^{\circ\prime}$ for this redox process is −0.423 V with a peak-to-peak separation of 115 mV. The large deviation of the peak separation from the Nernstian value of 0 mV is typical for nonaqueous solutions in the OTTLE due to uncompensated resistance inherent to the cell configuration.[23-25] The stability of the Re(III) and Re(II) forms in the thin-layer cell allows for the characterization of each species by spectroelectrochemistry. Spectra recorded during a spectropotentiostatic experiment are shown in Figure 3. Absorption maxima for the Re(III) species occur at 438 and 408 nm, while the Re(II) maxima are shifted to higher energy and occur at 383 and 345 nm. Values for the molar absorptivities are summarized in Table II. An isosbestic point is observed at 396 nm, which indicates that a clean interconversion between the two components of the redox couple occurs without concomitant ligand loss. A Nernst plot,[24] E_{app} vs. log ([O]/[R]), for the data at 408 nm in Figure 3 is linear and yields $E^{\circ\prime} = -0.433$ V and $n = 0.93$.

(ii) $[Re(dmpe)_2Br_2]^+$. Results similar to those obtained for the dichloro analogue are also observed for this complex in cyclic voltammetry and thin-layer electrochemistry experiments. The bulk-solution experiment exhibits the two characteristic reversible, one-electron processes described by eq 1 and 2; however, $[Re(dmpe)_2Br_2]^+$ is a better oxidant than $[Re(dmpe)_2Cl_2]^+$. The $E^{\circ\prime}$ values for the Re(III/II) and the Re(II/I) couples are −0.297 and −1.42 V, respectively, with corresponding peak separations of 62 and 74 mV. Thin-layer cyclic voltammetry yields $E^{\circ\prime} = -0.297$ V with a peak-to-peak separation of 99 mV. Figure 4 illustrates the spectra recorded during the spectropotentiostatic reduction of $[Re(dmpe)_2Br_2]^+$. The Re(III) complex has an absorption maximum at 467 nm with a shoulder at 434 nm, while the Re(II) form exhibits maxima at 408 and 343 nm. Isosbestic points are maintained at 421 and 334 nm. Analysis of the data via a Nernst plot at 467 nm yields $E^{\circ\prime} = -0.305$ V and $n = 0.97$.

(iii) $[Re(depe)_2Cl_2]^+$. The bulk-solution cyclic voltammogram of $[Re(depe)_2Cl_2]^+$ exhibits a reversible Re(III/II) couple with $E^{\circ\prime} = -0.450$ V. However, reduction of $[Re(depe)_2Cl_2]^0$ to $[Re(depe)_2Cl_2]^-$ is quasi-reversible; $E_{p,c}$ for this process is −1.63 V. No discrete oxidation wave is observed on the reverse scan for the conversion of Re(I) to Re(II), which indicates the chemical instability of the Re(I) species on the electrochemical time scale. Identical behavior is observed for scan rates up to 400 mV/s. In order to inhibit the rate of chemical decomposition, investigation of $[Re(depe)_2Cl_2]^+$ was conducted at −40 °C. The $E^{\circ\prime}$ of the Re(III/II) couple shifts to a slightly more negative potential, similar to the behavior previously observed for the analogous $[Tc(depe)_2Br_2]^+$ complex.[18] The peak separation for the Re(III/II) couple at −40 °C is 60 mV. This value is greater than the theoretical value of 46 mV for a reversible one-electron process at −40 °C and, as before,[18] can be attributed to the slow rate of heterogeneous electron transfer at −40 °C. Observation of the

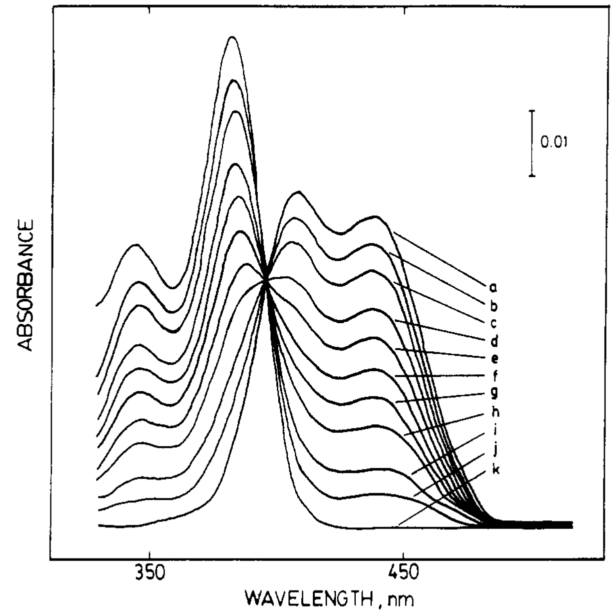

Figure 3. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 0.85 mM $[Re(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) 0.000; (b) −0.370; (c) −0.390; (d) −0.410; (e) −0.420; (f) −0.430; (g) −0.440; (h) −0.450; (i) −0.470; (j) −0.490; (k) −0.700.

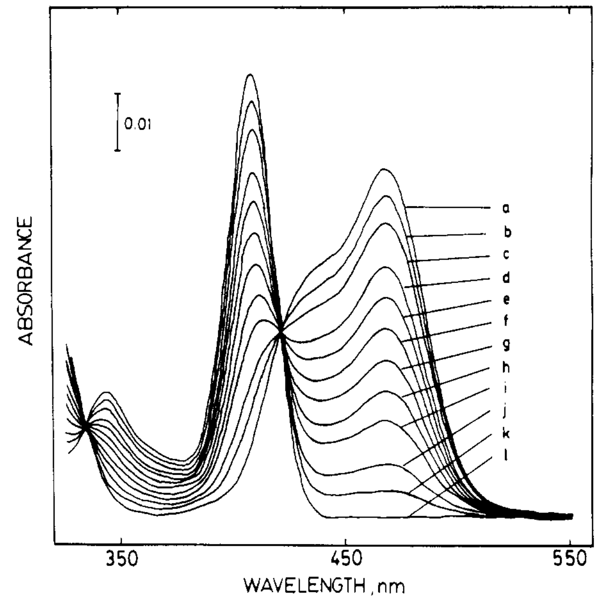

Figure 4. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 0.75 mM $[Re(dmpe)_2Br_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) 0.000; (b) −0.240; (c) −0.260; (d) −0.280; (e) −0.290; (f) −0.300; (g) −0.310; (h) −0.320; (i) −0.330; (j) −0.350; (k) −0.370; (l) −0.600.

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[27] Due to an impurity present in the $[Re(dppe)_2Cl_2]^+$ sample an estimate of the molar absorptivities was obtained by using the value of Cariati et al.[28] It should be noted that the impurity is nonelectroactive and spectroscopically silent in the region of interest.

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oxidation of Re(I) to Re(II) is also possible at -40 °C; $E_{p,a} = -1.49$ V vs. Ag wire.[29] After conversion to the Ag/AgCl reference potential and adjustment for the shift in peak potential with temperature, $E^{\circ\prime}$ for the Re(II/I) couple at 20 °C is estimated to be -1.61 V. The magnitudes of the peak currents decrease as the temperature decreases due to the increasing viscosity of the solution.

The changes in the absorption spectra that occur during the spectropotentiostatic experiment on $[Re(depe)_2Cl_2]^+$ are similar to those shown in Figure 3 for $[Re(dmpe)_2Cl_2]^+$. The Re(III) complex exhibits absorption maxima at 439 and 409 nm while the Re(II) complex has maxima at 385 and 344 nm; an isosbestic point is observed at 398 nm. Analysis of the data at 409 nm reveals $E^{\circ\prime} = -0.456$ V and $n = 0.99$.

(iv) $[Re(dppe)_2Cl_2]^+$. The electrochemical properties of $[Re(dppe)_2Cl_2]^+$ are analogous to those observed for $[Re(depe)_2Cl_2]^+$. Reversible behavior occurs for the Re(III/II) redox couple with an $E^{\circ\prime}$ of -0.205 V and a peak separation of 61 mV, while the Re(II/I) couple is quasi-reversible with a peak potential for the conversion of $[Re(dppe)_2Cl_2]^0$ to $[Re(dppe)_2Cl_2]^-$ at -1.26 V. However at -40 °C, the Re(II/I) redox couple is reversible; $E^{\circ\prime}$ for this process at 20 °C is estimated to be -1.20 V with a peak-to-peak separation of 85 mV. Thin-layer cyclic voltammetry gives an $E^{\circ\prime}$ value for the Re(III/II) couple of -0.205 V with a peak separation of 122 mV.

Spectropotentiostatic reduction of $[Re(dppe)_2Cl_2]^+$ reveals that the Re(III) complex exhibits an absorption maximum at 426 nm with a shoulder at 454 nm, while the Re(II) form has a maximum at 398 nm. A single isosbestic point is observed at 422 nm. Analysis of the data at 426 nm via a Nernst plot gives $E^{\circ\prime} = -0.210$ V and $n = 0.97$.

(v) $[Re(diars)_2Cl_2]^+$. Bulk-solution cyclic voltammetry and thin-layer cyclic voltammetry show behavior qualitatively similar to that observed for the other *trans*-$[ReD_2X_2]^+$ complexes. In bulk solution, both the Re(III/II) and the Re(II/I) couples are reversible and yield $E^{\circ\prime}$ values of -0.319 and -1.45 V with corresponding peak separations of 63 and 70 mV. Previous cyclic voltammetric measurements of *trans*-$[Re(diars)_2Cl_2]ClO_4$ in 0.1 M TEAP/CH_3CN show the presence of the Re(III/II) and Re(II/I) couples at -0.71 and -1.84 V vs. Ag/$AgClO_4$ in CH_3CN, respectively;[22] the corresponding potentials vs. Ag/AgCl are estimated to be ca. -0.38 and -1.51 V. The difference in $E^{\circ\prime}$ values observed in acetonitrile and DMF is in reasonable agreement with the difference in $E^{\circ\prime}$ values observed for the ferrocenium/ferrocene couple in these media and can be attributed to the relative basicity of the solvents.[18]

Thin-layer electrochemistry yields an $E^{\circ\prime}$ of -0.321 V; the peak separation is 128 mV. Results from the spectropotentiostatic experiment are depicted in Figure 5. The Re(III) complex has absorption maxima at 388 and 418 nm, while the Re(II) analogue has maxima at 363 and 446 nm. Isosbestic points are observed at 377 and 434 nm. Nernst analysis of the data in Figure 5 at 388 nm gives $E^{\circ\prime} = -0.324$ V and $n = 0.95$.

Comparison of $E^{\circ\prime}$ Values for the *trans*-$[ReD_2X_2]^{+/0/-}$ Couples. For all the complexes studied, the $E^{\circ\prime}$ values governing the Re(III/II) and Re(II/I) redox processes are sensitive to the nature of the D and X ligands. In the series of complexes with varying D ligands but common trans-chloride ligands, $E^{\circ\prime}$ for the Re(III/II) couple spans potentials ranging from -0.205 V for $[Re(dppe)_2Cl_2]^{+/0}$ to -0.450 V for $[Re(depe)_2Cl_2]^{+/0}$. Thus, $[Re(dppe)_2Cl_2]^+$ is a better oxidant by 245 mV than is $[Re(depe)_2Cl_2]^+$, the worst oxidant of this series. The Re(II/I) couple occurs on the average 1.11 V more negative than does the Re(III/II) couple and follows a similar trend in potentials throughout the series. The fact that the dppe complex exhibits the most positive $E^{\circ\prime}$ value is consistent with the enhanced π-acid character of the dppe ligand induced by the pendant aryl substituents. The net effect of enhanced π-acidity is to stabilize the lower oxidation states by delocalization of the excess charge density. π-Conjugation within the D ligand backbone, as well as with pendant groups on the D ligand, results in a positive shift in $E^{\circ\prime}$. For example, the Re(III/II) $E^{\circ\prime}$ value for $[Re(diars)_2Cl_2]^{+/0}$ is 104 mV more positive than that observed for $[Re(dmpe)_2Cl_2]^{+/0}$. However, coordination to arsenic seems to mitigate the effect of the potential shift since Warren and Bennett[22] have observed an even larger positive shift when D is diphos, 1,2-bis(dimethylphosphino)benzene. Variation of pendant alkyl groups on the D ligand only moderately affects the $E^{\circ\prime}$ value; thus, $[Re(dmpe)_2Cl_2]^+$ is only 25 mV easier to reduce than is $[Re(depe)_2Cl_2]^+$. However, variation of the X ligand generates a much larger effect; for $[Re(dmpe)_2X_2]^+$, the bromide complex is 126 mV easier to reduce than is the chloride complex. Analogous shifts in $E^{\circ\prime}$ values with variations in D and X ligands have been observed in the corresponding technetium complexes and have been attributed to the relative π-back-bonding interactions between the metal d orbitals and the orbitals located on the D and X ligands.[12]

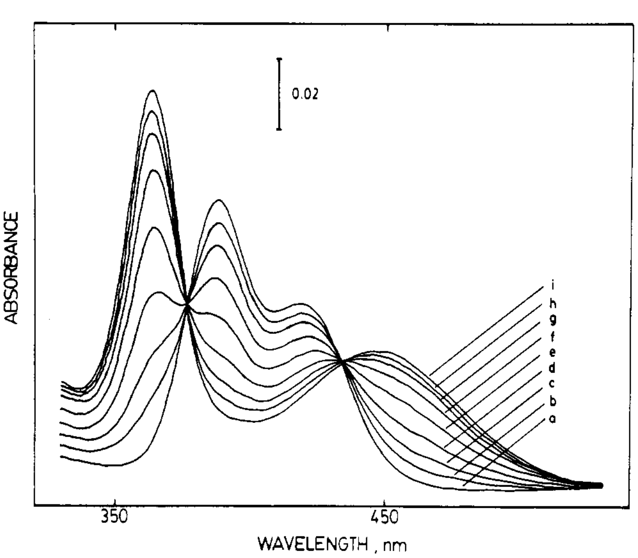

Figure 5. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 0.92 mM $[Re(diars)_2Cl_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) 0.000; (b) -0.270; (c) -0.290; (d) -0.310; (e) -0.330; (f) -0.350; (g) -0.370; (h) -0.390; (i) -0.600.

In all cases the *trans*-$[ReD_2X_2]^+$ complexes exhibit reversible behavior for the Re(III/II) couple, whereas the reversibility of the Re(II/I) couple depends on the D ligand and the conditions of the experiment. When D is dppe or depe, the Re(II/I) couple is quasi-reversible at the PDE and 20 °C. Upon cooling of the sample to -40 °C, the chemical decomposition of the Re(I) species is slowed enough so that reversible behavior can be observed. On the other hand when D is diars or dmpe, reduction at the PDE produces the stable anionic Re(I) complexes even at 20 °C. These results can be interpreted in terms of the ability of the D ligand to donate electron density; the better σ-donor ligands, dppe and depe, tend to destabilize the electron-rich Re(I) center and promote chemical decomposition. For all the complexes studied, regardless of the D ligand, the Re(II/I) couple is irreversible on the thin-layer time scale. Therefore, even the $[Re(diars)_2Cl_2]^-$ and $[Re(dmpe)_2X_2]^-$ complexes are stable for only seconds to minutes at room temperature in 0.5 M TEAP/DMF.

Electronic Spectra of the *trans*-$[ReD_2X_2]^{+/0}$ Complexes. Spectroscopic data for the *trans*-$[ReD_2X_2]^{+/0}$ complexes are summarized in Table II. The visible absorption spectra are similar to those observed for analogous Tc(III) and Tc(II) complexes. These spectra are dominated by intense halogen-to-metal charge-transfer band(s) (HTMCT).[12] The major difference is that the charge-transfer manifold for rhenium is split into two components. Splitting of the HTMCT band has also been observed in the absorption spectra of certain Ru(III) complexes that incorporate trans-halide ligands. It has been suggested that for these Ru(III) complexes the splitting results from loss of degeneracy of the chloride p_π orbitals induced by hydrogen bonding

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(29) Potentials are referenced to a Ag-wire reference electrode and ferrocene as an internal standard.

Table III. Variations in the Energies of the Halogen-to-Rhenium Charge-Transfer Transitions in *trans*-$[ReD_2X_2]^{+/0}$ Complexes as a Function of Rhenium Oxidation State[a,b]

	band	E_{III}	E_{II}	$E_{II} - E_{III}$
$Re(depe)_2Cl_2^{+/0}$	E_1	22780	25970	3190
	E_2	24450	29070	4620
$Re(dmpe)_2Cl_2^{+/0}$	E_1	22830	26110	3280
	E_2	24510	28990	4480
			22420[c]	
$Re(diars)_2Cl_2^{+/0}$	E_1	23920	27550	3630
	E_2	25770	*d*	
$Re(dppe)_2Cl_2^{+/0}$	E_1	22030[e]	25130	3100
	E_2	23470	*d*	
$Re(dmpe)_2Br_2^{+/0}$	E_1	21410	24510	3100
	E_2	23040[e]	29160	6120

[a] All energies in cm^{-1}. [b] E_{III} = energy of Re(III) band. E_{II} = energy of Re(II) band. E_1 = energy of low-energy component. E_2 = energy of high-energy component. [c] Not a HTMCT band. See text. [d] Not observed. [e] Shoulder. Energy assignment is only approximate.

between the trans chlorides and the equatorial ligand.[30-32] Although this explanation may not be directly applicable to the *trans*-$[ReD_2X_2]^{+/0}$ complexes, presumably the observed splitting also results from loss of degeneracy of the halide p_π orbitals.

Since Re(III) is a better oxidizing center than Re(II), the HTMCT transitions of the Re(III) complexes occur at lower energy than do those of the Re(II) analogues. The data of Table III show that this energy difference between analogous Re(II) and Re(III) bands ($E_{II} - E_{III}$) is fairly constant: 3260 ± 220 cm^{-1} ($n = 5$) for the low-energy component (E_1) of the HTMCT doublet and 5100 ± 900 cm^{-1} ($n = 3$) for the high-energy component (E_2). These average $E_{II} - E_{III}$ differences for rhenium complexes are larger than the average $E_{II} - E_{III}$ difference observed for related technetium complexes (2500 ± 370 cm^{-1}),[12] which is expected since for analogous complexes Re(III) is a stronger oxidant than Tc(III).

The band assignments given in Table III therefore form a self-consistent set, given that the high-energy bands of the $[Re(diars)_2Cl_2]^0$ and $[Re(dppe)_2Cl_2]^0$ complexes are obscured by UV absorptions of the diars and dppe ligands and that the high-energy band of $[Re(dmpe)_2Br_2]^+$ occurs as a shoulder and thus its energy assignment is only approximate. However, the spectrum of the Re(II) complex $[Re(diars)_2Cl_2]^0$ exhibits a puzzling band at very low energy (446 nm: Figure 5i). This cannot be a component of the HTMCT manifold since it occurs at *lower* energy than the lowest energy charge-transfer band observed in $[Re(diars)_2Cl_2]^+$. (Such a HTMCT assignment would make $E_{II} - E_{III}$ in Table III a negative number, which would be inconsistent with all other observations on related technetium and rhenium complexes.) This low-energy absorption could result from a metal-to-ligand charge-transfer (MLCT) transition, since Re(II) is a good reductant and diars may possess sufficiently low-lying empty π^* orbitals,[33] or from an unusually intense d–d transition. Even though the origins of this low-energy band are currently unclear, it is certain that it represents a transition inherent to $[Re(diars)_2Cl_2]^0$ and is not the result of decomposition of the complex during electrolysis. The latter point is firmly established by the maintenance of isosbestic points during spectroelectrochemistry and by independent chronoabsorptometry experiments which show that the spectrum of $[Re(diars)_2Cl_2]^+$ can be quantitatively regenerated by oxidizing $[Re(diars)_2Cl_2]^0$.

Table IV. Comparison of $E^{\circ\prime}$ for the M(III/II) Couple in *trans*-$[MD_2X_2]^+$ Complexes in 0.5 M TEAP/DMF[a]

	Tc	Re	$E^{\circ\prime}(Tc) - E^{\circ\prime}(Re)$
$M(depe)_2Cl_2^+$	−0.260[b]	−0.450	0.190
$M(dmpe)_2Cl_2^+$	−0.231[b]	−0.423	0.192
$M(diars)_2Cl_2^+$	−0.061[c]	−0.319	0.258
$M(dppe)_2Cl_2^+$	−0.010[c]	−0.205	0.195
$M(dmpe)_2Br_2^+$	−0.098[b]	−0.297	0.199

[a] $E^{\circ\prime}$ values are reported in volts vs. the Ag/AgCl (3 M NaCl) reference electrode. [b] From ref 18. [c] Conversion to Ag/AgCl (3 M NaCl) from NaSCE by addition of 0.030 V to the values reported in ref 17.

Table V. Comparison of the Energy of the HTMCT Band of *trans*-$[MD_2X_2]^+$ Complexes in 0.5 M TEAP/DMF[a]

	E_{Tc}[b]	E_{Re}[c]	$E_{Re} - E_{Tc}$[d]
$M(depe)_2Cl_2^+$	21280	22780; 24450 (23620)	2340
$M(dmpe)_2Cl_2^+$	21320	22830; 24510 (23670)	2350
$M(diars)_2Cl_2^+$	22730	23920; 25770 (24850)	2120
$M(dppe)_2Cl_2^+$	21050	22030; 23470 (22750)	1700
$M(dmpe)_2Br_2^+$	20040	21410; 23040 (22230)	2190

[a] All energies in cm^{-1}. [b] Taken from ref 17 and 18. [c] The values in parentheses represent the average energy of the charge-transfer manifold. [d] Calculated by using the average rhenium value.

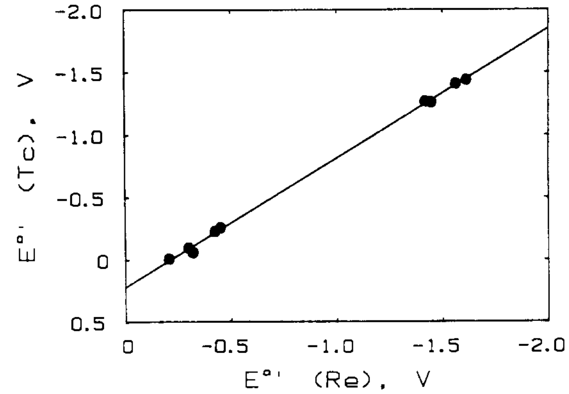

Figure 6. Plot of $E^{\circ\prime}$(Tc) vs. $E^{\circ\prime}$(Re) for the M(III/II) and M(II/I) redox couples. The linear regression line is drawn through the data.

Comparison of the Electrochemical and Spectroscopic Properties of *trans*-$[MD_2X_2]^{+/0/-}$ Complexes (M = Re, Tc). An important goal of this study is to increase the body of comparative electrochemical and spectral data available for analogous technetium and rhenium complexes and, in doing so, to try to understand how coordination environment affects the electrochemical and spectroscopic properties of these complexes. Table IV compares results from electrochemical studies on the *trans*-$[MD_2X_2]^{+/0}$ couple for a series of technetium and rhenium complexes. These data show that the complexes of Re(III) are on the average 207 ± 29 mV ($n = 5$) more difficult to reduce than the corresponding Tc(III) complexes. A slightly smaller potential difference of 165 ± 18 mV ($n = 4$) is observed on the average for the M(II/I) redox couple. These observations are consistent with established periodic trends based on a number of second- and third-row transition-metal pairs[22] and with previously reported comparative electrochemical data for analogous technetium and rhenium complexes.[17] It is noteworthy that the diars complexes exhibit significantly larger potential differences than do the other complexes in both series. Excluding the diars complexes from the correlations yields an average $E^{\circ\prime}$ difference of 194 ± 4 mV ($n = 4$) for the M(III/II) couple and 158 ± 13 mV ($n = 3$) for the M(II/I) couple. As discussed above, the larger $E^{\circ\prime}$ difference observed for the diars complexes may result from the unique orbital interactions available to the $[M(diars)_2Cl_2]^{+/0/-}$ system. The relationship between $E^{\circ\prime}$(Tc) and $E^{\circ\prime}$(Re) for the five pairs of complexes is presented in Figure 6, wherein both the M(III/II) and M(II/I) couples are considered. This plot of $E^{\circ\prime}$(Tc) vs. $E^{\circ\prime}$(Re) is adequately described by a linear function with a slope of 1.04 ± 0.01 and an intercept of 219 ± 15 mV ($n = 9$). The intercept provides a measure of the average potential difference between analogous

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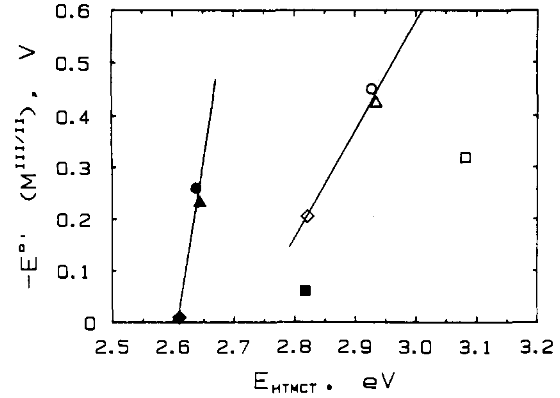

Figure 7. Plot of $E°'(M^{III/II})$ vs. E_{HTMCT} for M(III) complexes: ○, depe; △, dmpe; ◇, dppe; □, diars. The solid symbols represent Tc(III) complexes, and the open symbols represent the Re(III) analogues.

complexes of technetium and rhenium. Thus, for complexes of the type *trans*-$[MD_2X_2]^{+/0/-}$ the rhenium complex is on the average 219 ± 15 mV more difficult to reduce than the technetium analogue, and this potential difference is largely independent of metal oxidation state, trans-halide ligand, and equatorially coordinated D ligand.

For a given rhenium complex the charge-transfer manifold occurs at a higher energy than for the technetium analogue. The energy differences ($E_{Re} - E_{Tc}$) between the absorption maxima for analogous M(III) complexes are shown in Table V; the average spectral energy difference is 2140 ± 270 cm^{-1}, or 260 ± 30 mV. This spectral energy difference is thus both qualitatively and quantitatively in agreement with the electrochemical data; a given technetium center is electrochemically a better oxidizing agent than its rhenium analogue by 219 ± 15 mV, and concomitantly the HTMCT transition occurs at an energy 260 ± 30 mV lower for the technetium center than for the rhenium analogue.

Figure 7 compares plots of the M(III/II) $E°'$ value vs. the energy of the HTMCT band (E_{HTMCT}) for related *trans*-$[MD_2Cl_2]^+$ complexes. For each metal the data for the three complexes with related D ligands $R_2PCH_2CH_2PR_2$ (R = Me, Et, Ph) can be linearly correlated, but the data for the two diars complexes do not follow these trends. As noted above, this undoubtedly results from the unique bonding interactions available within the $[M(diars)_2Cl_2]^{+/0}$ system. A linear correlation between $E°'$ and E_{HTMCT} can be expected for a series of closely related complexes since both parameters are dependent upon the oxidizing power of the central metal.[12,34-36] However E_{HTMCT} should be less dependent than $E°'$ on the nature of D since π-back-bonding is more important for the M(II) complexes (which directly affect $E°'$) than for the M(III) complexes (which directly affect E_{HTMCT} for M(III)). This expectation is manifested in Figure 7 by the slopes of the two lines, which are both significantly greater than 1. The fact that the slope of the rhenium line is less than that of the technetium line (2.1 vs. 7.3) implies that π-back-bonding to the D ligands has a greater influence in the Re(III) complexes.

Summary

The electrochemical and spectroelectrochemical properties of a series of cationic *trans*-$[ReD_2X_2]^+$ complexes have been studied. All of the complexes exhibit a reversible one-electron reduction to the neutral $[ReD_2X_2]^0$ species in 0.5 M TEAP/DMF. Further reduction to $[ReD_2X_2]^-$ is also possible; however, the reversibility of this process depends on the nature of the coordinating phosphine or arsine ligand. The stability of the Re(III) and Re(II) complexes allows characterization of their electrochemical and spectroscopic properties by thin-layer spectroelectrochemistry. Comparison of the electrochemical properties of the *trans*-$[MD_2X_2]^{+/0/-}$ analogues of technetium and rhenium reveals several factors that affect the redox properties of the complexes. While a change in the metal center results in the greatest $E°'$ shift (ca. 220 mV), changes in the ligand environment also affect $E°'$ values. Therefore, the redox properties of a complex can be systematically varied by a judicious choice of the central metal and coordinating ligands. Since redox activity can control the biological behavior of transition-metal complexes used as radiopharmaceuticals, tuning of the redox potential by manipulation of the coordination environment provides a useful approach to the development of new classes of ^{99m}Tc and ^{186}Re imaging agents. From a more fundamental aspect, the electrochemical and spectroelectrochemical studies described in this report provide insight into the low oxidation state chemistry of rhenium and the less well explored chemistry of technetium. The results of these comparative studies help in establishing generalizations that can be applied to the chemistry of related second- and third-row transition-metal complexes.

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Registry No. $Re(depe)_2Cl_2^+$, 109242-13-9; $Re(depe)_2Cl_2$, 109242-14-0; $Re(depe)_2Cl_2^-$, 109242-15-1; $Re(dmpe)_2Cl_2^+$, 96192-45-9; $Re(dmpe)_2Cl_2$, 96109-57-8; $Re(dmpe)_2Cl_2^-$, 96109-58-9; $Re(diars)_2Cl_2^+$, 47512-03-8; $Re(diars)_2Cl_2$, 14325-13-4; $Re(diars)_2Cl_2^-$, 60489-94-3; $Re(dppe)_2Cl_2^+$, 109242-16-2; $Re(dppe)_2Cl_2$, 109428-32-2; $Re(dppe)_2Cl_2^-$, 109242-17-3; $Re(dmpe)_2Br_2^+$, 109242-18-4; $Re(dmpe)_2Br_2$, 109281-93-8; $Re(dmpe)_2Br_2^-$, 109242-19-5.

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