and monoalkoxo complex series **9–11**.

The substituents on chelate rings and monodentate ligands exhibit different inductive effects, which are responsible for various ligand-to-metal π-interactions among complexes. The π-donor ability of the ligands in complexes **1–11** increases in the following orders: (i) for the 2-mercaptoethanolato chelated complexes, **1** < **2** < **3**; (ii) for the alkoxo complex series, **6** < **7** < **8**; and (iii) for the alkanethiolato complex class, **9** < **10** < **11**. This parallels the electron-releasing tendency of the substituents of the ligands that are coordinated to the $[LMoO]^{2+}$ core.

The observed substituent effects in mononuclear monooxomolybdenum(V) complexes with chelated dithiolato ligands may not be directly applicable to Mo-co, because the cofactor is thought to possess a chelated dithiolene five-membered ring. However, with the exception of the 3,4-toluenedithiolato complex reported previously,[9] repeated attempts to synthesize complexes analogous to **5**, but containing a chelated dithiolene ligand, have been unsuccessful.

Acknowledgment. Support of this research by the National Institutes of Health (Grant GM 37773) is gratefully acknowledged. We acknowledge helpful discussions with Dr. M. A. Bruck, Dr. S. A. Roberts, Dr. K. Yamanouchi, Dr. A. G. Wedd, M. D. Carducci, P. J. Desrochers, and M. J. LaBarre.

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Technetium Electrochemistry. 7.[1] Electrochemical and Spectroelectrochemical Studies on Technetium(III) and -(II) Complexes Containing Polypyridyl Ligands[2]

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Received January 26, 1990

The redox properties of a series of technetium(III/II) complexes of the general formula *cis*(*X*),*trans*(*P*)-$[Tc^{III/II}X_2(PR_2R')_2L]^{+/0}$, where X = Cl or Br, PR_2R' = dimethylphenylphosphine or ethyldiphenylphosphine, and L = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), or 1,10-phenanthroline (phen), were investigated in 0.1 M TEAP/acetonitrile by cyclic voltammetry at a platinum-disk electrode. These complexes exhibit diffusion-controlled, 1-equiv Tc(IV)/Tc(III) redox couples in the range 1.044–0.965 V vs SCE and also Tc(III)/Tc(II) redox couples in the range −0.049 to −0.189 V vs SCE. Spectropotentiostatic experiments on three complexes of this class in 0.5 M TEAP/DMF confirm the 1-equiv character of the Tc(III)/Tc(II) couple. $E^{\circ\prime}$ values obtained from these spectropotentiostatic data are consistent with values determined from thin-layer cyclic voltammograms. The Tc(IV)/Tc(III) couple is not reversible on the time scale of the spectropotentiostatic experiment. The electrochemical behavior of Tc(II) complexes of the general formula *trans*(*P*)-$[TcX(PR_2R')_2terpy]^+$, terpy = 2,2′:6′,2″-terpyridine, was also investigated under the same conditions as above. These complexes exhibit diffusion-controlled, 1-equiv Tc(III)/Tc(II) redox couples in the range 0.491–0.440 V vs SCE and Tc(II)/Tc(I) redox couples in the range −1.067 to −1.123 V vs SCE. Spectropotentiostatic experiments on *trans*(*P*)-$[TcCl(PMe_2Ph)_2terpy]^+$ confirm the 1-equiv character of the Tc(III)/Tc(II) couple but show that the Tc(II)/Tc(I) couple is not reversible on the spectropotentiostatic time scale. These electrochemical results are discussed in terms of how Tc redox potentials, and thus the stabilities of various Tc oxidation states, can be controlled by manipulating the properties of the ligands bonded to technetium.

Introduction

We have recently reported the synthesis and characterization of technetium(III)[4] and -(II)[5] complexes of the general formula *cis*(*X*),*trans*(*P*)-$[Tc^{III/II}X_2(PR_2R')_2L]^{+/0}$, where X = Cl or Br, PR_2R' = dimethylphenylphosphine or ethyldiphenylphosphine, and L = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), or 1,10-phenanthroline (phen). The Tc(III) species were prepared by replacement of one halide and one phosphine ligand of the *mer*-$[Tc^{III}X_3(PR_2R')_3]$ starting material by the bidentate bipyridyl ligand. The Tc(II) analogues were prepared in good yield by hydroxide reduction of the Tc(III) analogues in ethanol. During these studies it was observed that slight variations in the ligands dictated the preferred oxidation state of the Tc center. For example, the bromo analogue of *cis*(*X*),*trans*(*P*)-$[Tc^{III/II}X_2(PMe_2Ph)_2bpy]^{+/0}$ is more easily obtained in the Tc(II) state and is not readily isolated in the solid form as a Tc(III) species, whereas the converse is true for the *cis*(*X*),*trans*(*P*)-$[Tc^{III/II}Cl_2(PMe_2Ph)_2(Me_2bpy)]^{+/0}$ pair.

Related Tc(II) complexes of the general formula *trans*(*P*)-$[TcX(PR_2R')_2terpy]^+$, where terpy = 2,2′:6′,2″-terpyridine, have also been synthesized and characterized.[5] They are analogously prepared by replacement of one phosphine and two halide ligands from the *mer*-$[Tc^{III}X_3(PR_2R')_3]$ starting materials, but in this system concomitant reduction of Tc(III) to Tc(II) occurs because of the greater stability of the Tc(II) form.

These qualitative observations suggest that these classes of complexes should exhibit a rich electrochemistry characterized by E° values that depend markedly on the nature of the coordinated ligands. The fact that both the Tc(II) and Tc(III) oxidation states are relatively stable also suggests that these systems should be amenable to spectroelectrochemical analysis. The characterization of these systems by both cyclic voltammetric and spectropotentiostatic methods is herein described.

Abbreviations and Acronyms. Definitions of abbreviations and acronyms used in this paper are as follows: $(acac)_2en$ = *N,N′*-ethylenebis(acetylacetone iminato); bpy = 2,2′-bipyridine; $(buac)_2en$ = *N,N′*-ethylenebis(*tert*-butyl acetoacetate iminato); CV = cyclic voltammogram; DMF = *N,N*-dimethylformamide; depe = $(CH_3CH_2)_2PCH_2CH_2P(CH_3CH_2)_2$; diars = *o*-bis(dimethylarsino)benzene; dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$; dppe = $Ph_2PCH_2CH_2PPh_2$; Et = ethyl; Me = methyl; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; Ophsal = *N*-(2-hydroxyphenyl)salicylideneaminato; OTTLE = optically transparent thin-layer electrode; PDE = platinum-disk electrode; $PEtPh_2$ = ethyldiphenylphosphine; Ph = phenyl; phen = 1,10-phenanthroline; phsal = *N*-phenylsalicylideneaminato; PMe_2Ph = dimethylphenylphosphine; SCE = saturated calomel electrode; TEA = tetraethylammonium ion; TEAP = tetraethylammonium perchlorate; terpy = 2,2′:6′,2″-terpyridine.

Experimental Section

Materials. *Caution!* All references to technetium in this paper are to the specific isotope ^{99}Tc, which emits a low-energy (0.292 MeV) β particle with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard,

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(1) Part 6: Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3608.

(2) Abstracted from the Ph.D. dissertation of B.E.W., University of Cincinnati, 1987.

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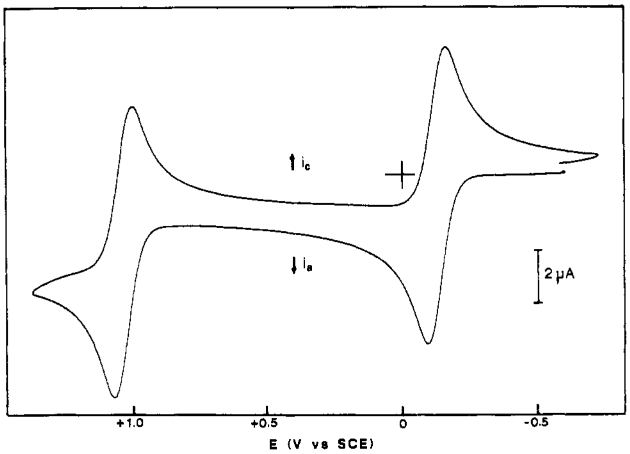

Figure 1. Cyclic voltammogram of 2.2 mM *cis(Cl)*,*trans(P)*-[$TcCl_2$(PMe_2Ph)$_2$bpy] in 0.1 M TEAP/acetonitrile at a PDE. Scan rate = 100 mV/s.

since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times, especially when dealing with solid samples, to prevent contamination and inadvertent inhalation. Complexes used in these experiments were prepared as previously described.[4,5] UV grade acetonitrile and DMF (Burdick and Jackson) were used as solvents. Polarographic grade TEAP (G. F. Smith), used as supporting electrolyte, was dried in vacuo at 60 °C over P_2O_5.

Instrumentation. All electrochemical measurements were performed by using a BAS CV-1B voltammograph. The potential was monitored with a Keithley 178 digital multimeter, and voltammograms were recorded on a Houston Instruments Omnigraphic 100 recorder. Bulk solution cyclic voltammetry experiments were performed with a platinum-disk working electrode (BAS), a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was isolated from the solution by a porous Vicor plug. Spectropotentiostatic and thin-layer cyclic voltammetric experiments were performed with an OTTLE constructed as previously described[6] by using 100 wires/in gold minigrid, a platinum-wire auxiliary electrode and a Ag/AgCl (3 M NaCl) reference electrode. Visible spectra were recorded on a Cary 210 spectrophotometer, the cell compartment of which was modified to accommodate the OTTLE, controlled atmosphere containment chamber, and electrical leads.

Methods. In general, experiments were performed as previously described[7-10] and are summarized as follows:

Cyclic voltammograms were obtained by using ca. 2 mM solutions of the complexes in acetonitrile that was 0.1 M in TEAP. The solutions were purged with a stream of Ar gas (saturated with acetonitrile) for a time sufficient to deoxygenate them (ca. 10 min). Potential scans were typically performed at a scan rate of 100 mV/s; however, various scan rates up to 400 mV/s were used to assess reversibility. Thin-layer cyclic voltammograms were obtained with DMF solutions of the complexes (ca. 1 mM) that were 0.5 M in TEAP. The sample solutions were sealed in serum vials and purged for 10–20 min with Ar. The OTTLE was mounted in a Plexiglas containment chamber fitted with quartz windows and then placed into the spectrophotometer sample compartment to obtain a baseline reading. The chamber was removed and purged with Ar, and the sample solution was transferred to the reservoir of the OTTLE with a glass syringe. The chamber was placed into the sample compartment, the compartment was purged with Ar, and the spectra were recorded at various stepped potentials. Each spectrum was recorded 5 min after potential application, a time that was sufficient to obtain equilibrium values of [O]/[R].

Results

All of the *cis(X)*,*trans(P)*-[$Tc^{III/II}X_2(PR_2R')_2L$]$^{+/0}$ complexes (X = Cl, Br; PR_2R' = PMe_2Ph, $PEtPh_2$; L = bpy, phen, Me_2bpy) studied herein exhibit both Tc(IV)/Tc(III) and Tc(III)/Tc(II) couples. Figure 1 depicts a typical bulk solution CV (PDE) obtained for the Tc(II) complex *cis(Cl)*,*trans(P)*-[$TcCl_2$(PMe_2Ph)$_2$bpy]. A positive potential scan initiated at −0.6 V reveals two oxidation waves with peak potentials at −0.098 and +1.065 V. Upon reversal of the scan at +1.37 V, reduction waves with peak potentials of +1.000 and −0.160 V are observed. The following observations establish that both redox events are reversible 1-equiv processes: (1) the peak currents are proportional to the square root of the scan rate, (2) the ratios of the anodic and cathodic peak currents are unity, and (3) the separations between related cathodic and anodic peaks are close to the Nernstian value of 59 mV for a 1-equiv process. Initiating a scan at −0.6 V and scanning in the negative direction yields a reduction wave with a peak potential at −1.57 V. Upon reversal of the scan at −1.70 V, no related oxidation wave is observed. However, several small oxidation waves appear over the entire previous scan range, indicating that the reduction process occurring at −1.57 V is quickly followed by chemical processes that alter the nature of the original complex. Repeating the experiment at a scan rate of 400 mV/s produces a small related oxidation wave, the intensity of which can be increased at the temperature of a dry ice/acetone bath. Even at this low temperature the anodic peak current is much less than the cathodic peak current. An identical CV is obtained when the Tc(III) analogue, *cis(Cl)*,*trans(P)*-[$TcCl_2$(PMe_2Ph)$_2$bpy]$^+$ is used. When the potential is held at −0.60 V and the solution is stirred, Faradaic current is observed for [$TcCl_2$(PMe_2Ph)$_2$bpy]$^+$ but not for [$TcCl_2$(PMe_2Ph)$_2$bpy]. Conversely, when the potential is held at +0.5 V and the solution is stirred, Faradaic current is observed for [$TcCl_2$(PMe_2Ph)$_2$bpy] but not for [$TcCl_2$(PMe_2Ph)$_2$bpy]$^+$. This behavior supports the assignments of the Tc(III) and Tc(II) oxidation states for the solid samples. The thin-layer CV of [$TcCl_2$(PMe_2Ph)$_2$bpy] in DMF (2 mV/s) shows a reversible Tc(III)/Tc(II) redox couple. Attempts to record a thin-layer cyclic voltammogram for the Tc(IV)/Tc(III) couple produce ever-increasing anodic current (positive scan) and multiple reduction waves upon reverse scan, indicating that the Tc(IV) product is not stable. Similar bulk solution voltammograms and thin-layer voltammetric behavior are observed for the other *cis(X)*,*trans(P)*-[$TcX_2(PR_2R')L$]$^{+/0}$ species. The results of the bulk solution experiments are presented in Table I.

Table I. Formal Redox Potentials of *cis(X)*,*trans(P)*-[$TcX_2(PR_2R')L$]$^{2+/+/0}$ and *trans(P)*-[$TcX(PR_2R')(terpy)$]$^{2+/+/0}$ Couples[a]

Tc(II) complex	$E°'$-(Tc^{IV}/Tc^{III})	$E°'$-(Tc^{III}/Tc^{II})	$E°'$-(Tc^{II}/Tc^{I})	$E_{p(c)}$
$TcBr_2(PMe_2Ph)_2$bpy	1.044	−0.049	n.o.[b]	−1.400
$TcCl_2(PEtPh_2)_2$bpy	1.080	−0.077	n.o.	−1.450
$TcCl_2(PMe_2Ph)_2$bpy	1.033	−0.128	n.o.	−1.570
$TcCl_2(PMe_2Ph)_2$phen	1.039	−0.130	n.o.	−1.600
$TcCl_2(PMe_2Ph)_2Me_2$bpy	0.965	−0.189	n.o.	−1.550
[$TcCl(PEtPh_2)_2$terpy]$^+$	n.o.	0.491	−1.072	n.o.
[$TcBr(PMe_2Ph)_2$terpy]$^+$	n.o.	0.467	−1.067	n.o.
[$TcCl(PMe_2Ph)_2$terpy]$^+$	n.o.	0.440	−1.123	n.o.

[a] Acetonitrile solutions. Potentials given in V vs SCE. The supporting electrolyte is 0.1 M TEAP. $E°'$ determined by averaging $E_{p(a)}$ and $E_{p(c)}$ of cyclic voltammogram. [b] n.o. = not observed within the scan range of +1.5 to −1.7 V vs SCE.

The *trans(P)*-[$TcX(PR_2R')_2$terpy]$^+$ complexes also exhibit two reversible redox processes, which, however, are assigned as Tc(III)/Tc(II) and Tc(II)/Tc(I) couples. Figure 2 depicts a typical bulk cyclic voltammogram for *trans(P)*-[$TcCl(PMe_2Ph)_2$terpy]$^+$. A negative potential scan starting at 0.0 V reveals a reduction wave with a peak potential of −1.158 V. Upon reversal of the scan at −1.64 V, an oxidation wave is observed with a peak potential of −1.088 V. Continuing the positive scan beyond 0 V reveals an oxidation wave with a peak potential of 0.475 V. Reversal of the scan at 0.900 V reveals a reduction wave with a peak potential of 0.405 V. By the same criteria noted above for the [$TcX_2(PR_2R')L$]$^{+/0}$ complexes, both of these redox events are reversible, 1-equiv processes. Extension of the positive scan beyond +0.9

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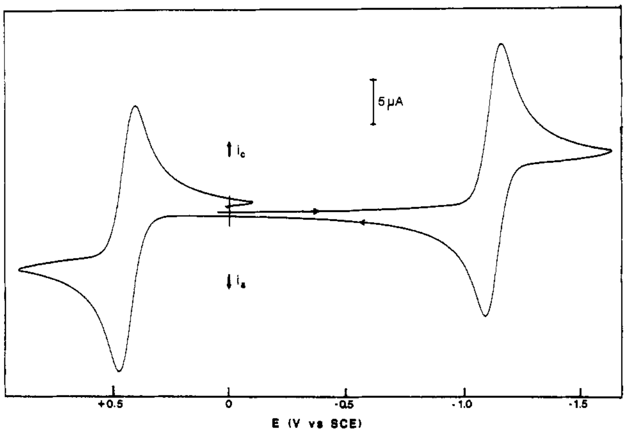

Figure 2. Cyclic voltammogram of 1.3 mM *trans(P)*-[TcCl$(PMe_2Ph)_2$terpy]$^+$ in 0.1 M TEAP/acetonitrile at a PDE. Scan rate = 100 mV/s.

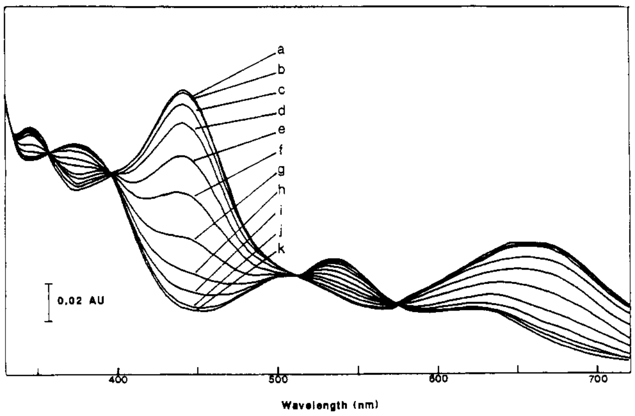

Figure 3. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 1.0 mM *cis(Br),trans(P)*-[$TcBr_2(PMe_2Ph)_2$bpy] in 0.5 M TEAP/DMF. Applied potentials in V vs Ag/AgCl: (a) -0.070; (b) 0.020; (c) 0.040; (d) 0.060; (e) 0.080; (f) 0.100; (g) 0.120; (h) 0.140; (i) 0.160; (j) 0.200; (k) 0.400.

Table II. Formal Redox Potentials and *n* Values Obtained from Thin-Layer Electrochemical Measurements of Tc(III)/Tc(II) Couples of Polypyridyl Complexes[a]

Tc(II) complex	$E^{\circ\prime\,b}$	$E^{\circ\prime\,b}$	*n*
trans(P)-[TcCl$(PMe_2Ph)_2$terpy]$^+$	0.498	0.502[d]	0.92[d]
cis(Br),trans(P)-$TcBr_2(PMe_2Ph)_2$bpy	0.108	0.109[e]	0.97[e]
cis(Cl),trans(P)-$TcCl_2(PMe_2Ph)_2$phen	0.028	0.016[f]	0.97[f]
cis(Cl),trans(P)-$TcCl_2(PMe_2Ph)_2$bpy	0.006	0.012[g]	0.99[g]

[a] Solutions in 0.5 M TEAP/DMF. $E^{\circ\prime}$ in V vs Ag/AgCl (3 M NaCl). [b] $E^{\circ\prime}$ = average of cathodic and anodic peak potentials from thin-layer cyclic voltammograms at a Au OTTLE at a scan rate of 2 mV/s. [c] Values determined from Nernstian plots of spectropotentiostatic data at a Au OTTLE. [d] 410-nm data. [e] 440-nm data. [f] 520- and 660-nm data. [g] 446- and 670-nm data.

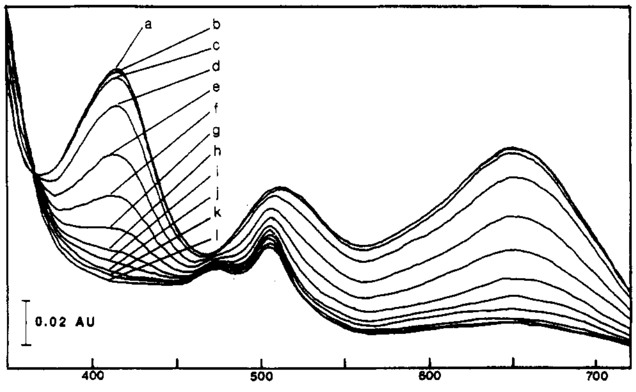

Figure 4. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 1.3 mM *trans(P)*-[TcCl$(PMe_2Ph)_2$terpy]$^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs Ag/AgCl: (a) 0.000; (b) 0.340; (c) 0.420; (d) 0.460; (e) 0.490; (f) 0.510; (g) 0.530; (h) 0.550; (i) 0.570; (j) 0.630; (k) 0.700; (l) 0.750.

V reveals an oxidation wave with a peak potential of +1.560 V, but reversal of the scan at +1.72 V reveals no related reduction wave. Continuing this scan over the entire accessible range reveals a number of baseline aberrations as well as small cathodic peaks, which indicate that new chemical species are generated as a result of the oxidation at 1.56 V. Similar cyclic voltammograms are obtained for *trans(P)*-[TcBr$(PMe_2Ph)_2$terpy]$^+$ and *trans(P)*-[TcCl$(PEtPh_2)_2$terpy]$^+$, and the CV results for all three complexes are summarized in Table I. For all three of these complexes, no Faradaic current is observed at 0.0 V, consistent with the two couples being assigned as Tc(III)/Tc(II) and Tc(II)/Tc(I) processes.

Because of the stability of the Tc(III) and Tc(II) forms of the *cis(X),trans(P)*-[$TcX_2(PR_2R')$L]$^{+/0}$ couples, *cis(Br),trans(P)*-[$TcBr_2(PMe_2Ph)_2$bpy]$^{+/0}$, *cis(Cl),trans(P)*-[$TcCl_2(PMe_2Ph)_2$phen]$^{+/0}$, and *cis(Cl),trans(P)*-[$TcCl_2(PMe_2Ph)_2$bpy]$^{+/0}$ were studied by the spectropotentiostatic method. Spectra recorded for the reversible Tc(III)/Tc(II) couples of *cis(Br),trans(P)*-[$TcBr_2(PMe_2Ph)_2$bpy]$^{+/0}$ during OTTLE spectropotentiostatic experiments are depicted in Figure 3. The observed absorption maxima, obtained in DMF, for all three systems are in good agreement with those previously observed for isolated Tc(III) and Tc(II) complexes in acetonitrile.[4,5] Isosbestic points (five for *cis(Br),trans(P)*-[$TcBr_2(PMe_2Ph)_2$bpy]$^{+/0}$ (Figure 3), four for *cis(Cl),trans(P)*-[$TcCl_2(PMe_2Ph)_2$phen]$^{+/0}$, and three for *cis(Cl),trans(P)*-[$TcCl_2(PMe_2Ph)_2$bpy]$^{+/0}$) are observed during the spectropotentiostatic experiments, consistent with simple interconversion of the Tc(III) and Tc(II) forms. The results from Nernstian analyses of these data are given in Table II.

Spectra obtained during a spectropotentiostatic experiment on the *trans(P)*-[TcCl$(PMe_2Ph)_2$terpy]$^{2+/+}$ Tc(III/II) couple are shown in Figure 4. The absorption maxima observed for the Tc(II) complex in DMF are in good agreement with those obtained previously for the isolated complex in acetonitrile.[5] One isosbestic point is observed in the visible region. The results from Nernstian analysis of these data are given in Table II. It should be noted that while the Tc(III) species appears to be sufficiently stable to perform the spectropotentiostatic experiment, this complex does undergo very slow decomposition, as evidenced by multiple reduction waves that appear in a reverse scan conducted after the potentiostatic experiment is completed. The Tc(I) complex is too unstable to permit the spectropotentiostatic experiment to be conducted on the Tc(II)/Tc(I) couple.

Discussion

General Considerations. Acetonitrile and DMF were chosen as solvents for these experiments because they permit a wide range of applied potentials and they provide good solubility for these complexes. Acetonitrile was used for the bulk cyclic voltammetry experiments in order to allow comparisons to results obtained for an analogous Re complex.[11] DMF is better suited to the spectropotentiostatic experiment because of its relatively low volatility.

The series of complexes *cis(X),trans(P)*-[$TcX_2(PR_2R')_2$L]$^{+/0}$ exhibit reversible Tc(IV)/Tc(III) and Tc(III)/Tc(II) couples in bulk cyclic voltammetry experiments according to eqs 1 and 2,

$$[Tc^{IV}X_2(PR_2R')_2L]^{2+} + e^- \rightarrow [Tc^{III}X_2(PR_2R')_2L]^+ \quad (1)$$

$$[Tc^{III}X_2(PR_2R')_2L]^+ + e^- \rightarrow [Tc^{II}X_2(PR_2R')_2L] \quad (2)$$

respectively. The $E^{\circ\prime}$ values obtained for the Tc(III)/Tc(II) couples (Table I) correlate with qualitative observations made during the syntheses of these complexes. The $E^{\circ\prime}$(III/II) values are not extreme, and therefore both forms of the couple are readily accessible. In fact, solid samples of most of the complexes in both oxidation states have been obtained; notable exceptions are the

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Table III. Redox Potentials for Analogous Technetium and Rhenium Complexes[a]

complex	couple	$E°'_{Tc}$	$E°'_{Re}$	$\Delta E°'_{Tc-Re}$	medium[b]
$[MO_4]^{-}$[c]	VII/IV	+0.74	+0.51	0.23	A
$[MO(SC(O)C(O)S)_2]^{-/2-}$[d]	V/IV	−0.27	−0.46	0.19	B
$[MOCl(phsal)_2]^{0/-}$	V/IV	−0.29[e,f]	−0.81[g]	0.52	C
$[MO(Ophsal)(phsal)]^{0/-}$	V/IV	−0.30[e]	−0.76[g]	0.46	C
$[M(NCS)_6]^{2-/3-}$[h]	IV/III	+0.66	+0.37	0.29	B
$[MCl_3(PMe_2Ph)_3]^{+/0}$	IV/III	+1.064[i]	+0.90[j]	0.16	C
$[MCl_2(PMe_2Ph)_2bpy]^{2+/+}$	IV/III	+1.274[k]	+1.12[j]	0.15	C
$[MCl_3(PMe_2Ph)_3]^{0/-}$	III/II	−0.51[i,l]	−0.77[i]	0.26	C
$[MCl_2(PMe_2Ph)_2bpy]^{+/0}$	III/II	+0.113[k]	−0.15[j]	0.262	C
$[M(depe)_2Cl_2]^{+/0}$	III/II	−0.054[m]	−0.244[n]	0.190	D
$[M(depe)_2Cl_2]^{+/0}$	III/II	−0.023[m]	−0.198[o]	0.175	E
$[M(dmpe)_2Cl_2]^{+/0}$	III/II	−0.025[m]	−0.217[n]	0.192	D
$[M(dmpe)_2Cl_2]^{+/0}$	III/II	−0.117[m]	−0.310[o]	0.193	E
$[M(dmpe)_2Br_2]^{+/0}$	III/II	−0.108[m]	−0.091[n]	0.199	D
$[M(dmpe)_2Br_2]^{+/0}$	III/II	−0.011[m]	−0.202[o]	0.191	E
$[M(dppe)_2Cl_2]^{+/0}$	III/II	+0.196[p]	+0.001[n]	0.195	D
$[M(diars)_2Cl_2]^{+/0}$	III/II	+0.145[p]	−0.17[n]	0.32	D
$[M(dmpe)_2Cl_2]^{0/-}$	II/I	−1.164[q]	−1.342[q]	0.178	D
$[M(diars)_2Cl_2]^{0/-}$	II/I	−1.05[q]	−1.24[n]	0.19	D
$[M(dmpe)_3]^{2+/+}$	II/I	+0.299[r]	+0.226[r]	0.073	F

[a] Potentials are in V vs the normal hydrogen electrode (NHE). The reported literature values have been converted as follows: SCE(Hg/Hg_2Cl_2, KCl saturated) = +0.241 V vs NHE; NaSCE(Hg/Hg_2Cl_2, NaCl saturated) = +0.236 V vs NHE; Ag/AgCl(3 M NaCl) = +0.206 V vs NHE; ferrocene/ferrocenium reference redox system in CH_3CN = +0.62 V vs NHE. [b] A = aqueous acidic medium; B = 0.1 M TBAP in CH_3CN; C = 0.1 M TEAP in CH_3CN; D = 0.5 M TEAP in DMF; E = 0.5 M KNO_3 in water; F = 0.1 M NaCl in H_2O; G = 0.5 M (TEA)Cl or 0.5 M (TEA)Br in DMF. [c] Reference 20. [d] Reference 21 by polaragraphy. [e] Reference 17. [f] −35 °C. [g] Reference 26. [h] Reference 22. [i] Reference 12. [j] Reference 11. [k] This work. [l] E_p for an irreversible reduction. [m] Reference 23. [n] Reference 7. [o] Reference 1; square-wave voltammetry. [p] Reference 10. [q] Reference 18. [r] Reference 25.

Tc(II) form of $[Tc^{III}Cl_2(PMe_2Ph)_2Me_2bpy]^+$ and the Tc(III) form of $[Tc^{II}Br_2(PMe_2Ph)_2bpy]$.[4,5] The $E°'$ values of Table I show that the $[Tc^{III}Cl_2(PMe_2Ph)_2Me_2bpy]^+$ complex is the most difficult of the series to reduce and thus is stable with respect to its Tc(II) analogue, while the $[Tc^{III}Br_2(PMe_2Ph)_2bpy]^+$ complex is the easiest to reduce and thus it is stable in its Tc(II) form.

Tc vs Re. The synthesis and electrochemical behavior of the analogous Re complex *cis*(*Cl*),*trans*(*P*)-$[ReCl_2(PMe_2Ph)_2bpy]^+$ have been reported previously.[11] This complex also exhibits reversible IV/III and III/II couples (at +0.88 and −0.39 V vs SCE in acetonitrile, respectively). These values are 153 and 262 mV more negative than those reported herein for the analogous Tc complex *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PMe_2Ph)_2bpy]^+$. That is, the Re analogue is more difficult to reduce. Similarly, from the data reported for $[Tc^{IV/III/II}Cl_3(PMe_2Ph)_3]^{+/0/-}$ [12] and its Re congener,[11] the $\Delta E°'_{Tc-Re}$ values are 0.160 V for the IV/III couple and 0.285 V for the III/II pair. The smaller difference ($\Delta E°'_{Tc-Re}$) for the IV/III couples with respect to the III/II couples appear to result from the high formal charge of the 2+ M(IV) species and not from its high oxidation state. This conclusion results from a comparison of $E°'$ values for all known Tc–Re congeners (Table III).[13,14] Consistent with established periodic trends,[13] in all cases a Re complex is more difficult to reduce than is its Tc analogue. Moreover, with only three exceptions the $\Delta E°'$ values ($E°'_{Tc} - E°'_{Re}$) are in the narrow range 0.15–0.32 V. The exceptions involve the *highly* charged (but low valent) $[M^{II/I}(dmpe)_3]^{2+/+}$ pair, which exhibits a $\Delta E°'_{Tc-Re}$ value *smaller* than any of the others reported (0.073 V), and the *low* charged (but high valent) Schiff base pairs $[M^{V/IV}OCl(phsal)_2]^{0/-}$ and $[M^{V/IV}O(Ophsal)(phsal)]^{0/-}$, which exhibit $\Delta E°'_{Tc-Re}$ values *higher* than any of the others reported (0.52 and 0.46 V, respectively).

Effects of Ligands on $E°'$. (1) Variation of the Phosphine Ligand. Of the two complexes $[TcCl_2(PMe_2Ph)_2bpy]^+$ and $[TcCl_2(PEtPh_2)_2bpy]^+$, the latter, which contains phosphine ligands with the greater number of phenyl groups, is more easily reduced to Tc(II) and is harder to oxidize to Tc(IV). This same phenomenon is seen for $[Tc^{II}Cl(PMe_2Ph)_2terpy]^+$ and $[Tc^{II}Cl(PEtPh_2)_2terpy]^+$ in that the complex containing $PEtPh_2$ is more difficult to oxidize to Tc(III) and easier to reduce to Tc(I). This effect occurs because the more phenyl-substituted phosphines are better π acids, which better stabilize lower oxidation states, while the less phenyl-substituted (more alkyl-substituted) phosphines are better σ donors, which better stabilize the higher oxidation states. This generalization is also manifested in the electrochemistry of free phosphines (the half-wave potential for the oxidation of the free phosphine ligand increases with increasing phenyl substitution)[15] and of technetium–phosphine–Schiff base complexes of the general formula *trans*-$[Tc^{III}(PR_2R')_2(\text{Schiff base})]^+$ (for a given Schiff base, increasing the phenyl substitution on the phosphine makes it easier to reduce both Tc(IV) to Tc(III) and Tc(III) to Tc(II)).[8]

For both the comparable bpy and terpy complexes, the difference in potential for the Tc(III)/Tc(II) couple when the phosphine is changed from PMe_2Ph to $PEtPh_2$ is 51 mV. This value is consistent with the results obtained by Libson and coworkers[16] in a study of technetium complexes of the form $[Tc^{III}(D)_2X_2]^+$, where D is a bisphosphine ligand. They observed that the bis(diphenylphosphino)ethane (dppe) complexes are easier to reduce, by an average of 218 mV, than the bis(dimethylphosphino)ethane (dmpe) analogues, which corresponds to a difference of +27 mV per methyl to phenyl exchange (eight exchanges per complex). By the same reasoning, they found a difference of −4 mV per methyl to ethyl exchange (the ethyl analogues being more difficult to reduce). With application of these values to the bpy and terpy species described herein, the exchange of two PMe_2Ph ligands for two $PEtPh_2$ ligands (2Me → 2Ph plus 2Me → 2Et) should result in a (2 × 27) + (2 × −4) or +46 mV change in potential. This value is close to the observed 51 mV difference.

The $\Delta E°'$ values for various phosphine substituent group changes in Tc and Re complexes are summarized in Table IV. The most extensive data available are for M(III/II) couples with Et → Ph substitutions, and for this exchange the $\Delta E°'$ values are around 30 mV (range = 25–51 mV). The corresponding Et → Ph $\Delta E°'$ values for the Tc(IV/III) couples in $[Tc^{IV/III}$(Schiff

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Table IV. Effect of Phosphine Substituents on Redox Potentials of Comparable Technetium and Rhenium Complexes[a]

(a) Complexes Containing Bidentate Phosphine Ligands

complex	couple	$E°'$ for L = depe	$E°'$ for L = dmpe	$E°'$ for L = dppe	$\Delta E°'$ per Me → Et exch[b]	$\Delta E°'$ per Et → Ph exch[b]	$\Delta E°'$ per Me → Ph exch[b]
$[Tc(L)_2Cl_2]^{+/0/-}$	III/II	-0.054[c,d]	-0.025[c,d]	+0.196[e]	-0.004	+0.031	+0.028
	III/II	-0.046[f]	-0.026[f]	+0.205[f]	-0.003	+0.031	+0.029
	II/I	-1.233[d,g]	-1.204[d]		-0.004		
$[Tc(L)_2Br_2]^{+/0/-}$	III/II	+0.075[c,d]	+0.108[c,d]		-0.004		
	III/II	+0.068[f]	+0.107[f]	+0.309[e]	-0.005	+0.030	+0.025
	II/I	-1.083[d,g]	-1.062[d]		-0.003		
$[Re(L)_2Cl_2]^{+/0/-}$	III/II	-0.244[h]	-0.217[h]	+0.001[h]	-0.003	+0.031	+0.027
	II/I	-1.40[g,h]	-1.35[h]	-0.99[h]	-0.006	+0.051	+0.045
$[Tc(L)_3]^{2+/+}$	II/I	+0.170[d]	+0.316[d]		-0.012		

(b) Complexes Containing Monodentate Phosphine Ligands[i]

complex	$E°'$(IV/III)	$E°'$(III/II)	$\Delta E°'$ per Et → Ph exch[a]	
			IV/III	III/II
$[Tc(acac_2en)(PEt_3)_2]^{2+/+/0}$	+0.896	-0.844	0.010	0.030
$[Tc(acac_2en)(PEt_2Ph)_2]^{2+/+/0}$	+0.916	-0.784	0.015	0.050
$[Tc(acac_2en)(PEtPh_2)_2]^{2+/+/0}$	+0.946	-0.684	0.025	0.025
$[Tc(acac_2en)(PPh_3)_2]^{2+/+/0}$	+0.996	-0.634	0.017 (av)	0.035 (av)
$[Tc(buac_2en)(PEt_2Ph)_2]^{2+/+/0}$	+0.806	-0.684	0.025	0.040
$[Tc(buac_2en)(PEtPh_2)_2]^{2+/+/0}$	+0.856	-0.604		

[a] Potentials are in V vs NHE (see Table III). Unless otherwise noted, values are determined by conventional cyclic voltammetry at a PDE; medium is 0.5 M TEAP in DMF. [b] Values determined by dividing $\Delta E°'$ of the complexes by the number of R groups (R = Me, Et, Ph) per complex. [c] Working electrode is a Au OTTLE. [d] Reference 23. [e] Reference 10. [f] Reference 16. [g] -40 °C. [h] Reference 7. [i] Medium is 0.1 M TEAP in CH_3CN.[24]

Table V. Redox Potentials of Technetium and Rhenium Complexes Containing Chloride and Bromide Ligands[a]

complex	couple	$E°'_{Cl}$ (X = Cl)	$E°'_{Br}$ (X = Br)	$\Delta E°'$ per Cl → Br exch[b]	medium[c]
cis(*X*),*trans*(*P*)-$[TcX_2(PMe_2Ph)_2bpy]^{2+/+}$[d]	IV/III	+1.274	+1.285	+0.006	C
cis(*X*),*trans*(*P*)-$[TcX_2(PMe_2Ph)_2bpy]^{+/0}$[d]	III/II	+0.113	+0.192	+0.040	C
trans(*P*)-$[TcX(PMe_2Ph)_2terpy]^{2+/+}$[d]	III/II	+0.681	+0.708	+0.027	C
trans-$[Tc(dmpe)_2X_2]^{+/0}$[e]	III/II	-0.025	+0.108	+0.067	D
trans-$[Tc(dmpe)_2X_2]^{+/0}$[e]	III/II	-0.122	-0.016	+0.053	E
trans-$[Tc(dmpe)_2X_2]^{+/0}$[e]	III/II	+0.016	+0.161	+0.073	G
trans-$[Tc(depe)_2X_2]^{+/0}$[e]	III/II	-0.023	+0.115	+0.069	E
trans-$[Tc(depe)_2X_2]^{+/0}$[e]	III/II	-0.054	+0.075	+0.065	D
trans-$[Re(dmpe)_2X_2]^{+/0}$[f]	III/II	-0.217	-0.091	+0.063	D
trans-$[Re(dmpe)_2X_2]^{+/0}$[g]	III/II[h]	-0.310	-0.202	+0.054	E
trans(*P*)-$[TcX(PMe_2Ph)_2terpy]^{+/0}$[d]	II/I	-0.882	-0.826	+0.056	C
trans-$[Tc(dmpe)_2X_2]^{0/-}$[e]	II/I	-1.204	-1.062	+0.071	D
trans-$[Tc(dmpe)_2X_2]^{0/-}$[e]	II/I	-1.163	-0.997	+0.078	G
trans-$[Tc(depe)_2X_2]^{0/-}$[e]	II/I[h]	-1.233	-1.083	+0.075	D
trans-$[Re(dmpe)_2X_2]^{0/-}$[g]	II/I	-1.35	-1.21	+0.070	D

[a] Potentials are in V vs the normal hydrogen electrode (see Table III). [b] Values determined by dividing $\Delta E°'$ of the complexes by the number of halide ligands per complex. [c] See Table III. [d] This work. [e] Reference 23. [f] Reference 7. [g] Reference 1. [h] -40 °C.

base)$(PR_2R')_2]^{2+/+}$ complexes are somewhat lower (range = 10–25 mV), presumably due to the higher formal charge of the Tc(IV) center.

(2) Variation of the Halogen Ligand. For the two Tc(III) complexes $[TcCl_2(PMe_2Ph)_2bpy]^+$ and $[TcBr_2(PMe_2Ph)_2bpy]^+$, the bromo analogue is easier to reduce to Tc(II) and harder to oxidize to Tc(IV). The same effect is seen for the Tc(II) complexes $[TcCl(PMe_2Ph)_2terpy]^+$ and $[TcBr(PMe_2Ph)_2terpy]^+$, wherein the bromo analogue is easier to reduce to Tc(I) and harder to oxidize to Tc(III). The differences in the Tc(III)/Tc(II) potential per Cl → Br interchange ($\Delta E°'_{Br-Cl}$) are similar for the two pairs (40 mV for the bpy pair and 27 mV for the terpy pair). The incorporation of bromide leads to a more reducible complex because bromide is a better π-acceptor ligand than chloride and is thus better able to stabilize lower oxidation states. Table V compares the differences in $E°'$ values per Cl → Br exchange ($\Delta E°'_{Br-Cl}$) for the complexes prepared in this study to the differences observed for Tc and Re complexes of the form $[M^{III/II/I}D_2X_2]^{+/0/-}$ (D = a bis(tertiary phosphine or arsine), X = Cl or Br, and M = Tc or Re). The values of $\Delta E°'_{Br-Cl}$ for the $[M^{III/II/I}D_2X_2]^{+/0/-}$ couples fall in the range 53–78 mV, while those for the higher charged 2+/+ bpy and terpy complexes are somewhat smaller (range = 6–27 mV). This is consistent with the previously noted leveling effect of formal charge on variations in $E°'$ values.

(3) Variation of the Polypyridyl Ligand. For the three Tc(III) complexes $[TcCl_2(PMe_2Ph)_2bpy]^+$, $[TcCl_2(PMe_2Ph)_2phen]^+$, and $[TcCl_2(PMe_2Ph)_2Me_2bpy]^+$, the bpy and phen species have essentially the same $E°'$ values, while the Me_2bpy analogue is considerably more difficult to reduce to Tc(II) and easier to oxidize to Tc(IV). This electrochemical property is manifested in the synthesis of the bpy and Me_2bpy analogues; both Tc(III) and Tc(II) forms of the bpy complex can be recovered, but the Tc(II) form of the Me_2bpy species is not readily accessible.[4,5] The difference in potential between the bpy and Me_2bpy species is understood in terms of the electron-donating properties of the methyl groups, which cause Me_2bpy to be a better σ donor and poorer π acceptor; this makes the Me_2bpy better able to stabilize Tc(IV) and less able to stabilize Tc(II). The same effect is observed in *trans*-$[Tc^{III}(PR_2R')_2$(Schiff base)$]^+$ complexes for Schiff base ligands of different π-accepting abilities.[8]

The Tc(III/II) couples $[TcX_2(PR_2R')_2bpy]^{+/0}$ and $[TcX(PR_2R')_2terpy]^{2+/+}$ differ in the replacement of a relatively poor π acid (the Cl or Br) by a better π acid (a pyridyl moiety). For each of the two chloride-containing $[TcCl_2(PR_2R')_2bpy]^{+/0}$/$[TcCl(PR_2R')_2terpy]^{2+/+}$ pairs studied, for a constant phosphine, the terpy complex is 568 mV easier to reduce from Tc(III) to Tc(II) than is the bpy analogue. The difference in potential for the bromide-containing $[TcBr_2(PMe_2Ph)_2bpy]^{+/0}/[TcBr(PMe_2Ph)_2terpy]^{2+/+}$ pair is 516 mV. The magnitude of these potential changes (>500 mV) reflects the great difference in ability to delocalize charge between a halide and a conjugated ring system. The smaller difference in potential for the bromide-containing pair is also as expected. Bromide stabilizes the lower oxidation state somewhat better than does chloride, and pyridyl stabilizes the lower oxidation state to a much greater extent than does either chloride or bromide. Therefore, the replacement of one bromide by one pyridyl moiety leads to a smaller stabilization effect (manifested as a smaller $\Delta E^{\circ\prime}$) than does the equivalent replacement of one chloride.

Spectropotentiostatic Measurements. The *cis*(*X*),*trans*(*P*)-$[Tc^{III/II}X_2(PR_2R')_2L]^{+/0}$ couples investigated herein are well suited for spectropotentiostatic analysis because of the stabilities of the component complexes, as evidenced by the thin-layer cyclic voltammetry results and the isolation of solid samples of each of the redox forms. The spectropotentiostatic experiments summarized in Figures 3 and 4 show that all of the $[TcX_2(PR_2R')_2L]^{+/0}$ complexes studied exhibit isosbestic behavior, and thus the Tc(III)/Tc(II) redox process involves simple electron transfer uncomplicated by ligand substitution or other reactions. The spectra of the Tc(III) and Tc(II) forms determined in these experiments are in good agreement with those obtained for isolated solid samples,[4,5] establishing that the solid samples and the electrogenerated species are identical. Nernstian analyses of the data from these experiments give $E^{\circ\prime}$ values that are in good agreement with those obtained from the thin-layer cyclic voltammograms and yield values of n close to unity. This latter observation confirms both the 1-equiv nature of the observed process and the oxidation state assignments previously made on the basis of elemental analyses.[4,5]

Figure 4 shows that the *trans*(*P*)-$[Tc^{III/II}Cl(PMe_2Ph)_2terpy]^{+/0}$ couple exhibits isosbestic behavior for the duration of the potentiostatic experiment. Nernstian analysis of the data gives an $E^{\circ\prime}$ value that is in good agreement with that obtained in the thin-layer cyclic voltammetry experiment (Table II). However, further investigation reveals that the Tc(III) form of this couple is not stable over long periods of time. The experiment requires a total of ca. 90 min, and the bulk of the complex is held in the Tc(III) form during the last 30 min. Upon reversal of the potential after the last visible spectrum is recorded and scanning in the negative direction at 2 mV/s, a Tc(III) to Tc(II) reduction wave is recorded; however the peak current is substantially smaller than that previously recorded for the corresponding oxidation. Additionally, two reduction waves are recorded that were not previously observed in thin-layer cyclic voltammograms. Both of these observations indicate that a slow decomposition of the Tc(III) form occurs on the prolonged time scale of the spectropotentiostatic experiment. In the case of the Tc(II)/Tc(I) couple, isosbestic behavior is seen only for the first four potential steps (ca. 20-min duration). After this, the visible spectrum changes continuously even with the potential held at values more positive than $E^{\circ\prime}$ of the couple. This behavior indicates that the electrogenerated Tc(I) complex decomposes spontaneously, possibly by loss of the chloride ligand.[17]

Summary. The ability to control the redox potential of technetium-based couples, especially the Tc(III/II) couple, is important to the development of new ^{99m}Tc radiopharmaceuticals.[14,18,19] While the qualitative principles underlying such control have been known for some time, the quantitative data necessary for precisely predicting the effects of ligand variations on Tc(III/II) potentials are only now becoming available. Data compiled in this work show that in complexes of formal charge <+1 (a) replacing a chloride ligand by a pyridyl moiety stabilizes Tc(II) by about 570 mV, (b) replacing a chloride ligand by a bromide ligand stabilizes Tc(II) by about 60 mV, (c) replacing a single P–Et substituent by a single P–Ph substituent stabilizes Tc(II) by about 30 mV, and (d) replacing a single P–Et substituent by a single P–Me substituent stabilizes Tc(II) by about 4 mV. These effects, ranging from gross (>500 mV) to subtle (<5 mV), allow for the design of ^{99m}Tc radiopharmaceuticals wherein the Tc(III/II) redox potential is precisely controlled by manipulation of the properties of the ligands bonded to technetium.

Acknowledgment. Financial support by the National Institutes of Health, Grant No. CA-42179 (E.D.), as well as the University of Cincinnati Department of Chemistry, University Research Council, and University Dean's Distinguished Dissertation fellowship programs (B.E.W.) is gratefully acknowledged. The assistance of Dr. J. R. Kirchhoff is also gratefully acknowledged.

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