yield. Me_2CO was evaporated and the residue recrystallized from $CH_2Cl_2/EtOH$ to give the crude product in 30% yield. The yield of crude product was raised to 51% by running the above reactions at −25 °C. Chromatography (silica gel, $CHCl_3$) gave the pure product as the third fraction (R_f 0.34) following the corresponding $(PhOP(OC_6H_4\text{-}p\text{-}Me)_2)_2$ (R_f 0.82; ^{31}P NMR ($CDCl_3$) δ 59.7 ($^1J_{PtP}$ = 5797 Hz)) and $(PhOP(OC_6H_4\text{-}p\text{-}Cl)_2)_2$ (R_f 0.65; ^{31}P NMR ($CDCl_3$) δ 61.0 ($^1J_{PtP}$ = 5761 Hz)) complexes, which were identified by comparison of their R_f and ^{31}P NMR data with those of authentic samples prepared analogously.

Resolution of (±)-1. Halide exchange of *cis*-$Cl_2Pt[(\pm)\text{-}\mathbf{1}]_2$ to the corresponding diiodide was carried out by following a previously reported method.[19] Chromatography (silica gel, CH_2Cl_2) of the crude material gave the desired product in 88% yield (mp 130 °C; ^{31}P NMR (acetone-d_6) δ 59.6 ($^1J_{PtP}$ = 5496 Hz)). In 150 mL of dry C_6H_6 were dissolved 0.2000 g (0.2021 mmol) of *cis*-$I_2Pt[(+)\text{-}\mathbf{3}]_2$ (see Scheme I), 0.2357 g (0.2021 mmol) of *cis*-$I_2Pt[(\pm)\text{-}\mathbf{1}]_2$, and 0.002 g of (+)-**3**. The reaction mixture was refluxed for 10 h under N_2. The solution was then filtered and the solvent evaporated to yield a yellow powder, which was dissolved in a minimum of CH_2Cl_2 and chromatographed (70 g of silica gel, CH_2Cl_2) at a flow rate of 1.0 mL/min. Five-milliliter fractions were collected and monitored by TLC. Four different fractions were collected and identified by ^{31}P NMR spectroscopy (band 1 R_f 0.72, *cis*-$I_2Pt[(\pm)\text{-}\mathbf{1}]_2$, band 2 R_f 0.41, diastereomer **4a** (see Scheme I); ^{31}P NMR ($CDCl_3$) δ 64.8 ($^1J_{PtP}$ = 5869 Hz), 63.6 ($^1J_{PtP}$ = 5481 Hz); band 3 R_f 0.31, diastereomer **4b** (see Scheme I); ^{31}P NMR ($CDCl_3$) δ 66.6 ($^1J_{PtP}$ = 5852 Hz), 64.5 ($^1J_{PtP}$ = 5487 Hz); band 4 R_f 0.14, *cis*-$I_2Pt[(-)\text{-}\mathbf{3}]_2$). To a solution of 0.1020 g (0.08718 mmol) of one of the resolved diastereomeric complexes **4a** or **4b** dissolved in 75 mL of CH_2Cl_2 was added 0.0340 g (0.8728 mmol) of dry NaCN. The solution turned colorless immediately and was allowed to stir at room temperature overnight under N_2. The colorless precipitate was filtered and the solvent evaporated to yield a colorless oil, which was dissolved in a minimum of C_6H_6 and chromatographed (silica gel, C_6H_6), giving (+)-**1** or (−)-**1** in the first fraction (R_f 0.76; yield 40%; $[\alpha]^{25}{}_{589}$ +21.4 ($CHCl_3$), −18.6 ($CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 127.8) with (+)-**3** (F_f 0.09[12]) arriving in the second fraction.

PhOP(OEt)[$\overline{\mathrm{N(CH_2)_3C}}\mathrm{HCO_2Et}$] (5). To 3.979 g (20.41 mmol) of $PhOPCl_2$ in 1.0 L of Et_2O at 0°C were added dropwise over a period of 2 h a solution of 2.923 g (20.41 mmol) of ethyl L-prolinate and 2.067 g (20.41 mmol) of Et_3N in 75 mL of Et_2O and a solution of 0.9390 g (20.41 mmol) of EtOH and 2.067 g (20.41 mmol) of Et_3N in 100 mL of Et_2O. The amine hydrochloride, after filtration, washing, and drying, gave 97% of the expected amount. The solvent was evaporated to an oil, which was purified by chromatography (silica gel, 8:1 $C_6H_6/CHCl_3$) to give both diastereomers in a single fraction (^{31}P NMR ($CDCl_3$) δ 141.2, 139.9; MS *m/e* 311 (P^+) (calcd 311)). Efforts[13] to separate the diastereomers failed.

PhOP(OEt)[$\overline{\mathrm{N(CH_2)_3C}}\mathrm{HCO_2Et\}\cdot BH_3}$ (6). Under dry N_2, 1.774 g (5.705 mmol) of **5a,b** was dissolved in 175 mL of Et_2O. After this solution was cooled to 0 °C, a 1.0 M solution containing 6.848 mmol (20% stoichiometric excess) of $THF\cdot BH_3$ was added dropwise over a period of 10 min. The reaction was allowed to warm slowly to room temperature followed by evaporation of the solvent. The crude product was obtained as a viscous oil, which was purified by chromatography (silica gel, 9:1 $C_6H_6/CHCl_3$). Upon evaporation of the eluant, the diastereomeric product was obtained as a colorless oil (^{31}P NMR ($CHCl_3$) δ 73.3, 70.2) that resisted separation efforts.[14]

Acknowledgment. J.G.V. thanks the National Science Foundation for a grant in support of this research.

Registry No. (±)-**1**, 96455-46-8; (+)-**1**, 96455-47-9; (−)-**1**, 96455-48-0; (+)-**3**, 75045-93-1; **4** (isomer 1), 96455-53-7; **4** (isomer 2), 96553-61-6; **5a**, 96455-49-1; **5b**, 96481-06-0; **6a**, 96455-54-8; (±)-**1**, phosphate derivative, 96455-52-6; **6b**, 96553-62-7; *cis*-$Cl_2Pt[(\pm)\text{-}\mathbf{1}]_2$, 96455-55-9; *cis*-$I_2Pt[(\pm)\text{-}\mathbf{1}]_2$, 96455-56-0; *cis*-$Cl_2Pt(NCPh)_2$, 15617-19-3; *cis*-$I_2Pt[(+)\text{-}\mathbf{3}]_2$, 72316-69-9; $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)_2$, 96455-50-4; $P(OPh)(OC_6H_4\text{-}p\text{-}Me)_2$, 96455-51-5; $PhOPCl_2$, 3426-89-9; $HOC_6H_4\text{-}p\text{-}Cl$, 106-48-9; $HOC_6H_4\text{-}p\text{-}Me$, 106-44-5; ethyl L-prolinate, 5817-26-5.

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Technetium Electrochemistry. 3.[1] Spectroelectrochemical Studies on the Mixed-Ligand Technetium(III) Complexes *trans*-$[Tc(PR_2R')_2L]^+$ Where L Is a Tetradentate Schiff Base Ligand and PR_2R' Is a Monodentate Tertiary Phosphine Ligand

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The redox chemistry of a series of eight well-characterized, robust, cationic technetium(III) complexes of the general formula *trans*-$[Tc(PR_2R')_2L]^+$, where PR_2R' represents a monodentate tertiary phosphine with R and R' being ethyl and/or phenyl and L represents a tetradentate Schiff base ligand, has been investigated in propylene carbonate by using spectroelectrochemistry with a gold minigrid optically transparent thin-layer electrode. The *trans*-$[Tc(PR_2R')_2L]^+$ complexes undergo a reversible 1-equiv reduction of Tc(III) to Tc(II) and a reversible 1-equiv oxidation of Tc(III) to Tc(IV). $E^{\circ\prime}$ values for the Tc(III)/Tc(II) couple range from −1.11 to −0.69 V (vs. Ag/AgCl/NaCl (3 M)) while $E^{\circ\prime}$ values for the Tc(IV)/Tc(III) couple range from +0.62 to +0.79 V (vs. the same reference). The difference between $E^{\circ\prime}{}_{IV/III}$ and $E^{\circ\prime}{}_{III/II}$ ranges from 1.5 to 1.75 V, reflecting the large range of stability of the Tc(III) state. The formal potentials of both redox processes depend on the nature of the phosphine and Schiff base ligands. These dependencies are readily explained in terms of π back-bonding from low-valent technetium to both the phosphine and Schiff base ligands. All the technetium complexes, including the electrogenerated Tc(II) and Tc(IV) species, exhibit characteristic metal-to-ligand charge-transfer (MTLCT) bands in the visible region of the spectrum. The energies of these MTLCT transitions are a function of the oxidation state of the technetium, the nature of the phosphine ligands, and the nature of the Schiff base ligand. The energy of the Tc(III) MTLCT band is linearly related to the redox potential of the Tc(IV)/Tc(III) couple.

Introduction

We have been investigating the electrochemistry of technetium complexes[1,3-5] both in order to characterize the chemistry of this relatively unstudied element and also in order to understand the biological behavior of technetium-99m complexes developed for use in diagnostic nuclear medicine.[6-8] Of particular concern to

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Table I. Formal Redox Potentials and *n* Values for *trans*-$[Tc(PR_2R')_2L]^{2+/+/0}$ Couples in 0.5 M TEAP–Propylene Carbonate[a]

code	Tc(III) complex	Tc(III)/Tc(II) $E^{\circ\prime}$,[b] V (n[b])	Tc(IV)/Tc(III) $E^{\circ\prime}$,[c] V (ΔE_p,[e] mV)	$\Delta E^{\circ\prime}$,[d] V
1	*trans*-$[Tc(PEt_3)_2((acac)_2en)]^+$	−1.108 (0.92)	+0.634 (65)	1.742
2	*trans*-$[Tc(PEt_2Ph)_2((acac)_2en)]^+$	−1.037 (1.00)	+0.674 (66)	1.701
3	*trans*-$[Tc(PEtPh_2)_2((acac)_2en)]^+$	−0.946 (0.98)	+0.685 (67)	1.631
4	*trans*-$[Tc(PPh_3)_2((acac)_2en)]^+$	−0.889 (1.00)	+0.716 (68)	1.605
5	*trans*-$[Tc(PEtPh_2)_2((bzac)_2en)]^+$	−0.874 (0.96)	+0.748 (66)	1.622
6	*trans*-$[Tc(PEtPh_2)_2((buac)_2en)]^+$	−0.829[c,e] (64)[e,b]	+0.619 (66)	1.448
7	*trans*-$[Tc(PEtPh_2)_2((brac)_2en)]^+$	−0.751[c,f] (62)[e,g]	+0.774 (72)	1.525
8	*trans*-$[Tc(PEtPh_2)_2((sal)_2en)]^+$	−0.693 (0.93)	+0.787 (69)	1.480

[a] $E^{\circ\prime}$ is vs. Ag/AgCl/NaCl (3 M). [b] From a Nernstian plot using OTTLE spectropotentiostatic data. [c] $E^{\circ\prime} = (E_{p,a} + E_{p,c})/2$ from cyclic voltammetry on a pltainum-disk electrode. [d] $\Delta E^{\circ\prime} = E^{\circ\prime}_{IV/III} - E^{\circ\prime}_{III/II}$. [e] Peak separation in cyclic voltammetry with a scan rate of 100 mV/s. [f] Anomalous behavior prevents spectropotentiostatic analysis. [g] Low solubility prevents spectropotentiostatic analysis.

Table II. Spectrophotometric Data for *trans*-$[Tc(PR_2R')_2L]^{2+/+/0}$ Complexes[a]

	λ_{max}, nm (ϵ, cm^{-1} M^{-1})		
complex	Tc(II)	Tc(III)	Tc(IV)[b]
trans-$[Tc(PEt_3)_2((acac)_2en)]^{n+}$	478 (3410), 397 (3300)	580 (1330), 416 (4080), 404 sh (3780), 364 (2430)	576 (700), 406 (3300)
trans-$[Tc(PEt_2Ph)_2((acac)_2en)]^{n+}$	464 (5980), 395 (4500)	594 (2270), 412 (7000), 396 sh (6360), 363 (5670)	588 (1800), 408 (6300)
trans-$[Tc(PEtPh_2)_2((acac)_2en)]^{n+}$	460 (6870), 393 (8080)	598 (2960), 408 (7230), 392 sh (6630), 364 (6100)	602 (2400), 399 (4900)
trans-$[Tc(PPh_3)_2((acac)_2en)]^{n+}$	460 sh (4430), 410 (7120)	606 (2890), 406 (6610), 390 sh (6410), 367 (5980)	620 (2000), 386 (5500)
trans-$[Tc(PEtPh_2)_2((bzac)_2en)]^{n+}$	529 (8230), 434 (9130)	619 (2660), 463 (11 160), 444 (11 010), 364 sh (9100)	640 (2700), 460 (11 200)
trans-$[Tc(PEtPh_2)_2((buac)_2en)]^{n+}$	*c*	621 (1840), 384 sh (5300), 370 (5710)	*c*
trans-$[Tc(PEtPh_2)_2((brac)_2en)]^{n+}$	*d*	632, 418, 408, 378	*d*
trans-$[Tc(PEtPh_2)_2((sal)_2en)]^{n+}$	520 (8150), 444 (9220)	634 (3190), 452 (9490), 400 (7890), 340 (9400)	568 (2700), 360 sh (8300)

[a] From spectroelectrochemical experiments in 0.5 M TEAP–propylene carbonate using an OTTLE. sh = shoulder. [b] ϵ values are approximate because of slow decomposition of the Tc(IV) complexes. [c] Too unstable to obtain reliable data. [d] Too insoluble to obtain reliable data.

us has been the electrochemistry of cationic technetium complexes that might be useful as ^{99m}Tc heart-imaging agents. These complexes contain ligands such as phosphines, arsines, and isonitriles, which stabilize technetium in the lower oxidation states, particularly III, II, and I.[1,3-7] Conversion of one oxidation state to another perforce alters the net charge on the complex, and this in turn can drastically alter the biodistribution of the complex.[9] Many of the complexes investigated to date have redox potentials that are biologically accessible, and thus the biodistributions of these species may be strongly dependent on their electrochemical properties.

The class of cationic technetium complexes containing tertiary phosphine ligands appears to be especially promising for heart imaging, and members of this class exhibit a rich electrochemistry. In order to more readily vary the chemical and physical properties of these cationic phosphine-containing technetium agents, we have developed a new series of complexes containing both phosphine and tetradentate Schiff base ligands.[10] Our original electrochemical characterization of these mixed-ligand Tc(III) complexes was accomplished by cyclic voltammetry in acetonitrile using a glassy carbon electrode, but under these conditions only quasi-reversible waves were observed.[10] This current work is based on the subsequent observation that these complexes exhibit reversible electrochemical behavior in propylene carbonate on both platinum and gold electrodes. Using this fact, we have conducted a spectroelectrochemical study of a series of the title *trans*-$[Tc(PR_2R')_2L]^+$ complexes, and the results of this study are reported herein. The inherent efficiency of the spectroelectrochemical technique, using optically transparent thin-layer electrodes (OTTLE),[11] allows simultaneous acquisition of quantitative electrochemical and spectrochemical data on the very small amounts of these radioactive technetium-99 complexes that are available.

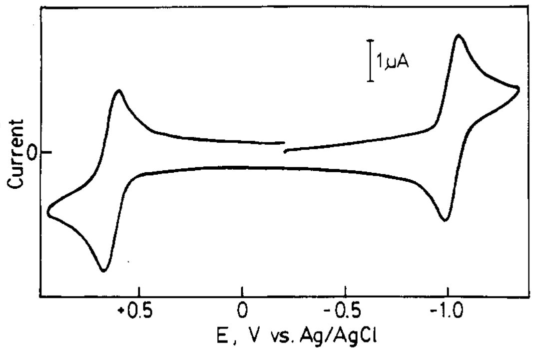

Figure 1. Cyclic voltammogram of 1.13 mM *trans*-$[Tc(PEt_2Ph)_2((acac)_2en)]^+$ in 0.5 M TEAP–propylene carboante (platinum electrode; scan rate 100 mV/s).

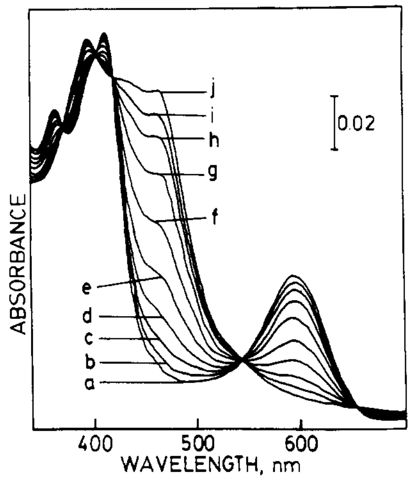

Figure 2. Spectra recorded during an OTTLE spectropotentiostatic experiment on 0.95 mM *trans*-$[Tc(PEt_2Ph)_2((acac)_2en)]^+$ in 0.5 M TEAP–propylene carbonate. Applied potentials in V vs. Ag/AgCl are as follows: (a) −0.800, (b) −0.960, (c) −0.980, (d) −1.000, (e) −1.020, (f) −1.040, (g) −1.060, (h) −1.080, (i) −1.100, (j) −1.300.

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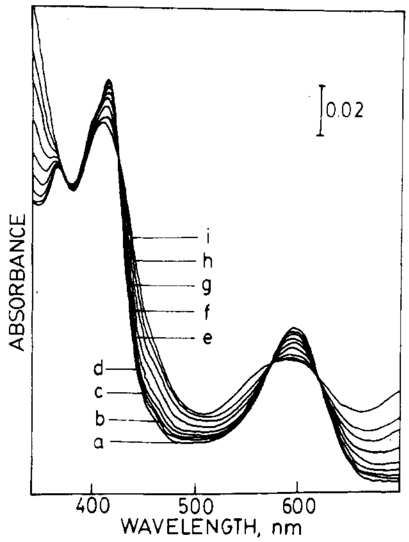

Figure 3. Spectra recorded during an OTTLE spectropotentiostatic experiment on 0.95 mM *trans*-[Tc(PEt$_2$Ph)$_2$((acac)$_2$en)]$^+$ in 0.5 M TEAP–propylene carbonate. Applied potentials in V vs. Ag/AgCl are as follows: (a) +0.400, (b) +0.560, (c) +0.580, (d) +0.600, (e) +0.620, (f) +0.640, (g) +0.660, (h) +0.680, (i) +0.900.

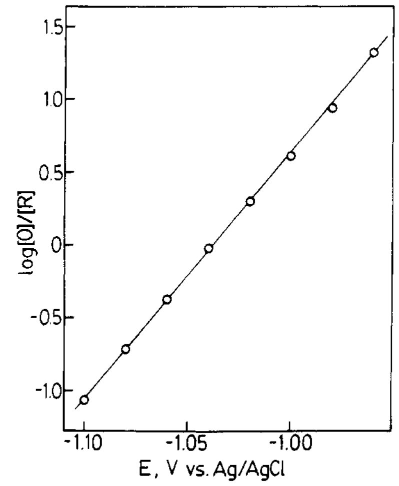

Figure 4. Nernstian plot of 464-nm data from Figure 2.

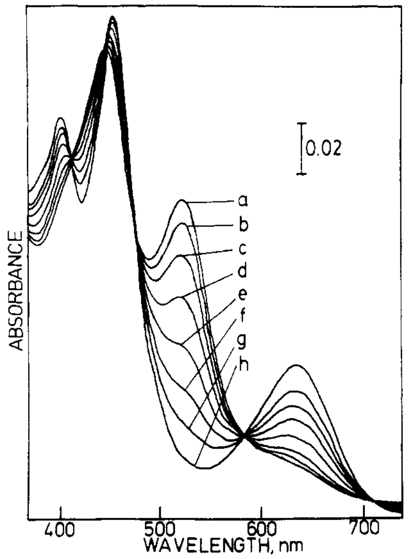

Figure 5. Spectra recorded during an OTTLE spectropotentiostatic experiment on 0.9 mM *trans*-[Tc(PEtPh$_2$)$_2$((sal)$_2$en)]$^+$ in 0.5 M TEAP–propylene carbonate. Applied potentials in V vs. Ag/AgCl are as follows: (a) −0.780, (b) −0.760, (c) −0.740, (d) −0.720, (e) −0.700, (f) −0.680, (g) −0.660, (h) −0.500.

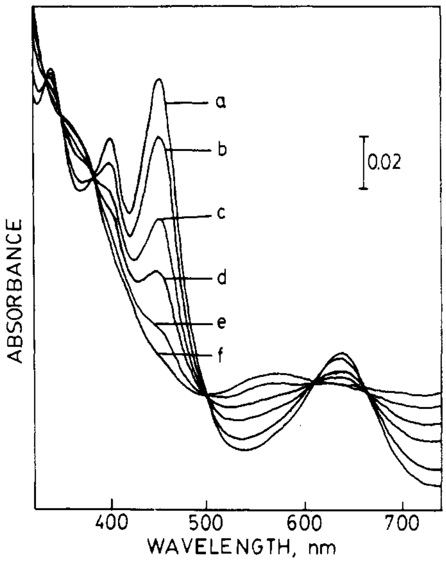

Figure 6. Spectra recorded during an OTTLE spectropotentiostatic experiment on 0.8 mM *trans*-[Tc(PEtPh$_2$)$_2$((sal)$_2$en)]$^+$ in 0.5 M TEAP–propylene carbonate. Applied potentials in V vs. Ag/AgCl are as follows: (a) +0.600, (b) +0.760, (c) +0.790, (d) +0.820, (e) +0.850, (f) +1.000.

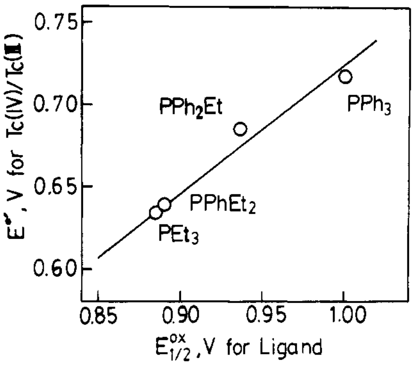

Figure 7. Correlation of $E^{\circ\prime}$ for the *trans*-[Tc(PR$_2$R′)$_2$((acac)$_2$en)]$^{2+/+}$ couple with the half-wave potential for the oxidation of PR$_2$R′.

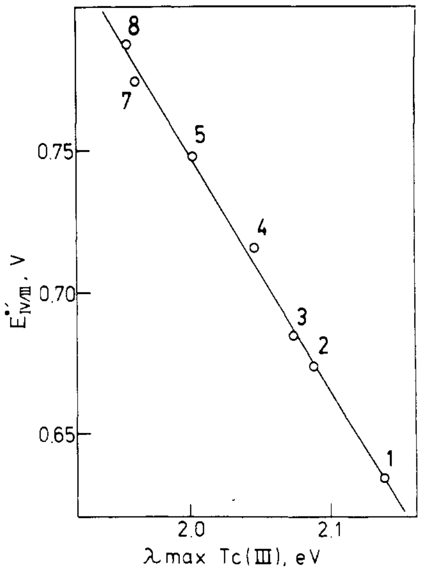

Figure 8. Plot of $E^{\circ\prime}$ for the reversible Tc(IV)/Tc(III) couple in V vs. the energy of the MTLCT (metal-to-ligand charge-transfer) transition of the Tc(III) complex in eV. Coding of entries is given in Table I.

Acronyms and Abbreviations

L = tetradentate Schiff base ligand

(acac)$_2$en = *N*,*N*′-ethylenebis(acetylacetone iminato), [CH$_3$—C(O$^-$)═CH—C(CH$_3$)═N—CH$_2$–]$_2$

$(\mathrm{buac})_2\mathrm{en}$ = *N*,*N'*-ethylenebis(*tert*-butyl acetoacetone iminato), $[(\mathrm{CH_3})_3\mathrm{CO{-}C(O^-){=}CH{-}C(CH_3){=}N{-}CH_2{-}}]_2$
$(\mathrm{bzac})_2\mathrm{en}$ = *N*,*N'*-ethylenebis(benzoylacetone iminato), $[\mathrm{C_6H_5{-}C(O^-){-}{-}CH{-}C(CH_3){=}N{-}CH_2{-}}]_2$
$(\mathrm{brac})_2\mathrm{en}$ = *N*,*N'*-ethylenebis(3–bromoacetoacetone iminato), $[\mathrm{CH_3{-}C(O^-){=}C(Br){-}C(CH_3){=}N{-}CH_2{-}}]_2$
$(\mathrm{sal})_2\mathrm{en}$ = *N*,*N'*-ethylenebis(salicylideneaminato), $[o\text{-}(\mathrm{O^-})\mathrm{C_6H_4{-}CH{=}N{-}CH_2{-}}]_2$
Et = ethyl
Ph = phenyl
TEAP = tetraethylammonium perchlorate
OTTLE = optically transparent thin-layer electrode
MTLCT = metal-to-ligand charge transfer

Experimental Section

General Information. Technetium-99 emits a low-energy (0.292-MeV) β particle with a half-life of 2.15×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard 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 to prevent contamination and inadvertent ingestion.

Reagents. Unless otherwise noted, all chemicals were of reagent grade. The *trans*-$[\mathrm{Tc(PR_2R')L}]\mathrm{PF_6}$ complexes were available from a previous study.[10] Propylene carbonate (Burdick and Jackson) and polarographic grade TEAP (G. F. Smith), dried over $\mathrm{P_2O_5}$ in vacuo at 60 °C, were used in electrochemical measurements. No significant electrochemical impurities were detected in either the solvent or the supporting electrolyte.

Apparatus and Instrumentation. Electrochemical measurements were made with a Bioanalytical System Inc. (BAS) CV-1A instrument. Potentials were monitored with a Keithley 178 digital multimeter. Visible spectra were recorded on a Cary 210 spectrophotometer, the cell compartment of which was modified to accommodate electrical leads and an inert-gas inlet. The working electrode for conventional cyclic voltammetry was a platinum-disk electrode (BAS, MF2013) with a surface area of 0.0244 cm^2 as determined by chronoamperometry of a standard potassium ferricyanide solution. OTTLE's were constructed with a 500 wire/in. gold minigrid as previously described.[12] The cell volume and the optical thickness were calibrated by coulometry and spectrophotometry and were 38 μL and 0.023 cm, respectively. An aqueous Ag/AgCl/NaCl (3 M) electrode (BAS, MF2020)[13] and a platinum wire were used as reference and auxilliary electrodes, respectively. The Ag/AgCl/NaCl (3 M) electrode was isolated from the solution by a porous Vycor plug. All potentials reported here are vs. the Ag/AgCl/NaCl (3 M) electrode.

Procedures. Experiments were generally conducted as previously described.[1,14] Each spectrum in the spectropotentiostatic experiments was recorded 5 min after potential application. This time was found to be sufficient to attain equilibrium values of [O]/[R].

Results

All the *trans*-$[\mathrm{Tc^{III}(PR_2R')_2L}]^+$ complexes studied herein undergo both reduction to Tc(II) and oxidation to Tc(IV) in propylene carbonate containing 0.5 M TEAP. Figure 1 shows a typical bulk solution cyclic voltammogram on a platinum electrode for *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^+$. A negative-potential scan initiated at −0.2 V reveals a reduction wave with a peak potential of −1.046 V. Upon reversal of the scan at −1.35 V, an oxidation wave with a peak potential of −0.986 V is observed. Continuing the scan in the positive direction results in an oxidation wave with a peak potential of +0.671 V. After scan reversal at +0.95 V, a reduction wave with a peak potential of +0.605 V is observed. Both reduction and oxidation processes are shown to be reversible 1-equiv electrochemical reactions from the spectroelectrochemical results presented below and the observations that (1) the peak currents are proportional to the square root of the scan rate, (2) the ratios of anodic peak current to cathodic peak current 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. Both redox couples were monitored by thin-layer cyclic voltammetry at a scan rate of 2 mV/s, confirming that the electrode reaction products *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^0$ and *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^{2+}$ are sufficiently stable to be studied by the spectropotentiostatic method. Spectra recorded for the reversible *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^{+/0}$ and *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^{2+/+}$ couples during a spectropotentiostatic experiment in the OTTLE are shown in Figures 2 and 3, respectively. For the Tc(III)/Tc(II) couple the Tc(III) complex exhibits absorption maxima at 594, 412, and 363 nm and a shoulder at 396 nm. These absorption maxima, determined in propylene carbonate, are in fair agreement with those previously observed for the Tc(III) complex in methanol.[10] The Tc(II) complex exhibits absorption maxima at 464 and 395 nm; five isosbestic points are seen in the visible region. Nernstian plots for the 594- and 464-nm data in Figure 2 yield $E°' = -1.037$ V and $n = 1.00$; a Nernstian plot for the 464-nm data is shown in Figure 4. For the Tc(IV)/Tc(III) couple the Tc(IV) complex exhibits absorption maxima at 588 and 408 nm, and isosbtic points are seen at 619, 573, 423, and 368, nm, respectively. A Nernstian plot of the 452-nm data gives $E°' = +0.637$ V and $n = 1.06$.

Other examples of the spectropotentiostatic experiments are shown in Figures 5 and 6 for the *trans*-$[\mathrm{Tc(PEtPh_2)_2((sal)_2en)}]^{+/0}$ and *trans*-$[\mathrm{Tc(PEtPh_2)_2((sal)_2en)}]^{2+/+}$ couples, respectively. A Nernstian plot for the 634-nm data in Figure 5 yields $E°' = -0.693$ V and $n = 0.93$ for the Tc(III)/Tc(II) couple, and a plot for the 452-nm data in Figure 6 yields $E°' = +0.794$ V and $n = 0.99$ for the Tc(IV)/Tc(III) couple.

As noted above, all the technetium complexes exhibit chemically and electrochemically reversible Tc(III)/Tc(II) and Tc(IV)/Tc(III) couples in bulk solution cyclic voltammetry on a platinum electrode. Also, the spectropotentiostatic experiment shows that all of the Tc(III)/Tc(II) couples, except for one of limited solubility and one of anomalous behavior, exhibit Nernstian behavior. However, the spectropotentiostatic experiment can be successfully conducted for only the three Tc(IV)/Tc(III) couples *trans*-$[\mathrm{Tc(PEt_3)_2((acac)_2en)}]^{2+/+}$, *trans*-$[\mathrm{Tc(PEt_2Ph)_2((acac)_2en)}]^{2+/+}$, and *trans*-$[\mathrm{Tc(PEtPh_2)_2((sal)_2en)}]^{2+/+}$) because of the inherent instability of the Tc(IV) complexes. All of the Tc(IV) complexes decompose slowly, the stability of individual *trans*$[\mathrm{Tc(PR_2R')_2L}]^{2+}$ species being strongly dependent on the nature of the phosphine and Schiff base ligands.

Electrochemical results are summarized in Table I, while spectrophotometric parameters for the Tc(II), Tc(III), and Tc(IV) complexes are given in Table II.

Discussion

General Electrochemistry. Propylene carbonate was chosen as the solvent for these spectroelectrochemical studies primarily because it provides sufficient solubility for the three *trans*-$[\mathrm{Tc(PR_2R')_2L}]^{n+}$ (n = 0, 1, 2) species. In addition, the *trans*–$[\mathrm{Tc^{III}(PR_2R')_2L}]^+$ complexes are more stable in this solvent than they are in acetonitrile or *N*,*N*-dimethylformamide. When the Tc(III) species are dissolved in these latter solvents, the color of the resulting solution changes (immediately in *N*,*N*-dimethylformamide and gradually in acetonitrile) from intense green to red. However, in propylene carbonate the characteristic green color of the technetium(III) complexes does not fade, presumably because this solvent is less basic and has less tendency to displace the phosphine ligands. In propylene carbonate the *trans*-$[\mathrm{Tc^{III}(PR_2R')_2L}]^+$ complexes undergo both an oxidation and a reduction, corresponding to the reversible one-electron conversion of Tc(III) to Tc(IV) (eq 1) and the reversible one-electron conversion of Tc(III) to Tc(II) (eq 2), respectively. The $E°'$ values

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

$$[\mathrm{Tc^{III}(PR_2R')_2L}]^+ + e^+ \rightarrow [\mathrm{Tc^{II}(PR_2R')_2L}]^0 \qquad (2)$$

of both electrochemical reactions monitored in propylene carbonate (Table I) nicely correlate with those values determined in acetonitrile on a glassy-carbon electrode,[10] although under these latter conditions[10] both processes are only quasireversible. The average difference in the $E°'$ values determined under the two sets of conditions is 50 mV; this most probably reflects the difference in liquid-junction potentials since the $E°'$ value of the ferrocenium/ferrocene couple exhibits a similar difference when measured

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(13) The potential of this electrode is 0.201 V relative to the NHE.
(14) Rohrbach, D. F.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 2536.

in these media (+0.371 V in 0.5 M TEAP–propylene carbonate vs. +0.417 V in 0.1 M TEAP–acetonitrile).

Effect of L and PR_2R' on $E^{\circ\prime}$. Both the L and PR_2R' ligands of the *trans*-$[Tc(PR_2R')_2L]^{2+/+/0}$ complexes strongly affect the $E^{\circ\prime}$ values governing the Tc(IV)/Tc(III) and Tc(III)/Tc(II) couples. The general patterns of these dependencies have been qualitatively described by using the previously available data.[10] In the paragraphs below, these patterns are quantitatively discussed by using the more reliable data of Table I.

(1) Considering complexes with a common Schiff base ligand but variable phosphine ligands (e.g. the four species *trans*-$[Tc(PR_2R')_2((acac)_2en)]^+$ with R and R′ being ethyl and phenyl), for phosphine ligands containing more phenyl groups, the Tc(III) complexes are more easily reduced to Tc(II) but are more difficult to oxidize to Tc(IV). This occurs because the phenyl-substituted phosphines are better π acids and therefore better stabilize the electron-rich Tc(II) state, while the alkyl-substituted phosphines are stronger σ donors, which better stabilize the electron-poor Tc(IV) state. The σ-donating properties of the various phosphine ligands can also be gauged by the tendency of the noncoordinated ligands to be oxidized, and it is well-known that alkyl-substituted phosphines are stronger reductants than phenyl-substituted phosphines. Indeed, Figure 7 shows that the half-wave potential for the oxidation of the free phosphine ligand (measured on a carbon-paste electrode in acetonitrile containing 0.1 M $NaClO_4$[15]) increases with increasing phenyl substitution and that this increase is linearly related to the increase observed in the $E^{\circ\prime}$ value of the Tc(IV)/Tc(III) couple of *trans*-$[Tc(PR_2R')_2((acac)_2en)]^{2+/+}$ as phenyl substitution on PR_2R' is increased. Viewed from another perspective, increasing the number of alkyl substituents on a phosphine ligand increases the σ-electron density on the phosphorus atom, thus making the noncoordinated ligand easier to oxidize and making the Tc(III) adduct easier to oxidize to the Tc(IV) state.

(2) Considering complexes with a common phosphine ligand but variable Schiff base ligands (e.g. the *trans*-$[Tc(PEtPh_2)_2L]^+$ complexes of Table I), the Tc(III) complexes with the better π-accepting Schiff ligands are easier to reduce and more difficult to oxidize. This is easily understood in terms of greater ligand π-acid character favoring the three oxidation states in the order IV < III < II, i.e. in the order of increasing metal π-electron density. Of the complexes studied, *trans*-$[Tc(PEtPh_2)_2((sal)_2en)]^+$ is the easiest to reduce and the most difficult to oxidize, and thus $(sal)_2en$ ligand appears to provide the maximum amount of π-electron delocalization in these systems.

(3) Variation of the phosphine ligands of *trans*-$[Tc(PR_2R')_2((acac)_2en)]^+$ leads to an excursion of 0.219 V in the $E^{\circ\prime}$ values governing the Tc(III)/Tc(II) couple but only an excursion of 0.082 V in the $E^{\circ\prime}$ values governing the Tc(IV)/Tc(III) couple. Similarly, variation of the L ligand of *trans*-$[Tc(PEtPh_2)_2L]^+$ leads to an excursion of 0.235 V in the $E^{\circ\prime}$ value governing the Tc(III)/Tc(II) couple but only an excursion of 0.102 V in the $E^{\circ\prime}$ values governing the Tc(IV)/Tc(III) couple. Thus, the Tc(III)/Tc(II) interconversion is more sensitive to variations in L and PR_2R' than is the Tc(IV)/Tc(III) interconversion. This is entirely as expected within the tenet that π back-bonding is the dominant electronic interaction that distinguishes closely related low-valent metal complexes, since among the three related *trans*-$[Tc(PR_2R')_2L]^{2+/+/0}$ species the Tc(II) complex enjoys the greatest metal–ligand π interactions while the Tc(IV) species has the least such interactions.

(4) For all complexes, except that of $(buac)_2en$, ligand-dependent variations in the $E^{\circ\prime}$ of the Tc(III)/Tc(II) couple ($E^{\circ\prime}{}_{III/II}$) are tracked by variations in the $E^{\circ\prime}$ of the Tc(IV)/Tc(III) couple ($E^{\circ\prime}{}_{IV/III}$). (The anomalous behavior of the $(buac)_2en$ complex has been noted previously[10] and is not yet understood.) However, since $E^{\circ\prime}{}_{III/II}$ is more sensitive to ligand variations than is $E^{\circ\prime}{}_{IV/III}$ (vide supra), the difference in $E^{\circ\prime}$ values ($\Delta E^{\circ\prime} = E^{\circ\prime}{}_{IV/III} - E^{\circ\prime}{}_{III/II}$) is not constant but rather systematically decreases as $E^{\circ\prime}{}_{III/II}$ becomes more positive (Table I). Thus, $\Delta E^{\circ\prime}$, which reflects the range of stability of the Tc(III) complex, is maximized by ligands that have minimum π-acid character since this property makes the Tc(III) complex most difficult to reduce. For the complexes studied, $\Delta E^{\circ\prime}$ is largest (at the remarkable potential exercusion of 1.74 V) for *trans*-$[Tc(PEt_3)_2((acac)_2en)]^+$ since both PEt_3 and $(acac)_2en$ are each the poorest π acid among the two classes of ligands investigated.

Effect of L and PR_2R' on Complex Stability. The stabilities of the electrogenerated Tc(II) and Tc(IV) complexes also depend on the nature of PR_2R' and L. All of the Tc(II) complexes investigated, except for *trans*-$[Tc(PEtPh_2)_2((buac)_2en)]^0$, are sufficiently stable (independent of PR_2R' or L) to study by spectroelectrochemical methods using the OTTLE. However, the Tc(IV) complexes are less stable than are the corresponding Tc(II) species. Spectroelectrochemical experiments on the *trans*-$[Tc(PR_2R')_2L]^{2+/+}$ couples exhibit good isosbestic points for complexes with PR_2R' = PEt_3 or PEt_2Ph, but for complexes with PR_2R' = $PEtPh_2$ or PPh_3 the isosbestic points are not maintained with time. In general, for the series of *trans*-$[Tc(PR_2R')((acac)_2en)]^{2+}$ complexes, the stability of the Tc(IV) species increases with increasing numbers of ethyl groups on the phosphine ligands presumably because of the enhanced σ-donating ability of alkylphosphines relative to that of arylphosphines. For the series of *trans*-$[Tc(PEtPh_2)_2L]^{2+}$ complexes only *trans*-$[Tc(PEtPh_2)_2((sal)_2en)]^{2+}$ is sufficiently stable to allow the spectropotentiostatic experiment to be conducted on the Tc(IV)/Tc(III) couple.

Visible–UV Spectra. Table II lists the characteristic absorptions associated with each of the *trans*-$[Tc(PR_2R')_2L]^{n+}$ (n = 0, 1, and 2) complexes. Because of the high intensities ($\epsilon > 10^3\ M^{-1}\ cm^{-1}$) associated with these absorptions, they are all assumed to arise from charge-transfer (CT) transitions. Data for the Tc(II) and Tc(IV) complexes were not available in our previous study[10] and have been acquired herein through application of the spectroelectrochemical technique.

The lowest energy band observed for the Tc(III) complexes has been assigned[10] as a metal-to-ligand charge-transfer (MTLCT) transition since the energy of this band increases with increasing electron-donating ability of both L and PR_2R'. The acceptor orbital involved in this transition could be located on either the phosphine or Schiff base ligand since the energy of the absorption is dependent on both L and PR_2R'. For five of the six Tc(IV) complexes investigated, the absorption maximum of the lowest energy band is linearly correlated with that of the Tc(III) analogue. This implies that the energy band of the Tc(IV) complexes also arises from a MTLCT transition. However, the nature of this CT transition must change over the series of complexes since (a) the $(sal)_2en$ complex does not follow the above correlation and (b) for some complexes the energy of the Tc(IV) CT is greater than that of the corresponding Tc(III) MTLCT, while for other complexes the opposite is true. It is possible that in one portion of the series one or the other MTLCT terminates in a PR_2R' orbital while in other portions of the series this MTLCT terminates in a Schiff base orbital.

The lowest energy band of the Tc(II) complexes does *not* track the lowest energy band of the Tc(III) complexes but does correlate with the *second* lowest energy band of the Tc(III) complexes. In fact, this correlation is linear with unit slope; on average the energy of the Tc(II) transition is 2850 ± 150 cm^{-1} lower in energy than that of the correlated Tc(III) transition. The energy of this Tc(II) band (and therefore the energy of the correlated Tc(III) band) does not depend strongly on the nature of the PR_2R' ligand but does depend on the nature of the Schiff base ligand. Taken together, these several observations strongly imply that the lowest energy Tc(II) band and the second lowest energy Tc(III) band arise from the same metal-to-Schiff base charge-transfer transition.

Relationship between $E^{\circ\prime}$ and MTLCT Energy. Since charge-transfer transitions involve a formal oxidation or reduction of the metal center, the energies of these processes are related to the redox potential of the complex. If, for a series of related complexes, the contribution of the ligand to the charge-transfer transition either remains constant or can be taken into account,

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then the energy of the charge-transfer process should depend linearly on the redox potential of the complex. Such linear relationships have been reported for ligand-to-metal charge-transfer (LTMCT) transitions in both technetium[4] and ruthenium[16] complexes, as well as in a series of tris(bipyridyl) complexes of several metals.[17,18] Figure 8 shows that a linear relationship (correlation coefficient 0.997, slope −0.83) also holds for the MTLCT transition of the Tc(III) complexes (except for the anomalous $(buac)_2en$ material). The MTLCT process in these complexes involves formal oxidation of Tc(III) to Tc(IV), and indeed the redox potential of the Tc(IV)/Tc(III) couple is linearly related to the energy of this process.

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Registry No. **1**, 96429-92-4; **1**$^+$, 93426-97-2; **1**$^{2+}$, 96429-97-9; **2**, 96429-93-5; **2**$^+$, 93426-99-4; **2**$^{2+}$, 96429-98-0; **3**, 96429-94-6; **3**$^+$, 93427-01-1; **3**$^{2+}$, 96429-99-1; **4**, 96429-95-7; **4**$^+$, 93427-03-3; **4**$^{2+}$, 96430-00-1; **5**, 96429-96-8; **5**$^+$, 93427-05-5; **5**$^{2+}$, 96430-01-2; **6**, 93453-71-5; **6**$^+$, 93453-71-5; **6**$^{2+}$, 96430-02-3; **7**, 96444-60-9; **7**$^+$, 93427-07-7; **7**$^{2+}$, 96430-03-4; **8**, 96444-61-0; **8**$^+$, 93427-09-9; **8**$^{2+}$, 96444-62-1; Au, 7440-57-5; TEAP, 2567-83-1; Pt, 7440-06-4.

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Electrochemistry and Spectroelectrochemistry of Indium(III) Porphyrins. Reactions of Five-Coordinate σ-Bonded Complexes

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The electrochemistry, NMR spectroscopy, and UV–visible spectroscopy of 16 different In(III) porphyrins with σ-bound alkyl or aryl groups were investigated in nonaqueous media. The ligands σ bonded to indium(III) octaethylporphyrins or tetraphenylporphyrins included simple alkyl groups such as CH_3 or C_2H_5 and aryl groups such as C_6H_5, $C_2H_2C_6H_5$, or $C_2C_6H_5$. All of the compounds could be oxidized or reduced by multiple single-electron-transfer steps in which the initial step yields $[(P)In(R)]^+$ or $[(P)In(R)]^-$, where P represents the porphyrin macrocycle and R is one of the σ-bonded ligands. In all cases, the singly reduced compound is stable. In contrast, the singly oxidized compounds undergo a metal–carbon bond cleavage, the rate of which depended upon the electron-donating properties of the axial ligand. The electron-donating properties of the σ-bonded ligand also influence the electronic absorption spectra and the ^{1}H NMR spectra of the neutral compounds, and linear free energy relationships with ^{1}H NMR shifts or ratios of molar absorptivities in the UV–visible spectra were obtained. Not surprisingly, complexes containing the $C_2C_6H_5$ group did not fit these trends, and the physical properties of these complexes more closely resembled those of the indium(III) porphyrins axially bound by ionic ligands such as Cl^-, ClO_4^-, or PF_6^-. Finally, comparisons between the electrochemical reactivities of the σ-bonded complexes and their physicochemical properties are discussed in terms of the general stability of the indium–carbon σ bond.

Introduction

Metal–alkyl (or –aryl) σ-bonded porphyrins are of considerable interest as model compounds for understanding the function and reactivity of several biological macromolecules. From this point of view, the syntheses of numerous iron,[2-11] cobalt,[2,12-17] and rhodium[18-26] porphyrins as well as other metalloporphyrins containing a metal–carbon σ bond have been described.[27-31]

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