

# Synthesis and Characterization of Mixed-Ligand Technetium(II) Complexes Containing Halides, Phosphines, and either 2,2'-Bipyridine, 1,10-Phenanthroline, or 2,2':6',2''-Terpyridine. X-ray Crystal Structures of *cis* (Cl), *trans* (P)-[TcCl<sub>2</sub>(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(phen)] and *trans* (P)-[TcBr(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub><sup>1</sup>

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Technetium(II) complexes of the general formula *cis*(X),*trans*(P)-[TcX<sub>2</sub>(PR<sub>2</sub>R')<sub>2</sub>L], where X = Cl or Br, PR<sub>2</sub>R' = dimethylphenylphosphine or ethyldiphenylphosphine, and L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), have been synthesized and characterized. They are prepared by replacement of one halide and one phosphine ligand of *mer*-TcX<sub>3</sub>(PR<sub>2</sub>R')<sub>3</sub> by the bidentate L ligand in refluxing ethanol, followed by reduction to the Tc(II) oxidation state and precipitation from solution by the addition of aqueous hydroxide. Additionally, related technetium(II) complexes of the general formula *trans*(P)-[TcX(PR<sub>2</sub>R')<sub>2</sub>(terpy)]<sup>+</sup>, where terpy = 2,2':6',2''-terpyridine, have been synthesized and characterized. They are prepared by terpy substitution onto and displacement of one phosphine and two halide ligands from *mer*-TcX<sub>3</sub>(PR<sub>2</sub>R')<sub>3</sub> in refluxing ethanol with concomitant reduction of Tc(III) to Tc(II). Evidence suggests a two-step synthetic process wherein the terpy ligand first displaces one halide and one phosphine moiety to form a Tc(III) complex in which terpy functions as a bidentate ligand, followed by subsequent displacement of the second halide ligand with coordination of the third heterocyclic nitrogen of the terpy ligand and reduction to the Tc(II) state. All of the complexes have been characterized by elemental analyses of prototypes, by UV-visible spectrophotometry, and by fast atom bombardment mass spectrometry in the positive ion mode. These "fingerprint" mass spectra exhibit peaks assigned to the molecular ion as well as peaks resulting from the loss of one or more monodentate ligands from the molecular ion. A single-crystal X-ray structure determination for *cis*(Cl),*trans*(P)-[TcCl<sub>2</sub>(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(phen)], formula weight 626.41, shows that the technetium(II) center resides in a distorted octahedral environment. This complex crystallizes in the tetragonal space group P4<sub>1</sub>2<sub>1</sub>2 with *a* = *b* = 10.666 (2) Å, *c* = 24.610 (4) Å, and *V* = 2799.4 (9) Å<sup>3</sup>, with *Z* = 4 for 1635 observed reflections with *F* > 3σ(*F*). The single-crystal X-ray structure determination for *trans*(P)-[TcBr(P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub>, formula weight 837.54, shows that this complex, which also contains technetium(II) in a distorted-octahedral coordination environment, crystallizes in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with *a* = 18.975 (3) Å, *b* = 19.336 (4) Å, *c* = 9.615 (1) Å, and *V* = 3527.7 (8) Å<sup>3</sup>, with *Z* = 4 for 3462 observed reflections with *F* > 3σ(*F*).

## Introduction

We have recently reported on the synthesis and characterization of mixed-ligand technetium(III) complexes containing 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands.<sup>3</sup> Prior to this report, polypyridyl complexes of technetium had been known only when the Tc center was in an oxidation states of +4 or higher.<sup>4,5</sup> These new Tc(III) complexes are of the form *cis*(X),*trans*(P)-[TcX<sub>2</sub>(PR<sub>2</sub>R')<sub>2</sub>L]<sup>+</sup> (where X represents Cl or Br, PR<sub>2</sub>R' represents dimethylphenylphosphine or ethyldiphenylphosphine and L represents bpy, 4,4'-Me<sub>2</sub>bpy, or phen). During this initial study it was observed that several of the technetium(II) analogues of these Tc(III) complexes were synthetically accessible by slight modifications of the procedures for the preparation of the Tc(III) species. Moreover, the Tc(II) analogues could also be generated electrochemically from the Tc(III) parents.<sup>6</sup> This paper details the synthesis and characterization of these Tc(II) *cis*(X),*trans*(P)-[TcX<sub>2</sub>(PR<sub>2</sub>R')<sub>2</sub>L]<sup>0</sup> complexes, as well as of related Tc(II) species containing 2,2':6',2''-terpyridine, and thus extends considerably our knowledge of low-valent technetium-polypyridyl complexes.

## Abbreviations

bpy = 2,2'-bipyridine

phen = 1,10-phenanthroline

Me<sub>2</sub>bpy = 4,4'-dimethyl-2,2'-bipyridine

terpy = 2,2':6',2''-terpyridine

PMe<sub>2</sub>Ph = dimethylphenylphosphinePEtPh<sub>2</sub> = ethyldiphenylphosphineDPPE = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>DMPE = (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>

Ph = phenyl

Me = methyl

Et = ethyl

## Experimental Section

**Materials.** All references to technetium in this paper are to the specific isotope <sup>99</sup>Tc, which was obtained as NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> from Oak Ridge National Laboratories. Technetium-99 emits a low-energy (0.292 MeV) β particle with a half-life of 2.12 × 10<sup>5</sup> 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, especially when dealing with solid samples, to prevent contamination and inadvertent inhalation. NH<sub>4</sub>TcO<sub>4</sub> was dissolved in water and then treated with a small amount of 30% H<sub>2</sub>O<sub>2</sub> (Fisher) to oxidize any TcO<sub>2</sub> impurity to pertechnetate.

All solvents and reagents used were of reagent grade. Dimethylphenylphosphine and ethyldiphenylphosphine (Strem Chemicals) and 2,2'-bipyridine (Aldrich), 1,10-phenanthroline, and 2,2':6',2''-terpyridine (GFS Chemicals) were used as received. The technetium(III) starting materials *mer*-TcCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>, *mer*-TcBr<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> and *mer*-TcCl<sub>3</sub>(PEtPh<sub>2</sub>)<sub>3</sub> were prepared as previously reported.<sup>7</sup> Chromatographic separations were performed on Sephadex LH-20 lipophilic resin (Pharmacia).

**Physical Measurements.** UV-visible spectra were recorded on a Cary 210 spectrophotometer (Varian Instruments) in acetonitrile solutions.

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**Table I.** Crystallographic Data for *cis*(Cl),*trans*(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)] (1) and *trans*(P)-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> (2)

	1	2
chem formula	TcC <sub>28</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub>	TcC <sub>32</sub> H <sub>33</sub> BrN <sub>3</sub> O <sub>3</sub> P <sub>2</sub> SF <sub>3</sub>
fw	626.41	837.54
space group	P4 <sub>1</sub> 2 <sub>1</sub> 2 (No. 92)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
a, Å	10.666 (2)	18.975 (3)
b, Å	10.666 (2)	19.336 (4)
c, Å	24.610 (4)	9.615 (1)
α = β = γ, deg	90	90
V, Å <sup>3</sup>	2799.4 (9)	3527.7 (8)
Z	4	4
T, °C	21	21
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.49	1.58
μ, cm <sup>-1</sup>	7.82	16.72
transm coeff	0.563–0.609	0.779–1.000
R(F <sub>o</sub> )	0.0481	0.0625
R <sub>w</sub> (F <sub>o</sub> ) <sup>a</sup>	0.0646 <sup>b</sup>	0.0408 <sup>c</sup>

<sup>a</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = [\sigma^2(F) + |g|(F)^2]^{-1}$ . <sup>b</sup>  $g = 0.000 524$ . <sup>c</sup>  $g = 0.000 100$ .

Mass spectra were recorded on a VG 30–250 quadrupole mass spectrometer (VG Masslab) with a fast atom bombardment (FAB) ionization source using xenon as the bombardment gas. Samples for mass analysis were prepared by dissolving or suspending solid samples in one of the following matrices: glycerol (Fisher), "Magic Matrix" (5:1 w/w dithiothreitol–dithioerythritol (Sigma Chemicals) with a small amount of methanol), or *m*-nitrobenzyl alcohol (Kodak). For mass analysis of chromatographic bands, portions of the fractions were allowed to evaporate to dryness in a depression of a spot plate and then were mixed with the matrix by using a glass pestle. For chromatographic bands that were very diffuse or that contained small amounts of material, it was often necessary to allow several portions to evaporate in the same depression in order to accumulate sufficient material for analysis. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Synthesis of Complexes.** *cis*(Cl),*trans*(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(bpy)] and Analogues. *mer*-TcCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (168 mg, 0.271 mmol) was dissolved in 20 mL of ethanol in a round-bottom flask. The solution was purged with nitrogen, and 209 mg (1.34 mmol) of bpy was added. The mixture was refluxed under nitrogen for 1 h. After the mixture had cooled, 10 mL of 0.1 M aqueous NaOH was added. The color of the solution turned immediately from red/purple to green, and a green precipitate slowly formed. The precipitate was collected by suction filtration, washed with small amounts of water, and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Yield: 115 mg (70%). Anal. Calcd for [TcP<sub>2</sub>N<sub>2</sub>Cl<sub>2</sub>C<sub>28</sub>H<sub>32</sub>]: C, 51.96; H, 5.03; N, 4.66; P, 10.32; Cl, 11.80. Found: C, 51.71; H, 5.08; N, 4.60; P, 10.31; Cl, 11.97.

Analogous complexes with phen instead of bpy, PEtPh<sub>2</sub> instead of PMe<sub>2</sub>Ph, and bromide instead of chloride were also prepared in a similar fashion. The phen analogue is blue/purple instead of green. Preparation of the analogue with 4,4'-dimethyl-2,2'-bipyridine was attempted; however, addition of the aqueous hydroxide solution produced a large amount of brown precipitate. Dissolution of this precipitate in dichloromethane, followed by purification on Sephadex LH-20 (dichloromethane elution), produced a large brown band and a small amount of a green band presumed to be the desired complex.

*trans*(P)-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> and Analogues. A 103-mg (0.137-mmol) sample of TcBr<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> was added to 15 mL of absolute ethanol that had been deoxygenated with a stream of nitrogen for 10 min. To this solution was added 170 mg (0.730 mmol) of 2,2':6',2''-terpyridine, and the resulting solution was degassed with a stream of nitrogen for another 5 min. The mixture (initially red-orange) was refluxed under nitrogen for 24 h and cooled to room temperature. The resulting green-brown solution was then evaporated to dryness in a rotary evaporator, dissolved in approximately 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and loaded onto a 2 × 20 cm (i.d. × l) Sephadex LH-20 column prepared in CH<sub>2</sub>Cl<sub>2</sub>. Elution of this column with CH<sub>2</sub>Cl<sub>2</sub> produced six bands of different colors (in order of elution): red-orange, dark purple, green (major), blue, faint purple, and yellow/gold. Only the green band contained a significant amount of material. (The second and third bands were not resolved; resolution could be achieved by initial elution with 90/10 (v/v) dichloromethane/carbon tetrachloride.) The third band (green) was collected, evaporated to dryness, and redissolved in 25 mL of acetone. To this was added 1 mL of 1 M NaSO<sub>3</sub>CF<sub>3</sub> in acetone and 5 mL of water. This mixture was evaporated until a solid product precipitated. The solid was collected by suction filtration, washed with small portions of water, and dried in vacuo over P<sub>2</sub>O<sub>5</sub>; yield 78.2 mg (0.104

mmol), 76%. Anal. Calcd for TcC<sub>32</sub>H<sub>33</sub>N<sub>3</sub>P<sub>2</sub>O<sub>3</sub>SF<sub>3</sub>BrC<sub>2</sub>H<sub>5</sub>OH: C, 46.22; H, 4.45; N, 4.75; P, 7.01; Br, 9.04; F, 6.45. Found: C, 46.81; H, 4.51; N, 4.89; P, 7.08; Br, 9.37; F, 6.40. These data give a N:P:Br:F ratio of 3:2:1:3.

The analogous complexes *trans*(P)-[TcCl(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup> and *trans*(P)-[TcCl(PEtPh<sub>2</sub>)<sub>2</sub>(terpy)]<sup>+</sup> were synthesized similarly with the following modifications.

*trans*(P)-[TcCl(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub>. A solution of 153 mg (0.247 mmol) of TcCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> and 300 mg (0.777 mmol) of terpy in 15 mL of deoxygenated ethanol was refluxed for 47 h under a nitrogen blanket. The reaction mixture was cooled, evaporated to dryness, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, chromatographed on an LH-20 column, and precipitated as the SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> salt as before.

*trans*(P)-[TcCl(PEtPh<sub>2</sub>)<sub>2</sub>(terpy)]PF<sub>6</sub>. A solution of 159 mg (0.188 mmol) of *mer*-TcCl<sub>3</sub>(PEtPh<sub>2</sub>)<sub>3</sub> and 216 mg (0.927 mmol) of terpy in 20 mL of deoxygenated ethanol was refluxed for 20 h under a nitrogen blanket. After the mixture was cooled and rotoevaporated to dryness, the reaction residue was dissolved in 10 mL of dichloromethane, 4 mL of this solution was loaded onto an LH-20 column prepared in CH<sub>2</sub>Cl<sub>2</sub> and eluted with dichloromethane. This column procedure gave results similar to those obtained for the analogues described above; however, the bands were not well resolved and seemed to be contaminated with materials from the top of the column, which appeared to slowly leach. A green band was collected as before, and precipitation of the trifluoromethanesulfonate salt was attempted. However, only a very small amount of solid product was formed. In order to improve the chromatography, 5 mL of the dichloromethane solution of the reaction residue was diluted to a total volume of 25 mL, and this solution was successively extracted with 15-mL portions of water until the aqueous layer was colorless (five extractions). The volume of the dichloromethane layer was then reduced to 5 mL and the layer loaded onto an LH-20 column as before. Elution with dichloromethane produced in order brown, green, and violet bands followed by a fourth major green band with no others eluting after this. The major green band was collected, rotoevaporated to dryness, and dissolved in a small amount of acetone. Then, 1 mL of 1 M NH<sub>4</sub>PF<sub>6</sub> in water was added along with 5 mL of water. Allowing the mixture to stand overnight produced a green precipitate, which was recovered by suction filtration, washed with water, and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Yield: 46.0 mg (52% based on half of the original reaction mixture).

**X-ray Crystal Structures.** *cis*(Cl),*trans*(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)] (1) and *trans*(P)-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> (2). Crystallographic data are presented in Table I and Table S1. Crystals of 1 were obtained by slow evaporation from dichloromethane/heptane under argon atmosphere and those of 2 were obtained by slow evaporation from an acetone/water mixture. Unit cell parameters of both were determined from the angular settings of 15 well-centered reflections (20° < 2θ < 27°). A total of 2147 and 5328 reflections, for 1 and 2, respectively, were measured and corrected for Lorentz-polarization and absorption effects (based on an ellipsoidal model and ψ-scan data from five azimuthal reflections). After averaging, 1635 unique reflections were obtained for 1 and 3462 observed reflections were obtained for 2 with  $F > 3\sigma(F)$ . The structure of 1 was successfully solved in the tetragonal space group P4<sub>1</sub>2<sub>1</sub>2 (No. 92). A combination of direct methods (SHELXS with TREF option)<sup>8</sup> and Fourier techniques was used to locate the positions of the non-hydrogen atoms. Isotropic refinement of this model with unit weights converged to  $R = 0.0757$  with uncorrected data. The structure was subsequently refined with absorption-corrected data, a weighting scheme based on  $\sigma(F)$ , and non-hydrogen positional and anisotropic temperature factors varying to give  $R = 0.0519$  and  $R_w = 0.0899$ .<sup>9</sup> (The corresponding enantiomeric structure was refined in the space group P4<sub>3</sub>2<sub>1</sub>2, and converged to  $R = 0.0535$  and  $R_w = 0.0911$ .) Further refinements included a riding model for the hydrogen atoms (C–H = 0.96 Å with fixed isotropic temperature factors ( $U(H) = 0.08 \text{ \AA}^2$ ) and an empirical isotropic extinction parameter. The structure refined smoothly to the final residuals  $R = 0.0418$  and  $R_w = 0.0646$ .

The structure of 2 was successfully solved in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19) and then refined by full-matrix least-squares methods. An initial sharpened Patterson map (XS:PATT)<sup>10</sup> and subsequent difference Fourier syntheses were used to locate the positions of the non-hydrogen atoms. Isotropic refinement of this non-hydrogen model with unit weights converged to  $R = 0.1229$  with uncorrected data. Anisotropic refinement of this model lowered the residuals to  $R = 0.0637$ . Subsequent cycles of least-squares refinement included absorption-cor-

(8) All computations were made with SHELXTL (Nicolet, VMS pre-release, 1986) on a MicroVAX II computer.

(9)  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = [\sigma^2(F) + |g|(F)^2]^{-1}$ ,  $g = 0.000 524$ .

(10) All computations were made with SHELXTL PLUS (Nicolet, 1986) on a MicroVAX II computer.

**Table II.** UV-Visible Spectrophotometric Parameters for Technetium(II) Bipyridine, Phenanthroline, and Terpyridine Complexes in Acetonitrile

complex	$\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
<i>cis(Cl),trans(P)</i> -[TcCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (phen)]	224 (41 800), 254 (37 500, 336 (5380), 398 (2810), 516 (5530), 655 (4400)
<i>cis(Br),trans(P)</i> -[TcBr <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (bpy)]	248 (25 600), 300 (14 600), 342 (4310), 441 (5060), 660 (2210)
<i>cis(Cl),trans(P)</i> -[TcCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (bpy)]	247 (34 500), 293 (17 200), 445 (6620), 670 (2560)
<i>cis(Cl),trans(P)</i> -[TcCl <sub>2</sub> (PEtPh <sub>2</sub> ) <sub>2</sub> (bpy)]	250 (31 400), 295 (17 200), 368 (4260), 441 (5630), 663 (2620)
<i>trans(P)</i> -[TcCl(PMe <sub>2</sub> Ph) <sub>2</sub> (terpy)] <sup>+</sup>	243 (40 900), 278 (17 700), 320 (24 000), 413 (5300), 510 (3200), 651 (3800)
<i>trans(P)</i> -[TcBr(PMe <sub>2</sub> Ph) <sub>2</sub> (terpy)] <sup>+</sup>	244 (40 800), 178 (17 000), 320 (26 000), 412 (5400), 510 (3400), 645 (3800)
<i>trans(P)</i> -[TcCl(PEtPh <sub>2</sub> ) <sub>2</sub> (terpy)] <sup>+</sup>	256 (39 900), 322 (22 800), 410 (4870), 510 (2800) 642 (3550)

**Table III.** Final Atomic Positional Parameters ( $\times 10^4$ ) for *cis(Cl),trans(P)*-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)]

atom	x	y	z
Tc	365.4 (6)	365.4 (6)	5000 <sup>a</sup>
Cl	747 (3)	2148 (2)	5595 (1)
P	-799 (2)	1698 (2)	4403 (1)
N	-1237 (7)	-178 (7)	5425 (3)
C(1)	-1809 (8)	-1244 (9)	5232 (4)
C(2)	-1775 (9)	381 (12)	5849 (4)
C(3)	-2855 (12)	-77 (16)	6104 (7)
C(4)	-3398 (12)	-1158 (17)	5913 (8)
C(5)	-2883 (10)	-1760 (12)	5463 (7)
C(6)	-3399 (12)	-2855 (13)	5226 (6)
C(7)	-997 (10)	1129 (10)	3721 (4)
C(8)	-173 (10)	3249 (9)	4282 (5)
C(9)	-2397 (7)	1987 (8)	4613 (4)
C(10)	-2679 (10)	2991 (10)	4968 (5)
C(11)	-3879 (13)	3155 (12)	5155 (6)
C(12)	-4811 (11)	2332 (13)	5027 (6)
C(13)	-4552 (11)	1329 (13)	4696 (4)
C(14)	-3343 (9)	1172 (10)	4506 (4)

<sup>a</sup>This parameter is required by symmetry to be 0.5 and was not varied.

rected data, a weighting scheme based on  $\sigma(F)$ , and hydrogen atoms riding on their respective carbon atoms with C-H = 0.96 Å. Two common hydrogen atom isotropic temperature parameters [ $U(H)$  for aromatic H atoms and  $U(H)'$  for methyl H atoms] were included and allowed to vary. The final residuals were  $R = 0.0625$  and  $R_w = 0.0408$ ,<sup>11</sup> with the goodness-of-fit ( $S$ )<sup>12</sup> being 1.27. The refined hydrogen atom isotropic parameters were  $U(H) = 0.092$  (9) Å<sup>2</sup>, and  $U(H)' = 0.120$  (13) Å<sup>2</sup>.

## Results

**Synthesis and Characterization.** Table II lists the UV-visible spectrophotometric parameters for the several complexes prepared in this work. All of the species exhibit strong absorbances between 300 and 700 nm and are intensely colored. The bpy complexes are dark emerald green while the phen complex is dark blue/purple. The terpy complexes are green and exhibit four absorbances in the visible region; the wavelengths of these absorbance maxima are nearly identical and the molar extinction coefficients are comparable. All complexes exhibit FAB/MS spectra in the

**Table IV.** Final Atomic Positional Parameters ( $\times 10^4$ ) for *trans(P)*-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub>

atom	x	y	z
Tc	734 (1)	405 (1)	-1223 (1)
Br	2061 (1)	604 (1)	-1454 (2)
P(1)	852 (2)	-411 (2)	-3081 (3)
P(2)	731 (2)	1284 (2)	543 (3)
N(1)	285 (4)	1102 (4)	-2633 (8)
N(2)	-300 (3)	223 (4)	-1009 (7)
N(3)	691 (5)	-394 (4)	258 (7)
C(1)	643 (5)	1561 (5)	-3425 (10)
C(2)	318 (6)	2009 (6)	-4338 (11)
C(3)	-406 (6)	1987 (5)	-4431 (11)
C(4)	-783 (5)	1542 (5)	-3599 (11)
C(5)	-433 (5)	1098 (5)	-2743 (10)
C(6)	-771 (5)	588 (4)	-1834 (9)
C(7)	-1480 (5)	470 (5)	-1683 (10)
C(8)	-1721 (5)	-24 (6)	-769 (12)
C(9)	-1244 (5)	-403 (6)	-8 (11)
C(10)	-528 (5)	-267 (5)	-113 (10)
C(11)	34 (5)	-619 (6)	629 (11)
C(12)	-60 (6)	-1146 (6)	1553 (12)
C(13)	511 (8)	-1441 (5)	2182 (12)
C(14)	1171 (7)	-1183 (6)	1880 (11)
C(15)	1248 (6)	-680 (6)	942 (10)
C(16)	1318 (6)	-74 (8)	-4590 (12)
C(17)	1290 (8)	-1214 (7)	-2650 (14)
C(18)	-10 (6)	-671 (7)	-3792 (16)
C(19)	-314 (9)	-353 (8)	-4918 (14)
C(20)	-989 (9)	-528 (10)	-5336 (17)
C(21)	-1376 (12)	-1001 (13)	-4654 (26)
C(22)	-1091 (12)	-1262 (11)	-3521 (23)
C(23)	-429 (10)	-1157 (7)	-3081 (16)
C(24)	1163 (7)	2092 (6)	40 (14)
C(25)	1151 (6)	1062 (6)	2203 (11)
C(26)	-176 (7)	1532 (6)	1016 (13)
C(27)	-539 (9)	2014 (7)	142 (13)
C(28)	-1256 (11)	2098 (9)	453 (21)
C(29)	-1543 (15)	1793 (13)	1543 (21)
C(30)	-1212 (14)	1363 (12)	2368 (25)
C(31)	-505 (8)	1225 (7)	2060 (15)
S	2176 (1)	2912 (2)	-6600 (3)
O(1)	2567 (4)	2576 (5)	-7643 (9)
O(2)	2435 (3)	3583 (3)	-6203 (12)
O(3)	1433 (3)	2849 (3)	-6646 (9)
C(32)	2381 (6)	2419 (9)	-5084 (17)
F(1)	2056 (4)	2639 (5)	-3965 (9)
F(2)	2214 (4)	1749 (4)	-5230 (8)
F(3)	3078 (4)	2414 (4)	-4831 (10)

positive ion mode wherein the peak of highest mass is assigned to the molecular ion M<sup>+</sup>. The mass spectra of the bpy and phen complexes also contain peaks that arise from the loss of one or more of the monodentate ligands. The FAB/MS spectra of the terpy complexes exhibit two clusters at masses corresponding to the loss of one and two phosphine ligands from the molecular ion. The mass spectrum of the second (purple) band observed during chromatographic isolation of the *trans*-[TcCl(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup> complex exhibits a large number of peaks, but notable among them are a cluster of peaks at  $m/e$  678, 680, and 682 and a fragmentation pattern (vide infra) similar to that obtained for the *cis(Cl),trans(P)*-[Tc<sup>III</sup>Cl<sub>2</sub>(P)<sub>2</sub>L]<sup>+</sup> complex (L = bpy, phen) described previously.<sup>3</sup>

**Crystal Structures of *cis(Cl),trans(P)*-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)] (1) and *trans(P)*-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> (2).** Final atomic positional parameters of the title complexes are found in Tables III and IV, respectively. Selected bond lengths and angles are found in Tables V and VI. Molecular structure plots with associated atom-numbering schemes are found in Figures 1 and 2. Additional molecular structure plots viewed down the P-Tc-P axes are shown in Figure 3. The following have been deposited as supplementary material: full crystallographic data collection and refinement parameters (Table S1); anisotropic temperature parameters (Table S2); hydrogen atom coordinates (Table S3); complete listings of bond lengths (Table S4) and angles (Table S5) and observed and calculated structure factors (Table S6).

(11) See ref 9;  $g = 0.000100$ .

(12)  $S = [\sum w(|F_o| - |F_c|)^2 / (M - N)]^{1/2}$ , where  $M$  is the number of observed reflections and  $N$  is the number of parameters refined.

**Table V.** Selected Bond Lengths (Å) and Angles (deg) for *cis(Cl),trans(P)*-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)]<sup>a</sup>

Bond Lengths			
Tc-Cl	2.435 (3)	Tc-N	2.086 (7)
Tc-P	2.391 (2)		
Bond Angles			
Cl'-Tc-Cl	95.8 (1)	P'-Tc-P	173.9 (1)
P-Tc-Cl	89.6 (1)	N-Tc-P	92.7 (2)
P'-Tc-Cl	86.4 (1)	N'-Tc-P	92.0 (2)
N-Tc-Cl	93.0 (2)	N'-Tc-N	78.2 (4)
N'-Tc-Cl	171.1 (2)		

<sup>a</sup>Numbers in parentheses represent the estimated standard deviations in the final digits.

**Table VI.** Selected Bond Lengths (Å) and Angles (deg) for *trans(P)*-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub><sup>a</sup>

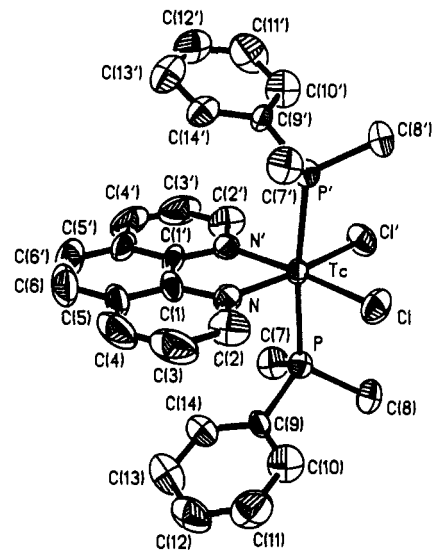
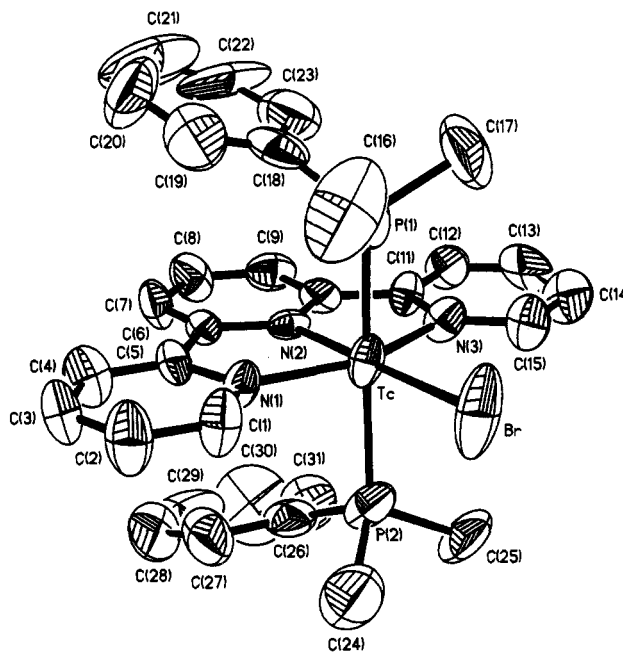
Bond Lengths			
Tc-Br	2.558 (8)	Tc-N(1)	2.093 (9)
Tc-P(1)	2.394 (8)	Tc-N(2)	2.004 (8)
Tc-P(2)	2.404 (8)	Tc-N(3)	2.101 (9)
Bond Angles			
P(1)-Tc-Br	86.7 (2)	N(2)-Tc-P(1)	93.0 (3)
P(2)-Tc-Br	87.5 (2)	N(2)-Tc-P(2)	92.9 (3)
P(2)-Tc-P(1)	173.6 (2)	N(3)-Tc-Br	102.0 (3)
N(1)-Tc-Br	104.3 (3)	N(3)-Tc-P(1)	91.5 (3)
N(1)-Tc-P(1)	88.8 (3)	N(3)-Tc-P(2)	92.3 (3)
N(1)-Tc-P(2)	90.1 (3)	N(3)-Tc-N(1)	153.7 (3)
N(2)-Tc-Br	178.3 (3)	N(3)-Tc-N(2)	76.3 (3)
N(2)-Tc-N(1)	77.3 (3)		

<sup>a</sup>Numbers in parentheses represent estimated standard deviations in the final digits.

## Discussion

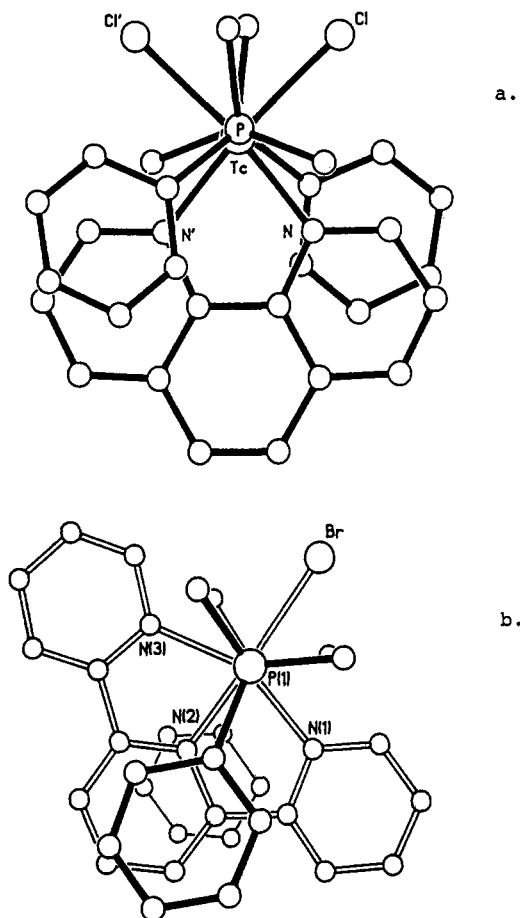
**Synthesis and Characterization.** The neutral technetium(II) complexes *cis(X),trans(P)*-[TcX<sub>2</sub>(P)<sub>2</sub>L] are prepared by L substitution onto the *mer*-trichlorotrakis(phosphine)technetium(III) starting material followed by base-induced reduction of Tc(III) to Tc(II). Neither the mechanism nor the driving force underlying this reduction are known. Hydroxide ion induces reduction of the Tc(III) species both in the reaction mixture and in an ethanol solution of the chromatographically purified products. However, the hydroxide-induced reduction does not occur in acetonitrile. Therefore, it is likely that the functional reducing agent is either the ethoxide formed in the ethanol/hydroxide mixture or ethanol itself. Metal ion oxidation of alcohols to aldehydes is well-known; e.g., Ru(III) oxidizes alcohols in the presence of PPh<sub>3</sub>.<sup>13</sup> Attempts to form the Tc(II) species in one step by adding hydroxide to the original reaction mixture proved unsuccessful. The solutions turned immediately from the clear orange of the *mer*-TcX<sub>3</sub>(P)<sub>3</sub> starting material to a dirty brown suspension. The Tc(II) complexes are generated in much smaller yields by allowing the original reaction mixture to reflux for 24 h or more instead of adding base. As noted previously,<sup>3</sup> the original reaction mixture provides both the Tc(II) and Tc(III) forms, and allowing the reaction to proceed for long periods of time, especially under anaerobic conditions, promotes the formation of the Tc(II) species. Of all of the systems studied, that containing bromide forms the Tc(II) species most readily because of the tendency of Br to stabilize lower oxidation states to a greater extent than does Cl. Solutions of the Tc(II) complexes that are not deoxygenated and that are exposed to air will change to the color of the technetium(III) form over several hours, except for the bromo species, which remains stable in solution for several days. The formation of the Tc(III) species is confirmed by UV-visible spectrophotometry.<sup>3</sup>

As with the Tc(III) analogues described previously,<sup>3</sup> these Tc(II) complexes are particularly well suited to analysis by fast atom bombardment mass spectrometry. The mass spectrum of the TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(bpy) species shows a cluster of peaks at *m/e* 601 that represents the molecular ion M<sup>+</sup> (in which Tc(II) has been oxidized to Tc(III)). It also has an isotope distribution

**Figure 1.** Molecular plot and atom-numbering scheme for *cis(Cl),trans(P)*-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)].**Figure 2.** Molecular plot and atom numbering scheme for *trans(P)*-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup>.

pattern that is consistent with a species containing two chlorine atoms. Additionally, the spectrum exhibits several other peaks all of which are assigned to fragments of the complex resulting from the loss of monodentate ligands. That is, a doublet at *m/e* 566 and 568 represents the molecular ion minus a chlorine, a triplet at *m/e* 463, 465, and 467 represents loss of a phosphine from the molecular ion, a peak at *m/e* 428 represents loss of one Cl and one phosphine, a peak at *m/e* 393 represents loss of two Cl atoms and one phosphine, etc. This fragmentation behavior results in a mass spectrophotometric "fingerprint", and observation of this "fingerprint" pattern for the other analogues allows identification of these species.

The cationic technetium(II) complexes *trans(P)*-[TcX(P)<sub>2</sub>(terpy)]<sup>+</sup> are prepared by substitution of terpy onto the *mer*-trichlorotrakis(phosphine)technetium(III) starting material in ethanol solution with concomitant reduction of Tc(III) to Tc(II). The functional reducing agent may be the free phosphine liberated by the replacement reaction or ethanol itself. These complexes exhibit "fingerprint" FAB mass spectra; the peak of greatest mass in each spectrum is assigned as the molecular ion M<sup>+</sup>, there are characteristic fragment peaks representing successive loss of the

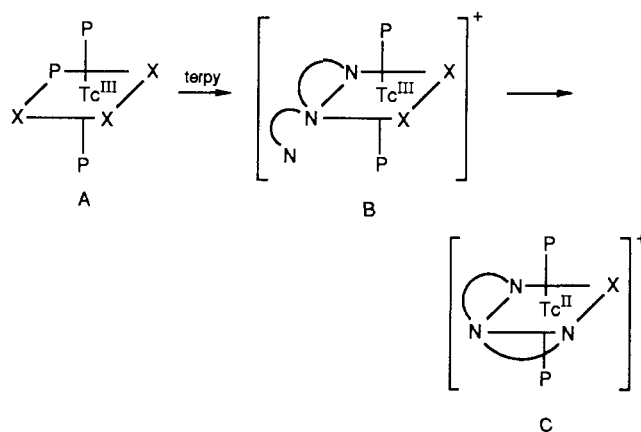


**Figure 3.** Molecular plots of (a) *cis(Cl),trans(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)]* and (b) *trans(P)-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup>* viewed down the P-Tc-P axes.

monodentate phosphine ligands, and there is a peak corresponding to loss of the phosphine ligands and the halide ligand.

As noted above, reaction of the bidentate ligands bpy or phen with *mer*-TcX<sub>3</sub>(P)<sub>3</sub> causes primarily the replacement of one X ligand and one P ligand by the bidentate ligand. This also appears to be the case with the potentially tridentate terpy ligand as evidenced by the FAB mass spectrum of a minor product in the preparation of *trans(P)-[TcCl(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup>*. This spectrum exhibits a molecular ion cluster centered at *m/e* 680 and a fragmentation pattern similar to those obtained for *cis(Cl),trans(P)-[TcX<sub>2</sub>(P)<sub>2</sub>L]<sup>+</sup>* species.<sup>3</sup> A cluster with peaks at *m/e* 678, 680, and 682 is consistent with the formulation [TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup> both in mass and in the distribution of isotopic peaks for a species containing two chlorine atoms. The formulation is also supported by the fragmentation pattern showing successive losses of Cl and PMe<sub>2</sub>Ph from the molecular ion. The UV-visible spectrum of this fraction in dichloromethane exhibits absorption maxima at 260, 304, 384, and 560 nm; these maxima are at wavelengths similar to those observed for *cis(Cl),trans(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(bpy)]<sup>+</sup>* in acetonitrile ( $\lambda_{\text{max}} = 262, 298, 364, 540 \text{ nm}$ ),<sup>3</sup> and thus it is likely that [TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup> is a six-coordinate complex with terpy functioning as a bidentate ligand, and is probably not a seven-coordinate complex with terpy functioning as a tridentate ligand. Bidentate coordination for terpy has been proposed for a number of complexes<sup>14</sup> and confirmed for *cis(C),trans(Br)-[Ru(CO)<sub>2</sub>Br<sub>2</sub>(terpy)]<sup>15</sup> by X-ray crystal-*

lography. Thus, the mechanism of formation of the [TcX(P)<sub>2</sub>(terpy)]<sup>+</sup> cations most likely involves the initial displacement of one halide and one phosphine ligand of the starting material (A)



and coordination of the terpy as a bidentate moiety. The resulting [TcX<sub>2</sub>(P)<sub>2</sub>(terpy)]<sup>+</sup> complex (B) is analogous to the [TcX<sub>2</sub>(P)<sub>2</sub>(bpy)]<sup>+</sup> Tc(III) complexes described previously.<sup>3</sup> In a subsequent step, a second halide is displaced by the third terpy nitrogen atom with concomitant reduction of the technetium center from Tc(III) to Tc(II) forming C. These technetium(II) species are stable toward oxidation in solution over long periods of time (unlike the [Tc<sup>III</sup>X<sub>2</sub>(P)<sub>2</sub>L] species) probably as a result of the greater  $\pi$ -back-bonding capabilities afforded by one tridentate terpy ligand relative to one bidentate bpy (or phen) and one halide ligand.

UV-visible spectrophotometric parameters for the complexes prepared in this study are listed in Table II. All complexes exhibit intense absorptions in the visible region which in turn give these complexes their specific colors (green for the bpy and terpy complexes and blue/purple for the phen complexes). Several lines of evidence indicate that these absorptions are most likely due to the metal-to-ligand ( $d\pi$ -to- $\pi^*$ ) charge-transfer (MTLCT) transitions that are characteristic of low-valent metal-bpy complexes.<sup>16</sup> (1) Previously reported spectra for the Tc(III) analogues of the Tc(II) bpy and phen complexes<sup>3</sup> exhibit comparable absorptions that are shifted to higher energies, consistent with the MTLCT assignment. For example, the lowest energy transitions for the Tc(II) complexes are in the 655–670-nm region (Table II), while those for the Tc(III) analogues are in the 535–540-nm region.<sup>3</sup> (2) For the terpy complex [TcCl(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]<sup>+</sup>, reduction from Tc(II) to Tc(I) causes the longest wavelength transition to shift to lower energy (651 to 690 nm), again consistent with the MTLCT assignment.<sup>6</sup> (3) There are only minor differences in the energies of the lowest energy bands (660 to 670 nm) of the bpy complexes, consistent with their assignment as Tc( $d\pi$ )-to-bpy( $\pi^*$ ) transitions, the energies of which are only slightly influenced by variations in the Cl, Br, and phosphine ligands. Similarly, the spectra of the three terpy complexes are not sensitive to the nature of the halogen or phosphine ligands, implying that they arise primarily from Tc-terpy interactions. (4) However, the energies of the transitions of the analogous bpy and phen complexes [TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>L] (L = bpy, phen) are markedly different, supporting the supposition that they arise from Tc-L interactions.

**Crystal Structures of *cis(Cl),trans(P)-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)] (1) and *trans(P)-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> (2).**** The single-crystal X-ray structure analyses of these complexes present rare glimpses of technetium(II) structural chemistry. The only other technetium(II) structure reports known to us are of *trans*-Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>,<sup>17</sup> *trans*-TcCl<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>,<sup>18</sup> and

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**Table VII.** Selected Bond Lengths for Related Tc(III), Tc(II), Re(II), and Ru(II) Complexes

metal center	complex	bond length, <sup>a</sup> Å			ref
		M-P	M-N	M-X	
Tc(III)	<i>cis</i> (Cl), <i>trans</i> (P)-[TcCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (phen)] <sup>+</sup>	2.461 (1)	2.114 (3)	2.354 (1)	3
Tc(II)	<i>cis</i> (Cl), <i>trans</i> (P)-[TcCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (phen)]	2.391 (2)	2.086 (7)	2.435 (3)	<i>b</i>
Tc(II)	<i>trans</i> -Tc(DPPE) <sub>2</sub> Cl <sub>2</sub>	2.429 (1)		2.438 (1) 2.410 (1)	19
Tc(II)	<i>trans</i> -Tc(DPPE) <sub>2</sub> (NCS) <sub>2</sub>	2.429 (5)	2.047 (8)		17
Tc(II)	<i>trans</i> -[TcBr(PMe <sub>2</sub> Ph) <sub>2</sub> (terpy)] <sup>+</sup>	2.399 (8)	2.097 (9) <sup>c</sup> 2.004 (8) <sup>d</sup>	2.558 (8)	<i>b</i>
Re(II)	<i>trans,trans,trans</i> -[Re(CNCMe <sub>3</sub> ) <sub>2</sub> (MeCN) <sub>2</sub> (PPH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	2.450 (2)	2.058 (7)		27
Re(II)	[Re(bpy) <sub>3</sub> ] <sup>2+</sup>		2.091		24
Ru(II)	<i>cis</i> -Ru(bpy) <sub>2</sub> Cl <sub>2</sub>		2.013 (2) <sup>e</sup> 2.054 (2) <sup>f</sup>	2.426 (2) <sup>f</sup>	21
Ru(II)	<i>cis</i> (S), <i>trans</i> (P)-[Ru(SOCPh) <sub>2</sub> (phen)(PMe <sub>2</sub> Ph) <sub>2</sub> ]	2.380 (3) 2.365 (3)	2.082 (7) <sup>g</sup> 2.091 (8) <sup>g</sup>		28
Ru(II)	<i>trans</i> (P)-Ru(OCOMe)(CO)Cl(PPh <sub>3</sub> ) <sub>2</sub>	2.373 (2)		2.364 (6)	25
Ru(II)	<i>trans</i> (Cl)-RuCl <sub>2</sub> (dppm) <sub>2</sub>	2.340 (1) 2.367 (1)		2.426 (1)	26
Ru(II)	<i>cis</i> (Cl)-RuCl <sub>2</sub> (dppm) <sub>2</sub>	2.303 (11) <sup>e</sup> 2.338 (11) <sup>d</sup>		2.440 (2) 2.451 (13)	26
Ru(II)	<i>cis</i> (Cl)-[RuCl <sub>2</sub> (CO)(terpy)]		2.081 (6) <sup>c</sup> 1.969 (7) <sup>d</sup>	2.420 (3) <sup>f</sup>	15

<sup>a</sup>Where applicable, bond lengths listed are average values for like bonds. <sup>b</sup>This work. <sup>c</sup>Terminal N. <sup>d</sup>Central N. <sup>e</sup>Trans to Cl. <sup>f</sup>Trans to N. <sup>g</sup>Trans to S. <sup>h</sup>Trans to P.

*trans*-Tc(DPPE)<sub>2</sub>Cl<sub>2</sub>.<sup>19</sup> Moreover, the analysis of **1** allows comparisons to be made to the analogous Tc(III) structure previously reported.<sup>3</sup> Selected bond lengths within these complexes and within some comparable Re(II) and Ru(II) complexes are presented in Table VII.

Both of the title complexes contain technetium(II) centers in a slightly distorted octahedral environment. In **1** the Tc atom is coordinated to two trans (axial) phosphorus atoms of the monodentate phosphine ligands and two cis (equatorial) chlorine atoms that are both trans to the two nitrogen atoms of the coordinating bidentate phen ligand. The technetium atom lies on a crystallographic 2-fold axis that bisects the Cl-Tc-Cl angle. In **2**, the Tc atom is coordinated to two trans (axial) phosphorus atoms of the monodentate PMe<sub>2</sub>Ph ligands, with the four remaining (equatorial) positions occupied by the three nitrogen atoms of the tridentate terpyridine molecule and one bromine atom. As can be seen in Figure 2, the phosphine moieties are not situated symmetrically over the terpy ligand, a fact that most likely accounts for the slight differences in Tc-N and Tc-P bond distances and the variations in bond angles about the technetium center (see Table VI).

The Tc-P bond distances within **1** and **2** (2.391 (2) and 2.399 (8) Å (av), respectively) are in good agreement with each other. These distances are significantly shorter than the average Tc(II)-P distances reported for *trans*-Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub> and *trans*-Tc(DPPE)<sub>2</sub>Cl<sub>2</sub> (average difference = 0.034 (6) Å; Table VII). This difference in Tc(II)-P bond distances is readily understood on the basis of the greater steric repulsion generated by the bulky phenyl groups of the DPPE ligand, relative to the single phenyl group of PMe<sub>2</sub>Ph. Differences in Tc(III)-P and Tc(II)-P bond lengths of similar magnitude have been previously observed and have also been successfully correlated with the steric bulk of groups bonded to the P atom.<sup>19,20</sup> The small differences among Tc(II)-P, Re(II)-P, and Ru(II)-P distances listed in Table VII are also readily explained on the basis of steric effects generated by the orientation of the phosphine ligands and by the bulk of the groups bonded to P. As expected, the Tc-P distance in **1** is significantly shorter than the Tc(III)-P distance in its Tc(III) analogue (average difference [III - II] = +0.070 (2) Å; Table VII) as a result of the greater  $\pi$ -back-bonding interactions in the lower oxidation state.<sup>19</sup>

The Tc(II)-N bonds within **1** are also shorter than the Tc(III)-N bonds within the analogous Tc(III) complex (average difference [III - II] = +0.028 (5) Å; Table VII), again due to

greater Tc-N  $\pi$ -back-bonding interactions in the lower oxidation state. This effect on the Tc-N bond length is attenuated, relative to the effect of oxidation state on the Tc-P bond length, due to the bite angle requirements of the rigid phen ligand (the N-Tc-N angles are 78.2° in both complexes). The Tc(II)-N distances within **1** compare well with the Tc(II)-N(terminal) distances within **2**, and with the analogous Ru(II)-N distances within the Ru-phen and Ru-terpy complexes listed in Table VII. As expected, because of the bite requirements of the tridentate terpy ligand, the Tc(II)-N(central) and Ru(II)-N(central) distances are significantly shorter than the M-N(terminal) distances (Table VII).

In contrast to the situation for the Tc-P and Tc-N distances, the Tc-Cl distances in the Tc(II) complex **1** are longer than those in the Tc(III) analogue (average difference [III - II] = -0.081 (2) Å; Table VII). This inversion in the sign of the [III - II] difference occurs because the Tc-Cl linkage is dominated by electrostatic interactions while the Tc-N and Tc-P linkages are dominated by  $\pi$ -back-bonding interactions. Similar observations and interpretations have been presented for the pair of complexes *trans*-[Tc<sup>III/II</sup>(DPPE)<sub>2</sub>Cl<sub>2</sub>]<sup>+0</sup>, wherein the [III - II] difference in Tc-Cl bond lengths is -0.105 (2) Å while the [III - II] difference in Tc-P bond lengths is +0.072 (2) Å.<sup>19</sup> The pair of ruthenium complexes *cis*-[Ru<sup>III/II</sup>(bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>+0</sup> also exhibits this inversion in the signs of the [III - II] differences for the Ru-N and Ru-Cl linkages.<sup>21</sup>

The effect of both shorter Tc-P and Tc-N bond lengths in the Tc(II) species **1** creates greater steric crowding between the phosphine and phen ligands than in the Tc(III) analogue, and this in turn results in the phosphine ligands being canted away from the phen ligand to a greater extent in the Tc(II) complex. The P-Tc-P angle in the Tc(II) analogue is 173.9 (1)°, whereas in the Tc(III) analogue it is 179.6 (1)°. This effect is probably also manifested in the terpy-Tc(II) complex **2** wherein the P-Tc-P angle is 173.6 (2)°. As expected, the stringent bite requirements of the terpy ligand generate a significant distortion in the octahedral coordination environment of **2**; the N(terminal)-Tc-N(terminal) angle of 153.7 (3)° in **2** is typical for transition-metal-terpy complexes.<sup>22</sup>

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**Supplementary Material Available:** Tables of crystallographic data (Table S1), anisotropic temperature parameters (Table S2), and hydro-

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gen atom coordinates (Table S3) and complete listings of bond lengths (Table S4) and bond angles (Table S5) for *cis(Cl),trans(P)*-[TcCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>(phen)] and *trans(P)*-[TcBr(PMe<sub>2</sub>Ph)<sub>2</sub>(terpy)]SO<sub>3</sub>CF<sub>3</sub> (13 pages); a listing of observed and calculated structure factors (Table S6) for both compounds (24 pages). Ordering information is given on any current masthead page.

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## Notes

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### 1,2-Difluorobenzene: A Relatively Inert and Noncoordinating Solvent for Electrochemical Studies on Transition-Metal Complexes

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The criteria required of a good solvent for electrochemical studies on metal complexes or organometallic compounds include that it should (1) be relatively easy to purify, (2) have good solvating properties for both electrolyte and metal complexes or compounds, and (3) have an extended potential "window".<sup>1</sup> Although these criteria are largely met by acetonitrile and other organic solvents such as DMF or DMSO, they have the ability to coordinate and often play a role as ligands in electrochemically induced substitution processes.<sup>2</sup> The solvents CH<sub>2</sub>Cl<sub>2</sub>, THF, 1,2-dimethoxyethane, and propylene carbonate have a lower tendency to coordinate, but all have limitations arising from restricted potential windows, poor solvating properties, or unwanted chemical reactivity. There have also been recent advances in the use of nonpolar solvents such as benzene for electrochemical studies.<sup>3-5</sup> Although useful in some studies, these solvents are often not conducive to large scale electrolyses, require specialized apparatus such as microelectrodes,<sup>3,4</sup> or utilize molten salt electrolytes above ambient temperature.<sup>5</sup>

We report here that 1,2-difluorobenzene (DFB) has some significant advantages as a solvent for electrochemical studies. It has a dielectric constant that is sufficiently high to dissolve many electrolyte and metal complex salts, it is noncoordinating, it is relatively inert chemically, it has a wide potential window, and it can be used in routine, small-scale, or large-scale electrochemical studies. We report here some illustrative examples from our own work where the utilization of DFB as an electrochemical solvent has been of value.

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### Experimental Section

Purification of 1,2-difluorobenzene (DFB) and electrochemical studies were carried out in a drybox (Vacuum/Atmospheres). The drybox was kept under a constant flow of N<sub>2</sub>, which acted as an atmospheric purge to prevent the contamination of DFB by other solvent vapors.

**Materials.** The liquid 1,2-difluorobenzene (Aldrich, 98% or Lancaster, 98+%) was purified by passing it through a column of activated alumina. DFB is expensive, and it was collected and recycled by distillation (bp = 92 °C) for reuse. To date, three recycling steps have not resulted in any noticeable degradation in the electrochemical properties of the solvent. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared and purified as reported previously.<sup>6</sup>

**Electrochemistry.** Platinum- and glassy-carbon-button electrodes of area ~0.1 cm<sup>2</sup> were seated in Teflon shrouds and cleaned by polishing with 1- $\mu$ m diamond paste (Buehler). Cuvette-sized optically transparent electrodes (In-doped SnO<sub>2</sub> on glass) were purchased from Delta Technologies. Electrochemical measurements were performed by using a PAR Model 173 potentiostat in conjunction with a PAR Model 175 universal programmer. Electrochemical data were recorded on a Hewlett-Packard Model 5017B X-Y recorder, and all potentials are referenced to a saturated sodium chloride calomel reference electrode (SSCE). Three-compartment cells were employed, where the reference and auxiliary (Pt mesh) electrodes were separated from the working compartment with fine- and medium-porosity frits, respectively. For controlled-potential electrolysis experiments, a Pt mesh served as the working electrode.

### Results and Discussion

**Solvating Properties.** The molecule 1,2-difluorobenzene is polar ( $\mu = 2.59$ )<sup>7</sup> and as a solvent has a higher dielectric constant ( $D_s = 13.8$  at 28 °C)<sup>8</sup> than either CH<sub>2</sub>Cl<sub>2</sub> ( $D_s = 8.9$ )<sup>1a</sup> or THF ( $D_s = 7.4$ ).<sup>1a</sup> The electrolyte TBAH is very soluble in DFB with a saturation limit at room temperature of ~1.5 M. Alkali-metal-based electrolytes such as Li(CF<sub>3</sub>SO<sub>3</sub>) are *not* soluble in DFB. The solvating ability of DFB toward transition-metal complexes is similar to that of CH<sub>3</sub>CN. Many neutral complexes—M<sub>2</sub>(CO)<sub>10</sub> (M = Mn and Re), ferrocene, *fac*-[Re(bpy)(CO)<sub>3</sub>X] (X = Cl, Br; bpy = 2,2'-bipyridine)—monocationic salts—*fac*-[Re(bpy)(CO)<sub>3</sub>(CH<sub>3</sub>CN)](PF<sub>6</sub>), *cis*-[Os(bpy)<sub>2</sub>(4-vinylpyridine)Cl](PF<sub>6</sub>)—and dicationic salts—[M(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (M = Fe, Ru, Os), *cis*-[Ru<sup>IV</sup>(bpy)<sub>2</sub>(4-*tert*-butylpyridine)(O)](PF<sub>6</sub>)<sub>2</sub>—have solubilities that are similar in CH<sub>3</sub>CN and 1,2-difluorobenzene. The neutral compounds [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] and [Re(bpy)(CO)<sub>3</sub>]<sub>2</sub> are only sparingly soluble in either solvent.

There are some solubility advantages to 1,2-difluorobenzene as a solvent. It will dissolve in reasonable concentrations some porphyrin and phthalocyanine complexes that are nearly or totally insoluble in acetonitrile. Ferrocene, although very soluble in DFB, leads to adsorptive behavior when oxidized to the ferrocenium ion.

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