have EPR spectra that are typical of high-spin Fe(III) porphyrins ($g$ = ca. 6). Thus, it is demonstrated that the amide groups do not bind to the iron center. Furthermore, Walker et al.[22] have also observed two sets of EPR signals in the crystal of [Fe(TPP)(ImH)$_2$]Cl. It has been shown from an X-ray crystallographic study[25] that two sets of EPR signals are due to the existence of two distinct species having different orientations ($\phi$) of axial bases. Therefore, it is speculated that the two sets of EPR signals observed in this work are due to the existence of the two species having different $\phi$'s. The crystal field parameters were calculated by the method of Taylor[26] and are summarized in Table III. The $V/\Delta$ values of species II were smaller than those of the corresponding species I, where both species I and II refer to those existing at low and high axial base concentrations, respectively. In species I the $V/\Delta$ values do not change as much as those found by Quinn et al.;[2] however, the $V/\Delta$ values decrease in the order [Fe(Az-P)(1-MeIm)$_2$]$^+$ > [Fe(Az-val$\beta\beta$)(1-MeIm)$_2$]$^+$ > [Fe(Az-piv$\beta\beta$)(1-MeIm)$_2$]$^+$. In species II, the $V/\Delta$ values decrease in the order [Fe(Az-P)(1-MeIm)$_2$]$^+$ > [Fe(Az-piv$\beta\beta$)(1-MeIm)$_2$]$^+$ > [Fe(Az-val$\beta\beta$)(1-MeIm)$_2$]$^+$. The changes in $V/\Delta$, and thus $\phi$, do not show the same trends in both species I and II. Therefore, our attempt to demonstrate that the axial base orientation is controlled by the steric restriction was unsuccessful.

The results obtained from this study are summarized as follows: (1) The reduction of $O_2$ affinities of jellyfish Fe(II) porphyrins is not in the same order as for the $O_2$ affinities of the corresponding Co(II) porphyrins. These changes in $O_2$ and CO affinities in the Fe(II) porphyrins cannot be explained only by the axial base orientation. (2) From the $^1$H NMR study, the conformations of cavities in both $O_2$ and CO adducts of [Fe(Az-piv$\beta\beta$)(1,2-Me$_2$Im)] were found to differ from each other. These conformational changes in the cavities are responsible for the reduced $O_2$ and CO affinities for [Fe(Az-piv$\beta\beta$)(1,2-Me$_2$Im)] as compared with those for [Fe(Az-P)(1,2-Me$_2$Im)]. Nevertheless, it is evident that the $O_2$ and CO affinities for the Fe(II) porphyrins are not fully explained by the conformational changes in the cavities, since the $^1$H NMR spectra of the cavities in [Fe(Az-P)(1,2-Me$_2$Im)(CO)] and [Fe(Az-val$\beta\beta$)(1,2-Me$_2$Im)(CO)] were virtually identical. Only the irregularity in these CO affinities remains as a question, and we propose further research to clarify these results.

**Acknowledgment.** This research was supported in part by Grant-in-Aid for Scientific Research No. 62740355 from the Ministry of Education, Science and Culture of Japan.

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# Thiolato-Technetium Complexes. 3.[1] Synthesis and X-ray Structural Studies on the Geometrical Isomers *cis*- and *trans*-Bis(*p*-chlorobenzenethiolato)bis(1,2-bis(dimethylphosphino)ethane)technetium(II)

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*Received October 12, 1988*

The reaction of *trans*-[Tc$^V$(OH)(O)(DMPE)$_2$]$^{2+}$ with excess *p*-chlorobenzenethiol and a small amount of base produces both cis and trans isomers of the air-stable arenethiolato-Tc(II) complex [Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$]. The geometries of these complexes are confirmed by X-ray crystallography. *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$], chemical formula $TcCl_2S_2P_4C_{24}H_{40}$, crystallizes in the orthorhombic space group *Iba*2 with $Z$ = 4 and lattice parameters $a$ = 10.4840 (14) Å, $b$ = 16.505 (2) Å, and $c$ = 17.783 (4) Å. The final weighted $R$ value is 0.024. The coordination sphere is octahedral with Tc occupying a crystallographic 2-fold axis. Important molecular parameters are Tc-S = 2.424 (3) Å, Tc-P(trans to P) = 2.385 (2) Å, Tc-P(trans to S) = 2.439 (3) Å, and Tc-S-C = 114.0 (3)°. Thus, there is a significant (0.054 (4) Å) sulfur-induced structural trans effect. *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$], chemical formula $TcCl_2S_2P_4C_{24}H_{40}$, crystallizes in the monoclinic space group $P2_1/c$ with $Z$ = 2 and lattice parameters $a$ = 9.882 (2) Å, $b$ = 15.311 (3) Å, $c$ = 10.285 (2) Å, and $\beta$ = 96.226 (12)°. The final weighted $R$ value is 0.032. The coordination sphere is octahedral with Tc occupying a crystallographic inversion center. Important molecular parameters are Tc-S = 2.424 (2) Å, Tc-P = 2.397 (2) Å, and Tc-S-C = 123.8 (2)°. The cis isomer is considerably more stable than the trans; trans → cis isomerization occurs with a half-life of about 74 min in dichloromethane at room temperature. The cis isomer exhibits a reversible Tc(III/II) redox couple at -0.182 V vs Ag/AgCl and a nonreversible Tc(II/I) couple at about -0.99 V vs Ag/AgCl. The remarkable stability of *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$] in the Tc(II) oxidation state and in the cis geometry is discussed in terms of the electronic and steric properties of the aryl substituent.

## Introduction

While thiolato-technetium complexes containing technetium in the +5 or +6 oxidation states are well-known,[5] such complexes containing low-valent technetium centers are relatively rare.[6,7] We have recently introduced[1] a general preparative route to the thiolato-Tc(III) comlexes *trans*-[Tc(SR)$_2$(DMPE)$_2$]$^+$, where $^-$SR is an alkane- or benzenemethanethiolato ligand and DMPE is 1,2-bis(dimethylphosphino)ethane. These complexes exhibit reversible Tc(III/II) redox couples, although the resulting Tc(II) species are not sufficiently stable to be isolated. In the hopes of generating more stable Tc(II) complexes, we have extended our preparative route to include arenethiolato ligands. In this paper we report the somewhat unexpected results of this investigation, including the isolation and characterization of both trans and cis

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[3] On leave from the Department of Chemistry, The University of Tsukuba, Sakura-Mura, Ibaraki 305, Japan.
[4] Wayne State University.
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isomers of the title arenethiolato–Tc(II) complex.

## Acronyms and Abbreviations

The following acronyms and abbreviations are used in this article: D = chelating diphosphine or diarsine; DEPE = 1,2-bis(diethylphosphino)ethane; DMF = *N,N*-dimethylformamide; DMPE = 1,2-bis(dimethylphosphino)ethane; DPPE = 1,2-bis(diphenylphosphino)ethane; Et = ethyl; Me = methyl; PDE = platinum-disk electrode; Ph = phenyl; STTCT = sulfur-to-technetium charge transfer; TEAP = tetraethylammonium perchlorate.

## Experimental Section

*Caution*! Technetium-99 emits a low-energy (0.292-MeV) $\beta$ particle with a half-life of $2.12 \times 10^5$ years. When handled in milligram amounts, $^{99}$Tc 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 $\beta$-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. In this paper the symbol Tc refers only to technetium-99; the metastable isotope $^{99m}$Tc was not used in these studies.

**Reagents.** Unless otherwise noted, all chemicals were of reagent grade. The starting complex, *trans*-$[Tc(O)(OH)(DMPE)_2](PF_6)_2$, was prepared by the method described in a previous paper.[1a] DMF labeled "suitable for spectrophotometry" from Burdick and Jackson Laboratories, Inc., and polarographic grade TEAP from G. F. Smith Chemicals were used in the electrochemical measurements.

**Synthesis. *cis*- and *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$.** To a suspension containing 100 mg of *trans*-$[Tc(O)(OH)(DMPE)_2](PF_6)_2$ ($1.4 \times 10^{-4}$ mol) in 20 mL of degassed ethanol was added 220 mg of *p*-chlorobenzenethiol ($1.5 \times 10^{-3}$ mol) in 2 mL of degassed ethanol, followed by 0.3 mL of 1 M NaOH ($3.0 \times 10^{-4}$ mol). The mixture was stirred at 60 °C for 20 min under an argon atmosphere, whereupon the solution became almost black. Cooling this black reaction solution to room temperature led to a crystalline precipitate that contained predominantly black *cis*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ as well as a very small amount of red *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$. This mixture of precipitates was collected by filtration; yield 40 mg, 42%.

Black crystals of *cis*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ suitable for X-ray structural analysis were obtained by recrystallization of the black/red mixture from $CH_2Cl_2$ at 4 °C. Anal. Calcd for *cis*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$, $C_{24}H_{40}P_4S_2Cl_2Tc$: C, 41.99; H, 5.87; Cl, 10.33. Found: C, 39.64; H, 5.63; Cl, 10.49. Visible–UV ($CH_2Cl_2$; $\lambda_{max}$, nm ($\epsilon$, $10^3$ M$^{-1}$ cm$^{-1}$)): 610 (3.33), 512 (3.47), 454 (4.39), 411 (3.62), 370 sh (3.89), 388 sh (1.74), 310 sh (7.32), 261 (44.17). These measured extinction coefficients represent lower limits to the actual values since this complex suffers some decomposition in solution, and this decomposition leads to decreasing measured absorbances (vide infra).

Red crystals of *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ were obtained by adding 5 mL of $CH_2Cl_2$ to the original black reaction mixture and removing the resulting black precipitate by filtration. The filtrate was cooled to 4 °C, and the resulting black crystals were again removed. When this final filtrate was stored at 4 °C for several days, a small amount (<5 mg) of red crystals of *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ suitable for X-ray structural analysis formed and could be collected by filtration. Visible ($CH_2Cl_2$; $\lambda_{max}$, nm): 533, 405. Accurate extinction coefficients could not be measured due to the rapid isomerization and decomposition of this isomer (vide infra).

**Measurements.** Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Visible–UV spectra were recorded in dichloromethane on a Cary 210 spectrophotometer (Varian) at ambient temperatures. Electrochemical measurements were made with a Bioanalytical Systems, Inc. (BAS), CV-1A apparatus using a platinum-disk working electrode (Bioanalytical Systems, Inc., MF 2013). An aqueous Ag/AgCl (3 M NaCl) electrode (BAS) and a platinum wire were used as reference and auxiliary electrodes, respectively. All potentials are reported vs this reference electrode. The electrochemical experiment was conducted in DMF with 0.5 M TEAP as supporting electrolyte and a complex concentration of ca. $10^{-3}$ M.

**Crystallography.** Single-crystal X-ray diffraction experiments were performed on a Nicolet R3 automated diffractometer with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) and a graphite monochromator at ambient temperature. Details of data collection in common were as follows: scan method, $\theta/2\theta$; scan range; 1.0° below K$\alpha_1$ to 1.0° above K$\alpha_2$; scan rate, variable 2–5°/min; ratio of background/scan time, 0.5. The agreement between equivalent reflections was <2%. Both structures were solved by Patterson methods and refined in a full matrix with the programs of SHELX-76.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in a combination of observed and calculated positions and held invariant. Isotropic temperature factors for the hydrogen atoms within each structure were set equal to a single variable, which was refined for each structure. Absorption corrections were made by empirical methods.[9] No correction for secondary extinction was made. Neutral-atom scattering factors and corrections for anomalous dispersion were from ref 10. Table I contains further crystallographic data.

**Table I.** Experimental Crystallographic Data for *cis*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ and *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$

| | cis | trans |
|---|---|---|
| formula | $TcS_2Cl_2P_4C_{24}H_{40}$ | $TcS_2Cl_2P_4C_{24}H_{40}$ |
| mol wt | 686.52 | 686.52 |
| cryst dimens, mm | 0.60 × 0.12 × 0.16 | 0.20 × 0.18 × 0.16 |
| cryst syst | orthorhombic | monoclinic |
| cryst color, habit | red-black, rods | red, irregular |
| space group | *Iba*2 | $P2_1/c$ |
| cell dimens[a] | | |
| *a*, Å | 10.4840 (14) | 9.882 (2) |
| *b*, Å | 16.505 (2) | 15.311 (3) |
| *c*, Å | 17.783 (4) | 10.285 (2) |
| $\beta$, deg | | 96.226 (12) |
| *V*, Å$^3$ | 3077.0 (7) | 1547.0 (4) |
| *Z* | 4 | 2 |
| calcd density, g cm$^{-3}$ | 1.482 | 1.474 |
| $2\theta$ range, deg | 5–52 | 6–52 |
| *hkl* ranges | $0 \le h \le 13$ | $0 \le h \le 13$ |
| | $0 \le k \le 21$ | $0 \le k \le 19$ |
| | $0 \le l \le 22$ | $-13 \le l \le 13$ |
| total no. of data | 1772 | 3458 |
| no. of unique data | 1578 | 3055 |
| no. of obsd data, $I_o \ge 3\sigma(I)$ | 1237 | 1821 |
| $\mu$, cm$^{-1}$ | 9.81 | 9.75 |
| transmissn coeff | 0.820–0.771 | 0.841–0.766 |
| $F_{000}$ | 1412 | 706 |
| $R$, $R_w$ for obsd rflns | 0.029, 0.024 | 0.046, 0.032 |
| $R$, $R_w$ for all rflns | 0.041, 0.025 | 0.088, 0.035 |
| *w* | $\sigma_F^{-2}$ | $\sigma_F^{-2}$ |

[a] Lattice parameters from 25 high-angle reflections constrained orthorhombic (cis) and from 22 high-angle reflections constrained monoclinic (trans).

## Results

**Synthesis.** The thiolato–Tc(II) complex $[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ is prepared in ethanol by a reduction–substitution route[1,5b] in which the Tc(V) starting material *trans*-$[Tc(OH)(O)(DMPE)_2]^{2+}$ is both reduced and ligated by excess *p*-chlorobenzenethiol in the presence of a small amount of NaOH. This reaction proceeds more rapidly and efficiently than the corresponding reduction–substitution reactions with alkanethiols.[1] The desired $[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ complex is produced in good yield as a mixture of cis (black) and trans (red) isomers, which may be separated by fractional crystallization. Since this synthesis generates the cis isomer in great preponderance (ratio of cis/trans >10), the fractional crystallization procedure affords good yields of the cis isomer but only very small amounts of the trans isomer.

**Properties.** Visible–UV absorption data for *cis*- and *trans*-$[Tc(SC_6H_4\text{-}p\text{-}Cl)_2(DMPE)_2]$ are given in the Experimental Section. The visible spectrum of the trans Tc(II) isomer is dominated by an intense band at 533 nm, while that of the cis Tc(II) isomer consists of several absorptions at 610, 512, 454, and 411 nm (see Figure 1). The absorption spectra of $CH_2Cl_2$ solutions of both the cis and trans isomers change with time. For the cis isomer, the intensities of all absorption bands slowly decrease with time (ca. 15% decrease at 610 nm in 60 min), but no isosbestic points are observed. For the trans isomer, much more

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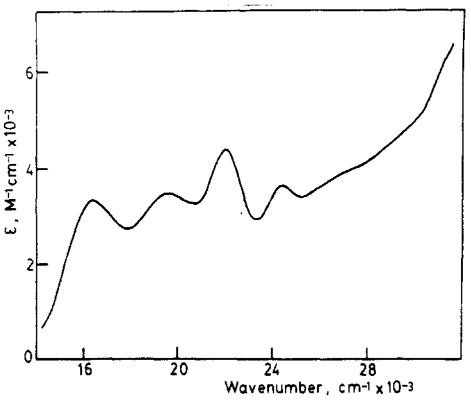

**Figure 1.** Visible spectrum of *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$] recorded in $CH_2Cl_2$.

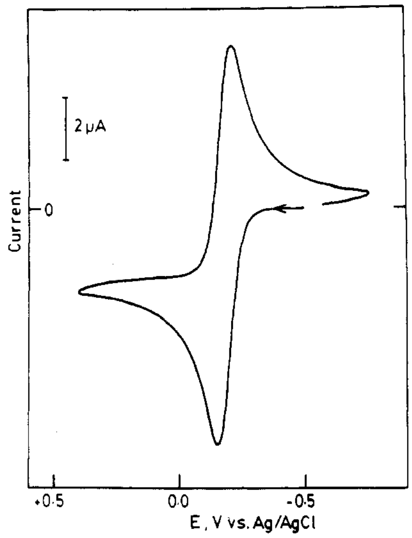

**Figure 2.** Cyclic voltammogram of 1 mM *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$] in 0.5 M TEAP/DMF at a PDE. The scan rate is 100 mV/s.

dramatic spectral changes occur; the original band at 533 nm decreases in intensity and shifts to slightly higher energy as new absorption bands appear at 610 and 454 nm. While these overall spectral changes reflect primarily conversion of the trans isomer to the cis isomer, isosbestic points (at about 660, 600, and 476 nm) are not well defined due to slow decomposition of the complexes. Standard first-order kinetic plots of ln $(A_t - A_\infty)$ vs $t$ (at 533 nm) are linear for more than 2 half-lives. From these plots the first-order rate constant governing the trans → cis isomerization in $CH_2Cl_2$ at ambient temperature is estimated to be $1.6 \times 10^{-4}$ s$^{-1}$ ($t_{1/2}$ = 74 min).

**Cyclic Voltammetry.** Electrochemical experiments were performed only on the more stable *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$] isomer. When a 1 mM solution of this Tc(II) complex in 0.5 M TEAP/DMF is exposed to a PDE held at 0.0 V, anodic electrolysis occurs. However, when the same experiment is conducted at −0.5 V, no electrolysis occurs. These observations establish that, with respect to the redox process which occurs between 0.0 and −0.5 V, the isolated complex exists in its reduced form. A cyclic voltammogram initiated at −0.5 V (Figure 2; positive potential scan) yields both an oxidation wave ($E_{pa}$ = −0.153 V) and a coupled reduction wave ($E_{pc}$ = −0.212 V). At a scan rate of 100 mV/s, the ratio of anodic to cathodic peak currents is approximately unity and the peak separation is 59 mV. These results establish that the redox process which occurs at $E°'$ = −0.182 V is electrochemically reversible.

Another cyclic voltammogram initiated at −0.5 V, but with a negative potential scan, shows that the Tc(II) *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$] complex can be reduced as well as oxidized. The peak potential for reduction occurs at −1.035 V, while the coupled reoxidation peak potential occurs at −0.945 V. The large difference in peak potentials (90 mV) indicates that this redox process ($E°'$ = ca. −0.99 V) is not reversible.

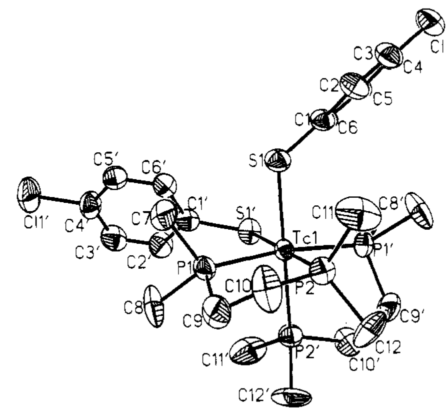

**Figure 3.** Perspective view of *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$] showing the assigned labeling. The Tc atom occupies a crystallographic 2-fold axis. Ellipsoids represent 50% probability.

**Table II.** Atomic Positional Parameters for *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$]

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Tc1 | 0.50000 | 0.50000 | 0.50000 |
| S1 | 0.4958 (3) | 0.3920 (2) | 0.4077 (2) |
| P1 | 0.7242 (2) | 0.4782 (1) | 0.5102 (2) |
| P2 | 0.4985 (2) | 0.3904 (2) | 0.5921 (2) |
| C1 | 0.3486 (8) | 0.3816 (4) | 0.3611 (4) |
| C2 | 0.2896 (8) | 0.3059 (4) | 0.3576 (4) |
| C3 | 0.1742 (8) | 0.2947 (4) | 0.3225 (5) |
| C4 | 0.1161 (7) | 0.3602 (5) | 0.2888 (4) |
| C5 | 0.1709 (7) | 0.4370 (4) | 0.2910 (4) |
| C(6) | 0.2883 (7) | 0.4461 (4) | 0.3261 (4) |
| C7 | 0.8102 (8) | 0.4092 (5) | 0.4477 (4) |
| C8 | 0.8398 (7) | 0.5631 (4) | 0.5143 (7) |
| C9 | 0.7580 (8) | 0.4279 (6) | 0.5999 (4) |
| C10 | 0.6621 (8) | 0.3581 (5) | 0.6124 (6) |
| C11 | 0.4279 (9) | 0.2929 (4) | 0.5638 (5) |
| C12 | 0.4374 (9) | 0.3989 (6) | 0.6886 (4) |
| Cl1 | −0.0314 (2) | 0.3480 (1) | 0.2425 (2) |

**Table III.** Bond Lengths (Å) and Angles (deg) for *cis*-[Tc($SC_6H_4$-*p*-Cl)$_2$(DMPE)$_2$]

| | | | |
|---|---|---|---|
| Tc1–S1 | 2.424 (3) | P2–C12 | 1.838 (9) |
| Tc1–P1 | 2.385 (2) | C1–C2 | 1.40 (1) |
| Tc1–P2 | 2.439 (3) | C1–C6 | 1.39 (1) |
| S1–C1 | 1.760 (9) | C2–C3 | 1.37 (1) |
| P1–C7 | 1.829 (9) | C3–C4 | 1.38 (1) |
| P1–C8 | 1.854 (7) | C4–C5 | 1.39 (1) |
| P1–C9 | 1.833 (9) | C4–Cl1 | 1.763 (8) |
| P1–C10 | 1.832 (9) | C5–C6 | 1.39 (1) |
| P2–C11 | 1.841 (9) | C9–C10 | 1.55 (1) |
| Tc1–S1–C1 | 114.0 (3) | S1–C1–C6 | 122.5 (6) |
| Tc1–P1–C7 | 122.3 (3) | P1–C9–C10 | 109.7 (6) |
| Tc1–P1–C8 | 122.2 (2) | P2–C10–C9 | 111.3 (6) |
| Tc1–P1–C9 | 109.0 (3) | C1–C2–C3 | 122.1 (7) |
| Tc1–P2–C10 | 110.0 (3) | C1–C6–C5 | 121.6 (7) |
| Tc1–P2–C11 | 117.9 (3) | C2–C1–C6 | 117.8 (7) |
| Tc1–P2–C12 | 124.9 (3) | C2–C3–C4 | 118.8 (7) |
| S1–Tc1–P1 | 87.59 (8) | C3–C4–C5 | 121.3 (7) |
| S1–Tc1–P2 | 84.8 (1) | C3–C4–Cl1 | 120.1 (6) |
| S1–Tc1–P1′ | 98.31 (8) | C4–C5–C6 | 118.5 (7) |
| S1–Tc1–P2′ | 179.18 (8) | C5–C4–Cl1 | 118.6 (6) |
| S1–Tc1–S1′ | 94.7 (1) | C7–P1–C8 | 100.0 (4) |
| P1–Tc1–P2 | 81.00 (8) | C7–P1–C9 | 98.7 (4) |
| P1–Tc1–P1′ | 171.3 (1) | C8–P1–C9 | 100.4 (5) |
| P1–Tc1–P2′ | 93.13 (8) | C10–P2–C11 | 100.1 (4) |
| P2–Tc1–P2′ | 95.7 (1) | C10–P2–C12 | 99.5 (5) |
| S1–C1–C2 | 119.8 (6) | C11–P2–C12 | 100.5 (4) |

In analogy to the well-characterized electrochemistry of the *trans*-[Tc$X_2D_2$]$^{+/0}$ systems,[11-16] the reversible redox process ob-

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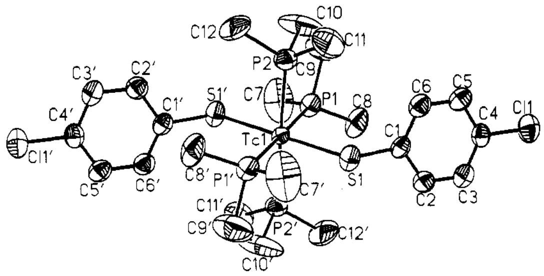

**Figure 4.** Perspective view of *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$] showing the assigned labeling. The Tc atom occupies a crystallographic inversion center. Ellipsoids represent 50% probability.

served for *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$] at −0.182 V vs Ag/AgCl (Figure 2) is assigned as the Tc(III/II) couple, while the nonreversible process observed at ca. −0.99 V vs Ag/AgCl is assigned as the Tc(II/I) couple.

**Crystal Structure of *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$].** Figure 3 illustrates the molecular geometry and adopted labeling scheme for the molecule. No solvent or ions are present in the lattice. Fractional atomic coordinates are listed in Table II. Bond lengths and angles are presented in Table III. The central technetium atom occupies a crystallographic 2-fold rotation axis, which relates the halves of the molecule. The ligand arrangement is roughly octahedral with the primary distortion being the restricted bite angles of the DMPE chelate (81.00 (8)° for P1–Tc–P2). As a result, the trans P1–Tc–P1′ angle is decidedly nonlinear at 171.3 (1)°. The monodentate thiolate ligands are mutually cis, which is a heretofore unknown geometry for [TcX$_2$D$_2$]$^{n+}$ complexes. The molecules exist in the lattice as discrete subunits with normal van der Waals contacts between them. Within the thiolato ligand the phenyl group is regular and planar. Substituent atoms S1 and Cl1 occupy the plane of the ring with deviations from it of −0.018 and 0.015 Å, respectively. The dihedral angle between the two related phenyl rings is 62.2 (2)°. In a view down the S1–Tc axis, the *p*-chlorobenzene substituent is neither staggered nor eclipsed with respect to that equatorial plane (consisting of atoms P1, P2, P1′, and S1′) but is positioned near the projection of the Tc–P1′ bond axis. Selected torsion angles describing the ring orientation are C1–S1–Tc–P1 = −171.2 (3)°, C1–S1–Tc–P2 = 107.6 (3)°, C1–S1–Tc–P1′ = 15.2 (3)°, and C1–S1–Tc–S1′ = −73.1 (3°). The rotational orientation of the ring about the S1–C1 bond can be described by the following torsion angles: Tc–S1–C1–C2 = −128.6 (6)° and Tc–S1–C1–C6 = 52.3 (7)°.

The Tc$^{II}$–S bond length is 2.424 (3) Å and the Tc–S1–C1 angle is 114.0 (3)°. Bond lengths in the thiolato moiety are S1–C1 = 1.760 (9) Å and C4–Cl1 = 1.763 (8) Å. The two Tc–P bonds are nonequivalent; the shorter is trans to another phosphorus atom (2.385 (2) Å), and the longer is trans to sulfur (2.439 (3) Å). The Tc–P bonds are lengthened trans to *p*-chlorobenzenethiol, and the magnitude of this structural trans effect is 0.054 (4) Å. The DMPE chelate exhibits its typical disorder with respect to the phosphine carbon atoms; this is manifested as large thermal ellipsoids in Figure 3.

**Crystal Structure of *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$].** Figure 4 illustrates the molecular geometry and adopted atomic labeling scheme for the molecule. No solvent or ions are present in the lattice. Fractional atomic coordinates are contained in Table IV. Bond lengths and angles are given in Table V. The technetium atom occupies a crystallographic inversion center in the lattice and is central to a trans-octahedral ligand arrangement. As usual, the acute bite angle of the DMPE chelate (82.50 (6)°) induces some distortion of the octahedron. The two independent phosphorus atoms and the Tc atom define an equatorial plane that the two inversion-related phosphorus atoms are required to occupy. The angle made by the axial Tc–S vector to this equatorial plane is 82.5 (6)°. The individual molecules are discrete with normal van der Waals contacts between them.

**Table IV.** Atomic Positional Parameters for *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$]

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Tc1 | 0.00000 | 0.00000 | 0.00000 |
| P1 | −0.1124 (2) | 0.0244 (1) | 0.1911 (2) |
| P2 | 0.1681 (2) | 0.0947 (1) | 0.1122 (2) |
| S1 | −0.1103 (2) | 0.1168 (1) | −0.1307 (2) |
| Cl1 | −0.5403 (2) | 0.3866 (1) | 0.0402 (2) |
| C1 | −0.2289 (7) | 0.1907 (4) | −0.0727 (6) |
| C2 | −0.3655 (7) | 0.1863 (4) | −0.1271 (6) |
| C3 | −0.4618 (7) | 0.2460 (4) | −0.0935 (6) |
| C4 | −0.4201 (7) | 0.3121 (4) | −0.0037 (6) |
| C5 | −0.2863 (7) | 0.3191 (4) | 0.0511 (6) |
| C6 | −0.1917 (7) | 0.2578 (4) | 0.0159 (6) |
| C7 | −0.123 (1) | −0.0670 (5) | 0.3114 (8) |
| C8 | −0.2839 (7) | 0.0682 (5) | 0.1904 (6) |
| C9 | −0.016 (1) | 0.1085 (7) | 0.2981 (8) |
| C10 | 0.129 (1) | 0.1145 (7) | 0.2776 (8) |
| C11 | 0.1873 (9) | 0.2062 (5) | 0.0488 (9) |
| C12 | 0.3488 (7) | 0.0587 (5) | 0.1451 (8) |

**Table V.** Bond Lengths (Å) and Angles (deg) for *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$]

| | | | |
|---|---|---|---|
| Tc1–P1 | 2.390 (1) | S1–C1 | 1.778 (7) |
| Tc1–P2 | 2.404 (2) | Cl1–C4 | 1.741 (7) |
| Tc1–S1 | 2.424 (2) | C1–C2 | 1.405 (9) |
| P1–C7 | 1.879 (8) | C1–C6 | 1.396 (9) |
| P1–C8 | 1.822 (7) | C2–C3 | 1.390 (9) |
| P1–C9 | 1.883 (9) | C3–C4 | 1.402 (9) |
| P2–C10 | 1.812 (8) | C4–C5 | 1.384 (9) |
| P2–C11 | 1.845 (8) | C5–C6 | 1.399 (9) |
| P2–C12 | 1.865 (8) | C9–C10 | 1.472 (11) |
| Tc1–P1–C7 | 119.4 (3) | Cl1–C4–C3 | 118.9 (5) |
| Tc1–P1–C8 | 124.7 (2) | Cl1–C4–C5 | 119.4 (5) |
| Tc1–P1–C9 | 109.7 (3) | C1–C2–C3 | 121.6 (6) |
| Tc1–P2–C10 | 110.1 (3) | C1–C6–C5 | 121.8 (6) |
| Tc1–P2–C11 | 118.7 (3) | C2–C1–C6 | 117.9 (6) |
| Tc1–P2–C12 | 120.5 (3) | C2–C3–C4 | 118.5 (6) |
| Tc1–S1–C1 | 123.8 (2) | C3–C4–C5 | 121.7 (6) |
| P1–Tc1–P2 | 82.50 (6) | C4–C5–C6 | 118.5 (6) |
| P1–Tc1–S1 | 96.88 (6) | C7–P1–C8 | 99.0 (4) |
| P1–C9–C10 | 113.4 (6) | C7–P1–C9 | 100.7 (4) |
| P2–Tc1–S1 | 93.81 (6) | C8–P1–C9 | 99.3 (4) |
| P2–C10–C9 | 115.8 (6) | C10–P2–C11 | 102.6 (4) |
| S1–C1–C2 | 118.4 (5) | C10–P2–C12 | 100.2 (4) |
| S1–C1–C6 | 123.4 (5) | C11–P2–C12 | 101.8 (4) |

Within the thiolato ligand the phenyl ring is regular and planar. The para substituent atom Cl lies in this phenyl plane (deviation −0.023 Å) while the sulfur atom is somewhat out of the plane (deviation 0.131 Å). The Tc–S1 vector is skewed toward the equatorial atom P1′, and the S1–C1 bond nearly eclipses the projection of the Tc–P1 bonds; overall, this lessens the contact between the *p*-chlorobenzenethiol group and the terminal methyl groups on the phosphines. Selected torsion angles describing the orientation of the phenyl ring are C1–S1–Tc–P1 = 2.3 (3)°, C1–S1–Tc–P2 = −80.6 (3)°, Tc–S1–C1–C2 = −112.1 (4)°, and Tc–S1–C1–C6 = 73.6 (6)°.

The Tc–S1 bond length is 2.424 (2) Å, and the Tc–S1–C1 angle is 123.8 (2)°. Linkages to the aryl fragment are S1–C1 = 1.778 (7) Å and C4–Cl1 = 1.741 (7) Å. The two Tc–P bond lengths are 2.390 (1) and 2.404 (2) Å (average 2.397 (7) Å). Bond distances and angles among the phosphine carbon atoms are considered to be unreliable due to disorder in both the chelate rings and the terminal methyl groups. This disorder manifests itself in large thermal ellipsoids for these carbon atoms (Figure 4).

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**Table VI.** Selected Tc(III/II) $E°'$ Values in 0.5 M TEAP/DMF

| couple[a] | $E°'$-(Tc(III/II))[b] | ref |
|---|---|---|
| *trans*-$[\mathrm{Tc(NCS)_2(DPPE)_2}]^{+/0}$ | +0.392 | 12 |
| *trans*-$[\mathrm{Tc(Br)_2(DPPE)_2}]^{+/0}$ | +0.103 | 11 |
| *trans*-$[\mathrm{Tc(Cl)_2(DPPE)_2}]^{+/0}$ | −0.001 | 11 |
| *trans*-$[\mathrm{Tc(Br)_2(DMPE)_2}]^{+/0}$ | −0.098 | 16 |
| *cis*-$[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]^{+/0}$ | −0.182 | this work |
| *trans*-$[\mathrm{Tc(Cl)_2(DMPE)_2}]^{+/0}$ | −0.231 | 16 |
| *trans*-$[\mathrm{Tc(SCH_2C_6H_5)_2(DMPE)_2}]^{+/0}$ | −0.513 | 1 |
| *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^{+/0}$ | −0.550 | 1 |
| *trans*-$[\mathrm{Tc(SCH_2C_6H_4\text{-}\mathit{p}\text{-}OCH_3)_2(DMPE)_2}]^{+/0}$ | −0.559 | 1 |
| *trans*-$[\mathrm{Tc(SC_2H_5)_2(DMPE)_2}]^{+/0}$ | −0.566 | 1 |
| *trans*-$[\mathrm{Tc(S\text{-}\mathit{n}\text{-}C_3H_7)_2(DMPE)_2}]^{+/0}$ | −0.622 | 1 |

[a] DPPE = 1,2-bis(diphenylphosphino)ethane; DMPE = 1,2-bis(dimethylphosphino)ethane. [b] In V vs Ag/AgCl (3 M NaCl) from cyclic voltammetry.

## Discussion

**Background.** Over 30 Tc(III) and Tc(II) complexes of general formula $[\mathrm{TcX_2D_2}]^{+/0}$ (where X is a halide or pseudohalide ligand and D is a chelating diphosphine or diarsine ligand) are known and have been extensively characterized, in many cases by single-crystal X-ray structural analysis.[1,5a–c,11–14] There are two especially noteworthy generalizations that can be made about this family of complexes: (1) *Every* $[\mathrm{TcX_2D_2}]^{+/0}$ complex prepared to date has been assigned the trans geometry, either on the basis of crystallographic analysis or on the basis of visible–UV spectral properties that mimic those exhibited by structurally characterized analogues. (2) *Every* complex exhibits an electrochemistry reversible Tc(III/II) redox couple at a readily accessible potential. When the D ligand contains pendant alkyl groups (e.g. DMPE or DEPE), the $E°'$ values governing the Tc(III/II) couple are sufficiently negative so that the Tc(II) complexes are air sensitive and thus only the Tc(III) forms can be readily isolated. However, when the D ligand contains pendant aryl groups (e.g. DPPE), the Tc(III/II) $E°'$ values often shift sufficiently positive so that the Tc(II) forms are reasonably stable in air and can be conveniently isolated. For example, both of the Tc(II) complexes *trans*-$[\mathrm{Tc(NCS)_2(DPPE)_2}]$ and *trans*-$[\mathrm{Tc(Cl)_2(DPPE)_2}]$ ($E°'$ values of +0.372 and −0.001 V vs Ag/AgCl, respectively) have been isolated and characterized by X-ray structural analysis.[13,14]

The most recently prepared members of this family are the *trans*-$[\mathrm{Tc(SR)_2(DMPE)_2}]^{+/0}$ complexes, in which X is an alkane- or benzenemethane-thiolato ligand.[1] The properties of these complexes comply with the above two generalizations; i.e., they have been assigned the trans geometry on the basis of structural characterization of the Tc(III) prototype *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^+$, and they all exhibit the relatively negative Tc(III/II) $E°'$ values typical of DMPE complexes, which allow their Tc(III) forms to be conveniently isolated but cause their Tc(II) forms to be air sensitive. From this perspective it is seen that replacing the alkane- or benzenemethanethiolato ligands of $[\mathrm{Tc(SR)_2(DMPE)_2}]^{+/0}$ complexes by the arenethiolato ligand *p*-chlorobenzenethiolate generates two dramatic effects: (1) It causes the Tc(II) state to be markedly stabilized with respect to the Tc(III) state. (2) It causes the cis isomer to be markedly stabilized with respect to the trans isomer. The following sections both describe these effects in more detail and also attempt to rationalize them on the basis of trends that have been observed during the extensive structural and electrochemical characterizations of *trans*-$[\mathrm{TcX_2D_2}]^{+/0}$ complexes.[11–16] Relevant Tc(III/II) $E°'$ values are summarized for convenience in Table VI.

**Synthesis.** The reaction of *trans*-$[\mathrm{Tc^V(OH)(O)(DMPE)_2}]^{2+}$ with excess *p*-chlorobenzenethiol and a small amount of base produces both cis and trans isomers of the air-stable arenethiolato–Tc(II) complex $[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]$. This preparative reaction proceeds more rapidly and efficiently than do the analogous reactions with alkanethiols, consistent with the supposition[1b] that the nucleophilicity of the thiol is an important factor in determining the efficacy of this reduction–substitution process. Also consistent with this supposition[1b] is the fact that addition of base is necessary in order for the preparative reaction to proceed at a reasonable rate.

It is difficult to isolate the trans isomer in substantial yields because of its relatively rapid isomerization to the more stable cis form. At room temperature, in dichloromethane, the half-life for this trans → cis isomerization is approximately 74 min. The cis isomer does not exhibit any detectable isomerization to the trans form. This marked preference of the $[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]$ complex for the cis geometry is in dramatic contrast to the geometrical preference in all other known $[\mathrm{TcX_2D_2}]^{+/0}$ complexes, which uniformly adopt a trans arrangement.[5a–c,11–14] Since this usual trans geometry is exhibited by the thiolato complexes $[\mathrm{Tc(SR)_2(DMPE)_2}]^{+/0}$ when R is a benzyl or alkyl group,[1] it is reasonable to assume that the extraordinary stability of the cis form of $[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]$ is directly due to the presence of the aryl moiety on the coordinated sulfur atom.

**Properties.** The relatively positive Tc(III/II) $E°'$ value of the arenethiolato complex *cis*-$[\mathrm{Tc(SC_6H_5\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]^{+/0}$ (−0.182 V vs Ag/AgCl), compared to those of the related alkane- and benzenemethanethiolato complexes *trans*-$[\mathrm{Tc(SR)_2(DMPE)_2}]^{+/0}$ (range −0.513 to −0.622 V vs Ag/AgCl for R = methyl, ethyl, *n*-propyl, benzyl, and *p*-methoxybenzyl), underlies the fact that the former is isolated in its Tc(II) form whereas the latter are isolated in their Tc(III) forms.[1] This relative stabilization of the arenethiolato–Tc(II) complex could result (i) directly from the properties of the aryl group itself, (ii) indirectly from the trans → cis conversion that is induced by the aryl group, or (iii) from a combination of these causes. While the trans vs cis geometry of a complex has been recognized as a factor determining the redox behavior of low-valent Cr and Mo phosphine complexes,[17] there are not sufficient data available to assess the effect of a trans → cis conversion on Tc(III/II) $E°'$ values. However, existing data on the effects of varying D and X substituents on the Tc(III/II) $E°'$ values of *trans*-$[\mathrm{Tc(X)_2(D)_2}]^{+/0}$ complexes support assigning at least a significant portion of the arenethiolato–Tc(II) complex stabilization to effects induced by the aryl group.

For example, the effect of varying organic moieties bonded directly to a coordinating atom is discerned by comparing Tc(III/II) $E°'$ values for *trans*-$[\mathrm{TcX_2(D)_2}]^{+/0}$ complexes, in which D is either DMPE or DPPE; converting the eight $\mathrm{P{-}CH_3}$ groups of *trans*-$[\mathrm{TcX_2(DMPE)_2}]^{+/0}$ complexes (X = Cl, Br) to the eight $\mathrm{P{-}C_6H_5}$ groups of *trans*-$[\mathrm{TcX_2(DPPE)_2}]^{+/0}$ complexes causes the Tc(III/II) $E°'$ value to shift positively by over 200 mV (202 mV for X = Br, 231 mV for X = Cl).[11] A similar, but more subtle, effect is seen by varying organic moieties that are separated from the coordinating atom by a methylene linkage; converting the two $\mathrm{(S{-}CH_2){-}H}$ groups of *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^{+/0}$ to the two $\mathrm{(S{-}CH_2){-}C_6H_5}$ groups of *trans*-$[\mathrm{Tc(SCH_2C_6H_5)_2(DMPE)_2}]^{+/0}$ causes the Tc(III/II) $E°'$ value to shift positively by 37 mV.[16] From these results it is clear that the addition of pendant aryl moieties to the *trans*-$[\mathrm{TcX_2(D)_2}]^{+/0}$ structure stabilizes the Tc(II) state and causes the Tc(III/II) $E°'$ value to shift to more positive values. Thus, the ordering of Tc(III/II) $E°'$ values *cis*-$[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]^{+/0}$ (−0.182 V) > *trans*-$[\mathrm{Tc(SCH_2C_6H_5)_2(DMPE)_2}]^{+/0}$ (−0.513 V) > *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^{+/0}$ (−0.550 V) can be understood at least qualitatively within this aryl group effect, and no special effect of the trans → cis transformation need be invoked. However, the available data do not permit a quantitative rationalization of this ordering (especially the relatively large 331-mV difference in potentials between the *cis*-$[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]^{+/0}$ and *trans*-$[\mathrm{Tc(SCH_2C_6H_5)_2(DMPE)_2}]^{+/0}$ couples) solely on the basis of the aryl group effect. Further data will be required in order to determine if the geometry of *cis*-$[\mathrm{Tc(SC_6H_4\text{-}\mathit{p}\text{-}Cl)_2(DMPE)_2}]^{+/0}$ plays a significant part in determining the surprisingly positive potential of this couple.

The fact that converting either pendant *P*-methyl groups to *P*-aryl groups or pendant *S*-methyl to *S*-aryl groups induces qualitatively similar effects on Tc(III/II) $E°'$ values implies that $\pi$ back-bonding, which is known to be an important component

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of the Tc–P interactions,[11-16] may also be an important factor in Tc–S interactions. However, it should also be noted that, in their recent review of thiolato–transition-metal complexes, Blower and Dilworth[18] have concluded that the involvement of sulfur 3d orbitals in $\pi$ back-bonding is "much less significant than is often supposed". Rather, they attribute many of the electronic interactions of coordinated thiols either to the polarizability of sulfur or to the participation of low-lying S–C antibonding $\sigma$ orbitals. Acquisition of detailed electrochemical and spectral data on a range of $[\mathrm{Tc(SR)_2(D)_2}]^{+/0}$ complexes containing different R and D groups should help decide whether or not $\pi$ back-bonding contributes significantly to the Tc–S interaction.

The visible–UV spectra of the cis and trans isomers of $[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ are quite different from one another and are easily distinguished. The trans isomer exhibits the two visible absorption bands that characterize the spectra of the related *trans*-$[\mathrm{Tc(SR)_2(DMPE)_2}]$ Tc(II) complexes, wherein R is an alkyl or benzyl group.[1] These bands have been assigned[1] as sulfur-to-technetium charge-transfer transitions,[1] with the higher intensity band (i.e., the one that occurs at lower energy) presumably being the $\mathrm{S}(\pi) \rightarrow \mathrm{Tc}$ transition. The visible absorption bands for the arenethiolato–Tc(II) complex occur at slightly higher energies ($18.8 \times 10^3$ and $24.7 \times 10^3$ cm$^{-1}$) than do the bands of the corresponding alkanethiolato– and benzenemethanethiolato–Tc(II) complexes (ranges 18.5–18.7 $\times 10^3$ and 22.2–22.7 $\times 10^3$ cm$^{-1}$ for five complexes);[1] this implies that the coordinated arenethiolato ligand is a slightly poorer reductant than are the coordinated alkane- and benzenemethanethiolato ligands.

The visible absorption spectrum of the cis isomer exhibits four distinct bands, which are assigned as CT transitions on the basis of their extinction coefficients (range 3000–5000 M$^{-1}$ cm$^{-1}$; Figure 1). The average energy ($18.0 \times 10^3$ cm$^{-1}$) of the two bands at higher wavelengths (610 and 512 nm) is approximately equal to the energy ($18.8 \times 10^3$ cm$^{-1}$) of the higher wavelength band of the trans isomer (533 nm), implying that these two transitions of the cis isomer arise from splitting of the corresponding $\mathrm{S}(\pi) \rightarrow \mathrm{Tc}$ transition of the trans isomer. This symmetry-induced splitting presumably occurs in orbitals associated with the sulfur atom since the spin-paired $\mathrm{d}^5$ Tc(II) center provides a single STTCT target orbital independent of coordination geometry.

**Structures.** For a given oxidation state of a metal, most $[\mathrm{MX_2B_2}]^{n+}$ complexes (where X is a monodentate ligand and B is a bidentate chelate) show a marked preference for either cis or trans geometry. Thus, only a few cis–trans pairs of such complexes have been structurally characterized. When B is a chelating diphosphinoethane ligand, the only such pair known to us (other than the pair introduced in this paper) involves the Mo(II) complex $[\mathrm{MoCl_2(DPPE)_2}]$.[19,20] Furthermore, chelating diphosphinoethane ligands tend to favor formation of *trans*-$[\mathrm{MX_2B_2}]^{n+}$ complexes,[11-14,21] and relatively few examples of cis complexes are known. These examples include *cis*-$[\mathrm{Cr(CO)_2(DMPE)_2}]$,[22] *cis*-$[\mathrm{RuH_2(DPPE)_2}]$,[23] *cis*-$[\mathrm{IrH_2(DPPE)_2}]$,[24] *cis*-$[\mathrm{Ru(CN)_2(DMPE)_2}]$,[25] and most recently *cis*-$[\mathrm{ReH(PPh_3)(DMPE)_2}]$,[26] which NMR studies show to be in equilibrium with the trans isomer.

Analysis of structural details within the cis–trans pair of $[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ complexes provides some insight into why for these arenethiolato–Tc(II) complexes the cis isomer is more stable than the trans, even though the analogous methanethiolato–Tc(III) complex $[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^+$ prefers the usual trans geometry.[1a] The following observations implicate steric repulsion between S-bonded groups and P-bonded methyl groups as an important factor in determining which geometry is more stable.

(i) Intramolecular close contacts less than the sum of the van der Waals radii are present in both isomers of $[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$, but they are generally shorter within the trans geometry. For example, the most severe nonbonding interaction occurs between the sulfur atom and a P-bonded methyl group: 3.209 Å for S1⋯C7 in the trans isomer vs 3.299 Å for S1⋯C11 in the cis isomer.

(ii) For the two trans complexes *trans*-$[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ and *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^+$ the Tc–S–C angle is relatively large (123.8 (2) and 122.9 (2)°, respectively), while for the cis complex *cis*-$[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ the Tc–S–C angle is closer to the tetrahedral value at 114.0 (3)°. A recently reported[7] Tc(III) complex containing very sterically hindered arenethiolato ligands, $[\mathrm{Tc(MeCN)_2(SC_6HMe_4)_3}]$, relieves the steric strain associated with the aryl groups by assuming a five-coordinate structure in which the arenethiolato ligands occupy the less sterically demanding equatorial positions. In this complex the Tc–S–C bond angles range from 109 to 115°.[7] More generally, arenethiolato complexes of second- and third-row metals often assume coordination numbers less than 6, and in these complexes the M–S–C angles rarely exceed 116° (for example, Mo,[27] Re,[28] Ru,[29] Os[30]). Thus, it appears that the Tc–S–C angle within *cis*-$[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ is close to a normal, unstrained value, whereas the Tc–S–C angles within the two trans isomers are unusually large and reflect steric strain within the *trans*-$\mathrm{Tc(SR)_2}$ arrangement.

The Tc(II)–S distances in cis and trans isomers of $[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ are the same at 2.424 Å, significantly longer than the $\mathrm{Tc^{III}}$–S distance of 2.300 (3) Å in *trans*-$[\mathrm{Tc(SCH_3)_2(DMPE)_2}]^+$. This lengthening of the $\mathrm{Tc^{II}}$–S(aryl) bond with respect to the $\mathrm{Tc^{III}}$–S(methyl) bond is consistent with there being greater steric strain in the arenethiolato complexes, and indeed an analogous lengthening of $\mathrm{Tc^{III}}$–P(aryl) bonds over $\mathrm{Tc^{III}}$–P(methyl) bonds has been established.[1a] However, this comparison of Tc–S distances is not completely direct since the oxidation states of the technetium centers differ. A recent crystallographic comparison of the Tc(III) and Tc(II) complexes *trans*-$[\mathrm{TcCl_2(DPPE)_2}]^{+/0}$[14] has shown that the primarily ionic Tc–Cl bonds shorten 0.105 Å upon going from Tc(II) to Tc(III), whereas the primarily covalent Tc–P bonds lengthen 0.072 Å upon going from Tc(II) to Tc(III) because of reduced $\pi$ back-bonding in the Tc(III) state. The extent to which electrostatic and covalent interactions contribute to Tc–S bonding is yet unknown, and thus it is currently impossible to separate the electronic and steric contributions to the 0.124-Å shortening observed upon going from $\mathrm{Tc^{II}}$–S(aryl) to $\mathrm{Tc^{III}}$–S(methyl).

The details of structural comparisons between complexes of cis and trans geometries can be especially revealing with regard to ligand competition for electron density. For the cis–trans pair of $[\mathrm{Tc(SC_6H_4\text{-}}p\mathrm{\text{-}Cl)_2(DMPE)_2}]$ complexes, the most striking structural change in the first coordination sphere is the discrepancy in Tc–P bond lengths. In the cis isomer there is a sulfur-induced

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structural trans effect; the Tc–P bonds trans to sulfur are 0.054 (4) Å longer than those trans to phosphorus. This surprising result indicates that the electronic requirements of the sulfur atom are being met at some expense to the trans Tc–P bond. Since the $Tc^{II}$–P bond is known to be dominated by $\pi$-back-bonding interactions[14] we can speculate that either the arenethiolato ligand is itself a potent $\pi$-acceptor ligand which competes effectively with the trans-situated phosphine or that the arenethiolato ligand is such a poor $\sigma$ donor that maximum utilization of $Tc^{II}$–P $\pi$ back-bonding is not required.

The average length of the two Tc–P bonds that are trans to P in *cis*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$] is only marginally less than the average Tc–P length in the trans complex (2.385 (2) vs 2.397 (2) Å, respectively). These Tc–P bond lengths are in harmony with previously established correlations concerning the effects of Tc–P distances of technetium oxidation state and bulk of the P-bound group. (i) Several studies,[11-14] including a detailed structural analysis of the Tc(III)/Tc(II) pair of complexes *trans*-[$TcCl_2(DPPE)_2]^{+/0}$,[14] have established that $\pi$-back-bonding effects cause Tc–P bond lengths to decrease with increasing technetium oxidation state. Consistent with this, the $Tc^{II}$–P lengths observed in the title structure are shorter than the average $Tc^{III}$–P length (2.43 (1) Å) observed in *trans*-[$Tc(SCH_3)_2(DMPE)_2]^+$.[1a] (ii) We have previously correlated Tc–P bond lengths with the bulk of the pendant group attached to phosphorus and have documented that complexes with pendant methyl groups consistently exhibit shorter Tc–P distances than do those with pendant phenyl groups.[1a] Thus, the $Tc^{II}$–P distances in the title complexes are somewhat shorter than the $Tc^{II}$–P distances observed in complexes containing phenyl-substituted phosphine ligands: [$Tc(NCS)_2(DPPE)_2$], 2.44 (1) Å (average);[13] [$TcCl_2(DPPE)_2$], 2.43 (2) Å (average);[14] [$Tc(PPh(OEt)_2)_4Cl_2$], 2.412 (9) Å (average).[31]

The S–C(aryl) lengths in the two title structures are not significantly different (1.760 (9) and 1.778 (7) Å for the cis and trans isomers, respectively). However, both are shorter than the S–C(methyl) lengths in *trans*-[$Tc(SCH_3)_2(DMPE)_2]^+$ and *trans*-[$Tc(SCH_3)_2(DEPE)_2]^+$ (1.842 (7) and 1.821 (4) Å, respectively)[1a] due to the change in hybridization of the carbon atom from $sp^2$ to $sp^3$. At the other end of the *p*-chlorobenzenethiolato ligand, the observed Cl–C bond lengths are also not significantly different (1.763 (8) and 1.741 (7) Å for the cis and trans isomers, respectively) and are consistent with previously reported values. A survey of the Cambridge Structural Database[32] generates precise structural parameters for 10 examples of *p*-chlorobenzenethiolate fragments, some being bound to transition metals and others being part of organic moieties. For this set of fragments the Cl–C bond length averages 1.74 (3) Å and ranges from 1.675 to 1.784 Å.

There has been some discussion in the literature about S···S bonding interactions when coordinated arenethiolato ligands are cis and are appropriately oriented.[33] However, in the *cis*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$] complex the S···S distances and ring orientations preclude any such interactions.

## Conclusions

The unusual stability of the cis isomer of the arenethiolato title complexes, relative to that of the trans isomer, which is the stable form of the alkanethiolato analogues, is ascribed as resulting primarily from the steric requirements of the aryl group. The unusual stability of the Tc(II) form of the arenethiolato title complexes, relative to that of Tc(III), which is the stable oxidation state of the alkanethiolato analogues, is ascribed at least partially to the $\pi$-accepting electronic properties of the aryl group. The extent to which these two aryl group effects, steric and electronic, may be interrelated is not yet clear. The surprising structural trans effect exerted by the arenethiolato ligand on the strongly covalent Tc–P linkage highlights how little is known about the electronic factors that govern thiolato–metal interactions.

**Acknowledgment.** Financial support was provided in part by the National Institutes of Health (Grants Nos. HL-21276 and CA-42179) and by Mallinckrodt, Inc. The diffractometer used herein was purchased through an NSF equipment grant to Wayne State University. M.J.H. continues to appreciate the expertise of L. Boulet and the WSU Electronics Shop.

**Supplementary Material Available:** Tables A–D, listing thermal parameters for *cis*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$], hydrogen parameters for *cis*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$], thermal parameters for *trans*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$], and hydrogen parameters for *trans*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$], respectively (4 pages); Tables E and F, listing observed and calculated structure factors for *cis*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$] and *trans*-[$Tc(SC_6H_4$-*p*-$Cl)_2(DMPE)_2$], respectively (31 pages). Ordering information is given on any current masthead page.

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