w, 1489 s, 1453 s, 1404 s, 1380 m, sh, 1310 m, sh, 1310 s, 1290 s, 1240 vs, 1163 vs, 1109 m, 1070 s, 1040 vs, 982 vs, 877 s, 838 s, 810 s, 760 m, 670 s, 627 w, 571 m, sh, 550 s, 528 s, b, 490 s, 429 w cm^{-1}. MS (EI$^+$) [m/e (species), intensity]: 235 (M$^+$), 5.2; 216 (M$^+$ − F), 13.0; 162 (CF$_3$CH$_2$N(H)PO$_2$H$^+$), 51.5; 110 (C$_2$H$_5$OPO$_2$H$_2^+$), 100; 92 (P(O)-OC$_2$H$_5^+$), 22.5; 81 (P(O)(OH)$_2^+$), 28.0; 69 (CF$_3^+$), 38.0. ^{19}F NMR: ϕ −75.1 (t). ^{31}P{H} NMR: δ 6.8 (s). ^{1}H NMR: δ 1.2 (t), 3.5 (q, b), 4.33 (p), 5.1 (b); $J_{CF_3CH_2} = 8.2$ Hz, $J_{CH_3-CH_2} = 7.1$ Hz.

Preparation of CF$_3$CH$_2$N(H)P(O)(OH)$_2$. A 1.87-mmol sample of pure CF$_3$CH$_2$N(H)P(O)(OC$_2$H$_5$)$_2$ was combined with 3.9 mmol of (CH$_3$)$_3$SiBr in a round-bottomed Pyrex vessel equipped with a Teflon stopcock. The mixture was stirred at 40 °C for 12 h and at 45 °C for 18 h, after which excess (CH$_3$)$_3$SiBr was removed under vacuum. Water

(20 mL) was then added, and stirring at room temperature was continued for 24 h. The solvent was then removed under vacuum to leave the white solid product CF$_3$CH$_2$N(H)P(O)(OH)$_2$ in approximately 20% yield. Spectral data obtained were as follows. IR (KBr): 3460 b (OH), 3200 cm^{-1} vb (NH). MS (CI$^+$) [m/e (species), intensity]: 180 (M$^+$ + 1), 72.0; 160 (M$^+$ − F), 30.4; 138 (M$^+$ − F − 2H), 29.6; 110 (M$^+$ − CF$_3$), 33.6; 80 (P(O)$_2$OH$^+$), 14.0; 69 (CF$_3^+$), 1.2. ^{19}F NMR: ϕ −73.6 (t). ^{31}P{H} NMR: δ −10.9 (s). ^{1}H NMR: δ 3.66 (b), 5.87 (b), 4.2 (q); $J_{CF_3-CH_2} = 7.9$ Hz.

Synthesis and Structural Characterization of Trimethylphosphine Complexes of Technetium(III)

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The first structurally characterized technetium(III) complexes containing trimethylphosphine as a ligand are reported. A novel cationic technetium(III) phosphine hydride complex was prepared by reaction of [Tc(S-tu)$_6$][PF$_6$]$_3$ (tu = η^1-S=C(NH$_2$)$_2$) with excess trimethylphosphine in methanol. The complex, [TcH{η^2-N,S-NHC(NH$_2$)S}(PMe$_3$)$_4$][PF$_6$] (1) was characterized spectroscopically and crystallographically, and shown to contain the unusual bidentate ligand [η^2-N,S-NHC(NH$_2$)S]$^-$ and a hydride ligand. Stirring 1 in methanol-d_4 led to formation of a spectroscopically identified technetium(III) deuteride, [TcD{η^2-N,S-NDC(ND$_2$)S}(PMe$_3$)$_4$][PF$_6$]. Crystallographic data for 1 are as follows: monoclinic, *Cc*, $a = 9.305$ (2) Å, $b = 16.726$ (2) Å, $c = 19.951$ (3) Å, $\beta = 91.24°$, $V = 3104.4$ Å^3, $Z = 4$, $R = 0.062$ ($R_2 = 0.060$) for 2043 observed reflections having $F_o > 3\sigma(F_o)$. Reaction of a Tc(V) substrate, [NBu$_4$][TcOCl$_4$], with excess trimethylphosphine yielded *mer*-TcCl$_3$(PMe$_3$)$_3$ (2). Crystals of 2 suitable for X-ray analysis were obtained by cocrystallizing 2 with triphenyl isocyanurate, [(PhNCO)$_3$]. The resulting material, [*mer*-TcCl$_3$(PMe$_3$)$_3$][(PhNCO)$_3$], crystallized in the orthorhombic space group *Pnma* in a unit cell of dimensions $a = 18.461$ (1) Å, $b = 13.934$ (2) Å, $c = 14.035$ (1) Å, $V = 3610.3$ Å^3, and $Z = 4$, with $R = 0.044$ ($R_w = 0.039$) for 3699 observed reflections having $F_o > 3\sigma(F_o)$. The closest intermolecular distances revealed no bonding between the two components in the crystal, 2 and [(PhNCO)$_3$].

Introduction

The increased use of radiodiagnostic compounds labeled with the metastable isotope ^{99m}Tc ($\gamma = 140$ keV, $t_{1/2} = 6$ h) has led to numerous studies exploring the basic coordination chemistry of technetium. Technetium compounds containing tertiary phosphine ligands have been studied extensively.[2-5] However, the reports of technetium compounds containing trimethylphosphine as a ligand are limited. Deutsch[6] reported the preparation of a cationic Tc(III) complex containing a tetradentate Schiff-base ligand and trans trimethylphosphine ligands. The reaction of sodium pertechnetate and excess trimethylphosphine was claimed[7] to yield the cationic Tc(I) species [Tc(PMe$_3$)$_6$]$^+$, which was not isolated. Neither of these compounds has been structurally identified. We now report the synthesis and structural

characterization of two trimethylphosphine complexes of technetium, as well as their spectroscopic and electrochemical properties.

Experimental Section

Materials. Technetium-99, as NH$_4$^{99}TcO$_4$, was purchased from Oak Ridge National Laboratories, Oak Ridge, TN. *Caution!* ^{99}Tc is a weak β-emitter with a half-life of 2.12×10^5 years, and a particle energy of 0.292 MeV. When handled in milligram amounts, ^{99}Tc does not present a significant health hazard since common laboratory materials (glass, Lucite) provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission. All manipulations were carried out in a fume hood, on a conventional vacuum line, as appropriate, or in a drybox under dinitrogen. Standard techniques for handling air-sensitive compounds were employed throughout. The work area was routinely monitored for residual radiation by using a calibrated Technical Associates Model TBM-3 contamination meter. All solvents were water and dioxygen free. Methanol, acetonitrile, and methylene chloride (Baker, Reagent Grade) were purged with dinitrogen, dried twice over activated molecular sieves (3 Å), and filtered through $^1/_4$-in. of activated alumina prior to use. Diethyl ether and tetrahydrofuran (THF; Baker, Reagent Grade) were distilled under dinitrogen from the sodium ketyl of benzophenone, stored over activated molecular sieves (3 Å), and filtered through $^1/_4$-in. of activated alumina prior to use. Trimethylphosphine and thallium hexafluorophosphate was purchased from Strem Chemicals Inc. All other chemicals were purchased from Aldrich Chemical Co. All reagents were used as received. [NBu$_4$][TcOCl$_4$][8] and [Tc(S-tu)$_6$][Cl]$_3$[9] were prepared by standard methods (tu = thiourea, i.e., S=C(NH$_2$)$_2$).

(1) (a) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19176. (b) Visiting Research Scientist, 1987–1988.
(2) (a) Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 3917. (b) Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1743. (c) Deutsch, E.; Lisbon, K.; Vanderheyden, J. L. In *Technetium Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven: New York, 1985; Vol. 2, p 161 and references therein.
(3) Pearlstein, R. M.; Davis, W. M.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3332 and references therein.
(4) (a) Bandoli, G.; Nicolini, M.; Mazzi, U.; Refosco, F.; Tisato, F. *Inorg. Chim. Acta* **1989**, *157*, 227. (b) Mazzi, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1988**, 847 and references therein.
(5) Batsanov, A. S.; Struchkov, Yu. T.; Lorenz, B.; Olk, B. *Z. Anorg. Allg. Chem.* **1988**, *564*, 129 and references therein.
(6) Deutsch, E.; Vanderheyden, J.-L.; Gerudini, P.; Lisbon, K.; Hirth, W.; Colomobo, F.; Savi, A.; Fazio, F. *J. Nucl. Med.* **1987**, *28*, 1870.
(7) Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T.; Schreifels, J. A.; Hunt, J. E. *Inorg. Chim. Acta* **1987**, *131*, 163.
(8) Davison, A.; Trop, H. S.; DePamphilis, B. V.; Jones, A. G. *Inorg. Synth.* **1982**, *21*, 160.
(9) Abrams, M. J.; Davison, A.; Faggiani, R.; Jones, A. G.; Lock, C. J. L. *Inorg. Chem.* **1984**, *23*, 3184.

Physical Measurements. NMR spectra were obtained on a Bruker WM400 high-resolution NMR spectrometer, operating at 400.13 MHz for proton, 100.60 MHz for ¹³C, 161.98 MHz for ³¹P, 90.06 MHz for ⁹⁹Tc, and 61.4 MHz for deuterium. A 10-mm broad-band probe was used for all measurements, except for ¹³C where a 5-mm probe was used to obtain data. Proton spectra were simulated by using the PANIC version of LAOCOON as modified by Bruker for an ASPECT 3000 computer. The experimental design used to obtain proton-decoupled ³¹P spectra is described in the supplementary material.

In all cases, positive chemical shift values are reported in parts per million downfield from the reference. Proton and ¹³C NMR spectra were referenced to residual solvent peaks (¹H, δ = 1.73 ppm for THF, δ 1.93 ppm for acetonitrile; ¹³C, δ = 27.3 ppm for THF). ³¹P NMR spectra were referenced by taking the center peak of the PF₆⁻ counterion resonance as −143.7 ppm.[10] ⁹⁹Tc NMR spectra were referenced to external NH₄⁹⁹TcO₄. For differences greater than the maximum spectral width (100 KHz) obtainable, chemical shifts could be calculated on the basis of spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. Spectral folding was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved with the spectral window by the appropriate amount and in the expected direction. Deuterium NMR spectra were referenced by running the sample in neat protonated solvent, opening the tube, adding a drop of the corresponding deuterated solvent, resealing the NMR tube, and rerunning the spectrum. The natural-abundance solvent resonance ion the neat protonated solvent was identified and referenced (²H, δ = 5.32 ppm, d, J(¹H–²H) = 1 Hz, for CD₂Cl₂).

Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer as Nujol mulls on CsI plates. Positive fast-atom-bombardment (FAB) mass spectra were obtained on a ZAB-E mass spectrometer with samples dissolved in a nitrobenzyl alcohol matrix. The source was equipped with an FAB gun producing a beam with 6–8-keV xenon neutrals. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Cyclic voltammetric experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat and a PAR Model 175 universal programmer. The typical experiment consisted of an acetonitrile solution that was 0.001 M in technetium compound and 0.1 M in supporting electrolyte, [NBu₄][PF₆]. The ferrocene/ferrocenium couple[11] was used as an internal reference. A polished platinum working electrode, a platinum-wire counter electrode, and a silver chloride coated silver-wire reference electrode were used.

Data for both crystals were collected on a Enraf-Nonius CAD-4 instrument at low temperatures; complete crystallographic data are listed in the supplementary material. All crystallographic calculations were performed on a DEC/CRAY computer network, using a system of programs developed by J. C. Calabrese. Plots were made with the ORTEP program (C. K. Johnson, 1971). Scattering factors were taken from ref 34.

Synthesis of Complexes. Conversion of [Tc(S-tu)₆][Cl]₃[9] **to [Tc(S-tu)₆][PF₆]₃.** In a 200-mL round-bottomed flask, [Tc(S-tu)₆][Cl]₃[9] (1.29 g, 1.95 mmol) was dissolved in methanol (100 mL), and TlPF₆ (2.05 g, 5.86 mmol, in 10 mL methanol) was added dropwise. TlCl precipitated as a heavy white solid, which was removed by filtration (recovered, 1.34 g (96%)). After the filtrate was stirred for 30 min, the methanol was removed under reduced pressure. The resulting orange-red solid was dissolved in 50 mL of acetonitrile and filtered to remove any excess [Tc(S-tu)₆][Cl]₃.[9] The acetonitrile was removed to give an orange-red solid. Anal. Found (calcd) for C₆H₂₄F₁₈N₁₂P₃S₆Tc: C, 7.16 (7.28); H, 2.61 (2.44); F, 33.96 (34.52); N, 17.17 (16.97); P, 8.86 (9.38); S, 18.79 (19.42).

Preparation of Hydrido(η²-N,S-aminomethanethioamido)tetrakis-(trimethylphosphine)technetium(III) Hexafluorophosphate. Into a thick-walled glass tube were placed a magnetic stir bar, [Tc(S-tu)₆][PF₆]₃ (0.500 g, 0.505 mmol), methanol (20 mL), and PMe₃, (0.812 g, 10.7 mmol). The tube was sealed, stirred, and heated to 75 °C for 12 h. During this time, the reaction mixture turned yellow and some white solid precipitated. After filtration, the methanol was removed in vacuo, and the resultant orange-yellow solid was dissolved in 25 mL of methylene chloride. The orange-yellow methylene chloride solution was stirred for 5 min and filtered to remove further white precipitate. The solvent was removed, and the resultant orange oil was dissolved in 5 mL of THF, layered with 2 mL of diethyl ether, and cooled to −30 °C overnight (ca. 16 h). The orange-yellow product precipitated and was collected and dried under reduced pressure. A yield of 240 mg (76%) was collected.

(10) Reddy, G. S.; Schmutzler, R. Z. *Naturforsch.* **1970**, *25B*, 1199.
(11) (a) E₀[Fe(C₅H₅)₂⁰/⁺] = 0.315 V in acetonitrile at platinum electrode versus SCE: Little, W. F.; Reilley, C. N.; Johnson, J. D.; Lynn, K. N.; Sanders, A. P. *J. Am. Chem. Soc.* **1964**, *86*, 1376. (b) Koepp, H. M.; Wendt, H.; Strehlow, H. Z. *Elektrochem.* **1960**, *64*, 483.

Table I. Crystallographic Data for [Tc(H)(η²-N,S-HNC(NH₂)S)(PMe₃)₄][PF₆]·[THF] (1·THF) and [mer-TcCl₃(PMe₃)₃]·[(PhNCO)₃] (2·[(PhNCO)₃])

	1·THF	2·[(PhNCO)₃]
formula	C₁₇H₄₈ON₂P₅F₆STc	C₃₀H₄₈O₃N₃P₃Cl₃Tc
fw	696.51	797.01
space group	Cc (No. 9)	Pnma (No. 62)
a, Å	9.305 (2)	18.641 (1)
b, Å	16.726 (2)	13.934 (2)
c, Å	19.951 (3)	14.035 (1)
β, deg	91.24 (1)	
V, Å³	3104.4	3610.3
Z	4	4
D_calc, g cm⁻¹	1.48	1.47
μ, cm⁻¹	8.16	7.78
T, °C	−70	−65
total no. of reflcns collcd	3819	8664
no. of observed reflcns with F₀ > 3σ(F₀)	2043	3699
R	0.062	0.044
R_w	0.060	0.039

Anal. Found (calcd) for C₁₃H₄₀F₆N₂P₅STc: C, 25.06 (25.01); H, 5.97 (6.46); N, 4.51 (4.49); P, 24.43 (24.81); F, 16.63 (18.26). IR (Nujol mull, CsI plates): 3495 (sm), 3384 (sm), 1989 (sw), 846 (bs), 720 (sm), 668 (sm), 400 (bm) cm⁻¹. ¹H NMR (25 °C, THF-d₈): −8.9, ddt, J(³¹P–¹H) = 60.8, 57.4, and 22.9 Hz, 1 H, TcH; 1.43, br s, 18 H, PCH₃(ax); 1.52, d, J(³¹P–¹H) = 7.9 Hz, 9 H, PCH₃(eq); 1.58, d, J(³¹P–¹H) = 8.9 Hz, 9 H, PCH₃(eq); 5.79, br s, 1 H, NH; 5.93, s, 2 H, NH₂. ¹H (−80 °C, THF-d₈): −9.17, tt, J(³¹P–¹H) = 58.1 and 22.8 Hz, 1 H, TcH; 1.41, br s, 18 H, PCH₃(ax); 1.48, d, J(³¹P–¹H) = 8.0 Hz, 9 H, PCH₃(eq); 1.57, d, J(³P–¹H) = 9.4 Hz, 9 H, PCH₃(eq); 5.75, s, 1 H, NH; 5.91, s, 2 H, NH₂. ¹³C{¹H} (35 °C, THF-d₈): 17.5, s, PCH₃(eq); 18.2, s, PCH₃(eq); 19.2, t, J(³¹P–¹³C) = 12.5 Hz, PCH₃(ax); not found, (HNC(NH₂)₂)⁻. ³¹P{¹H} (25 °C, THF-d₈): −25 to −10 ppm, broad hump. ³¹P{¹H} (−80 °C, THF-d₈): 23, br s; 14, br s; 0.5, br s, ratio 1:1:2, half-width at half-height for each peak = ca. 300 Hz. ⁹⁹Tc (35 °C, CD₂Cl₂) −543 ppm, br s, half-width at half-height 2500 Hz. FAB(+) MS: m/e 479.21 [M]⁺; m/e 403.05 [M − PMe₃]⁺.

Preparation of mer-Trichlorotris(trimethylphosphine)technetium(III). Into a thick-walled tube were placed a magnetic stir bar, [NBu₄]-[TcOCl₄][8] (330 mg, 0.661 mmol), and acetonitrile (15 mL). Addition of trimethylphosphine (695 mg, 9.13 mmol) caused an immediate color change from green to dark brown. The tube was sealed and heated to reflux for 3 h, during which the color turned orange. The solvent was removed and the orange oil was dissolved in THF. The THF solution (4 mL), layered with 2 mL of diethyl ether, was cooled to −30 °C, causing the precipitation of NBu₄Cl. Following filtration, the THF was removed from the filtrate and an NMR spectrum of the orange solid indicated that some NBu₄Cl remained. The solid was dissolved in 2 mL of THF and loaded onto a short (3 × 0.5 inch) alumina column (neutral grade, activated). The desired complex eluted with THF, as the first fraction as a yellow band. The yellow solution was stripped of volatiles, and a yellow-orange solid was obtained. A yield of 120 mg (44%) was collected. Anal. Found (calcd) for C₉H₂₇Cl₃P₃Tc: C, 24.82 (24.94); H, 6.35 (6.28); P, 20.80 (21.44). ¹H NMR (CD₃CN, 25 °C): −15.30, br s, 18 H, P(CH₃)₃, axial; −26.35, br s, 9 H, P(CH₃)₃ equatorial. FAB(+) MS: m/e 432.05 [M]⁺; m/e 397.06 [M − Cl]⁺; m/e 355.98 [M − PMe₃]⁺; m/e 321.01 [M − Cl − PMe₃]⁺.

X-ray Crystallography

(a) [Tc(η²-N,S-tu′)(H)(PMe₃)₄][PF₆] (1). A single crystal, obtained from the slow evaporation of a THF solution of 1 at −30 °C, was mounted and sealed under a dinitrogen atmosphere. Unit cell parameters were determined by a least-squares fit of 25 well-centered reflections. The data were corrected for Lorentz polarization and for a 26% decrease in reflection intensity. Selected crystal data are shown in Table I. Atomic coordinates are listed in Table II. Pertinent bond lengths and angles are collected in Table III.

The structure was solved via an automated Patterson analysis. The crystallographic repeating unit consists of the complex as its PF₆⁻ salt cocrystallized with one molecule of THF. The acentric space group is justified by the orientation of the cation with respect to the unique axis. The refinement revealed disorder of the PF₆⁻ anion and one of the trimethylphosphine groups, as well as a random orientation of the oxygen in the THF ring. The disorder was satisfactorily modeled with simple anisotropic thermal parameters (Table II) with the exception of one fluorine atom of the PF₆⁻ anion, which was refined isotropically. The refinement included anomalous dispersion terms for Tc, S, and P.

Table II. Atomic Coordinates (×10⁴) for [Tc(H)(η^2-N,S-HNC(NH$_2$)S)(PMe$_3$)$_4$][PF$_6$]·[THF] (1·THF)

	x	y	z	B_{iso}, Å^2
Tc	5000	5064 (1)	5000	2.6 (1)
S(1)	7521 (4)	5343 (3)	4591 (3)	4.1 (1)
P(1)	5354 (5)	6303 (3)	5599 (3)	4.8 (2)
P(2)	5165 (5)	3916 (3)	4271 (3)q	4.0 (1)
P(3)	2517 (4)	5196 (2)	4925 (3)	3.6 (1)
P(4)	5739 (6)	4319 (3)	5939 (3)	4.9 (2)
P(5)	6069 (9)	1447 (4)	2549 (3)	6.0 (2)
F(11)	7492 (15)	1172 (13)	2795 (11)	14.0 (9)
F(12)	4480 (22)	1729 (12)	2305 (11)	12.7 (9)
F(13)	6216 (24)	2249 (13)	2764 (16)	20.5 (14)
F(14)	6672 (32)	1674 (12)	1898 (10)	18.8 (12)
F(15)	5746 (28)	667 (17)	2329 (14)	16.5 (8)
F(16)	5241 (19)	1138 (18)	3157 (10)	18.0 (12)
N(1)	5121 (14)	5786 (7)	4087 (7)	3.2 (4)
N(2)	7121 (16)	6190 (9)	3451 (8)	5.9 (5)
C(1)	6498 (17)	5822 (9)	3982 (9)	3.7 (5)
C(11)	5371 (25)	7188 (10)	5105 (14)	7.7 (9)
C(12)	4116 (26)	6620 (13)	6257 (12)	8.1 (9)
C(13)	7080 (23)	6421 (14)	6058 (12)	7.5 (8)
C(21)	3921 (22)	3095 (10)	4262 (11)	6.0 (7)
C(22)	5114 (26)	4141 (11)	3374 (10)	6.2 (7)
C(23)	6843 (22)	3332 (10)	4362 (12)	6.4 (7)
C(31)	1612 (22)	4745 (16)	4229 (16)	11.4 (11)
C(32)	1476 (23)	4885 (32)	5598 (18)	22.0 (23)
C(33)	1795 (21)	6179 (14)	4795 (16)	9.8 (10)
C(41)	5269 (27)	4642 (15)	6794 (10)	7.9 (8)
C(42)	7679 (23)	4182 (15)	6028 (11)	7.7 (8)
C(43)	5117 (27)	3287 (13)	6027 (12)	7.4 (8)
C(61)	9367 (32)	3680 (13)	2734 (18)	9.2 (11)
C(62)	9781 (39)	2936 (18)	3165 (16)	12.0 (14)
C(63)	10861 (22)	2565 (16)	2869 (14)	9.3 (9)
C(64)	11602 (26)	3114 (18)	2489 (13)	8.8 (10)
C(65)	10488 (41)	3596 (19)	2239 (20)	12.4 (15)

Table III. Pertinent Bond Lengths and Bond Angles for [Tc(H)(η^2-N,S-HNC(NH$_2$)S)(PMe$_3$)$_4$][PF$_6$]·[THF] (1·THF) and [mer-TcCl$_3$(PMe$_3$)$_3$]·[(PhNCO)$_3$] (2·[(PhNCO)$_3$])

	1·THF		2·[(PhNCO)$_3$]
Bond Lengths (Å)			
Tc–S	2.543 (4)	Tc–Cl(1)	2.440 (1)
Tc–P(1)	2.411 (5)	Tc–Cl(2)	2.352 (1)
Tc–P(2)	2.416 (5)	Tc–Cl(3)	2.370 (1)
Tc–P(3)	2.323 (4)	Tc–P(1)	2.387 (1)
Tc–P(4)	2.340 (5)	Tc–P(2)	2.4528 (8)
Tc–N(1)	2.190 (13)	O(1)–C(8)	1.209 (5)
S–C(1)	1.724 (16)	O(2)–C(7)	1.201 (4)
N(1)–C(1)	1.304 (18)	N(1)–C(7)	1.386 (3)
N(2)–C(1)	1.367 (20)	N(2)–C(7)	1.381 (3)
		N(1)–C(21)	1.454 (4)
Bond Angles (deg)			
S–Tc–P(1)	83.4 (2)	Cl(1)–Tc–Cl(2)	86.82 (5)
S–Tc–P(2)	83.2 (2)	Cl(1)–Tc–Cl(3)	96.58 (5)
S–Tc–P(3)	152.3 (1)	Cl(2)–Tc–Cl(3)	176.60 (6)
S–Tc–P(4)	95.6 (2)	Cl(1)–Tc–P(1)	168.04 (6)
S–Tc–N(1)	64.4 (4)	Cl(1)–Tc–P(2)	87.11 (2)
N(1)–Tc–P(1)	86.0 (4)	Cl(2)–Tc–P(1)	81.22 (5)
N(1)–Tc–P(2)	86.1 (4)	Cl(2)–Tc–P(2)	96.91 (2)
N(1)–Tc–P(3)	87.9 (4)	Cl(3)–Tc–P(1)	95.38 (5)
N(1)–Tc–P(4)	160.0 (3)	Cl(3)–Tc–P(2)	83.29 (2)
P(1)–Tc–P(3)	94.3 (2)	P(1)–Tc–P(2)	94.30 (2)
P(1)–Tc–P(2)	166.3 (2)	P(2)–Tc–P(2a)	164.68 (3)
P(1)–Tc–P(4)	91.5 (2)	O(1)–C(8)–N(1)	122.5 (2)
P(2)–Tc–P(3)	96.5 (2)	O(2)–C(7)–N(2)	122.0 (3)
P(3)–Tc–P(4)	112.2 (2)	C(7)–N(1)–C(21)	116.5 (2)
P(2)–Tc–P(4)	92.2 (2)	N(1)–C(7)–N(2)	115.6 (3)
Tc–N(1)–C(1)	103 (1)		
Tc–S–C(1)	79.2 (6)		
N(1)–C(1)–N(2)	125 (2)		
S–C(1)–N(1)	113 (1)		
S–Cl(1)–N(2)	121 (1)		

Idealized hydrogen atoms were included as fixed atom contributions (d(C–H) and d(N–H) = 0.95 Å). The usual crystallographic difficult resolving metal hydrides was compounded by the disorder described

Table IV. Atomic Coordinates (×10⁴) for [mer-TcCl$_3$(PMe$_3$)$_3$]·[(PhNCO)$_3$] (2·[(PhNCO)$_3$])

	x	y	z	B_{iso}, Å^2
Tc	2006.0 (2)	2500.0	4937.0 (2)	1.7 (1)
Cl(1)	3030 (1)	2500	3838 (1)	3.4 (1)
Cl(2)	2865 (1)	2500	6174 (1)	3.1 (1)
Cl(3)	1086 (1)	2500	3760 (1)	3.2 (1)
P(1)	1196 (1)	2500	6262 (1)	2.6 (1)
P(2)	1954.3 (5)	4244.6 (5)	4714.2 (5)	2.2 (1)
O(1)	5180 (2)	2500	3924 (2)	2.9 (1)
O(2)	3790 (1)	4121 (2)	1795 (2)	3.3 (1)
N(1)	4540 (1)	3340 (2)	2815 (2)	2.0 (1)
N(2)	3806 (2)	2500	1740 (2)	1.9 (1)
C(1)	246 (3)	2500	5965 (5)	5.0 (2)
C(2)	1282 (2)	3491 (3)	7087 (2)	4.0 (1)
C(3)	1066 (2)	4813 (2)	4789 (2)	3.1 (1)
C(4)	2239 (2)	4625 (3)	3535 (2)	3.2 (1)
C(5)	2529 (2)	4930 (2)	5506 (2)	3.0 (1)
C(7)	4026 (2)	3377 (2)	2096 (2)	2.2 (1)
C(8)	4776 (2)	2500	3247 (3)	2.2 (1)
C(11)	3223 (2)	2500	1043 (3)	2.0 (1)
C(12)	3381 (2)	2500	91 (3)	2.7 (1)
C(13)	2821 (3)	2500	−573 (3)	3.6 (1)
C(14)	2125 (3)	2500	−266 (4)	3.7 (1)
C(15)	1967 (3)	2500	666 (4)	3.3 (1)
C(16)	2516 (3)	2500	1339 (3)	2.7 (1)
C(21)	4772 (2)	4255 (2)	3204 (2)	2.2 (1)
C(22)	4349 (2)	4720 (3)	3864 (2)	2.8 (1)
C(23)	4581 (2)	5603 (3)	4208 (2)	3.7 (1)
C(24)	5219 (3)	5999 (3)	3900 (3)	4.3 (1)
C(25)	5637 (2)	5521 (3)	3246 (3)	4.3 (1)
C(26)	5419 (2)	4636 (3)	2893 (2)	3.3 (1)

above. The highest residual density is 0.47 e/Å³ near the technetium atom.

(b) [*mer*-TcCl$_3$(PMe$_3$)$_3$] (2). A single cocrystal of 2 with [(PhNCO)$_3$], obtained from the evaporation of a THF solution of *mer*-TcCl$_3$(PMe$_3$)$_3$ and excess [(PhNCO)$_3$], was mounted and sealed without precaution to exclude oxygen. Unit cell parameters were determined by a least-squares fit of 25 reflections. A correction for a 5% decrease in reflection intensity was applied to the data collected. Selected crystal data are in Table I, atomic coordinates are listed in Table VI, and pertinent bond lengths and angles are found in Table III.

The technetium atom was located from the Patterson map and the remaining non-hydrogen atoms were found by subsequent Fourier synthesis and least-squares refinement. Both molecules were constrained to lie on the crystallographic mirror plane along the *b* axis. All non-hydrogen atoms were refined anisotropically (including anomalous terms for Pc, P, and Cl). Hydrogen atoms were calculated and fixed as idealized isotropic contributions (d(C–H) = 0.95 Å). The largest peak in the final difference Fourier map, 0.85 e/Å³, was located near the technetium atom.

Results and Discussion

Synthesis, Characterization, and Reactivity of [Tc(η^2-N,S-tu')(H)(PMe$_3$)$_4$][PF$_6$] (1). [Tc(S-tu)$_6$][PF$_6$]$_3$ is readily prepared from the chloride [Tc(S-tu)$_6$][Cl]$_3$ by the reaction with TlPF$_6$. This hexafluorophosphate salt proves to be a useful starting reagent because it is more soluble than the chloride salt in common polar organic solvents such as THF and acetonitrile. The sealed tube reaction of bright red [Tc(S-tu)$_6$][PF$_6$]$_3$ with an excess of trimethylphosphine in methanol at 75 °C yields [Tc(H)(η^2-N,S-HNC(NH$_2$)S)(PMe$_3$)$_4$][PF$_6$] (1), with the solution becoming yellow as the reaction progresses. Workup of the reaction mixture yielded water- and oxygen-sensitive yellow crystals of 1.

1 was initially characterized by multinuclear NMR and infrared spectroscopy. The room-temperature proton and ¹³C NMR spectra suggested that the complex contained four PMe$_3$ ligands, in a 2:1:1 ratio. In the ¹³C spectrum a triplet (characteristic of trans phosphine ligands that are virtually coupled[12]) was observed at 19.2 ppm, while the remaining two singlets at 17.5 and 18.2 ppm were assigned to nonequivalent equatorial phosphine ligands. These assignments ruled out the possibility that the thiourea ligand was symmetrically S-bound or N,N-bound. In fact, two signals

(12) Pregosin, P. S.; Kunz, R. W. ³¹P and ¹³C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: Berlin, 1979; p 66.
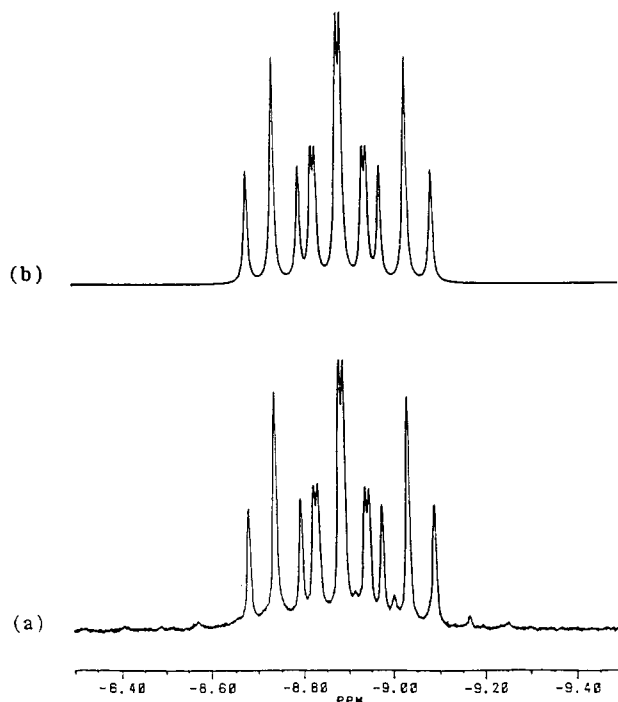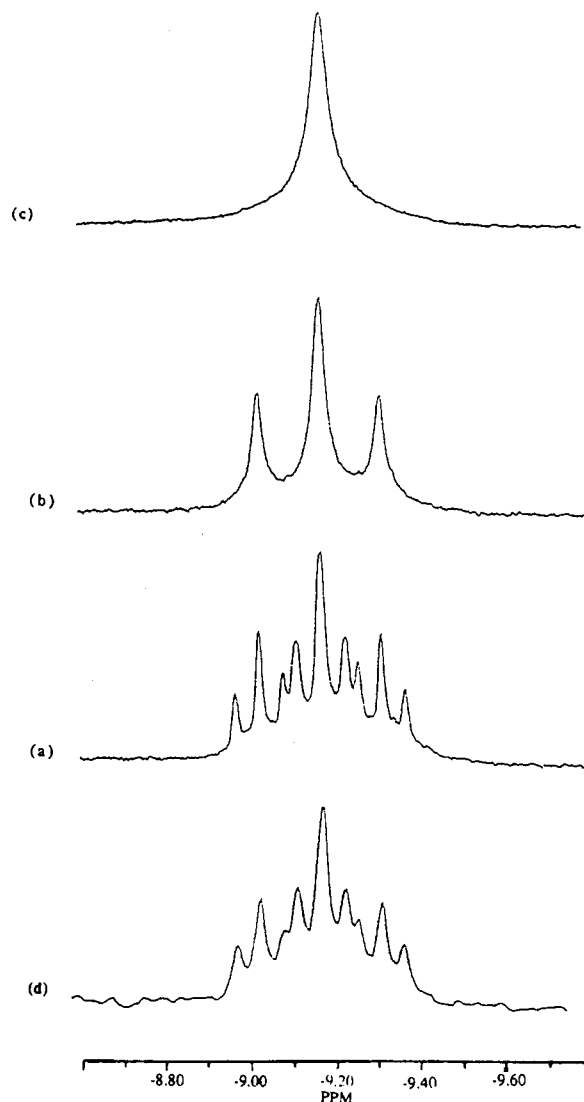
Figure 1. (a) Hydride portion of proton spectrum of 1 at room temperature in THF-d_8. (b) Simulation of hydride portion of proton spectrum.

Figure 2. (a–c) Hydride portion of proton spectrum of 1 at −80 °C in THF-d_8: (a) unirradiated; (b) irradiation of axial phosphine ligands; (c) irradiation of all phosphine ligands. Identical spectra were obtained in methylene chloride. (d) Deuteride portion of deuterium spectrum of 1-d, in methylene chloride, 25 °C.

in the N–H region of the proton NMR spectrum, of relative integration 2:1, suggested an anionic [NH⇌C(NH2)⇌S]⁻ ligand. Two bands in the N–H region of the IR spectrum at 3495 and 3384 cm⁻¹ gave further evidence that the thiourea ligand was bound asymmetrically.

At room temperature, the hydride resonance of 1 at −8.9 ppm appeared as an apparent doublet of doublets of triplets (see Figure 1a) due to the coupling to four phosphine ligands, two of which are magnetically equivalent. This A₂BC pattern was readily computer-simulated (see Figure 1b), without invoking any phosphine site exchange. At −80 °C, the hydride portion of the proton spectrum was slightly broader than at room temperature (See Figure 2a), and irradiation of the two axial phosphorus ligands removed the smaller triplet splitting from the hydride resonance (Figure 2b). As expected, simultaneous decoupling of all the phosphorus ligands resulted in collapse of the hydride resonance to a single peak (Figure 2c). Further evidence of the hydride ligand came from the infrared spectrum, where a band characteristic[13] of the Tc–H stretching mode was observed at 1989 cm⁻¹.
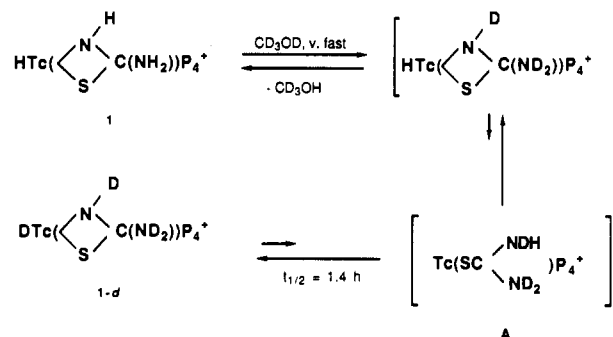
The ³¹P spectrum of 1 at room temperature showed a barely visible broad resonance in the region −10 to −25 ppm. The low-temperature ³¹P spectrum consists of three broad peaks ($\omega_{1/2}$ ca. 300 Hz), in a ratio of 1:1:2. These spectra indicate that the quadrupolar Tc nucleus effectively relaxes the P nuclei at room temperature but not at −80 °C. The observed temperature-dependent quadrupolar effect is analogous to that described[14] in detail for vanadium complexes.

The mechanism of formation of 1 is unknown, but methanol appears to play a role. In THF solvent, a mixture of products was formed, together with a small amount (<5%) of 1, whereas the hydride complex 1 was the only detected product when the reaction was carried out in methanol. The composition of 1

(13) (a) Kaden, L.; Lorenz, B.; Schmidt, K.; Sprinz, H.; Wahren, M. *Z. Chem.* **1981**, *21*, 232. (b) Fisher, E. O.; Schmidt, M. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 93. (c) Ginsburg, A. P. *Inorg. Chem.* **1964**, *3*, 567.
(14) Roe, D. C. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; ACS Symposium Series 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 8, p 208. (b) Domaille, P. *J. Am. Chem. Soc.* **1984**, *106*, 7677.

Scheme I. Proposed Qualitative Mechanism of Formation for 1-d in Methanol-d_4 (P = PMe₃)

suggests its formation via intramolecular oxidative addition of the N–H bonds of a coordinatively unsaturated putative Tc(I) precursor such as [Tc(S-tu)(PMe₃)₄][PF₆] (A in Scheme I). Reduction of the Tc(III) starting material to such a Tc(I) intermediate could be accomplished by either methanol or PMe₃. However, we have no direct evidence for this postulated intermediate.

Ease of hydride–deuteride exchange (Scheme I) was explored. A 20-mg sample was stirred at room temperature for 4 days in

Table V. Selected Bond Distances for Related Technetium(III) Complexes

	bond dist, Å				
complex	Tc–P	Tc–Cl	Tc–N	Tc–S	ref
[Tc(S-tu)$_6$][Cl]$_3$				2.427 (1)	9
[Tc(η^2-N,S-tu')(PMe$_3$)$_4$H][PF$_6$]·	2.413 (5)^a		2.190 (13)^a	2.543 (4)^a	this work
[THF] (1·THF)	2.340 (5)^b				
	2.323 (4)^c				
[TcCl$_3$(PMe$_2$Ph)$_3$(CO)]	2.44 (1)	2.48 (1)			27
[Tc(PPh$_3$)(S$_2$COC$_4$H$_9$)$_3$]	2.381 (2)^d			2.462 (2)	16
[Tc(PMe$_2$Ph)(S$_2$CNEt$_2$)$_3$]	2.330 (3)^d			2.476 (3)	28
				2.505 (3)	
[mer-TcCl$_3$(PMe$_3$)$_3$]·[(PhNCO)$_3$],	2.387 (1)^e	2.361 (1)^e			this work
(2·[(PhNCO)$_3$])	2.453 (1)^a	2.440 (1)^a			
mer-TcCl$_3$(PMe$_2$Ph)$_3$	2.42 (1)^e	2.33 (1)^e			24
	2.47 (1)^a	2.46 (1)^a			
trans(Cl)-[Tc(DMPE)$_2$Cl$_2$]$^+$	2.436 (1)	2.323 (4)			29
trans(Cl)-[Tc(DPPE)$_2$Cl$_2$]$^+$	2.501 (1)	2.319 (1)			30

^{a} Trans to P. ^{b} Trans to N. ^{c} Trans to S. ^{d} Capping ligand. ^{e} Trans to Cl.

1 mL of methanol-d_4. After the volatiles were removed, the residual yellow solid was collected and an IR spectrum showed that the hydride band at 1989 cm^{-1} had disappeared. A band at 1835 cm^{-1} was assigned to the Tc–D stretch. The half-life of the Tc–H/Tc–D exchange reaction was determined to be approximately 1.4 h at 50 °C in neat CD$_3$OD. The rate at which the Tc–H/Tc–D exchange occurred did not significantly increase upon addition of 1 equiv of base. This suggests that the exchange is not base-catalyzed. The likelihood remains that intramolecular reductive elimination to form A is quickly followed by the proposed oxidative addition step forming 1-*d*.

The product deuteride from the exchange reaction, [Tc(D)-(PMe$_3$)$_4$(η^2-N,S-tu')][PF$_6$], was dissolved in methylene chloride and fully characterized by ^{2}H NMR. The Tc–*D* resonance was observed at –8.8 ppm as a triplet ($J(^{31}$P–^{2}H) = 9.1 Hz) of triplets ($J(^{31}$P–^{2}H) = 3.5 Hz), with an integrated intensity about the same as the total intensity observed in the region from 2.5 to 0.6 ppm. The proton spectrum confirmed little or no deuterium enrichment of the phosphine ligands has occurred under the hydride/deuteride exchange conditions. Figure 2d illustrates that the hydride and deuteride portion of the proton and deuterium spectra, respectively, are superimposable when plotted on a ppm scale.

A cyclic voltammogram of 1 revealed an irreversible oxidation wave approximately 0.20 V more anodic than the reference ferrocene/ferrocenium couple.[11] No attempt was made to identify the product(s) formed.

Crystal Structure of 1. While the NMR studies revealed that this complex contained a hydride ligand, four trimethylphosphine ligands, and an asymmetrically bound thiourea ligand, the bonding mode of the thiourea ligand (i.e., N,N vs N,S) was not clearly established.

An X-ray crystal structure determination was performed to clarify the bonding mode of the proposed thiourea anion ligand in 1. The structure of 1 (depicted in Figure 3) adds to the few structurally characterized[15,16] seven-coordinate, mononuclear Tc(III) compounds known. The asymmetric unit consisted of the complex as the PF$_6^-$ salt, cocrystallized with a THF molecule. The geometry about the metal center cannot be fully described since the technetium-bound hydride was not located. Ignoring the hydride ligand, the geometry around the Tc atom in 1 appeared as a distorted octahedron. The largest vacancy in the coordination sphere lies trans to the η^2-N,S-tu' ligand between P(3) and P(4), and the hydride ligand could reside in this position. The crystal structure does establish an unusual η^2-N,S bonding mode for the deprotonated thiourea ligand.

The axial phosphine ligand bond lengths of 2.413 (5) Å were within the range previously reported for other Tc(III) complexes, listed in Table V. The values for the equatorial phosphines, 2.332 (5) Å were relatively short. There was surprisingly little difference
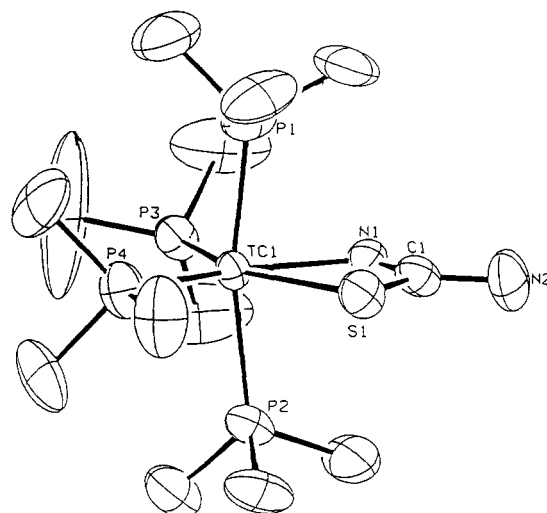

Figure 3. Molecular structure of [Tc(H)(η^2-N,S-HNC(NH$_2$)S)-(PMe$_3$)$_4$][PF$_6$]·[THF] 1·THF. The PF$_6$ counterion and lattice THF molecule have been omitted for clarity.

(Δ = 0.02 Å) in the equatorial phosphine bond distances trans to the thiourea ligand.

The Tc–N distance, 2.190 (13) Å, is long when compared to known Tc(III) complexes. The range[15] for Tc–N bonds was found to be 2.041 Å (for the *trans*(P)-[Tc(PPh$_3$)$_2$((acac)en)]$^+$ cation[17]) to 2.124 Å (for *trans*(P), *cis*(Cl)-[Tc(PMe$_2$Ph)$_2$(Cl)$_2$(phen)$^{+2b}$]). This reflects delocalization of negative charge within the bidentate deprotonated thiourea ligand. This elongation is also seen in the Tc–S bond, 2.543 (4) Å, which is significantly longer than Tc–S bonds in the parent compound [Tc(S-tu)$_6$][Cl]$_3$[9] and longer than the Tc–S bonds found in seven-coordinate Tc(III) complexes (Table V). The bite angle of the N–C–S moiety is 113°, similar to a reported S–C–S angle of 113.1° in [Tc(PPh$_3$)(S$_2$COC$_4$H$_9$)].[16] We are unaware of any other structurally characterized coordination compounds containing the [η^2-N,S-HNC(NH$_2$)S]$^-$ ligand.

Synthesis and Characterization of *mer*-Tc(PMe$_3$)$_3$Cl$_3$ (2). *mer*-Trichlorotris(trimethylphosphine)technetium(III) was prepared by the reduction of [NBu$_4$][TcOCl$_4$] with excess trimethylphosphine in acetonitrile. Reaction conditions were similar to those for the preparation of TcCl$_3$(PPh$_3$)$_2$(CH$_3$CN)[3] but the isolation of the desired product was more complicated. It is well documented[18] that excess phosphine ligand acts as a oxygen acceptor to reduce Tc(V)–oxo complexes to the corresponding

(15) Melnik, M.; Van Lier, J. E. *Coord. Chem. Rev.* **1987**, *77*, 275.
(16) Nicholson, T.; Thornback, J.; O'Connell, L.; Morgan, G.; Davison, A.; Jones, A. G. *Inorg. Chem.* **1990**, *29*, 89.

(17) Jurrsion, S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743.
(18) (a) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728. (b) Davison, A.; de Vries, N.; Dewan, J. C.; Jones, A. G. *Inorg. Chim. Acta* **1986**, *120*, L15. (c) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.
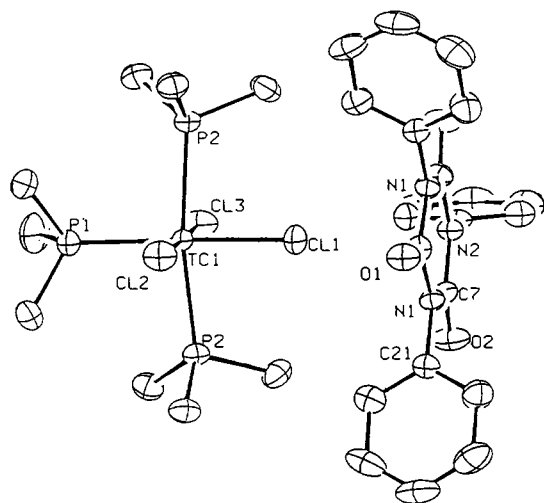
Figure 4. Molecular structure of [*mer*-TcCl₃(PMe₃)₃] in 2·[(PhNCO)₃].

Tc(III) species. Technetium(III) phosphine halide complexes were prepared by other synthetic routes,[19] but, trimethylphosphine analogues of these compounds were not reported.

Identification of paramagnetic *mer*-trichlorotris(trimethyl-phosphine)technetium(III) (2) was straightforward. The proton NMR spectrum at room temperature exhibited two upfield broad resonances with a relative integration of 2:1 assigned to the axial and equatorial phosphine ligands, respectively. Similar upfield chemical shifts were also observed for *mer*-Tc(PMe₂Ph)₃Cl₃[19] and, though less, for the rhenium analogue *mer*-ReCl₃(PMe₃)₃.[20] A rationalization of this phenomenon was offered by Randall and Shaw.[21]

Crystal Structure of 2. Crystals of *mer*-Tc(PMe₃)₃Cl₃ were obtained by cocrystallizing the technetium complex from a solution containing an excess of triphenyl isocyanurate, [(PhNCO)₃].[22] The crystals contained a 1:1 ratio of 2 and [(PhNCO)₃]. However, no evidence of bonding between the two components in the crystal was observed. From a comparison of the bond lengths and bond angles, the [(PhNCO)₃] molecule in 2·[(PhNCO)₃] and the independently structurally characterized[23] cyclic trimer were found to be almost identical. In addition, no significant change for ν(C=O) of the trimer was observed in the IR spectrum,[22,24] and we conclude that [(PhNCO)₃] is a useful and innocent cocrystallite.

The molecular structure of 2·[(PhNCO)₃] is shown in Figure 4. The metal center is surrounded by a *meridional* arrangement of trimethylphosphines and chlorines. The Tc–P distances in complex 2 are typical for six-coordinate Tc(III) complexes (Table

V). The Tc–Cl(1) distance of the Cl trans to phosphine is considerably lengthened with respect to the other two Tc–Cl bonds and can be ascribed to the trans effect exerted by P(1). Both the average Tc–P and the average Tc–Cl distances are relatively short when compared to those in *mer*-TcCl₃(PMe₂Ph)₃[25] and other technetium(III) phosphine–chloride compounds (Table V). This is probably a reflection of the less demanding steric requirements and better σ-donating ability of the PMe₃ groups versus PMe₂Ph and other bulkier phosphines. This observation follows the trend recognized by Deutsch.[2b]

Cyclic voltammetric experiments with *mer*-Tc(PMe₃)₃Cl₃ showed the occurrence of a reversible couple at 0.39 V more anodic than the ferrocene/ferrocenium couple,[11] assigned to the Tc-(III)/Tc(IV) [*mer*-TcCl₃(PMe₃)₃]⁰/⁺ couple. Comparison of peak heights between the technetium complex and an equimolar solution of ferrocene, showed this to be a one-electron transfer. An irreversible reduction was found at 1.30 V more cathodic than the ferrocene/ferrocenium couple.[11] Similar redox potentials were reported for *mer*-TcCl₃(PMe₂Ph)₃.[26]

Summary. The seven-coordinate complex, 1, and the six-coordinate compound, 2, are the first structurally characterized trimethylphosphine complexes of technetium. No evidence of the previously reported[7] [Tc(PMe₃)₆]⁺ cation was observed during the either of the preparations. We expect that [Tc(PMe₃)₆]⁺ cation to be extremely sterically hindered, possibly lying in equilibrium with [Tc(PMe₃)₄(η²-CH₂PMe₂)H]⁺, by comparison with known homoleptic (trimethylphosphine)molybdenum[31] and -tungsten[32] complexes.[33]

Registry No. 1, 136238-04-5; 1·THF, 136238-06-7; 2, 136238-05-6; 2·[(PhNCO)₃], 136238-07-8; tu, 62-56-6; [Tc(*S*-tu)₆]Cl₃, 89172-46-3; [Tc(*S*-tu)₆][PF₆]₃, 136238-02-3; [NBu₄][TcOCl₄], 92622-25-8; HNC-(NH₂)S, 121782-79-4; D₂, 7782-39-0.

Supplementary Material Available: Tables SIII–SXII, listing complete bond lengths and angles, isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom coordinates, and crystallographic data for 1 and 2 and a complete description of the phosphorus-decoupled proton NMR experiment (9 pages); Tables SI and SII, listing calculated and observed structure factors for 1 and 2 (16 pages). Ordering information is given on any current masthead page.

(19) Mazzi, U.; De Paoli, G.; Di Bernardo, P.; Magon, L. *J. Inorg. Nucl. Chem.* **1976**, *38*, 721.

(20) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

(21) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867.

(22) Anal. Found (calcd) for 2·[(PhNCO)₃], C₃₀H₄₈O₃P₃Cl₃Tc: C, 45.78 (45.56); H, 5.46 (5.78); N, 5.23 (5.10); P, 12.17 (11.75); Cl, 13.50 (13.45). A proton NMR spectrum, in CD₃CN, revealed no unusual changes. A multiplet observed at 7.3 ppm, 15 H, was assigned to the cyclic trimer. The IR spectrum, Nujol on CsI plates, showed a strong absorption at 1705 cm⁻¹, assigned to ν(C=O).

(23) Usanmaz, A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1117.

(24) [(PhNCO)₃] carbonyl stretch was reported at 1710 cm⁻¹ as a KBr disk. Martelli, E.; Pelizzi, C.; Predieri, G. *J. Mol. Catal.* **1983**, *22*, 89.

(25) Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1976**, 125.

(26) Mazzocchin, G. A.; Seeber, R.; Mazzi, U.; Roncari, E. *Inorg. Chim. Acta* **1978**, *29*, 1.

(27) Bandoli, G.; Clemente, D.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1978**, 373.

(28) Batsanov, A. S.; Struchkov, Yu. T.; Lorenz, B.; Wharen, M. *Z. Anorg. Allg. Chem.* **1984**, *510*, 117.

(29) Vanderheyden, J. L.; Ketring, A. R.; Lisbon, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, R.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184.

(30) Lisbon, K.; Doyle, M. N.; Thomas, R. W.; Nelesnik, T.; Woods, M.; Sullivan, J. C.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3614.

(31) Cloke, F. G. N.; Cox, P. K.; Green, M. L. H.; Baskin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393.

(32) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 5381.

(33) For a complete review, see refs 1–3 in ref 32.

(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.