Synthesis of a Novel Class of Trigonal Bipyramidal Nitrido Tc(V) Complexes with Phosphino−Thiol Ligands. Crystal Structure of [^{99g}Tc(N)(L^1)$_2$] [L^1 = 2-(Diphenylphosphino)ethanethiolato] and [^{99g}Tc(N)(L^5)$_2$] [L^5 = 2-(Ditolylphosphino)propanethiolato]

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Reactions of the precursor complexes [^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$] and [^{99g}Tc(N)Cl$_4$]$^-$ with phosphine−thiol ligands (HL^n) of the type R$_2$PCH$_2$CH$_2$SH (R = phenyl, methoxypropyl), R$_2$′PCH$_2$CH$_2$CH$_2$SH (R′ = phenyl, tolyl), and R$_2$″P-*o*-C$_6$H$_4$SH (R″ = phenyl) afforded the five-coordinated, disubstituted nitrido technetium(V) complexes [^{99g}Tc(N)(L^n)$_2$]. The complexes were characterized by elemental analysis, ^{1}H and ^{31}P NMR spectroscopy, FT IR, and positive FAB MS spectra. Structural characterization of [^{99g}Tc(N)(L^1)$_2$] (**1**) [HL^1 = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$SH] and [^{99g}Tc(N)(L^5)$_2$] (**5**) [HL^5 = (*o*-CH$_3$C$_6$H$_4$)$_2$PCH$_2$CH$_2$CH$_2$SH] showed that the bidentate phosphino−thiol ligands are coordinated to the technetium center through the neutral phosphorus atom and the deprotonated thiol sulfur atom. These complexes possess an uncommon trigonal bipyramidal geometry with the two phosphorus atoms occupying the two transaxial positions and the two sulfur atoms on the equatorial plane along with the nitrido nitrogen atom. Compound **1** crystallizes in the monoclinic space group *C*2/*c*, $a = 24.84(2)$ Å, $b = 7.327(6)$ Å, $c = 31.52(2)$ Å, $\beta = 111.06(10)°$, and $Z = 8$. Compound **5** crystallizes in the monoclinic space group $P2_1/n$, $a = 11.090(1)$ Å, $b = 14.387(2)$ Å, $c = 11.087(1)$ Å, $\beta = 113.62(1)°$, and $Z = 2$.

Introduction

Radiopharmaceuticals containing the γ-emitting isotope ^{99m}Tc still continue to occupy a prominent position in diagnostic nuclear medicine due to the favorable nuclear properties (E_γ = 142 keV, $t_{1/2}$ = 6.02 h) and availability of this radionuclide. In the last two decades, dramatic advancements of the studies of the basic chemistry of technetium complexes have led to the introduction into clinical application of useful tracers for heart, brain, and kidneys.[5]

A considerable number of these tracers belong to the class of complexes containing the monoxo, [Tc═O]$^{3+}$, and trans dioxo, [O═Tc═O]$^+$, cores. The recent introduction of an efficient method for the preparation of nitrido technetium(V) species at the "carrier free" level[6−8] has made this class of compounds more attractive for the development of ^{99m}Tc radiopharmaceuticals, whose production has been focused in the past primarily on oxo−technetium complexes.

Some years ago, Baldas and co-workers first explored nitrido technetium chemistry.[9−13] Following these pioneering investigations, our research group and others have further studied the coordination chemistry and biological properties of technetium complexes characterized by the presence of the terminal Tc≡N multiple bond.[14−20] Extensive studies have been carried out on the synthesis and biological evaluation of square pyramidal nitrido technetium(V) complexes with dithiocarbamate,[21,22]

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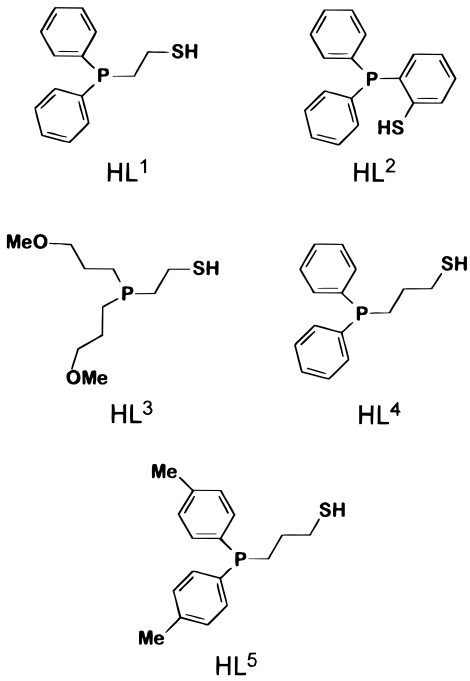
dithiocarboxylate,[23,24] and dithiophosphinate ligands,[25] and with ONS-type Schiff base ligands.[26,27] Five- and six-coordinated nitrido technetium(V) complexes have been also prepared with N_2S_2-type ligands,[28,29] diphosphines, and polyphosphines,[30,31] and cyclic and acyclic polydentate amine ligands.[32−34]

In spite of the well-developed technetium chemistry with thiolate and phosphine ligands, studies on the reactivity of mixed polydentate phosphine−thiol ligands toward technetium,[35−38] and more generally toward other transition metals,[39−42] have appeared in the literature only recently. Examples are represented by the five-coordinate and six-coordinate technetium(III) species of the type $[^{99g}Tc\{P(C_6H_4S\text{-}o)_3\}(CNPr^i)_n]$ ($n = 1$ or 2),[38] prepared by reduction−substitution reactions of the potentially tridentate ligand $P(C_6H_4SH\text{-}o)_3$ onto $[^{99g}TcO_4]^-$ in the presence of isonitriles. In addition, a few more technetium(III) complexes, such as octahedral *mer*-$[^{99g}Tc(L^2)_3]$ and trigonal bipyramidal $[^{99g}Tc(L^n)_2(S\text{-}L^n{=}O)]$ ($n = 1$, 4), have been prepared by our group.[35,38] The paucity of investigations in this area probably reflects the lack of commercially available functionalized phosphines, the syntheses of which require a multistep approach and tedious procedures.[43−45]

In this study we report an extensive investigation on the synthesis and structural characterization of novel, five-coordinate, disubstituted nitrido technetium(V) complexes of the type $[^{99g}Tc(N)(L^n)_2]$, where HL^n ($n = 1-5$) is a mixed, bidentate phosphine−thiol ligand [HL^1 = 2-(diphenylphosphino)ethanethiol; HL^2 = 2-(diphenylphosphino)thiophenol; HL^3 = 2-(dimethoxypropylphosphino)ethanethiol; HL^4 = 2-(diphenylphosphino)propanethiol; HL^5 = 2-(ditolylphosphino)-propanethiol] (Chart 1). Biodistribution studies in rats and primates have demonstrated that this new category of agents accumulate selectively in myocardium tissue and that washout from blood, lung, and liver is extremely fast.[46] A detailed description of these biological results will be reported elsewhere.[47] The compound $[^{99g}Tc(N)(L^2)_2]$ has been briefly described previously by Dilworth and co-workers.[48] A preliminary report on this chemistry has been communicated.[49]

Chart 1



Experimental Section

CAUTION! ^{99g}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in laboratories approved for low-level radioactivity using monitored hoods and gloveboxes. When handled in milligram amounts, ^{99g}Tc does not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation.

Materials. Technetium-99g as $[NH_4][^{99g}TcO_4]$ was obtained from Oak Ridge National Laboratory. Samples were dissolved in water and treated with excess aqueous ammonia and H_2O_2 (30%) at 80 °C prior to use to eliminate residual TcO_2. Solid samples of purified ammonium pertechnetate were obtained by slow evaporation of the solvent under heating at 40 °C. General literature methods were applied to the preparation of the precursor complexes $[As(C_6H_5)_4][^{99g}Tc(N)Cl_4]$[50] and

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[^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$].[51] Common laboratory solvents were reagent grade and used as purchased.

Physical Measurements. Elemental analyses (C, H, N, S) were performed on a Carlo Erba 1106 elemental analyzer. Analysis of radioactive technetium was performed as previously described[25] by dissolving weighed samples in HNO_3/H_2O_2 mixtures and counting the resulting radioactivity in a Packard TRICARB 3000 scintillation counter. FT IR spectra were recorded on a Nicolet 510P Fourier transform spectrometer, in the range 4000−200 cm^{-1} and in KBr mixtures, using a Spectra-Tech diffuse-reflectance collector accessory. Proton and ^{31}P NMR spectra were collected on a Bruker AC-200 instrument, using $SiMe_4$ as internal reference (^{1}H) and 85% aqueous H_3PO_4 as external reference (^{31}P). Positive ion fast atom bombardment mass spectra (FAB$^+$) of selected complexes in an NBA matrix were recorded on a VG 30-250 spectrometer (VG Instrument) at the probe temperature. Xe was used as the primary beam gas, and the ion gun was operated at 8 keV (ca. 1.28×10^{-15} J) and 100 μA. Chromatographic separations were accomplished on a SiO_2 column (45 × 2 cm, 70−230 mesh, Aldrich).

Synthesis of the Ligands. HL^1 and HL^4 were synthesized according to the method reported by Blower et al.[52] (for HL^4, ethylene sulfide was replaced by propylene sulfide), while HL^2 was prepared as described elsewhere.[53,54] HL^3 and HL^5 were purchased from Argus Chemicals. Since all mixed phosphino−thiol ligands discussed here are air sensitive, they were stored under an inert atmosphere and all reactions and manipulations were routinely performed under a nitrogen atmosphere using standard Schlenk techniques.

Syntheses of ^{99g}Tc Complexes. All of the complexes [^{99g}Tc(N)(L^n)$_2$] (n = 1−5) were prepared according to the same general procedure. [^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$] (0.045 g, 0.065 mmol) was suspended in 10 mL of dichloromethane, and an excess (1:10) of the appropriate ligand HL^n (n = 1, 2, 4, 5) was added with stirring (with the ligand HL^2 a 1:3 ratio was used). The mixture was refluxed for 1 h, and the initial pink-orange color turned yellow. After cooling, the solvent was removed by passing an argon stream through the reaction solution thus causing the precipitation of a yellow solid. The crude material was washed with ethanol and diethyl ether and dried under vacuum. The resulting pale-yellow solid was recrystallized by slow evaporation from a dichloromethane/methanol mixture.

[^{99g}Tc(N)(L^1)$_2$] (1). Yield: 94% (based on ^{99g}Tc). FT IR (cm^{-1}): 1053 [ν(Tc≡N)]. FAB MS: m/z 604 [MH$^+$]. ^{1}H NMR (CDCl$_3$, ppm): 2.75 (m, 8H), 8.10−7.20 (20H, aromatic). Anal. Calcd for $C_{28}H_{28}P_2S_2$-NTc: C, 55.72; H, 4.64; N, 2.32; S, 10.61; Tc, 16.42. Found: C, 55.68; H, 4.60; N, 2.34; S, 10.14; Tc, 17.01.

[^{99g}Tc(N)(L^2)$_2$] (2). Yield: 93% (based on ^{99g}Tc). FT IR (cm^{-1}): 1041 [ν(Tc≡N)]. FAB MS: m/z 700 [MH$^+$]. ^{1}H NMR (CDCl$_3$, ppm): 8.10−6.60 (aromatic). Anal. Calcd for $C_{36}H_{28}P_2S_2$NTc: C, 61.80; H, 4.01; N, 2.00; S, 9.16; Tc, 14.16. Found: C, 61.67; H, 2.06; N, 1.95; S, 9.03; Tc, 14.09.

[^{99g}Tc(N)(L^4)$_2$] (4). Yield: 92% (based on ^{99g}Tc). FT IR (cm^{-1}): 1045 [ν(Tc≡N)]. FAB MS: m/z 632 [MH$^+$]. ^{1}H NMR (CDCl$_3$, ppm): 2.26 (m, 8H), 2.57 (m, 4H), 8.00−7.25 (20H, aromatic). Anal. Calcd for $C_{30}H_{32}P_2S_2$NTc: C, 57.05; H, 5.07; N, 2.22; S, 10.14; Tc, 15.69. Found: C, 57.08; H, 5.12; N, 2.20; S, 9.65; Tc, 15.22.

[^{99g}Tc(N)(L^5)$_2$] (5). Yield: 90% (based on ^{99g}Tc). FT IR (cm^{-1}): 1039 [ν(Tc≡N)]. FAB MS: m/z 688 [MH$^+$]. ^{1}H NMR (CDCl$_3$, ppm): 2.24 (m, 4H), 2.34 (s, 12H), 2.57 (m, 8H), 7.90−7.10 (16H, aromatic). Anal. Calcd for $C_{34}H_{40}P_2S_2$NTc: C, 59.39; H, 5.82; N, 2.04; S, 9.32; Tc, 14.41. Found: C, 58.92; H, 5.82; N, 2.00; S, 8.95; Tc, 14.37.

Compounds **1**, **2**, **4**, and **5** are soluble in chlorinated solvents, benzene, and toluene and insoluble in alcohols, acetonitrile, and diethyl ether.

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Table 1. ^{31}P NMR Spectral Parameters of Five-Coordinate Phosphino−Thiolato ^{99g}Tc Complexes

complex	δ ^{31}P, ppm	$\Delta\gamma_{1/2}$, Hz[a]	δ ^{31}P (free ligand), ppm
[Tc^V(N)(L^1)$_2$] (**1**)	66.2	250	−20.0
		140 (273 K)	
		110 (250 K)	
		65 (235 K)	
[Tc^{III}(L^1)$_2$(S-L^1)]	71.8	170	−20.0
	−5.9[b]	50	
[Tc^{III}(L^1)$_2$(S-L^1═O)]	69.9	240	−20.0
	27.7[c]	40	
[Tc^V(N)(L^2)$_2$] (**2**)	63.5	280	−14.7
[Tc^V(N)(L^3)$_2$] (**3**)	65.6	220	−32.8
[Tc^V(N)(L^4)$_2$] (**4**)	22.3	260	−19.0
		155 (273 K)	
		90 (250 K)	
		55 (235 K)	
[Tc^{III}(L^4)$_2$(S-L^4═O)][d]	22.4	200	−19.0
	31.4[c]	40	
[Tc^V(N)(L^5)$_2$] (**5**)	21.1	240	−21.0
[Tc^V(N)Cl$_2$(PPh$_3$)$_2$][e]	33.1	300	−7.4

[a] Measured at 298 K unless otherwise noted. [b] Uncoordinated P(III) of the S-L^1 ligand. [c] O═P(V) of the S-L^1═O ligand. [d] Taken from ref 10b. [e] Trace amounts of free PPh$_3$ (δ = −7.4 ppm) and oxidized O═PPh$_3$ (δ = 27.5 ppm) are present.

[^{99g}Tc(N)(L^3)$_2$] (3). The same procedure described above was applied to the reaction of [^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$] with the ligand HL^3. The final product was isolated as a yellow oily residue after evaporation of the reaction solvent. This oil was found to dissolve in all common solvents, and any attempt to convert it into a solid material was unsuccessful. The compound was purified by column chromatography on silica gel using ethanol/chloroform/benzene (0.1:2.0:1.5) as the mobile phase, and collected as a yellow band. Characterization was carried out only through NMR and FAB mass spectroscopy. FAB MS: m/z 588 [MH$^+$]. ^{1}H NMR (CDCl$_3$, ppm): 1.96 (m, 20H), 2.82 (m, 4H), 3.28 (s, 12H), 3.36 (m, 8H).

^{31}P NMR spectral data for complexes **1**−**5** are collected in Table 1.

Alternatively, the complexes [^{99g}Tc(N)(L^n)$_2$] could be prepared starting from the tetrachloro nitrido Tc(VI) complex [As(C$_6$H$_5$)$_4$][^{99g}Tc(N)Cl$_4$]. However, in these preparations, a careful selection of the experimental conditions was required to achieve final yields comparable with those obtained with the precursor complex [^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$]. A typical preparation was carried out as described below.

A 10-fold molar excess of the appropriate ligand HL^n (n = 1, 2, 4, 5) (with HL^2 the metal-to-ligand ratio was 1:3) was dissolved in 5.0 mL of ethanol. To this solution was added 50 μL (0.65 mmol) of trifluoroacetic acid (TFA), previously diluted with water (1:10), followed by the addition of 5.0 mL of an ethanolic solution containing 0.05 g (0.08 mmol) of [As(C$_6$H$_5$)$_4$][^{99g}Tc(N)Cl$_4$]. The mixture was refluxed for 1 h, and the initial red-orange color turned quickly to yellow. After cooling to room temperature, a yellow precipitate formed, which was collected by filtration, washed with ethanol and diethyl ether, and dried under vacuum. Recrystallization was carried out as described above. The final yields ranged between 70% and 83%.

It should be noted that the presence of TFA was found to be essential for obtaining the final complexes starting from [As(C$_6$H$_5$)$_4$][^{99g}Tc(N)Cl$_4$]. When the synthesis was conducted without addition of a proton source, the yields of the compounds [^{99g}Tc(N)(L^n)$_2$] were always lower than 40% because of the concomitant formation of a series of secondary Tc(III) byproducts, which were studied in detail only with the ligand HL^1 (see Results and Discussion). The synthesis and characterization of the Tc(III) complex [^{99g}Tc(L^1)$_2$(S-L^1)], where S-L^1 represents a monodentate, deprotonated L^1 ligand, is reported below.

[^{99g}Tc(L^1)$_2$(S-L^1)]. [As(C$_6$H$_5$)$_4$][^{99g}Tc(N)Cl$_4$] (0.05 g, 0.08 mmol) was dissolved in 5.0 mL of dichloromethane, and to the resulting solution was added a 10-fold molar excess of the ligands HL^1 [HL^1 = 2-(diphenylphosphino)ethanethiolato (Ph$_2$PCH$_2$CH$_2$SH)]. The color of the mixture turned from orange to fuchsia. A small drop of the reaction solution was placed on a silica gel plate (60 F$_{254}$, Merck) through a

Table 2. Crystal Data and Details of Data Collection for Complexes **1** and **5**

compd	**1**	**5**
formula	$C_{28}H_{28}NP_2S_2Tc$	$C_{34}H_{40}NP_2S_2Tc$
space group	*C*2/*c*	$P2_1/n$
cryst syst	monoclinic	monoclinic
fw, g mol^{-1}	602.6	686.7
a, Å	24.84(2)	11.090(1)
b, Å	7.327(6)	14.387(2)
c, Å	31.52(2)	11.087(1)
β, deg	111.06(10)	113.62(1)
T, °C	21	21
λ, Å	0.710 73	0.710 73
Z	8	2
F(000)	2464	712
V, Å^3	5353(7)	1620.9(3)
ρ_{calc}, g cm^{-1}	1.495	1.407
μ, cm^{-1}	8.31	6.96
2ϑ range, deg	5.2−40.1	4.9−46.1
obs reflns	2057	1778
R1[a]	0.057	0.060
wR2[a]	0.140	0.165
GOF[a]	1.060	1.066
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.33−0.72	0.51−0.81

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ (n = number of reflections, p = number of parameters).

syringe. Thin-layer chromatography (TLC) was performed using ethanol/chloroform/benzene (0.1:2:1.5) showing the presence of three colored spots (fuchsia, $R_f = 0.22$, yellow, $R_f = 0.78$, pink, $R_f = 0.95$). These products were separated through column chromatography on SiO_2 using the same mobile phase given above for TLC. Elution yields a first pink band followed by a yellow one, the fuchsia component being retained on the column. Evaporation of the solvent led to isolation of the corresponding pink and yellow solids. The yellow compound was identified as the nitrido Tc(V) complex [^{99g}Tc(N)(L^1)$_2$]. The pink product was found to convert slowly into the fuchsia Tc(III) complex [^{99g}Tc(L^1)$_2$(S-L^1═O)] when it was dissolved in chloroform and the resulting solution was allowed to evaporate under air. The crystal structure of the complex [^{99g}Tc(L^1)$_2$(S-L^1═O)] has been reported previously.[35,36] It comprises two bidentate L^1 ligands and an oxidized form of L^1 (S-L^1═O) acting as a monodentate ligand through the deprotonated thiol sulfur atom, and carrying the oxo−phosphorus(V) group. On the basis of these findings, we speculated that the structure of the pink complex could be formulated as [^{99g}Tc(L^1)$_2$(S-L^1)] where S-L^1 represents the ligand L^1 that is coordinated to the metal center only through the negative sulfur atom. Yield: 28% (based on ^{99g}Tc). FAB MS: *m*/*z*, 835 [MH$^+$]. ^{1}H NMR ($CDCl_3$, ppm): 7.65−7.10 (30H, aromatic), 3.10−1.8 (12H, aliphatic). Anal. Calcd for $C_{42}H_{42}P_3S_3Tc$: C, 60.43; H, 5.04; S, 11.51; Tc, 11.87. Found: C, 60.28; H, 5.02; S, 11.29; Tc, 11.37. The ^{31}P NMR spectrum showed a peak at $\delta = 71.8$ ppm assigned to the two phosphorus atoms of the two bidentate L^1 ligands, and one peak at $\delta = -5.9$ ppm assigned to the phosphorus atom of the monodentate ligand S-L^1.

Crystallographic Data Collection and Refinement. The intensity data were measured on a Siemens Nicolet R3m/V four-circle diffractometer using Mo Kα radiation and the $\omega-2\vartheta$ scan mode at 294 K. Absorption corrections were made according to ψ curves of four reflections at χ ca. 90°. The crystal parameters and the other experimental details of data collection and refinement procedures are summarized in Table 2. The structures were solved by standard Patterson methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL/PC[55] and SHELXL-93[56] programs.

The diffracting ability of sample **1** (Figure 1) fell off rapidly with increasing Bragg angle, and much of the higher angle data were flagged as weak. As a consequence, the data collection for **1** was restricted to $2\Theta_{max} = 40°$. In spite of this, all non-hydrogen atoms were refined anisotropically and refinement resulted satisfactorily. For compound **5** (Figure 2) the solution of the structure was rather difficult due to the siting of the Tc atom at 0, 0, $^1/_2$. The metal, P(1), S(1), and S(1′) atoms were located from a Patterson synthesis, and subsequent observed Fourier synthesis showed the positions of the C(1A)−(7A) atoms, along with a double image of the molecule from which the C(1B)−(7B) and C(1B′)−(7B′) atoms were identified (Figure 3). After five cycles of refinement of the parameters of these atoms, a difference Fourier synthesis gave reliable coordinates for the six carbons of the two propylene groups. The heavy atoms were assigned anisotropic thermal

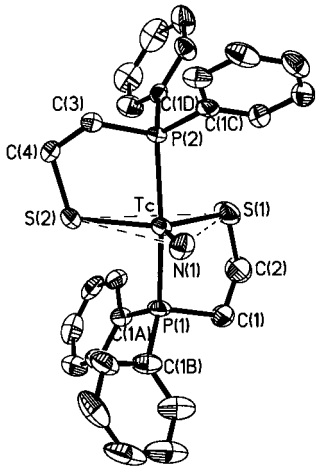


Figure 1. ORTEP representation of complex **1** showing thermal ellipsoids at the 40% probability level.

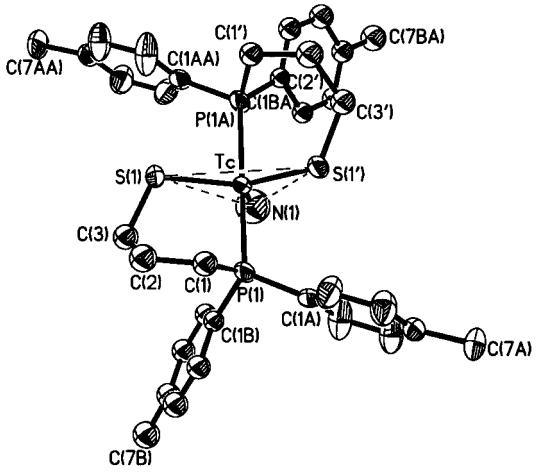


Figure 2. ORTEP representation of complex **5** showing thermal ellipsoids at the 40% probability level.

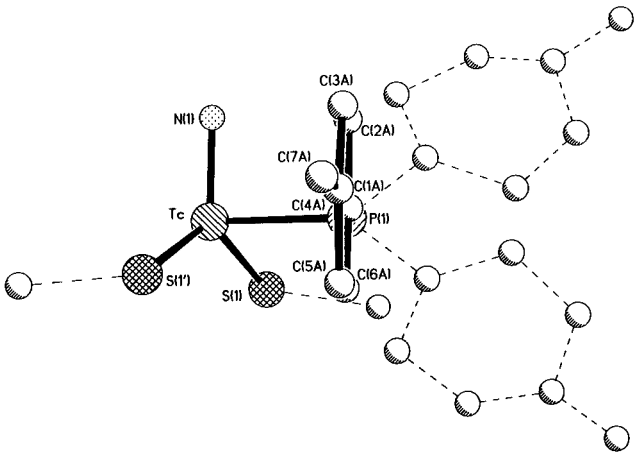


Figure 3. The double image of complex **5** derived by Fourier synthesis.

(55) Sheldrick, G. M. *SHELXTL/PC Version 5.3*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, USA, 1994.
(56) Sheldrick, G. M. *SHELXL-93 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Tc−P(1)	2.415(3)	P(1)−C(1)	1.83(1)
Tc−P(2)	2.399(3)	P(1)−C(1A)	1.82(1)
Tc−S(1)	2.342(4)	P(1)−C(1B)	1.81(1)
Tc−S(2)	2.353(4)	P(2)−C(3)	1.81(1)
Tc−N(1)	1.638(9)	P(2)−C(1C)	1.81(1)
S(1)−C(2)	1.83(1)	P(2)−C(1D)	1.82(1)
S(2)−C(4)	1.87(1)	C(1)−C(2)	1.50(2)
		C(3)−C(4)	1.50(2)
P(1)−Tc−P(2)	165.5(1)	S(2)−Tc−N(1)	112.5(3)
P(1)−Tc−S(1)	83.3(1)	Tc−P(1)−C(1)	104.0(4)
P(1)−Tc−S(2)	92.1(1)	Tc−P(2)−C(3)	105.6(3)
P(1)−Tc−N(1)	97.2(3)	Tc−S(1)−C(2)	108.8(4)
P(2)−Tc−S(1)	90.7(1)	Tc−S(2)−C(4)	108.8(4)
P(2)−Tc−S(2)	82.8(1)	P(1)−C(1)−C(2)	110.1(9)
P(2)−Tc−N(1)	97.3(3)	P(2)−C(3)−C(4)	111.1(7)
S(1)−Tc−S(2)	135.0(1)	S(1)−C(2)−C(1)	113.6(9)
S(1)−Tc−N(1)	112.5(3)	S(2)−C(4)−C(3)	113.3(8)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Tc−P(1)	2.407(2)	C(1)−C(2)	1.55(2)
Tc−S(1)	2.336(4)	C(1′)−C(2′)	1.55(2)
Tc−S(1′)	2.337(4)	C(2)−C(3)	1.53(2)
Tc−N(1)	1.65(1)	C(2′)−C(3′)	1.53(3)
P(1)−C(1)	2.12(2)	S(1)−C(3)	1.83(2)
P(1A)−C(1′)	2.11(2)	S(1′)−C(3′)	1.82(2)
S(1)−Tc−P(1)	91.7(1)	P(1)−C(1)−C(2)	111(1)
S(1′)−Tc−P(1A)	91.7(1)	P(1A)−C(1′)−C(2′)	111(1)
S(1)−Tc−S(1′)	131.5(2)	C(1)−C(2)−C(3)	119(2)
S(1)−Tc−N(1)	114.5(5)	C(1′)−C(2′)−C(3′)	119(2)
S(1′)−Tc−N(1)	113.9(5)	S(1)−C(3)−C(2)	116(1)
P(1)−Tc−N(1)	90.1(4)	S(1′)−C(3′)−C(2′)	116(1)
P(1A)−Tc−N(1)	89.9(4)	Tc−S(1)−C(3)	112.4(6)
Tc−P(1)−C(1)	99.9(4)	Tc−S(1′)−C(3′)	112.1(6)

parameters, the phenyl rings were treated as "rigid body", and the atoms with the same *y* value were satisfactorily refined with a fixed occupancy of 0.5. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.51, and −0.81 e Å^{-3}, in the vicinity of the Tc atom. Refinement in the two alternative space groups of higher symmetry (*Cmca* or *Aba*2) resulted in unacceptable *R* factor values (0.11 and 0.12, respectively), with some high peaks (up to 4.2 e Å^{-3}) in the proximity of phosphorus and sulfur atoms, and unrealistic metrical parameters.

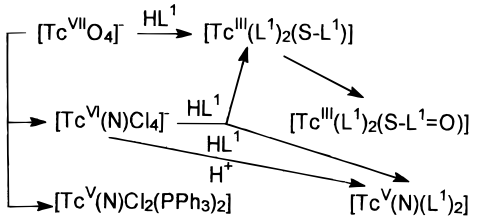
Selected bond distances and angles are summarized in Tables 3 and 4 for **1** and **5**, respectively.

Results and Discussion

Synthesis and Characterization. The nitrido Tc(V) complexes **1**−**5** were easily prepared by treating the precursor complex [^{99g}Tc(N)Cl$_2$(PPh$_3$)$_2$] with an excess of the appropriate phosphino−thiol ligand in dichloromethane solutions, and isolated as yellow crystals (except for the complex with the ligand L^3, see Experimental section) from dichloromethane/methanol mixtures in almost quantitative yields.

Starting from the precursor Tc(VI) complex [^{99g}Tc(N)Cl$_4$]$^-$, the reactions with phosphine−thiol ligands HL^n (n = 1, 2, 4, 5), in acidic media, afforded the same symmetric, bis-substituted nitrido Tc(V) complexes **1**, **2**, **4**, and **5**, which were collected in high yield. However, when these reactions were conducted without addition of a proton source, a more pronounced reduction of the metal oxidation state, with the concomitant removal of the Tc≡N terminal group, was observed. Under these conditions, a series of chemically related Tc(III) derivatives were obtained, which were fully characterized only with the ligand HL^1. This series comprised both the five-coordinated complexes [^{99g}Tc^{III}(L^1)$_2$(S−L^1)] and [^{99g}Tc^{III}(L^1)$_2$(S-L^1═O)] and the octahedral, tris-substituted complex [^{99g}Tc(L^1)$_3$] (Scheme 1). In [^{99g}Tc^{III}(L^1)$_2$(S−L^1)], S-L^1 represents a monodentate L^1 ligand coordinated to the metal ion through the deprotonated sulfur atom, while in [^{99g}Tc^{III}(L^1)$_2$(S-L^1═O)], S-L^1═O indicates the oxo phosphorus(V) form of the same phosphine−thiol ligand still coordinated through the sulfur atom. The influence of acidic conditions on the outcome of the reactions of ligands HL^n with [^{99g}Tc(N)Cl$_4$]$^-$ can be easily explained by assuming that high proton concentrations should keep the thiol group of the ligands protonated, thus reducing its donor affinity toward the metal center. Consequently, the phosphorus atom of the phosphine−thiol ligand may react first by substituting a chlorine atom and, in turn, stabilizing the +5 metal oxidation state in the resulting [Tc≡N]$^{2+}$ group, in much the same way as it is commonly observed when [^{99g}Tc(N)Cl$_4$]$^-$ reacts with simple monophosphine ligands.[50] Under more basic conditions, deprotonation of the thiol group would be enhanced and competitive displacement of the nitrido group with the concomitant formation of Tc(III) species would occur. Nucleophilic attack of the thiolate sulfur atom of the phosphine−thiol ligand at the nitrido nitrogen atom is most likely responsible of the removal of the Tc≡N multiple bond. These reactions constitute rare examples of displacement of a terminal nitrido group from a technetium complex, which have been previously observed only with simple bidentate thiol ligands.[57] It is worthy to note here that complex **1** is converted into the related Tc(III) complexes only through prolonged heating in solution and in the presence of a large excess of the ligand HL^1. Thus, the sudden formation of the complex [^{99g}Tc^{III}(L^1)$_2$(S-L^1)] must involve the first removal of the Tc≡N bond from [^{99g}Tc(N)Cl$_4$]$^-$ and not from **1**.

Scheme 1



Elemental analyses of complexes **1**, **2**, **4**, and **5** were in excellent agreement with the proposed formulation. FT IR spectra exhibited the characteristic ν(Tc≡N) stretching vibration in the range 1030−1053 cm^{-1}. FAB$^+$ mass spectra of **1**−**5** showed the presence of the parent molecule with no detectable fragmentation.

All [^{99g}Tc(N)(L^n)$_2$] (n = 1−5) are diamagnetic as expected for d^2 complexes containing the [Tc^V≡N]$^{2+}$ core. Proton NMR spectra exhibited multiplet signals in the aromatic and aliphatic regions consistent with the presence of methylene and/or phenyl groups, with the correct integration ratio. At the opposite, ^{31}P NMR spectra showed very broad signals at ambient temperature (Table 1). On lowering the temperature, lines became narrower, with half line width decreasing from 250 Hz at room temperature to 60 Hz at 235 K. This behavior parallels that found by Abram and co-workers in six-coordinate [^{99g}Tc(N)X$_2$(PMe$_2$Ph)$_3$] (X = Cl, Br) complexes.[51] In these latter compounds, line broadening has been attributed to the coupling of the ^{31}P nuclei with the quadrupolar ^{99g}Tc nucleus. As summarized in Table 1, ^{31}P NMR spectra of [^{99g}Tc(N)(L^n)$_2$] complexes exhibited a remarkable downfield shift of the phosphorus signal upon phosphino−thiolato coordination. The position of this peak in the spectral

(57) Colmanet, S. F.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1987**, 2305−2310.

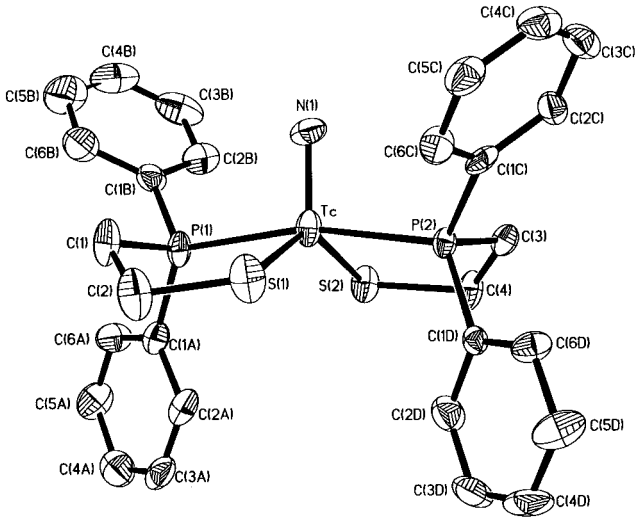


Figure 4. Alternative ORTEP representation of complex **1** showing thermal ellipsoids at the 40% probability level.

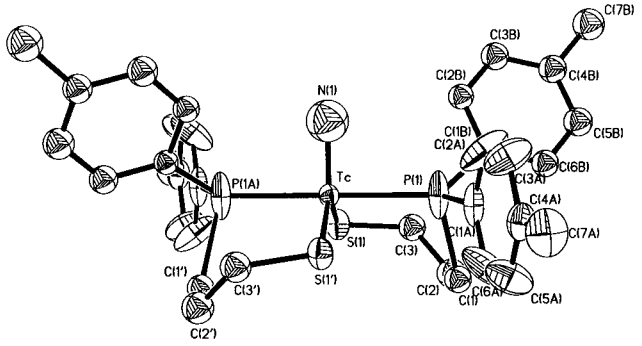


Figure 5. Alternative ORTEP representation of complex **5** showing thermal ellipsoids at the 40% probability level.

window appears to be dependent on the length of the carbon chain between P and S atoms. Specifically, phosphinoethanethiolato ligands generating a five-membered chelate ring gave rise to larger deshielding effects than the corresponding phosphinopropanethiolato ligands (six-membered chelate ring). This behavior was observed also in diamagnetic five-coordinated Tc(III) derivatives of the type $[^{99g}Tc(L^n)_2(S\text{-}L^n{=}O)$ (n = 1, 4).[35,38]

Structure. In complexes **1** and **5** the $[Tc{\equiv}N]^{2+}$ core is coordinated by two phosphino−thiol ligands and the P(1)- - -P(2) line has the appearance of the axis in an approximate trigonal bipyramidal structure (Figures 1 and 2), in which the equatorial positions are occupied by N(1), S(1), and S(2) atoms. Alternatively, the coordination geometry can be described as a distorted rectangular pyramid, with the P_2S_2 donor atom set in the basal positions, identical atoms being diametrically opposed, and the nitrido ligand occupying the apical position (Figures 4 and 5). In the square pyramidal description, the P and S donor atoms lie out of the P_2S_2 plane on opposite sides by ±0.30 Å in **1** and ±0.48 Å in **5**, while the Tc atom is above this plane by 0.60 Å in **1** and 0.48 Å in **5** toward the nitrido ligand. The P- - -S bite distance of 3.15 Å in **1** lengthens to 3.40 Å in **5**, and accordingly, the P−Tc−S angle of 83.3° in **1** enlarges to 91.7° in **5**. In **1**, the two five-membered $TcSC_2P$ rings assume the envelope (C_s) conformation with C(1) and C(3) atoms out of the pertinent TcSCP mean plane by 0.67 and 0.64 Å, respectively. These TcSCP mean planes are roughly perpendicular to the S(1)N(1)S(2) plane, both dihedral angles being 93.2° (Figure 1). In **5**, the two six-membered $TcSC_3P$ rings adopt the boat (C_{2v}) conformation with P(1) and C(3) atoms above the TcS(1)C(2)C(1) mean plane by 1.18 and 0.74 Å, respectively (Figure 2).

The bond lengths and angles in the coordination sphere are similar to those observed in the other five-coordinate Tc(V) nitrido complexes listed in Table 5 and need no comment. In crystals of both **1** and **5**, the molecules are packed individually and interact via normal van der Waals contacts.

Using the structural index parameter τ[58] [$\tau = (\beta - \alpha)/60$, where α and β are the two largest angles around Tc], its value is 0.50 and 0.81 for **1** and **5**, respectively. This suggests that the trigonal bipyramidal geometry has to be preferred for **5** (τ = 1 for ideal trigonal bipyramidal geometry, and τ = 0 for ideal square pyramidal geometry), while for **1** the geometry has to be considered as intermediate between the two ideal limits. Table 5 reports τ values for a number of monomeric five-coordinate nitrido Tc(V) complexes. These data indicate that the situation encountered here with phosphino−thiol Tc(V) nitrido complexes is quite uncommon since the preferred coordination geometry is usually square pyramidal, while complexes **1** and **5** exhibit the highest values of τ index. Examination of Table 5 shows that only six complexes have a τ value greater than 0.35. The structures of these complexes are characterized by two distinct features: (i) only donor atoms of group 15 lie in the two apical positions, and (ii) only donor atoms of group 16 and/or 17 span the positions in the equatorial plane along with the nitrido ligand. This observation may suggest a possible way to account for the change from square pyramidal to trigonal bipyramidal geometry by carefully considering the effect of varying the chemical nature of the set of atoms placed on the remaining four positions of a five-coordinated arrangement where one position is always occupied by the Tc≡N group. Crystal data (Table 5) clearly show that, in complexes where the Tc≡N group is coordinated to ligands through four π-donor atoms such as S^- and X^- (X = halogen), the resulting geometry is invariably square pyramidal with four,

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Table 5. τ Values in Monomeric, Five-Coordinate Nitrido Tc(V) Complexes[a]

complex	τ	ref	complex	τ	ref
$[Tc(N)(SCOCOS)_2]^{2-}$	0.00	59	$[Tc(N)(i\text{-}mns)_2]^{2-}$	0.09	70
$[Tc(N)(SCOS)_2]^{2-}$	0.00	60	$[Tc(N)Cl_2(PP^1)]$	0.10	30
$[Tc(N)(mnt)_2]^{2-}$	0.00	61	$[Tc(N)(S_2N_2)]$	0.10	26
$[Tc(N)(SCOCOS)_2]^{2-}$[b]	0.01	62	$[Tc(N)(ecbap)(PPh_3)]$	0.18	71
$[Tc(N)(S_2CNEt_2)_2]$	0.02	9	$[Tc(N)Cl(cys)(PPh_3)]$	0.20	18
$[Tc(N)(mnt)(PMe_2Ph)]$	0.02	63	$[Tc(N)(SC_6HMe_4)_2\{NHC(NMe_2)_2\}_2]$	0.26	17
[Tc(N)(SNNS)]	0.02	64	$[Tc(N)(SB1)(PPh_3)]$	0.28	27
$[Tc(N)Cl(14S4)]^{+}$[c]	0.03	65	$[Tc(N)Cl_2(PPh_3)_2]$	0.36	72
$[Tc(N)Cl(18S6)]^{+}$[c]	0.05	65	$[Tc(N)Cl_2(AsPh_3)_2]$	0.38	73[
$Tc(N)Cl\{16S4\text{-}(OH)_2\}]^{+}$[c]	0.06	65	[Tc(N)Cl{PhNC(OEt)S}]	0.39	74
$[Tc(N)(HEt_2tcb)_2]$	0.07	66	$[Tc(N)(SB2)_2]$	0.42	27
$[Tc(N)(dmit)_2]^{2-}$	0.08	67	$[Tc(N)Cl_2(PP^2)]$	0.43	30
$[Tc(N)(S_2CNEt_2](SCOCOS)]^{-}$	0.08	68	$[Tc(N)(quin)_2]$	0.47	50
$[Tc(N)\{N(SPPh_2)_2\}_2]$	0.08	69			

[a] Abbreviations: mnt = 1,2-dicyanoethenedithiolato(1−); SNNS = *N*,*N*′-ethylenebis(methyl-2-aminocyclopentene-1-dithiocarboxylato)(2−); HEt_2tcb = *N*,*N*-diethylthiocarbamoylbenzaminidato(1−); dmit = isotrithionedithiolato(1−); i-mns = 1,1-dicyanoethene-2,2-diselenolato(1−); PP^1 = bis(diphenylphosphinoethyl)propylamine; S_2N_2 = *N*,*N*′-ethylenebis(thioacetylacetarylideneiminato(2−); ecbap = *N*-(2-ethoxycarbonyl-3-oxo-but-1-en(1)yl-2-aminophenolato(2−); cys = *O*-ethyl-L-cysteinato(1−); SB1 = *S*-methyl-3-(2-hydroxyphenylmethylene)dithiocarbazato(2−); SB2 = *S*-methyl-3-isopropylidenedithiocarbazato(1−); PP^2 = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane; quin = 8-quinolinethiolato(1−). [b] Monoclinic modification of ref 59. [c] Thiacrown ether.

almost equivalent, basal bonds resulting in an approximate C_{4v} symmetry. Since the phosphine−thiol ligands utilized in this study comprise a mixed set of coordinating atoms, including one π-donor, negative sulfur and one π-acceptor, neutral phosphorus atom, it is straightforward to assume that, on changing the coordinating set of four equivalent π-donor atoms to a mixed P_2S_2 set, the almost regular C_{4v} symmetry cannot longer be maintained. In particular, the crystallographic results shown here seem to indicate that the two π-acceptor phosphorus atoms prefer to occupy a reciprocal trans position of the five-coordinated arrangement, the two π-donor sulfur atoms still keeping a relative cis position. Obviously, only a trigonal bipyramidal arrangement can accommodate such a distribution of coordinating atoms around the Tc≡N group, thus forcing the system to achieve this final geometry. As predicted for trigonal bipyramidal compounds, the transaxial π-acceptor phosphorus atoms should be bound to the $[Tc{\equiv}N]^{2+}$ core using a set of equivalent orbitals that is different from that utilized by the two equatorial π-donor sulfur atoms.

Conclusions

A novel series of five-coordinated, nitrido technetium(V) complexes with phosphine−thiol ligands has been described. Structural characterization of these complexes showed that they possess an uncommon trigonal bipyramidal geometry in contrast with most nitrido Tc(V) complexes, which exhibit a square-pyramidal geometry. The stability of the trigonal bipyramidal arrangement appears to be related to the specific set of coordinating atoms composed of two π-donor sulfur atoms and two π-acceptor phosphorus atoms. P atoms were found to occupy the two transaxial positions while S atoms span two positions on the equatorial plane along with the N^{3-} nitrogen atom. A more extended survey of the relationships between geometry and specific sets of coordinating atoms in nitrido Tc(V) complexes may contribute to elucidate both electronic and steric factors favoring each type of five-coordinated arrangement.

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Supporting Information Available: Listings, from the Cambridge Crystallographic Data Centre, the crystallographic methods, fractional atomic coordinates and the equivalent thermal parameters for all atoms, anisotropic thermal parameters, and bond lengths and angles for **1** and **5** and description of the synthesis of $[^{99g}Tc(L^1)_2(S\text{-}L^1)]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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