Inorg. Chem. **2000,** *39,* 5757−5762

Syntheses of New Ionic Technetium(III) Complexes Containing Four Monodentate Phosphine Ligands. Crystal Structures of *trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$, *trans*-$[Tc(PMe_3)_4Cl_2]BPh_4$, and *trans*-$[Tc(PMe_3)_4Cl_2]PF_6$

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Received June 3, 1999

New ionic technetium complexes of the type *trans*-$[Tc(PR_3)_4Cl_2]^+$ are synthesized by various methods. The simplest method is the reaction of $[TcO_4]^-$ with the phosphine in methanol in the presence of a chloride salt. Compounds containing PMe_2Ph and PMe_3 are synthesized and characterized by crystallographic methods. The complexes containing the less bulky phosphine can be prepared from complexes containing the bulkier phosphine. The compounds are paramagnetic, with two unpaired electrons. The complexes studied by X-ray diffraction methods are the trans isomers. $[Tc(PMe_2Ph)_4Cl_2]PF_6$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.511(2)$ Å, $b = 26.713(7)$ Å, $c = 12.688(3)$ Å, $\beta = 92.79(1)°$, $Z = 4$, and R1 = 0.0574. $[Tc(PMe_3)_4Cl_2]BPh_4$ (**II**) crystallizes in the orthorhombic space group *Pbcn*, with $a = 18.213(5)$ Å, $b = 22.950(5)$ Å, $c = 19.428(6)$ Å, $Z = 8$, and R1 = 0.0691. $[Tc(PMe_3)_4Cl_2]PF_6$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 18.152(7)$ Å, $b = 16.838(9)$ Å, $c = 18.090(6)$ Å, $\beta = 106.63(1)°$, $Z = 8$, and R1 = 0.0670. The compounds all have octahedral coordination, but an important tetrahedral deformation of the plane containing the Tc and the four P atoms is observed in each case. In **II**, the two independent Tc atoms are both located on 2-fold axes.

Introduction

The isotope ^{99m}Tc is widely used as a diagnostic agent in nuclear medicine. It has greatly increased the importance of developing the chemistry of technetium. ^{99m}Tc has been used for many years in bone scanning and more recently for studying diseases of the heart, brain, kidneys, liver, and other organs as well as imaging tumor tissue.

We have been involved for several years in the synthesis of technetium-99 compounds. The main objective of our research is to synthesize new Tc complexes with ligands that could have some significance in the radiopharmaceutical field. To be useful, the preparative methods must be simple and adaptable to the use of the industrial kits, where the starting material $[^{99m}TcO_4]^-$ is synthesized *in situ* and the ^{99m}Tc radiopharmaceutical must be prepared rapidly, by a “one-pot” method.

Phosphine derivatives are one type of ligands under study in our laboratory, mainly because of their significance as heart agents. The latter are generally cationic species of Tc in a low oxidation state, such as $[Tc(diphosphine)_3]^+$ and $[Tc(diphosphine)_2Cl_2]^+$.[1] $[Tc(MIBI)_6]^+$ (MIBI = methoxyisobutylisonitrile) is now currently used for myocardial perfusion imaging.[2] This agent accumulates rapidly in the heart and has a long retention time. But it also accumulates in other organs, especially the liver, which partly limits its use. Therefore, the search for a more specific agent is continuing. More recently, a Tc(V) cationic dioxo complex containing a bidentate phosphine ligand with ether groups, *trans*-$[Tc(tetrofosmin)_2O_2]^+$, where tetrofosmin = 1,2-bis(bis(2-ethoxyethyl)phosphino)ethane, was evaluated for potential use in myocardial diagnostic studies.[3] The results of the biodistribution studies seemed very promising for myocardial perfusion imaging, especially because of its substantially increased clearance from nontarget tissue, particularly the liver.

The linear organoimido unit (Tc−N−R) is formally isoelectronic with the Tc═O unit, which is present in several Tc radiopharmaceuticals. A simple method was reported for the preparation of $Tc(NPh)(PPh_3)_2Cl_3$, from the reaction of $NH_4[TcO_4]$ with PPh_3, Ph-NH−NH−$COCH_3$, and HCl in methanol.[4] The phenylimido unit was generated through the cleavage of the N−N bond in the hydrazine derivative. We decided to synthesize such Tc compounds with phosphines less bulky than PPh_3. A similar reaction with $PMePh_2$ produced the expected compound $Tc(NPh)(PMePh_2)_2X_3$.[5] When PMe_2Ph was used, the reaction was quite different. A complex containing an organodiazenido unit, $Tc(NNPh)(PMe_2Ph)_2Br_3$, was isolated with a 30% yield.[5] A phenylimido complex, $[Tc(NPh)(PMe_2Ph)_3Br_2]^+$, was also formed in the reaction. The ligand PMe_2Ph is less bulky and the complex contains three phosphine ligands. Since the latter Tc compound is ionic, it did not precipitate in the reacting medium. The synthesis of $[Tc(NPh)(PMe_2Ph)_3X_2]BPh_4$ was later reported, but it was synthesized by a different method,

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10.1021/ic9906454 CCC: $19.00

namely, from the reaction of $Tc(NPh)(PPh_3)_2X_3$ with excess PMe_2Ph.[6]

In an effort to prepare the ionic compound $[Tc(NPh)(PR_3)_3X_2]^+$ with even less bulky phosphines, we have studied the reaction of $Tc(NPh)(PPh_3)_2X_3$ with PEt_3 following the method published for the PMe_2Ph compound.[6] The experimental details, however, were not well described. We isolated crystals that were identified by X-ray diffraction as a new type of ionic dioxo compound, $[TcO_2(PEt_3)_3]^+$.[7] We then repeated the reaction with PMe_2Ph following the published method[6] to prepare $[Tc(NPh)(PMe_2Ph)_3X_2]^+$, and the crystals obtained were studied by X-ray diffraction methods. The results showed a totally different compound containing four phosphine ligands. To our knowledge, Tc compounds with four monodentate phosphine ligands have not, until now been reported, although compounds with two or three bidentate phosphines have been known for a long time.[1,8,9] Compounds with six phosphite ligands have also been known for many years, but in these complexes, the steric requirements around the binding site are much reduced.[10,11]

Following the isolation of these very interesting new compounds, we attempted to develop simpler methods for their preparation. We were quite successful, and in this paper, these new methods are described. The crystal structures of three such complexes were determined, and the results are discussed below.

Experimental Section

Ammonium pertechnetate ($NH_4{}^{99}TcO_4$) was obtained from Oak Ridge National Laboratory. It was recrystallized from nitric acid (*caution*: ammonium pertechnetate in acid medium will produce some radioactive volatile compounds) and dissolved in water. A ~0.3 M aqueous solution was then prepared. All manipulations were performed in a laboratory approved for low-level radioactive material (^{99}Tc is a β-emitter with a particle energy of 0.292 MeV and a half-life of 2.13×10^5 years). The ligands were purchased from Aldrich.

$Tc(PMe_2Ph)_2Cl_4$ and $Tc(PMe_2Ph)_3Cl_3$. These two compounds were prepared according to the literature procedures.[12,13]

***trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$ (I).** (a) This compound was first synthesized exactly as described in the literature for the preparation of $[Tc(NPh)(PMe_2Ph)_3Cl_2]^+$ from the reaction of $Tc(NPh)(PPh_3)_2Cl_3$ with excess dimethylphenylphosphine in hot methanol.[6] NH_4PF_6 was added to the cooled solution instead of $NaBPh_4$. The solvent was evaporated to dryness, and the oily residue was washed several times with ether. The residue was dissolved in methanol and allowed to slowly crystallize. Orange crystals identified as *trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$ by X-ray diffraction methods were later isolated.

(b) For a second synthesis, a 0.2 mL portion of PMe_2Ph was added with constant stirring to a 20 mL ethanol solution containing 0.05 g of $Tc(PMe_2Ph)_2Cl_4$. The mixture was refluxed for 6 h, after which the orange solution was cooled to room temperature and filtered. The volume of the filtrate was concentrated to a few milliliters, 5 mL of water was added, and the resulting mixture was filtered. A 0.2 g quantity of NH_4PF_6 was added to the filtrate, whereupon a precipitate appeared immediately and was collected by filtration. Yield: 70%. The compound was recrystallized from methanol−dichloromethane for the X-ray diffraction study. IR (cm^{-1}): 1320 w, 1300 w, 1285 s, 1150 m, 1100 s, 1000 w, 940 s, 905 vs, 840 vs (br), 745 vs, 700 vs, 685 w, 630 m, 565 vs, 490 vs, 420 s (br), 345 s (ν(Tc−Cl)). $\mu = 3.1\ \mu_B$.

Table 1. Crystallographic Data for **I**−**III**

	I	II	III
empirical formula	$C_{32}H_{44}Cl_2F_6P_5Tc$	$C_{36}H_{56}BCl_2P_4Tc$	$C_{12}H_{36}Cl_2F_6P_5Tc$
MW	866.42	792.40	618.16
space group	$P2_1/c$	*Pbcn*	$P2_1/c$
a (Å)	11.511(2)	18.213(5)	18.152(7)
b (Å)	26.713(7)	22.950(5)	16.838(9)
c (Å)	12.688(3)	19.428(6)	18.090(6)
β (deg)	92.79(1)		106.63(1)
V (Å^3)	3896.6(18)	8121(4)	5298(4)
Z	4	8	8
ρ_{calcd} (g cm^{-3})	1.477	1.296	1.550
μ(Mo Kα) (mm^{-1})	0.763	0.667	1.087
λ (Å)	0.71073	0.71073	0.71073
T (°C)	21	21	21
R1 ($I > 2\sigma(I)$)	0.0574	0.0691	0.0670
wR2 (all data)	0.1173	0.1202	0.1194
S	1.054	0.845	0.998

***trans*-$[Tc(PMe_3)_4Cl_2]BPh_4$ (II) and *trans*-$[Tc(PMe_3)_4Cl_2]PF_6$ (III).** These compounds were prepared by two different methods, from $Tc(PMe_2Ph)_2Cl_4$ and from $NH_4[TcO_4]$.

(a) Method b described above for the preparation of the PMe_2Ph compound was used. $Tc(PMe_2Ph)_2Cl_4$ dissolved in methanol was reacted with 3 mL of a PMe_3 toluene solution (1 M). For the BPh_4^- compound, NH_4PF_6 was replaced by $NaBPh_4$. The yields were about 60%.

(b) For an alternative synthesis, a 5 mL methanol solution containing 0.1 mmol of $NH_4[TcO_4]$ was added to a 15 mL methanol solution containing 0.07 g of aniline hydrochloride. A 3 mL portion of PMe_3 solution (1 M in toluene) was added to the mixture. The resulting solution was stirred (becoming green due to the formation of $Tc(PMe_3)_2Cl_4$) and refluxed overnight, whereupon the solution turned orange. Its volume was concentrated to a few milliliters, 5 mL of water was added, and the mixture was filtered. A 0.2 g quantity of NH_4PF_6 (or $NaBPh_4$) was added to the filtrate, and the orange-yellow precipitate was collected by filtration. Yield: 80%. Data for **III**: IR (cm^{-1}) 1320 s, 1295 s, 1285 sh, 1070 w, 940 vs (br), 835 vs (br), 735 sh, 720 s, 674 w, 555 vs, 485 w, 345 sh, 330 s (ν(Tc−Cl)); $\mu = 3.2\ \mu_B$; NMR (ppm; $CDCl_3$) 1.519 d, $^2J(^{31}P-^1H) = 12.9$ Hz. Anal. Calcd for **III**: C, 23.30; H, 5.87; P, 25.05. Found: C, 23.53; H, 5.57; P, 25.32. Calcd for **II**: C, 54.57; H, 7.12; P, 15.64. Found: C, 54.13; H, 6.88; P, 15.34.

Crystallographic Measurements and Structure Resolutions. The crystals were selected after examination under a polarizing microscope for homogeneity. The unit cell parameters were obtained by least-squares refinement of the angles 2θ, ω, and χ for about 33 well-centered reflections on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation. The Siemens XSCANS program[14] was used for the crystal-centering, data collection, and data reduction procedures. The background time to scan time ratio was 0.5. The crystal data are listed in Table 1.

The coordinates of the Tc atoms were determined from direct methods or from a Patterson map calculations, and the positions of all other non-hydrogen atoms were found by the usual Fourier methods. The refinements of the structures were performed on F^2, by full-matrix least-squares analysis. The H atoms were fixed at their calculated positions (riding model), each with $U_{eq} = 1.2$ (1.5 for CH_3 groups) $\times\ U_{eq}$ of the atom to which it is bonded. The refinements of the scale factors, coordinates, and anisotropic temperature factors of all the non-hydrogen atoms converged to the R1 and wR2 values shown in Table 1. All calculations were performed using the Siemens SHELXTL system.[15] The crystallographic data were those incorporated in the system.

Results and Discussion

In an attempt to synthesize phenylimido Tc complexes of the type $Tc(NPh)(PR_3)_2X_3$ or $[Tc(NPh)(PR_3)_3X_2]^+$ with phos-

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phines less bulky than the triphenyl derivative, we have repeated the published procedure for the preparation of $[Tc(NPh)(PMe_2Ph)_3Cl_2]BPh_4$ from the reaction of $Tc(NPh)(PPh_3)_2X_3$ with an excess of dimethylphenylphosphine in methanol:[6]

$$Tc(NPh)(PPh_3)_2Cl_3 + PMe_2Ph\ (excess) \rightarrow [Tc(NPh)(PMe_2Ph)_3Cl_2]^+$$

Our reaction did not proceed as described. There were a few experimental differences from the published method, namely, that we used normal methanol instead of anhydrous methanol, we might have refluxed for a slightly longer time, and we replaced the salt $NaBPh_4$ by NH_4PF_6. Furthermore, the excess amount of PMe_2Ph might have been different (not mentioned in the published procedure). After the addition of NH_4PF_6, there was no precipitate as reported. Therefore, the solvent was evaporated and the dark oil was washed with ether. Orange crystals suitable for X-ray diffraction analysis were obtained by recrystallizing the residue from methanol. The results of our crystallographic study showed that the compound was completely different from the expected one. It was identified as a new kind of cationic Tc(III) complex: *trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$.

$$Tc(NPh)(PPh_3)_2X_3 + PMe_2Ph\ (excess) \xrightarrow{\text{methanol}} trans\text{-}[Tc(PMe_2Ph)_4X_2]^+$$

The presence of four bonded PMe_2Ph ligands was quite surprising, since, to our knowledge, Tc compounds containing four monodentate phosphine ligands have not, until now, been reported. Tetrakis(phosphine) compounds have been reported, but they all contain bidentate phosphine ligands. It was believed that the steric hindrance was too large for the synthesis of tetrakis(phosphine) complexes. It has been shown that the reaction of $[TcO_4]^-$ with a great excess of triphenylphosphine produces *trans*-$Tc(PPh_3)_2Cl_4$, while the reaction with a less crowded phosphine like $PPhMe_2$ produces *mer*-$Tc(PPhMe_2)_3Cl_3$.[12] The steric requirements for tri- or tetra-substituted phosphine complexes are not very different. Therefore, the synthesis of tetrakis(phosphine) compounds is possible, especially with less sterically demanding ligands. Tetrasubstituted Tc phosphite compounds have been known for many years[10,11] because the steric requirements around P are much smaller.

We concentrated our next efforts toward the development of simpler methods to synthesize these new types of tetrasubstituted complexes. We were successful in developing a much better method using as starting materials $Tc(PR_3)_2Cl_4$ or $Tc(PR_3)_3Cl_3$ complexes, which are more readily available than the phenylimido compound:

$$Tc(PMe_2Ph)_{2\text{ or }3}Cl_{4\text{ or }3} + PMe_2Ph \xrightarrow{\text{ethanol, }\Delta} trans\text{-}[Tc(PMe_2Ph)_4X_2]^+$$

The mixture is refluxed in ethanol for 6 h. The less sterically demanding ligands such as PMe_3 can also produce tetrasubstituted Tc complexes by ligand exchange from complexes containing more crowded ligands as follows:

$$Tc(PMe_2Ph)_{2\text{ or }3}Cl_{4\text{ or }3} + PMe_3 \xrightarrow{\text{methanol, }\Delta} trans\text{-}[Tc(PMe_3)_4X_2]^+$$

$$trans\text{-}[Tc(PMe_2Ph)_4X_2]^+ + PMe_3 \xrightarrow{\text{methanol, }\Delta} trans\text{-}[Tc(PMe_3)_4X_2]^+$$

Ethanol was used in the preparation of the PMe_2Ph complexes, since it can be heated at a higher temperature than in methanol, which shortens the refluxing time. In the synthesis of the PMe_3 complexes, methanol was preferred, since PMe_3 has a low boiling point and refluxing in ethanol led to an important loss of ligand. The yields are about 60%.

This method is quite simple, but it is not very useful for the preparation of radiopharmaceuticals, since the starting material $Tc(PR_3)_2Cl_4$ or $Tc(PR_3)_3Cl_3$ must be isolated. We have made several attempts to develop a one-pot preparation from $[TcO_4]^-$. Recently, we were quite successful in the development of an easy one-step method:

$$[TcO_4]^- + PR_3 + Cl^- \xrightarrow{\text{methanol, }\Delta} [Tc(PR_3)_4X_2]^+$$

The aqueous $[TcO_4]^-$ solution was evaporated to dryness, and the residue was dissolved in methanol. A small quantity of $PhNH_3^+Cl^-$ was used in addition to the phosphine ligand. This is a very simple method, and the reaction requires about 15 h. The yields are close to 80%. This method could probably be adapted to the commercial kits used in hospitals for the preparation of the ^{99m}Tc radiopharmaceuticals. The aqueous $[^{99m}TcO_4]^-$ solution obtained from the generator could be evaporated to dryness, and the residue could be dissolved in alcohol. In all these reactions, no reducing agent was used, since, when needed, the phosphine acts as the reducing agent, being oxidized to the phosphine oxide.

Only compounds containing PMe_2Ph and PMe_3 could be prepared with PF_6^- and BPh_4^- anions. The preparations of these compounds seem to be very dependent on the phosphines used. Similar reactions with $PMePh_2$ were not successful because of the greater bulkiness of the ligand. The reactions with PEt_3 were also investigated, and only dark decomposed products were isolated. It was not possible to purify the residues or to identify some of the compounds formed. The two phosphines PMe_2Ph and PMe_3 seem to have similar reactivities toward Tc even if their sizes are quite different.

The PMe_2Ph and PMe_3 compounds could be prepared with PF_6^- and BPh_4^- anions. The complexes with a d^4 configuration are paramagnetic, with two unpaired electrons. The magnetic moments are around 3.0−3.2 μ_B. The ^1H NMR spectrum of *trans*-$[Tc(PMe_3)_4Cl_2]PF_6$ could be measured and confirmed the purity of the compound. The three complexes *trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$ (**I**), *trans*-$[Tc(PMe_3)_4Cl_2]BPh_4$ (**II**), and *trans*-$[Tc(PMe_3)_4Cl_2]PF_6$ (**III**) were characterized by X-ray diffraction methods.

***trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$ (I).** A labeled diagram of the complex cation in *trans*-$[Tc(PMe_2Ph)_4Cl_2]PF_6$ is shown in Figure 1. The molecule is the trans isomer, and the geometry around the Tc atom is approximately octahedral. Selected bond distances and angles are listed in Table 2. The cis P−Tc−P angles are very close to the expected value (90.01(3)−91.24(3)°), but the P−Tc−Cl angles show considerable distortions of the octahedron (83.76(4)−96.96(3)°). The trans angles P−Tc−P are 168.17(3) and 170.84(3)°, while the Cl−Tc−Cl angle is 176.97(3)°. The Tc−Cl bond distances are 2.325(1) and 2.330(1) Å, close to the average value of 2.335 Å reported for 11 published similar Tc(III) structures.[16] The Tc−P bonds vary between 2.490(1) and 2.536(1) Å. These values are slightly long for Tc(III) compounds. In a short review, the average value found for Tc(III)−P bond distances for monodentate phosphines located in trans positions to other phosphines is 2.478 Å (based

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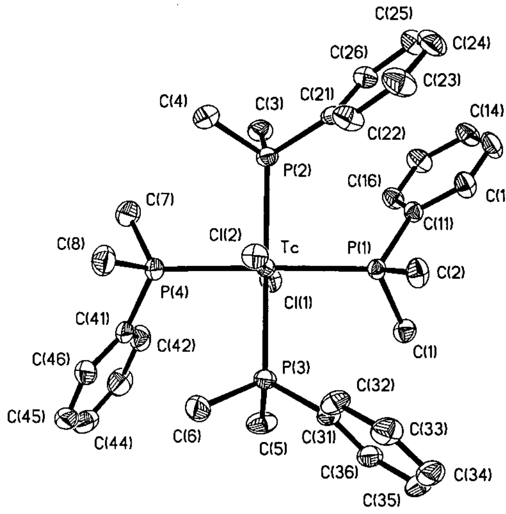

Figure 1. Labeled diagram of the cation in *trans*-$[\text{Tc}(\text{PMe}_2\text{Ph})_4\text{Cl}_2]\text{PF}_6$ (**I**). The ellipsoids correspond to 30% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **I**−**III**

trans-$[\text{Tc}(\text{PMe}_2\text{Ph})_4\text{Cl}_2]\text{PF}_6$ (**I**)			
Tc−Cl(1)	2.3251(10)	Tc−Cl(2)	2.3299(10)
Tc−P(1)	2.4900(10)	Tc−P(2)	2.5075(11)
Tc−P(3)	2.5159(11)	Tc−P(4)	2.5364(10)
P(1)−C(1)	1.841(4)	P(1)−C(2)	1.802(3)
P(1)−C(11)	1.827(3)	P(2)−C(3)	1.813(4)
P(2)−C(4)	1.822(4)	P(2)−C(21)	1.835(4)
P(3)−C(5)	1.804(4)	P(3)−C(6)	1.831(4)
P(3)−C(31)	1.837(3)	P(4)−C(7)	1.837(4)
P(4)−C(8)	1.812(4)	P(4)−C(41)	1.849(4)
P−CMe (ave)	1.820(4)	P−C(Ph) (ave)	1.833(3)
P−F (ave)	1.488(5)		
Cl(1)−Tc−Cl(2)	176.97(3)	Cl(1)−Tc−P(1)	85.88(3)
Cl(1)−Tc−P(2)	96.59(4)	Cl(1)−Tc−P(3)	95.22 (4)
Cl(1)−Tc−P(4)	84.96(3)	Cl(2)−Tc−P(1)	96.96(3)
Cl(2)−Tc−P(2)	84.48(4)	Cl(2)−Tc−P(3)	83.76(4)
Cl(2)−Tc−P(4)	92.19(4)	P(1)−Tc−P(2)	90.01(3)
P(1)−Tc−P(3)	90.17(3)	P(1)−Tc−P(4)	170.84(3)
P(2)−Tc−P(3)	168.17(3)	P(2)−Tc−P(4)	91.24(3)
P(3)−Tc−P(4)	90.46(3)	Tc−P−Ph	118.74(12)
Tc−P−CH_3 (ave)	114.82(14)	C(Ph)−P−CMe (ave)	101.4(2)
CMe−P−CMe (ave)	103.4(2)	P−C−C (ave)	120.7(3)
F−P−F (*cis*, ave)	90.0(3)	F−P−F (*trans*, ave)	174.2(3)
trans-$[\text{Tc}(\text{PMe}_3)_4\text{Cl}_2]\text{BPh}_4$ (**II**)			
Tc(1)−Cl(1)	2.342(2)	Tc(2)−Cl(2)	2.346(2)
Tc(1)−P(1)	2.484(2)	Tc(2)−P(3)	2.451(2)
Tc(1)−P(2)	2.454(2)	Tc(2)−P(4)	2.486(2)
P−C (ave)	1.815(6)	B−C (ave)	1.653(8)
Cl(1)−Tc(1)−Cl(1)′	178.93(8)	Cl(2)−Tc(2)−Cl(2)′	179.15(8))
Cl(1)−Tc(1)−P(1)	97.35(6)	Cl(2)−Tc(2)−P(3)	97.53(6)
Cl(1)−Tc(1)−P(1′)	81.89(6)	Cl(2)−Tc(2)−P(3′)	81.87(6)
Cl(1)−Tc(1)−P(2)	97.92(6)	Cl(2)−Tc(2)−P(4)	80.89(6)
Cl(1)−Tc(1)−P(2′)	82.84(6)	Cl(2)−Tc(2)−P(4′)	99.71(6)
P(1)−Tc(1)−P(1)′	91.39(7)	P(3)−Tc(2)−P(3)′	91.12(10)
P(2)−Tc(1)−P(2)′	90.58(8)	P(4)−Tc(2)−P(4)′	90.96(8)
P(1)−Tc(1)−P(2)	164.73(6)	P(3)−Tc(2)−P(4)	91.54(6)
P(1)−Tc(1)−P(2)′	91.04(6)	P(3)−Tc(2)−P(4)′	162.75(6)
Tc(1)−P−C (ave)	116.5(2)	Tc(2)−P−C (ave)	116.2(2)
C−P(1,2)−C (ave)	101.6(3)	C−P(3,4)−C (ave)	101.9(3)
C−B−C (ave)	109.5(4)	B−C−C (ave)	122.8(5)
C−C(B)−C (ave)	114.4(5)	C−C(*ortho*)−C (ave)	123.4(6)
other C−C−C (ave)	119.6(6)		
trans-$[\text{Tc}(\text{PMe}_3)_4\text{Cl}_2]\text{PF}_6$ (**III**)			
Tc(1)−Cl(1)	2.340(3)	Tc(1)−Cl(2)	2.347(3)
Tc(1)−P(1)	2.485(3)	Tc(1)−P(2)	2.475(3)
Tc(1)−P(3)	2.479(3)	Tc(1)−P(4)	2.469(3)
Tc(2) −Cl(3)	2.345(3)	Tc(2)−Cl(4)	2.340(3)
Tc(2)−P(5)	2.474(3)	Tc(2)−P(6)	2.476(3)
Tc(2)−P(7)	2.485(3)	Tc(2)−P(8)	2.470(3)
P−C (ave)	1.823(10)	P−F (ave)	1.491(7)
Cl(1)−Tc(1)−Cl(2)	179.93(10)	Cl(3)−Tc(2)−Cl(4)	179.09(10))
Cl(1)−Tc(1)−P(1)	97.25(9)	Cl(3)−Tc(2)−P(5)	97.26(10)
Cl(1)−Tc(1)−P(2)	81.29(10)	Cl(3)−Tc(2)−P(6)	81.73(9)
Cl(1)−Tc(1)−P(3)	82.14(9)	Cl(3)−Tc(2)−P(8)	81.98(10)
Cl(1)−Tc(1)−P(4)	97.52(9)	Cl(3)−Tc(2)−P(7)	98.72(10)
Cl(2)−Tc(1)−P(1)	82.81(9)	Cl(4)−Tc(2)−P(5)	82.30(10)
Cl(2)−Tc(1)−P(2)	97.92(6)	Cl(4)−Tc(2)−P(6)	97.47(9)
Cl(2)−Tc(1)−P(3)	98.73(10)	Cl(4)−Tc(2)−P(8)	98.83(10)
Cl(2)−Tc(1)−P(4)	82.41(9)	Cl(4)−Tc(2)−P(7)	81.71(10)
P(1)−Tc(1)−P(2)	90.96(10)	P(5)−Tc(2)−P(6)	91.19(9)
P(1)−Tc(1)−P(3)	91.23(9)	P(5)−Tc(2)−P(8)	92.33(10)
P(1)−Tc(1)−P(4)	165.22(10)	P(5)−Tc(2)−P(7)	164.00(10)
P(2)−Tc(1)−P(3)	163.43(10)	P(6)−Tc(2)−P(8)	163.64(10)
P(2)−Tc(1)−P(4)	91.12(10)	P(6)−Tc(2)−P(7)	90.52(9)
P(3)−Tc(1)−P(4)	90.25(9)	P(7)−Tc(2)−P(8)	90.47(10)
Tc(1)−P−C (ave)	115.8(3)	Tc(2)−P−C (ave)	115.7(4)
C−P(1−4)−C (ave)	102.4(5)	C−P(5−8)−C (ave)	102.5(5)
F−P−F (*cis*, ave)	90.0(5)	F−P−F (*trans*, ave)	177.1(5)

on nine structures).[16] The slightly longer value observed in crystal **I** (average 2.512(1) Å) probably results from the strain caused by the presence of four relatively bulky phosphine ligands.

The steric hindrance of the four relatively bulky phosphine ligands can be further seen in the results of the calculation of the best plane containing the Tc atom and the four P atoms. The deviations of the five atoms from the best plane are as follows: Tc, −0.023 Å; P(1), −0.227 Å; P(2), 0.235 Å; P(3), 0.235 Å; P(4), −0.220 Å. The first pair of *trans* P atoms (P(1) and P(4)) are located 0.23 Å on one side and the second pair (P(2) and P(3)) are located 0.23 Å on the other side of the best plane forming a tetrahedral distorted plane. This distortion can also be observed in the smaller P(1)−Tc−P(4) and P(2)−Tc−P(3) angles (168.17(3) and 170.84(3)°).

The average P−CH_3 bond distance is 1.820(4) Å, while the average P−Ph distance is 1.833(3) Å. These bond distances and angles are usually slightly influenced by the bulkiness of the substituents. The Tc−P−C angles are larger than normal tetrahedral angles, while the C−P−C bond angles are smaller than the tetrahedral value. Furthermore, the Tc−P−CH_3 angles (average 114.8(1)°) are smaller than the Tc−P−Ph angles (average 118.7(1)°) because of the greater steric hindrance of the phenyl groups. These values are similar to those observed in other Tc−PMe_2Ph complexes.[5,13,16,17] The average CH_3−P−CH_3 angle is 103.4(2)°. It is interesting to note that the two CH_3−P−Ph angles on the same ligand are significantly different. For the four phosphine ligands, one angle varies from 97.9(2) to 98.9(2)°, while the second angle is between 104.2(2) and 104.8(2)°.

The bond distances and angles in the PF_6^- anions are normal. The average P−F bond distance is 1.488(5) Å, and the average *cis* and *trans* angles are 90.0(3) and 174.2(3)°, respectively. The thermal factors of these atoms are quite large, as usually observed in these ions.

***trans*-$[\text{Tc}(\text{PMe}_3)_4\text{Cl}_2]\text{BPh}_4$ (II) and *trans*-$[\text{Tc}(\text{PMe}_3)_4\text{Cl}_2]\text{PF}_6$ (III).** These two PMe_3 complexes have a trans geometry. There are two independent Tc atoms in the BPh_4^- compound (**II**), both located on 2-fold axes. The BPh_4^- ion is located on a general position. A labeled diagram of the two cations in **II** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The Tc−Cl bond distances are 2.342(2) and 2.346(2) Å, while the Tc−P bond distances vary between 2.451(2) and 2.486(2) Å. The latter values are sligthly shorter than those observed in **I** and are normal for Tc(III) compounds.[16]

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(17) Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chim. Acta* **2000**, *300−302*, 43−48.

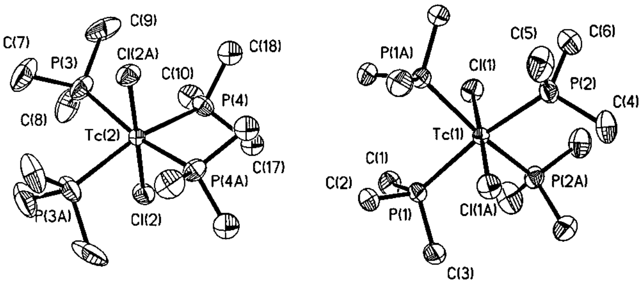

Figure 2. Labeled diagram of the two cations in *trans*-[Tc(PMe$_3$)$_4$-Cl$_2$]BPh$_4$ (**II**). The ellipsoids correspond to 30% probability.

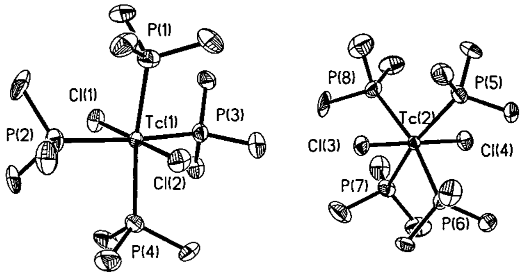

Figure 3. Labeled diagram of the two cations in *trans*-[Tc(PMe$_3$)$_4$-Cl$_2$]PF$_6$ (**III**). The ellipsoids correspond to 30% probability.

The coordination around the Tc atoms is octahedral, although some relatively important distortions are observed. The *cis* P−Tc−P angles are normal (90.58(8)−91.54(6)°), but the Cl−Tc−P angles are quite distorted, ranging from 80.89(6)−97.92(6)°. The *trans* Cl−Tc−Cl angles are normal (178.93(8) and 179.15(8)°), while the *trans* P−Tc−P angles have been reduced to 162.75(6) and 164.73(6)°. These deformations result from the steric hindrance caused by the coordination of the four phosphine ligands. The best plane was calculated through the Tc atom and the four P atoms for each cation. The results show an important tetrahedral deformation. In the first molecule (Tc(1)), two *trans* P atoms are 0.328 Å on the same side of the best plane, while the two other *trans* P atoms are −0.328 Å on the other side of the plane. In the second molecule (Tc(2)), the deformation is even larger, the deviation from the best plane being 0.370 Å. This type of deformation was not observed in the crystal structure of *trans*-[Tc(DMPE)$_2$Cl$_2$]$^+$ (DMPE = 1,2-bis(dimethylphosphino)ethane).[18] In the complexes containing bidentate ligands, the strain is seen in the smaller bidentate angles (≈81°), while the other two angles are much larger than 90°. In our PMe$_3$ complexes, the strain is relieved in a tetrahedral deformation of the four phosphine ligands located in the same plane.

There are also two independent Tc cations in the PF$_6^-$ compound (**III**), both located on general positions. The average Tc−Cl bond distance is 2.343(3) Å, and the average Tc−P bond distance is 2.477(3) Å. These values are identical to those found in **II**. The coordination sphere around the Tc atom is again a distorted octahedron. The *cis* P−Tc−P angles are normal (90.25(9)−92.33(10)°), but the Cl−Tc−P angles are again distorted, ranging from 81.29(10) to 98.72(10)°. The *trans* Cl−Tc−Cl angles are normal (179.09(10) and 179.93(10)°), while the *trans* P−Tc−P angles have been reduced to values ranging from 163.43(10) to 165.22(10)°. The best plane was calculated through each Tc atom and its four P-bonded ligands. The deviations from the best planes are as follows. Molecule 1: Tc(1), 0.018 Å; P(1), 0.332 Å; P(2), −0.343 Å; P(3), −0.342 Å; P(4), 0.335 Å. Molecule 2: Tc(2), −0.002 Å; P(5), −0.343 Å; P(6), 0.348 Å; P(7), −0.348 Å; P(8), 0.345 Å. Again, the tetrahedral deformation of each plane containing a Tc atom and four P atoms can be well visualized.

The average P−C bond distance is 1.815(6) Å for **II** and 1.823(10) Å for **III**, while the average Tc−P−C angles are 116.4(2) and 115.8(4)° for **II** and **III**, respectively. These values are larger than the C−P−C angles (average 101.7(3)° for **II** and 102.5(5)° for **III**), as observed in other Tc−phosphine complexes.[16,19−23]

The cations in **II** and **III** are not significantly different. Therefore, the anions do not seem to influence the structure of the *trans*-[Tc(PMe$_3$)$_4$Cl$_2$]$^+$ cations. The average P−F bond distance in **III** is 1.491(7) Å. The average *cis* and *trans* angles are 90.0(5) and 177.1(5)°, respectively. The thermal factors of the F atoms are large, as observed in **I**. The average B−C bond distance in the BPh$_4^-$ anions of **II** is 1.653(8) Å. The C−B−C angles are normal (average 109.5(4)°). The external B−C−C angles are significantly larger (average 122.8(5)°) than the internal C−C(B)−C angle (average 114.4(5)°). The internal *ortho* angles are also significantly larger (123.4(6)°) than the remaining other internal angles (average *meta* and *para* angles 119.6(6)°).

Conclusion

Tetrasubstituted ionic Tc complexes of the type *trans*-[Tc(PR$_3$)$_4$X$_2$]$^+$ containing monodentate phosphines have been synthesized by different methods. These reactions are very dependent on the phosphines used and the experimental conditions. Complexes containing less sterically demanding ligands can be prepared by ligand exchange from complexes containing more crowded ligands. Compounds with phosphines of different sizes, namely, PMe$_2$Ph and PMe$_3$, have been studied and characterized by X-ray diffraction methods. All the compounds show octahedral coordination, but an important tetrahedral deformation of each plane containing a Tc atom and four P atoms has been observed. The strain caused by the presence of four phosphine ligands is evident even with PMe$_3$, the least sterically demanding phosphine ligand. Furthermore, in the PMe$_2$Ph complex, the strain is relieved not only in a tetrahedral deformation of the four phosphine ligands located in the same plane but also in sligthly longer Tc−P bonds.

The synthesis of Tc(III) compounds of the type *trans*-[Tc(PR$_3$)$_4$X$_2$]$^+$ is important, since these complexes could be used as starting materials for the syntheses of mixed-ligand complexes, particularly those in the lower oxidation states. The chloro ligands could be exchanged for a more interesting ligand such as dithiocarbamate or NCS$^-$. This possibility is presently being investigated in our laboratories.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to The DuPont Merck Pharmaceutical Co., Radiopharmaceutical Division, N. Billerica, MA, for the gift of NH$_4$[TcO$_4$].

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Supporting Information Available: Listings of crystal data, structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles for **I**−**III**. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic files, in CIF format, for **I**−**III** are available from the Cambridge Crystallographic Data Centre (CCDC Nos. 149409−149411).

IC9906454