Synthesis and Crystal Structure of a New Type of Ionic Technetium(V) Dioxo Phosphine Complexes, $[Tc(O)_2(PR_3)_3]^+$. Reactions with Pyridine and Crystal Structures of *trans,cis,cis*-$[Tc(O)_2(PR_3)_2(py)_2]^+$ Compounds

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New ionic technetium complexes of the type $[TcO_2(PR_3)_3]^+$ have been synthesized from the reaction of $[TcO_4]^-$ with the phosphine in methanol. The crystal structures of two crystallographic forms of $[TcO_2(PEt_3)_3](BPh_4)$ were determined. The first form is monoclinic, space group $P2_1/n$ with $a = 14.353(3)$ Å, $b = 11.731(2)$ Å, $c = 26.478(6)$ Å, $\beta = 101.22(1)°$, and $Z = 4$. The second form is also monoclinic, space group $P2_1/c$ with $a = 10.043(3)$ Å, $b = 21.122(4)$, $c = 20.994(5)$ Å, $\beta = 97.43(2)°$, and $Z = 4$. $[TcO_2(PPr_3)_3](BPh_4)$ belongs to the monoclinic $C2/c$ space group with $a = 34.097(7)$ Å, $b = 16.944(4)$ Å, $c = 19.033(4)$ Å, $\beta = 102.99(1)°$, and $Z = 8$. The geometry around the Tc atom is a trigonal bipyramid with the two oxo ligands in the trigonal plane. The Tc−O bond distances are between 1.707(4) and 1.726(3) Å, while the Tc−P bonds vary from 2.507(2) to 2.528(2) Å for the axial ligands and between 2.395(1) and 2.403(1) Å for the equatorial bond. The O−Tc−O angles are in the range 141.5(2)−143.4(2)°. The reaction of these complexes with pyridine produced *trans,cis,cis*-$[Tc(O)_2(PR_3)_2(py)_2]^+$ (py = pyridine). $[Tc(O)_2(PMe_3)_2(py)_2](BPh_4)$ is monoclinic, space group $P2_1/c$ with $a = 30.346(8)$ Å, $b = 12.865(4)$ Å, $c = 21.464(9)$ Å, $\beta = 110.35(2)°$, and $Z = 8$, while $[Tc(O)_2(PEt_3)_2(py)_2](BPh_4)$ is monoclinic, space group $P2_1/c$ with $a = 10.594(6)$ Å, $b = 19.921(7)$ Å, $c = 21.306(10)$ Å, $\beta = 95.31(5)°$, and $Z = 4$. The geometry around the Tc atom is a distorted octahedron with the oxo ligands located in *trans* positions to each other, while the phosphine and the pyridine ligands are *cis* to each other.

Introduction

The chemistry of technetium has become very important, especially in relation to the use of the isotope ^{99m}Tc as a diagnostic agent in nuclear medicine. It has been used for many years in bone scanning and more recently in studying different diseases of the heart, brain, kidneys, liver, and other organs as well as tumor tissue. We have now been involved for several years in the synthesis of technetium-99 compounds. The main objective of our research project is to synthesize new Tc complexes with ligands which could have some interest for the radiopharmaceutical industry. In order to be useful, the preparative methods must be simple and adaptable to the use of the industrial kits, where the starting material is $[^{99m}TcO_4]^-$, and the active compound must be prepared by a "one pot" method.

Phosphine derivatives are one type of ligands under study in our laboratory, mainly because of the interest in them as heart agents. These compounds are usually cationic species of Tc in a low oxidation state. Tc(I) complexes based on phosphorus donor ligands like $[Tc(diphosphine)_3]^+$ show high heart and liver uptake and slow washout from the heart. Compounds of the type $[Tc^{III}(diphosphine)_2Cl_2]^+$ have also been shown to accumulate in the hearts of animals.[1,2] Nevertheless, the retention time in the heart of humans is too short, probably because of a reduction of the complex to a neutral Tc(II) species, which washes out of the heart rapidly.[3,4] $[Tc(MIBI)_6]^+$ (MIBI = methoxyisobutylisonitrile) known as "cardiolite" is now currently used for myocardial perfusion imaging.[5] 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.

The linear organoimido unit (Tc−N−R) is formally isolectronic with the Tc═O unit, which is present in several Tc radiopharmaceuticals. The physical and chemical properties of the complexes containing this group can be specifically tuned by changing the organic −R substituent on the ligand. 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.[6] The phenylimido unit is generated through the cleavage of the N−N bond in the hydrazine derivative. We have decided to synthesize such Tc compounds with phosphines less bulky than PPh_3. A similar reaction with $PMePh_2$ produced the expected compound $Tc(NPh)(PMePh_2)_2X_3$.[7] When PMe_2Ph was used, the reaction was quite different. A complex containing an organodiazenido unit,

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Table 1. Crystallographic Data for the Four Compounds

	IA,B	**II**	**III**	**IV**
chem formula	$C_{42}H_{65}BO_2P_3Tc$	$C_{51}H_{83}BO_2P_3Tc$	$C_{40}H_{48}BN_2O_2P_2Tc$	$C_{46}H_{60}BN_2O_2P_2Tc$
M_w	803.7	929.9	759.6	843.7
space group	$P2_1/n$, $P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	14.354(3) 10.043(3)	34.097(7)	30.346(8)	10.594(6)
b (Å)	11.731(2), 21.122(4)	16.944(4)	12.865(4)	19.921(7)
c (Å)	26.478(6), 20.994(5)	19.033(4)	21.464(9)	21.306(10)
β (deg)	101.220(10), 97.432(15)	102.990(10)	110.35(2)	95.31(5)
V (Å^3)	4373.4(15), 4416.1(25)	10728(4)	7857(5)	4477(4)
Z	4	8	8	4
ρ_{calcd} (g cm^{-3})	1.221, 1.209	1.152	1.284	1.252
μ(Mo Kα) (cm^{-1})	4.71, 4.66	3.92	4.83	4.30
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (°C)	21	21	21	21
R^a	0.052, 0.047	0.059	0.067	0.072
$R_w{}^b$	0.052, 0.047	0.057	0.058	0.058

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

$Tc(NNPh)(PMe_2Ph)_2Br_3$, was isolated with a 30% yield. The phenylimido complex was also formed $[Tc(NPh)(PMe_2Ph)_3Br_2]^+$, but since the phosphine is less bulky, it contained three phosphine ligands and it is ionic. The synthesis of this compound $[Tc(NPh)(PMe_2Ph)_3X_2](BPh_4)$ was reported recently, but it was synthesized by a different method, namely, from the reaction of $Tc(NPh)(PPh_3)_2X_3$ with an excess of PMe_2Ph.[8] In order to prepare the ionic compound $[Tc(NPh)(PR_3)_3X_2]^+$ with even less bulky phosphines, we have studied the reaction of the $Tc(NPh)(PPh_3)_2X_3$ with PEt_3. We obtained a noncrystalline product, which after several recrystallizations gave brown crystals suitable for X-ray diffraction. The results of the crystallographic study were very surprising and are described below.

Experimental Section

Ammonium pertechnetate ($NH_4{}^{99}TcO_4$) was obtained from Oak Ridge National Laboratory. It was recrystallized in nitric acid (*Caution*: ammonium pertechnetate in acid medium will produce some radioactive volatile compounds) and dissolved in water. An aqueous solution (about 0.3 M) was prepared. All manipulations were made 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 $\times$ 10^5 years). The phosphine ligands were bought from Aldrich.

$[TcO_2(PR_3)_3]$ (BPh_4) (R = C_2H_5 (Et; Crystal IA) and C_3H_7 (Pr; Crystal II). The phosphine (for R = Et, 0.1 mL and for R = Pr, 0.3 mL) was added at room temperature to a solution of 0.018 g of NH_4TcO_4 dissolved in 6 mL of methanol. After 1 h, 0.14 g of $NaBPh_4$ dissolved in 4 mL of methanol was added to the mixture. Brown crystals started to precipitate after a few hours. Yield: 60−70%. The quality of the crystals were adequate for X-ray diffraction studies. $[TcO_2(PEt_3)_3](BPh_4)$. IR (cm^{-1}), 1260 w, 1180 w, 1130 w, 1035 s, 890 m, 850 s, 750 s, 730 s, 715 m, 700 s, 610 s, 470 w, 420 w, 305 w. ^{1}H NMR (in $CDCl_3$, ppm): δ 1.15 (large CH_3), 1.73 (large CH_2), 6.92 (t, *p*-Ph), 7.063 (t, *m*-Ph), 7.42 (m, *o*-Ph). $[TcO_2(PPr_3)_3](BPh_4)$. IR (cm^{-1}): 1220 w, 1080 m 1035 w, 890 w, 855 s, 755 m, 735 s, 710 s, 615 s, 485 w, 440 w, 305 w. ^{1}H NMR (in $CDCl_3$, ppm): δ 1.060 (t, CH_3), 1.5 (large CH_2), 1.68 (large CH_2), 6.93 (t, *p*-Ph), 7.071 (t, *m*-Ph), 7.44 (m, *o*-Ph).

$[TcO_2(PEt_3)_3](BPh_4)$ (Crystal IB). Crystal **IB** was obtained by following the above method and adding a small quantity of LiCl (≈50 mg) along with the phosphine. The IR and NMR spectra of the compound were identical to the above spectra, but the crystallographic data were different.

$TcO_2(PMe_3)_2(py)_2](BPh_4)$ (py = Pyridine; Crystal III). A quantity of 0.022 g of $NH_4[TcO_4\ ]$ was dissolved in 10 mL of methanol. To this solution, 1 mL of a PMe_3−toluene solution (1 M) and 0.2 mL of pyridine were added. The mixture was left at room temperature overnight. The next day, 0.1 g $NaBPh_4$ was added. The solution was evaporated to dryness, and an oily paste was obtained. The latter was dissolved in 5 mL of methanol, and the mixture was filtered. The filtrate was placed in a beaker, which was sealed with paraffin paper. A few days later, the orange crystals were collected by filtration. These crystals were adequate for an X-ray structure determination. IR (cm^{-1}): 1305 w, 1290 s, 1210 w, 1150 m, 1070 m, 1060 m, 1040 m, 1030 sh, 1015 m, 960 sh, 940 vs, 835 s, 805 s, 765 m, 755 sh, 745 sh, 730 s, 705 vs, 695 vs, 630 m, 615 s, 605 s. ^{1}H NMR (in $CDCl_3$, ppm): δ 1.354 (m, CH_3, $^2J(^{31}P-^1H) = 10.2$ Hz), 7.30 (m, *m*-py), 7.80 (tt, *p*-py), 8.830 (d, *o*-py), 6.90 (t, *p*-Ph), 7.02 (t, *m*-Ph), 7.40 (m, *o*-Ph).

$[TcO_2(PR_3)_2(py)_2](BPh_4)$ (R = Et (Crystal IV) and Pr). About 0.04 mmol of $[TcO_2(PR_3)_3](BPh_4)$ was suspended in 10 mL of methanol, and 0.2 mL of pyridine was added to the mixture which was then stirred overnight. The next day, the yellow solution was concentrated to about 2 mL and filtered. The precipitate was dissolved in 2 mL of CH_2Cl_2, and 2 mL of methanol was then added to the solution which was left standing at room temperature until orange crystals appeared. $[TcO_2(PEt_3)_2(py)_2](BPh_4)$. ^{1}H NMR (in $CDCl_3$, ppm): δ 1.099 (quintet, CH_3), 1.706 (quintet, CH_2), 7.273 (m, *m*-py), 7.718 (tt, *p*-py), 8.870 (d, *o*-py), 6.687 (t, *p*-Ph), 7.031 (t, *m*-Ph), 7.416 (m, *o*-Ph). $[TcO_2(PPr_3)_2(py)_2](BPh_4)$. IR (cm^{-1}): 1215 s, 1150 m, 1080 s, 1065 vs, 1040 s, 1035 s, 1015 s, 1005 s, 835 s, 810 vs, 790 s, 765 s, 755 s, 745 s, 725 vs br, 700 vs, 695 sh, 610 vs, 465 w, 420 w. ^{1}H NMR (in $CDCl_3$, ppm): δ 0.952 (t, CH_3), 1.515 (large CH_2), 1.645 (large CH_2), 7.245 (m, *m*-py), 7.680 (tt, *p*-py), 8.844 (d, *o*-py), 6.878 (t, *p*-Ph), 7.028 (t, *m*-Ph), 7.418 (m, *o*-Ph).

Crystallographic Measurements and Structure Resolution. 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 (12−25°), ω, and χ for 30−45 well-centered reflections on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation. The Siemens XSCANS program was used for the data collection. The background time to scan time ratio was 0.5. The crystal data are listed in Table 1. All of the calculations were done using the Siemens SHELXTL system.[9] The crystallographic data were taken from the International Tables for X-ray Crystallography.[10]

The coordinates of the Tc atom were determined from direct methods[9] or from Patterson map calculations, and the positions of all of the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structure was done by full matrix least-squares analysis minimizing $\sum w(|F_o| - |F_c|)^2$. $[TcO_2(PEt_3)_3](BPh_4)$

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was found to crystallize in two different crystallographic forms (crystals **IA** and **IB**). The **IB** form was isolated when LiCl was added in the solution. The ethyl groups of one phosphine ligand (P(3)) in the two crystals **IA** and **IB** were found to be disordered. The following atoms were refined on two positions: **IA** (occupancy factors 65%, 35%), C(19), C(20), C(27), and C(29); **IB** (occupancy factors 60%, 40%), C(19), C(27), and C(29). The H atoms were fixed at their calculated positions (riding model) with $U_{eq} = 0.080$ Å^2. The H atoms on the disordered groups were neglected. The refinement of the scale factor, coordinates, and anisotropic temperature factors of all of the non-hydrogen atoms converged to the R and R_w values shown in Table 1. There were a few residual peaks (<0.78 e Å^{-3}) in the close environment of the Tc atom.

Results and Discussion

In an attempt to synthesize phenylimido Tc complexes of the type $Tc(NPh)(PR_3)_2X_3$ or $[Tc(NPh)(PR_3)_3X_2]^+$ from the reaction of $Tc(NPh)(PPh_3)_2X_3$ with phosphines less bulky than the phenyl derivatives, we have isolated, with PEt_3, dark brown crystals which were studied by X-ray diffraction methods. The results have shown that the compound was completely different from what was expected. It was identified as a new kind of cationic dioxo technetium(V) complex, $[TcO_2(PEt_3)_3]^+$, with a trigonal bipyramid structure, not yet known in the literature. *trans*-Dioxo octahedral Tc compounds have been reported, but none of this type. The structure of this complex suggested to us that it could be of interest for heart imaging. It is charged +1, but the oxidation state is high (V). Recently, a new 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.[11] 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.

We speculated that our new type of dioxo complexes could be synthesized directly from $[TcO_4]^-$. We were successful in developing a new and simple "one pot" method for preparing the ionic compounds $[TcO_2(PR_3)_3]^+$. The method could probably be adapted to the commercial kits used in hospitals for the preparation of the ^{99m}Tc radiopharmaceuticals. The biodistribution of the compounds has not been studied yet.

$[TcO_2(PR_3)_3]^+$ Complexes. The compounds can be prepared from the following reaction in methanol:

$$NH_4[TcO_4] + PR_3 \xrightarrow{CH_3OH} [TcO_2(PR_3)_3]^+$$

An excess of ligand is used (about 10×). No reducing agent is needed, since the phosphine acts as the reducing agent, being oxidized to the phosphine oxide. NH_3 is produced in the reaction. The yields vary between 60 and 70%. The method is extremely simple. The aqueous ammonium pertechnetate solution is evaporated to dryness. The residue is dissolved in methanol, and the phosphine is added. After 1 h, $Na(BPh_4)$ was added and crystals adequate for crystal structure determinations were isolated. No attempts were made to increase the yields.

Compounds with PEt_3 (crystal **IA**) and PPr_3 (crystal **II**) ligands were prepared. A similar reaction with PMe_3 behaved quite differently. Only crystals of $PMe_3H(BPh_4)$ could be isolated and characterized by X-ray diffraction methods. The reaction seems much more complicated, and a mixture of products is probably formed. The investigation with PMe_3 is presently under study.

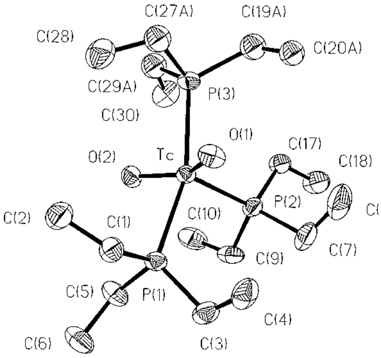

Figure 1. Labeled diagram of the cation $[TcO_2(PEt_3)_3]^+$ (**IA**). The disorder on P(3) is not shown (the ellipsoids correspond to 30% probability).

When a small quantity of LiCl was added to the solution in the preparation of the PEt_3 and PPr_3 compounds, the same products were obtained. The IR and NMR spectra of the products obtained in the presence of LiCl were identical to those prepared without LiCl. A crystallographic investigation of the compound obtained with PEt_3 in the presence of LiCl showed a different crystallographic form (crystal **IB**). The two structures (crystals **IA** and **IB**) are very similar, and the results of the two crystals are shown in this paper. When the reaction with PMe_3 was done in the presence of LiCl, a crystalline compound was obtained. Several crystals were studied by X-ray diffraction methods. All crystals showed very important disorder, and no reasonable structure has been resolved yet.

The PEt_3 and PPr_3 compounds were characterized by IR spectroscopy. The stretching ν(Tc−O) band was observed around 850 cm^{-1}, at intermediate frequency between the *trans*-dioxo octahedral compounds (bond order of Tc═O is 2[12]), which are observed at 800 cm^{-1} and the monooxo square pyramidal complexes where the Tc≡O bond (formally triple bond, but because of unfavorable charge distribution, the bond order is between 2 and 3[13]) absorbs at higher energy (≈950 cm^{-1}).[14] The NMR spectra showed large peaks, confirming that the compounds are paramagnetic (d^2). The two unpaired electrons are probably in the d_{xz} and d_{yz} orbitals (the trigonal plane is in the xy plane).

The ionic complexes $[TcO_2(PR_3)_3](BPh_4)$ (R = C_2H_5 (crystals **IA** and **IB**), R = C_3H_7 (crystal **II**)) were characterized by X-ray diffraction methods. Labeled diagrams of the two compounds are shown in Figures 1 and 2. The ethyl groups on P(3) of crystals **IA** and **1B** were found to be disordered. The complexed cations have a distorted trigonal bipyramid structure with the two oxo ligands in the trigonal plane. The selected bond distances and angles are shown in Table 2. The trigonal plane is distorted with O−Tc−O angles of 143.5(2) (**IA**), 142.4(2) (**IB**), and 141.5(2)° (**II**). The other trigonal angles (P−Tc−O) are smaller as expected and vary between 107.3(2) and 111.1(1)°. The angles involving the apical P atoms with the atoms located in the trigonal planes are close to 90°, but there are some deviations. The apical phosphine ligands are pushed away from the third phosphine ligand, and the *trans* apical

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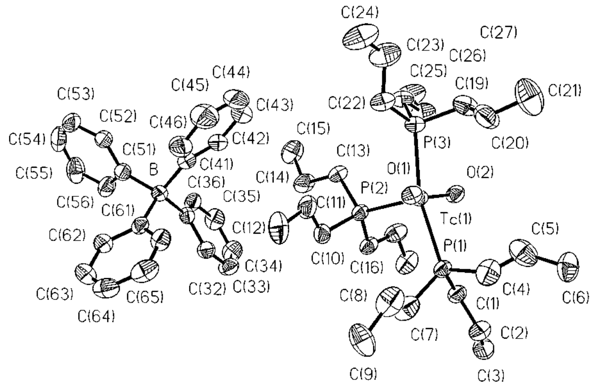

Figure 2. Labeled diagram of $[TcO_2(PPr_3)_3](BPh_4)$ (**II**) (the ellipsoids correspond to 30% probability).

P−Tc−P angle is 160.9(1) (**IA**), 159.3(1) (**IB**), and 163.4(1)° (**II**). The angles P_{apical}−Tc−$P_{trigonal\ plane}$ are larger than the expected 90° (96.9(1), 102.1(1)° (**IA**), 97.5(1), 103.2(1)° (**IB**), and 97.5(1), 99.1(1)° (**II**)). The P_{apical}−Tc−O angles are slightly smaller than 90° (average 87.0(1) for **IA**, 86.7(1) for **IB**, and 87.3(1)° for **II**).

The Tc−O bond distances are 1.712(4), 1.726(3) Å (**IA**), 1.714(3), 1.716(3) Å (**IB**), and 1.710(4), 1.707(4) Å (**II**). These values are longer than the one found in monooxo complexes (≈1.64 Å)[14−18] where the bond order is formally 3.[13] For *trans*-dioxo octahedral complexes, where the Tc═O bond order is 2,[12] the bond distances are longer. Values in the 1.74 Å region have been reported.[17,18] Our values appear slightly shorter from the latter value. These results are in agreement with the IR spectra, where the absorption *ν*(Tc−O) vibration band was observed at slightly higher energy than the one in *trans*-dioxo octahedral complexes. These structures are the first example of trigonal bipyramidal dioxotechnetium complexes. There are several reports of *trans*-dioxo octahedral complexes, but *cis*-dioxo complexes are rare in the literature. Only one Tc structure, namely, the one of TcO_2F_3, was published.[19] The compound has a fluoro-bridged "zigzag" chain structure and the environment around each Tc atom has a distorted octahedral geometry. The oxo ligands are in *cis* position to each other with O−Tc−O angles between 102.4(5) and 104.1(5)°. The Tc−O bond lengths in TcO_2F_3 are shorter (1.643(10)−1.657(9) Å) than in our Tc(V) complexes, but the oxidation state of the Tc atom is higher (VII).

The apical Tc−P bond distances are 2.507(2), 2.528(2) Å for **IA**, 2.520(1), 2.514(2) Å for **IB**, and 2.521(2), 2.512(2) Å for **II**. The bond in the trigonal plane is much shorter, 2.403(1) for **IA**, 2.395(1) for **IB**, and 2.400(2) Å for **II**. In general, values ranging between 2.40 and 2.52 Å have been reported for the Tc(V)−P bond distances.[18] Trigonal bipyramidal Tc compounds are not very common in the literature. None was reported with three phosphine ligands. In the neutral trigonal bipyramid Tc(V) compounds $TcNCl_2(PPh_3)_2$, $TcNCl_2(PPr_3)_2$, and $TcNBr_2(PMePh_2)_2$, the phosphine ligands are located in the apical positions and the Tc−P bond distances are 2.464(3),[20] 2.445(2),[21] and 2.450(3)[21] Å, respectively. Our apical distances seem significantly longer than these values, probably to reduce the steric hindrance with the third phosphine ligand located in the trigonal plane.

The average P−C distance is 1.836(7) for **I** and 1.821(7) Å for **II**. The Tc−P−C angles (average 113.6(3) for **I** and 114.1(2)° for **II**) are larger than normal tetrahedral angles, while all of the C−P−C bond angles are smaller than the tetrahedral value with average angles of 104.5(4) for **I** and 104.4(3)° for **II**. The average P−C−C angles are 115.3(5) for **I** and 116.8(5)° for **II**. These values are not very precise for crystal **I** (even if the estimated standard deviations are acceptable), because of the important disorder of the ethyl groups on P(3), but similar angles were observed in other technetium−phosphine complexes.[22−27] The C−C−C angles of the PPr_3 compound are slightly flattened averaging 113.9(7)°.

The bond distances and angles in BPh_4^- are normal. The average B−C bond distance is 1.652(8) Å, and the average angle C−B−C is 109.5(5)°. The external angles B−C−C are larger (average 122.7(4)°) than the internal angle C−C(B)−C (average 114.6(5)°).

$[TcO_2(PR_3)_2(py)_2]^+$ Complexes. The ionic $[TcO_2(PR_3)_3]^+$ complexes described above are good starting material for the preparation of other dioxo mixed-ligand species. The reaction of the PEt_3 or the PPr_3 complexes with pyridine (py) in methanol solution produced the cationic dioxo octahedral compound $[TcO_2(PR_3)_2(py)_2]^+$. One of the phosphine ligands was replaced by two pyridine ligands. Complexes with PEt_3 and PPr_3 were prepared by this method.

$$[TcO_2(PR_3)_3]^+ + py \xrightarrow{CH_3OH} [TcO_2(PR_3)_2(py)_2]^+$$

The pyridine complex with PMe_3 was prepared directly from $[TcO_4]^-$. The starting material $NH_4[TcO_4]$ was mixed with PMe_3 and pyridine in methanol overnight. The next day, $NaBPh_4$ was added, and after a few days crystals of $[TcO_2(PMe_3)_2(py)_2]BPh_4$, adequate for a crystallographic investigation, were isolated. This simple one pot method for preparing mixed-ligand complexes could probably be adapted for use in the commercial kits used to prepare the ^{99m}Tc compounds.

$$NH_4[TcO_4] + py + PMe_3 \xrightarrow{CH_3OH} [TcO_2(PMe_3)_2(py)_2]^+$$

The PMe_3 (**III**) and PEt_3 (**IV**) compounds were studied by X-ray diffraction methods. Labeled diagrams of the complexed cations are shown in Figures 3 and 4. The bond distances and bond angles are shown in Table 2. For crystal **III**, there are two independent Tc cations and BPh_4^- in the unit cell (identified as molecules IIIA and IIIB in Table 2). For the two crystals, the geometry around the Tc atom is a distorted octahedron. The two oxo ligands are located in *trans* positions to each other, while the phosphine and the pyridine ligands are in *cis* positions

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Table 2. Selected Bond Distances (Å) and Angles (deg)

	$[TcO_2(PR_3)_3](BPh_4)$			$[TcO_2(PMe_3)_2(py)_2](BPh_4)$ (**III**)					
	R = Et								
	IA	**IB**	R = Pr (**II**)	molecule IIIA		molecule IIIB		$[TcO_2(PEt_3)_2(py)_2](BPh_4)$ (**IV**)	
Tc−P(1)	2.506(1)	2.520(1)	2.521(2)	Tc(1)−P(1)	2.433(6)	Tc(2)−P(3)	2.401(6)	Tc−P(1)	2.426(4)
Tc−P(2)	2.403(1)	2.395(1)	2.400(2)	Tc(1)−P(2)	2.437(5)	Tc(2)−P(4)	2.402(6)	Tc−P(2)	2.439(4)
Tc−P(3)	2.528(2)	2.514(1)	2.512(2)	Tc(1)−O(1)	1.715(13)	Tc(2)−O(2)	1.693(14)	Tc−O(1)	1.728(7)
Tc−O(1)	1.712(3)	1.714(3)	1.710(4)	Tc(1)−O(3)	1.725(14)	Tc(2)−O(4)	1.705(13)	Tc−O(2)	1.736(7)
Tc−O(2)	1.726(3)	1.716(3)	1.707(4)	Tc(1)−N(1)	2.252(13)	Tc(2)−N(3)	2.287(14)	Tc−N(1)	2.255(9)
P−C (av)	1.834(7)	1.838(6)	1.821(7)	Tc(1)−N(2)	2.215(13)	Tc(2)−N(4)	2.257(12)	Tc−N(2)	2.287(11)
B−C (av)	1.649(8)	1.658(6)	1.648(9)	P−C (av)	1.796(20)	P−C (av)	1.785(22)	P−C (av)	1.805(12)
P(1)−Tc−P(2)	96.9(1)	97.5(1)	97.5(1)	N−C (av)	1.309(28)	N−C (av)	1.329(27)	N−C (av)	1.323(16)
P(1)−Tc−P(3)	160.9(1)	159.3(1)	163.4(1)	B−C (av)	1.643(26)	B−C (av)	1.643(26)	B−C (av)	1.654(18)
P(1)−Tc−O(1)	88.7(1)	86.8(1)	87.0(1)	P(1)−Tc(1)−P(2)	95.0(2)	P(3)−Tc(2)−P(4)	94.6(2)	P(1)−Tc−P(2)	94.5(1)
P(1)−Tc−O(2)	86.7(1)	87.5(1)	88.1(1)	P(1)−Tc(1)−O(1)	95.9(4)	P(3)−Tc(2)−O(2)	93.5(4)	P(1)−Tc−O(1)	95.2(3)
P(2)−Tc−P(3)	102.1(1)	103.2(1)	99.1(1)	P(1)−Tc(1)−O(3)	88.0(4)	P(3)−Tc(2)−O(4)	88.0(4)	P(1)−Tc−O(2)	90.6(3)
P(2)−Tc−O(1)	108.4(1)	109.3(1)	111.1(1)	P(1)−Tc(1)−N(1)	91.3(4)	P(3)−Tc(2)−N(3)	89.9(3)	P(1)−Tc−N(1)	92.3(3)
P(2)−Tc−O(2)	108.1(1)	108.3(1)	107.3(2)	P(1)−Tc(1)−N(2)	173.5(4)	P(3)−Tc(2)−N(4)	172.7(4)	P(1)−Tc−N(2)	172.4(3)
P(3)−Tc−O(1)	86.9(1)	86.8(1)	86.4(1)	P(2)−Tc(1)−O(1)	87.5(4)	P(4)−Tc(2)−O(2)	90.1(4)	P(2)−Tc−O(1)	91.3(3)
P(3)−Tc−O(2)	85.9(1)	85.7(1)	87.8(1)	P(2)−Tc(1)−O(3)	95.1(4)	P(4)−Tc(2)−O(4)	94.3(4)	P(2)−Tc−O(2)	92.0(3)
O(1)−Tc−O(2)	143.5(2)	142.4(2)	141.5(2)	P(2)−Tc(1)−N(1)	172.2(4)	P(4)−Tc(2)−N(3)	174.5(4)	P(2)−Tc−N(1)	173.2(3)
Tc−P−C (av)	113.8(3)	113.3(2)	114.1(2)	P(2)−Tc(1)−N(2)	90.8(4)	P(4)−Tc(2)−N(4)	91.9(3)	P(2)−Tc−N(2)	92.5(3)
C−P−C (av)	104.7(4)	104.3(3)	104.4(3)	O(1)−Tc(1)−O(3)	175.1(5)	O(2)−Tc(2)−O(4)	175.1(5)	O(1)−Tc−O(2)	173.1(4)
P−C−C (av)	115.6(5)	115.0(5)	116.8(5)	O(1)−Tc(1)−N(1)	87.2(6)	O(2)−Tc(2)−N(3)	86.4(6)	O(1)−Tc−N(1)	88.3(3)
C−C−C (av PPr_3)			113.9(7)	O(1)−Tc(1)−N(2)	87.4(6)	O(2)−Tc(2)−N(4)	89.9(6)	O(1)−Tc−N(2)	87.6(4)
C−B−C (av)	109.5(4)	109.5(3)	109.5(5)	O(3)−Tc(1)−N(1)	89.7(6)	O(4)−Tc(2)−N(3)	88.9(6)	O(2)−Tc−N(1)	87.7(3)
B−C−C (av)	122.6(4)	122.6(4)	122.8(5)	O(3)−Tc(1)−N(2)	88.4(6)	O(4)−Tc(2)−N(4)	88.0(6)	O(2)−Tc−N(2)	86.2(4)
C−C(B)−C (av)	114.6(5)	114.8(4)	114.3(6)	N(1)−Tc(1)−N(2)	83.2(5)	N(3)−Tc(2)−N(4)	83.8(4)	N(1)−Tc−N(2)	80.7(4)
C−C−C (other aromatic, av)	121.1(5)	121.0(4)	121.1(7)	Tc(1)−P−C (av)	114.5(7)	Tc(2)−P−C (av)	115.6(8)	Tc−P−C (av)	114.8(4)
				Tc(1)−N−C (av)	122.3(14)	Tc(2)−N−C (av)	120.7(13)	C−P−C (av)	103.7(6)
				C−P−C (av)	104.0(10)	102.6(11)		P−C−C (av)	115.5(9)
				C−N−C (av)	117.1(15)			C−N−C	118.1(11)
				N−C−C (av)	122.6(20)			Tc−N−C (aav)	120.8(8)
				C−C−C (av py)	119.2(20)			C−C−C (av in py)	118.8(13)
				C−B−C (av)	109.5(14)			N−C−C (av)	122.8(12)
				B−C−C (av)	123.2(16)			C−B−C (av)	109.5(9)
				C−C(B)−C (av)	113.4(17)			B−C−C (av)	122.8(10)
				C−C−C (others in BPh_4^-, av)	121.1(18)			C−C(B)−C (av)	114.2(11)
								C−C−C (others in BPh_4^-, av)	121.1(13)

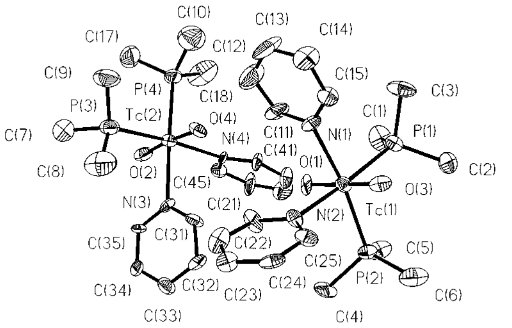

Figure 3. Labeled diagram of the two cations in $[TcO_2(PMe_3)_2(py)_2]$-(BPh_4) (**III**) (the ellipsoids correspond to 30% probability).

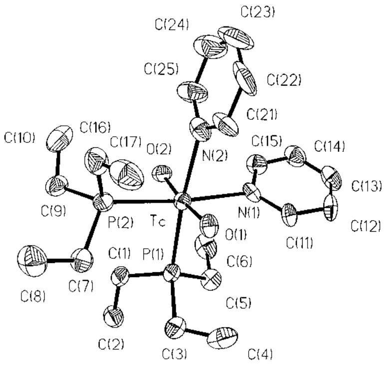

Figure 4. Labeled diagram of $[TcO_2(PEt_3)_2(py)_2]^+$ (**IV**) (the ellipsoids correspond to 30% probability).

to each other. The angles P−Tc−P are slightly larger than 90° (95.0(2) and 94.6(2)° for **III** and 94.5(1)° for **IV**) in order to reduce the steric hindrance between the two *cis*-phosphine ligands. This strain is further reduced by the conformation of the pyridine rings. The dihedral angles between the pyridine planes and the Tc plane containing the two P and the two N atoms are 104 and 79° for molecule **IIIA**, 69 and 82° for molecule **IIIB**, and 74 and 89° for **IV**. Therefore the pyridine rings are not too far from being perpendicular to the Tc plane containing the greatest steric hindrance. The dihedral angles between the two *cis*-pyridine rings are 104 and 83° for **III** and 109° for **IV**. The N−Tc−N angles have been reduced to 83.2(5) and 83.8(4)° for **III** and 80.7(4)° for **IV**. The O−Tc−O angles are 175.1(5)° (**III**) and 171.1(4)° (**IV**), and the two oxo ligands are pushed away from the phosphine ligands, the deformation being slightly larger for the more bulky phosphine.

The Tc−O bond distances vary between 1.693(13) and 1.725(13) Å for **III** and between 1.728(7) and 1.736(7) Å for **IV**. These values are close to those observed in the $[TcO_2(PR_3)_3]^+$ complexes described above. The IR band located around 805−810 cm^{-1} was assigned to the stretching ν(Tc═O) vibrations as observed in the literature for *trans*-dioxo complexes.[13] This band is observed at slightly lower energy than the one observed for $[TcO_2(PR_3)_3]^+$ (≈850 cm^{-1}).

The Tc−P bond distances vary from 2.401(6) to 2.437(5) Å for **III** and are 2.426(4), 2.439(4) Å for **IV**. At first sight, they seem slightly short for Tc(V) compounds where π-bonding should not be important. These distances are usually dependent on the *trans* ligands. Pyridine ligands are not known to have a large *trans* influence. Furthermore, since the two d electrons are paired, the bond distances should be slightly shorter. Therefore these Tc(V)−P bonds are probably normal. The Tc−N bond lengths are in the range 2.215(13)−2.287(13) Å for **III** and are 2.255(9) and 2.287(11) Å for **IV**. These values are larger than those reported for *trans*-[TcO_2(4-*tert*-butylpyridine)$_4$]$^+$ (average value of 2.144(7) Å).[28] In our case, the pyridine ligands are located in *trans* position to the phosphines, which are known to possess a large *trans* influence. We have not found any reported values on such bond distances. In Tc(III) compounds (d^4 configuration), the average Tc−N bond is 2.140(5) Å in *mer*-Tc(4-picoline)$_3$Cl$_3$,[29] while the bond located in *trans* position to a phosphine ligand in Tc(4-picoline)(PMe$_2$Ph)$_2$Cl$_3$ is longer (2.198(3) Å).[29] The average Tc−N−C angles are 121.0(13) (**III**) and 120.8(8)° (**IV**), while the average C−N−C angles are 117.1(15) (**III**) and 118.1(11)° (**IV**). The ortho angles N−C−C (122.6(20) (**III**) and 122.8(12)° (**IV**)) are slightly larger than the other pyridine C−C−C angles (average 119.2(20) (**III**) and 118.8(13)° (**IV**)).

The average P−C distance is 1.796(20) for the PMe_3 complex and 1.805(12) Å for the PEt_3 compound. These bonds seem slightly shorter for phosphines less bulky than PPh_3. The Tc−P−C angles (average 115.0(8) for **III** and 114.8(4)° for **IV**) are larger than normal tetrahedral angles, while all of the C−P−C bond angles are smaller than the tetrahedral value with average angles of 103.3(10) for **III** and 103.7(6)° for **IV**. These angles are similar to those observed in the [$TcO_2(PR_3)_3$]$^+$ complexes described above. The P−C−C angles in **IV** are slightly flattened, averaging 115.5(9)°.

The [$TcO_2(PR_3)_2(py)_2$]$^+$ compounds are diamagnetic, indicating an important deformation of the octahedron. The two 4d electrons are paired in a nondegenerate orbital. If the two *trans*-dioxo ligands are along the *z* axis, the orbital of lowest energy might be the d_{xy} orbital. The ^{1}H NMR were measured in $CDCl_3$. The resonances are listed in the Experimental Section. The phosphine protons located in α and β positions show enlarged peaks due to coupling with ^{31}P and with ^{99}Tc, which has a spin $I = {}^9/_2$. The resonances of the *ortho* protons of BPh_4^- are also quite large due to coupling with the two isotopes ^{10}B ($I = 3$, 19.6% abundance) and ^{11}B ($I = {}^3/_2$, 80.4% abundance)

The bond distances and angles in BPh_4^- are similar to those observed in the [$TcO_2(PR_3)_3$]$^+$ compounds. The average B−C bonds are 1.643(26) (**III**) and 1.654(18) Å (**IV**). The average external angles B−C−C are 123.2(16) (**III**) and 122.8(10)° (**IV**), while the internal angles C−C(B)−C are significantly smaller (113.4(17) for **III** and 114.2(11)° for **IV**) than the other internal angles (average 121.1(18) for **III** and 121.1(13)° for **IV**).

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic temperature factors, hydrogen coordinates, and bond distances and angles (35 pages). Ordering information is given on any current masthead page.

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