Complexes of technetium(I) (^{99}Tc, ^{99m}Tc) pentacarbonyl core with π-acceptor ligands (*tert*-butyl isocyanide and triphenylphosphine): Crystal structures of [Tc(CO)$_5$(PPh$_3$)]OTf and [Tc(CO)$_5$(CNC(CH$_3$)$_3$)]ClO$_4$

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Abstract

A procedure was developed for preparing [^{99m}TcX(CO)$_5$] (X = Cl, Br, I) in a reasonable yield by high-pressure carbonylation with CO of ^{99m}TcO$_4^-$ in aqueous solutions. In the synthesis, the substantial part of the target product is accumulated in the gas phase and can be transferred from the autoclave into various solvents when relieving the pressure. Compounds [^{99m}TcX(CO)$_5$] (X = Cl$^-$, Br$^-$, I$^-$) are stable in solutions for several hours, but in the course of longer storage they gradually decompose to give the tricarbonyl species. Substitution of the halide ligands in [^{99}TcX(CO)$_5$] and [^{99m}TcX(CO)$_5$] with *tert*-butyl isocyanide and triphenylphosphine was studied. The structures of the complexes [Tc(CO)$_5$(PPh$_3$)]OTf and [Tc(CO)$_5$(CNC(CH$_3$)$_3$)]ClO$_4$ are presented.
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1. Introduction

Recently, there has been a great deal of interest in technetium triaquatricarbonyl complex, [Tc(CO)$_3$(H$_2$O)$_3$]$^+$, as a promising precursor for development of new radiopharmaceuticals [1]. In this complex, three facially arranged water molecules can be readily replaced by other donor ligands. Various complexing groups for linking the tricarbonyltechnetium core to biomolecules were proposed, and numerous complexes were prepared and characterized (see, e.g. [2]). The triaquatricarbonyl complex can also be prepared on the tracer level with ^{99m}Tc. For this purpose, a reagent kit based on the boranocarbonate anion as carbonylation agent and a procedure for normal-pressure synthesis have been developed [3]. However, with the [Tc(CO)$_3$]$^+$ core, it is necessary to use tripodal chelating groups or to combine bidentate and monodentate ligands so as to saturate the coordination sphere of technetium. The first approach involves fine organic synthesis. The second one is simpler from the synthetic viewpoint, but it may be difficult to find ligand combinations that would form a single complex species with [Tc(CO)$_3$]$^+$ on the tracer level. It seems very promising to use precursors

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containing $[Tc(CO)_4]^+$ or even $[Tc(CO)_5]^+$ cores, to label a biomolecule via bidentate or monodentate ligands, respectively.

Unfortunately, higher Tc(I) carbonyls are relatively unstable. For example $[^{99}TcCl(CO)_5]$ completely decomposes in a noncoordinating (e.g., CCl_4) solvent at room temperature into dimeric tetracarbonyl chloride within a day and polymerizes on heating in the solid state to form tetrameric tricarbonyl chloride [4]. In coordinating solvents (e.g., acetonitrile, THF) the decarbonylation is slightly faster [5]. $[^{99}TcBr(CO)_5]$ and its iodide analogue decompose more slowly. The degree of decarbonylation of $[TcI(CO)_5]$ in a noncoordinating solvent in 24 h at room temperature is about 10%. Such a level of stability may be sufficient for performing certain chemical transformations and even biodistribution experiments.

Substitution of the halide in $[TcX(CO)_5]$ by various anionic ligands was usually accompanied by partial decarbonylation with formation of tricarbonyl species, but some tetra- and pentacarbonyl derivatives were also obtained [6,7]. In particular, $[Tc(OC(O)CF_3)(CO)_5]$ was prepared by the heterogeneous reaction of $[TcCl(CO)_5]$ with silver trifluoroacetate under a layer of $CHCl_3$ and purified by vacuum sublimation. The compound is relatively stable in CCl_4 solution but sensitive to atmospheric moisture [6]. Heterogeneous reactions of $[TcCl(CO)_5]$ with potassium β-diketonates under a layer of CCl_4 with gentle heating yielded tetracarbonyltechnetium β-diketonates, which slowly decomposed to tricarbonyl species in the course of days and weeks [7]. The kinetic stability of pentacarbonyl complexes, which was studied comprehensively for manganese(I) [analog of technetium(I)] in relation to the nature of the sixth ligand [8], grows in going from harder to softer bases.

Thus, linking of higher technetium carbonyls to biomolecules seems possible. However, synthetic approaches developed for ^{99}Tc are not yet fully applicable to ^{99m}Tc.

Further synthetic possibilities may arise from the volatility of $[TcX(CO)_5]$. The saturated vapor pressure of $[TcI(CO)_5]$ at room temperature was estimated at 0.2 Pa [9]. Moreover, according to our experimental data, pentacarbonylrhenium halides are steam-distillable, and therefore formation of a water azeotrope with $[TcX(CO)_5]$ is possible. These facts suggested the possibility of transferring $[^{99m}TcX(CO)_5]$ through the gas phase from the reaction mixture in high-pressure carbonylation and trapping it in an aqueous or nonaqueous solvent.

In this study, we examined the possibility of preparing $[^{99m}TcX(CO)_5]$ (X = Cl, Br, I) by high-pressure carbonylation of $^{99m}TcO_4^-$ with CO. We also studied reactions of $[^{99}TcX(CO)_5]$ and $[^{99m}TcX(CO)_5]$ with monodentate ligands such as *tert*-butyl isocyanide (TBI) and triphenylphosphine (PPh_3) with the aim to evaluate the formation conditions and stability of the $[^{99m}Tc(CO)_5L]^+$ core (L = RNC, PR_3). The structures of $[Tc(CO)_5(PPh_3)]OTf$ and $[Tc(CO)_5(CNC(CH_3)_3)]ClO_4$ have been determined.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Fluka (St. Petersburg, Russia). Except HI, the reagent grade chemicals and solvents were used without additional purification. $[^{99}TcI(CO)_5]$ was prepared by carbonylation of $KTcO_4$ with an HCOOH–HI mixture in an autoclave (at 170 °C, 160 atm, 40 min) according to the previously published procedure [10]. Prior to synthesis, aqueous hydroiodic acid was treated with a benzene solution of tributyl phosphate to remove traces of free I_2. The resulting white crystals of $^{99}Tc(CO)_5I$ (yield ~60–65%) were separated from the solution, washed with water, and dried in air. $Na^{99m}TcO_4$ was obtained from a $^{99}Mo/^{99m}Tc$ extraction generator (Khlopin Radium Institute, St. Petersburg, Russia) using 0.9% saline.

HPLC analysis was performed on a Waters 1525 chromatograph equipped with a Waters 2487 UV detector and a Raytest NaI γ-ray detector. A 4.6×150 mm Atlantis™ dC_{18} 5 μm column was used. HPLC solvents consisted of 0.1% aqueous trifluoroacetic acid (TFA) (solvent A) and acetonitrile (solvent B). The elution was started with 100% A (5 min). The eluent switched at 5 min to 75% A and 25% B and at 9 min to 66% A and 34% B, which was followed by a linear gradient from 66% A and 34% B to 100% B during the period from 9 to 20 min. This was followed by 100% B for 2 min before switching back to 100% A. The flow rate was 1 ml/min. The NMR spectra were recorded on a Varian Gemini 2000 spectrometer. The ^{99}Tc shifts are given relative to external aqueous $KTcO_4$ reference. The IR spectra were recorded on a Shimadzu FT-IR 8700. The mass spectra were taken on an MKh-5311 ESI-TOF mass spectrometer (Institute of Analytical Instrument Making, Russian Academy of Sciences, St. Petersburg, Russia) at electrospray voltage of 3.7 kV, with the calibration against gramicidin as external reference. The device resolution was about 6500. The technetium content of the synthesized compounds was determined photocolorimetrically with thiourea after decomposition of the compounds to pertechnetate ion with hydrogen peroxide [11].

2.2. Synthesis of $[^{99m}TcI(CO)_5]$

Synthesis was performed in a high-pressure laboratory microreactor developed at the Khlopin Radium Institute (St. Petersburg, Russia). To produce CO pressure, an external CO source was used. To a penicillin vial containing 1–2 ml of a $Na^{99m}TcO_4$ eluate (activity from 0.5 to 2 GBq), KI (10 mg) and H_2SO_4 (0.06–0.12 ml) were added [12]. The vial was nonhermetically sealed with a Teflon ribbon and placed into the high-pressure cell. The cell was closed and pressurized with carbon monoxide to a pressure of 100–150 atm. The cell was kept at 170 °C for 30–40 min and then was cooled to 80–90 °C. At this temperature carbon monoxide was slowly released from the cell through a vial (or reaction flask) with

1–2 ml of appropriate solvent (e.g., water, alcohols, CH_2Cl_2, THF, etc.). The yield of the target product in an aqueous solution in the autoclave was almost quantitative. HPLC showed a single radioactive peak with a retention time of 16.4 min. $[^{99m}TcI(CO)_5]$ was transferred with a carbon monoxide stream into the vial. $[^{99m}TcBr(CO)_5]$ and $[^{99m}TcCl(CO)_5]$ were prepared by similar procedure using HBr and HCl instead of a mixture of KI and H_2SO_4. In all the cases synthesis was performed at acid concentration of about 1 M.

2.3. Preparation of $[^{99}Tc(CO)_5TBI]ClO_4$

$[TcI(CO)_5]$ (0.3 mmol) was dissolved in dry CH_2Cl_2. Solid $AgClO_4$ (0.6 mmol) was added. The mixture was stirred for 2 h. The AgI precipitate was filtered off and a slight excess of TBI (0.034 ml) was added to the filtrate. The reaction mixture was stirred at room temperature for 2 h. Crystallization of $[Tc(CO)_5TBI]ClO_4$ was induced by adding diethyl ether. Tc exp. 23.41%, calc. 23.48%; IR (CaF_2, $CHCl_3$, cm^{-1}): ν_{CO} 2071.4; $\nu_{C\equiv N}$ 2162.1. ^{99}Tc NMR (CH_2Cl_2): δ_{Tc} 2016.3 ppm. MS: m/z 321.93 ($[^{99}Tc(CO)_5$-$TBI]^+$, calcd. 321.95), 265.87 ($[^{99}Tc(CO)_5TBI- C_4H_8]^+$, calcd. 265.89), 181.96 ($[^{99}Tc(CO)_5TBI-5CO]^+$, calcd. 181.98). HPLC: retention time 9.2 min.

2.4. Preparation of $[^{99m}Tc(CO)_5(TBI)]OTf$

To 0.5 ml of $[^{99m}TcI(CO)_5]$ in dry CH_2Cl_2 prepared by releasing CO from the reaction vessel, solid AgOTf (10–15 mg) was added. The mixture was stirred for 30 min at room temperature, and the solid was filtered off. A 10^{-3} M solution of TBI in dry CH_2Cl_2 (0.1 ml) was added. The reaction mixture was stirred at room temperature for 30 min and then was analyzed by HPLC. The retention time of $[^{99m}Tc(CO)_5(TBI)]OTF$ was 9.6 min (radiochemical purity 9.8%).

2.5. Preparation of $[^{99}Tc(CO)_5PPh_3]OTf$

A solution of $[TcI(CO)_5]$ (0.13 mmol) in dry CH_2Cl_2 (5 ml) was treated with solid AgOTf (0.26 mmol). The mixture was stirred for 30 min at room temperature. The solution was filtered and an equimolar amount of PPh_3 in dry CH_2Cl_2 was added. The mixture was stirred overnight. Crystalline $[Tc(CO)_3PPh_3]OTf$ was precipitated with diethyl ether. Colorless plates suitable for single crystal X-ray diffraction were prepared by slow evaporation of a $CHCl_3$/isopropanol solution. Tc exp. 13.81%, calc. 15.22%; IR (CH_2Cl_2) 2057.9 cm^{-1}. ^{99}Tc NMR (CH_2Cl_2, ppm): δ 1958 (d), J_{TcP} 364 Hz. MS: m/z 500.93 ($[^{99}Tc(CO)_5PPh_3]^+$, calcd. 500.97), 360.96 ($[^{99}Tc(CO)_5PPh_3-5CO]^+$, calcd. 361.00). HPLC: retention time 13.6 min.

2.6. Preparation of $[^{99m}Tc(CO)_5(PPh_3)]OTf$

To 0.5 ml of $[^{99m}TcI(CO)_5]$ in dry CH_2Cl_2 prepared by releasing CO from the reaction vessel, solid AgOTf

(10–15 mg) was added. The mixture was stirred for 30 min at room temperature. The solid was separated by filtration. A 10^{-3} M solution of PPh_3 in dry CH_2Cl_2 (0.1 ml) was added. The reaction mixture was stirred at room temperature for 30 min and then was analyzed by HPLC. The retention time of $[^{99m}Tc(CO)_5(PPh_3)]OTf$ was 13.6 min (radiochemical purity 93.3%).

2.7. X-ray diffraction measurements

Crystallographic data for $[^{99m}Tc(CO)_5(PPh_3)]OTf$ and $[Tc(CO)_5TBI]ClO_4$ were collected at 183(2) and 100 K, respectively, on STOE IPDS and Bruker SMART APEX (Mo Kα radiation, $\lambda = 0.71073$ Å) diffractometers, respectively, using a graphite-monochromated radiation. Suitable crystals were coated with Paratone N oil, mounted on the top of a glass fiber, and immediately transferred to the diffractometer. For $[^{99m}Tc(CO)_5(PPh_3)]OTf$, a maximum of 8000 reflections distributed over the whole limiting sphere were selected by the SELECT program and used for unit cell parameter refinement with the CELL program [13]. Data were corrected for Lorenz and polarization effects as well as for absorption (numerically). Structures were solved with direct methods using SIR97 program [14] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97 program [15]. For $[Tc(CO)_5TBI]ClO_4$, the intensity data were processed using standard Bruker software. Data were corrected for Lorenz and polarization effects as well as for absorption (semi-empirically).

3. Results and discussion

3.1. Synthesis of $[^{99m}TcX(CO)_5]$

High-pressure carbonylation of $^{99}TcO_4^-$ in aqueous solution in the presence of HCl yields different products depending on the technetium concentration. At high technetium concentrations, a precipitate of $[^{99}TcCl(CO)_5]$ is formed, whereas at lower concentrations (10^{-3} M) only the tricarbonyl species is formed in a quantitative yield, as follows from the ^{99}Tc NMR spectrum of the reaction mixture [10]. Apparently, the pentacarbonyl chloride may also be formed in this case as an intermediate, but it partially decomposes in solution on relieving the CO pressure (NMR data). Carbonylation of $^{99m}TcO_4^-$ under the similar conditions also yields the $[^{99m}Tc(CO)_3(H_2O)_3]^+$ ion in the solution [16].

To develop a procedure for preparing $[^{99m}TcI(CO)_5]$, we studied carbonylation of $^{99}TcO_4^-$ with HI at such technetium concentration when solid $[^{99}TcI(CO)_5]$ did not form, but the ^{99}Tc NMR spectrum could be recorded. A 0.02 M solution of $KTcO_4$ in aqueous ethanol (1:1 v/v) was carbonylated with CO ($P = 160$ atm, $T = 170$ °C, $t = 40$ min) in the presence of 1 M HI. The ^{99}Tc NMR spectrum of the resulting mixture contained two signals at -1728 and -1952 ppm (relative to $KTcO_4$). The former signal belongs to an unidentified species, and the latter

signal, to $Tc(CO)_5I$ (−1991 ppm in CH_2Cl_2 for an authentic sample). It should be noted that the chemical shift of this signal is typical for technetium complexes with soft π-acceptor ligands (e.g., the signal of the hexacarbonyltechnetium(I) cation lies at −1961 ppm [17]), and the signals of tricarbonyltechnetium iodide complexes are also observed in appreciably higher field than the signals of their chloride and bromide analogs [18].

Carrier-free $[^{99m}TcI(CO)_5]$ was prepared in a special laboratory autoclave. The reductive carbonylation of $^{99m}TcO_4{}^-$ was performed in the presence of HI generated *in situ* from a mixture of KI and H_2SO_4 at 170 °C and a working pressure of carbon monoxide of 80–200 atm; the synthesis time was 30 min. The yield of the target product in an aqueous solution was almost quantitative. HPLC showed a single radioactive peak with a retention time of 16.4 min, which coincided with the retention time of a reference sample of $[^{99}TcI(CO)_5]$ under similar conditions corrected for the solution flow time between the UV and γ-ray detectors.

$[^{99m}TcI(CO)_5]$ was isolated from the reaction mixture by relieving excess CO pressure from the reaction vessel at 80–90 °C. Approximately 40–60% of the initial ^{99m}Tc activity was transferred with the CO flow into an appropriate solvent by gas bubbling. $[^{99m}TcBr(CO)_5]$ and $[^{99m}TcCl(CO)_5]$ were prepared similarly. These compounds were transferred into the solvent in amounts of 30% and 20% of the initial activity, respectively.

3.2. Reactions of $[^{99}TcI(CO)_5]$ with neutral ligands: tert-butyl isocyanide and triphenylphosphine

We studied reactions of $[^{99}TcI(CO)_5]$ with monodentate ligands with the aim to develop a procedure for labeling biomolecules with the $[^{99m}Tc(CO)_5]^+$ moiety. Monodentate ligands to be used for substitution of the halide ion to form $[Tc(CO)_5L]$ should meet the following requirements. On one hand, they should form very stable complexes resistant to exchange with strong chelating ligands. On the other hand, the substitution product $[Tc(CO)_5L]$ should be resistant to decarbonylation to form the tricarbonyl species. Soft ligands with π-acceptor properties, such as isocyanides, meet these requirements. Isocyanides form very stable complexes with Tc (one of them, hexakis(methoxyisobutylisonitrile)technetium(I), MIBI, is a commercially used radiopharmaceutical for heart imaging). They form (in combination with dithiocarbamates) stable 2+1 complexes with the tricarbonyltechnetium fragment [19]. On the other hand, linking of the isonitrile functional group to biomolecules seems quite feasible (using, e.g., commercially available ethyl isocyanoacetate).

The direct substitution of iodide ion with *tert*-butyl isocyanide does not proceed in inert solvents. Therefore, substitution of the iodide ligand in $[TcI(CO)_5]$ with TBI was performed in two steps. The first step is substitution of iodide ion with weakly coordinated $ClO_4{}^-$. For this purpose, $[TcI(CO)_5]$ was treated with two equivalents of solid

$AgClO_4$ in dichloromethane solution under stirring for 2 h at room temperature. The substitution of ligands in the solid-phase reaction was confirmed by the fact that the $^{99}TcNMR$ spectrum of the resulting reaction mixture contained the major signal at −1353.2 ppm (relative to $KTcO_4$), whereas the signal of the initial $[TcI(CO)_5]$ in CH_2Cl_2 was observed at −1993.0 ppm. The Ag-containing precipitate was filtered off and a slight excess of TBI (over the 1:1 stoichiometry) was added to the filtrate. Precipitation was induced by adding diethyl ether. The IR spectrum of the product in dichloromethane in the carbonyl region contained a strong band at 2071.4 cm^{-1} corresponding to pentacarbonyl group. The weak bands at 2219.9 and 2202.6 cm^{-1} can be assigned to the coordinated TBI by the analogy with the IR spectra of $[(OC)_5ReCNCMe_3]BF_4$ [20]. The ^{99}Tc NMR spectrum of the compound in CH_2Cl_2 contained a single signal at 2016.3 ppm (Fig. 1). Along with the chemical analysis of the precipitate for the Tc content, these facts indicate formation of the compound $[Tc(CO)_5TBI]ClO_4$. The HPLC pattern of $[^{99}Tc(CO)_5TBI]ClO_4$, recorded in the CH_3CN–0.1%TFAA gradient system, contained a single peak with a retention time of 9.2 min.

The reaction of $[^{99m}TcI(CO)_5]$ with TBI also required preliminary activation with a silver salt [in this case we used $AgSO_3CF_3$ (AgOTf)]. For this purpose, a solution of $[^{99m}TcI(CO)_5]$ in dry CH_2Cl_2 containing solid AgOTf, prepared by relieving the pressure from the reaction vessel through this mixture, was stirred for 30 min at room temperature. Then the mixture was filtered and TBI (10^{-3} M) was added to the filtrate. The reaction mixture was stirred at room temperature for 30 min and analyzed by HPLC. The yield of $[^{99m}Tc(CO)_5TBI]^+$ (9.6 min) was low (radiochemical purity ∼10%), and the major product (retention time 13.9 min) was tentatively identified as $[^{99m}Tc(CO)_3(TBI)_3]^+$ in accordance with data of Schibli [21].

As a monodentate ligand for binding to the $[Tc(CO)_5]^+$ core we also studied triphenylphosphine. This compound exhibits π-acceptor properties, and ligands of this type, according to Atwood and Brown [8], exert relatively weak *cis*-labilization effect on the carbonyl groups of the pentacarbonyl core. A solution of $[TcI(CO)_5]$ in dry CH_2Cl_2
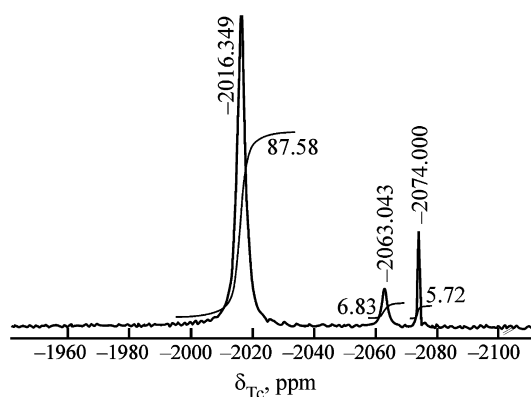

Fig. 1. ^{99}Tc NMR spectrum of $[Tc(CO)_5TBI]ClO_4$ in CH_2Cl_2.

was treated with 2 equiv. of AgOTf. The solution was filtered, and an equimolar amount of PPh$_3$ in dry CH$_2$Cl$_2$ was added. The mixture was stirred overnight, and crystalline [Tc(CO)$_5$PPh$_3$]OTf was precipitated by adding diethyl ether. The IR spectrum of the complex in CH$_2$Cl$_2$ contained a strong CO band at 2057.9 cm^{-1}, assignable to the pentacarbonyl group [22]. The ^{99}Tc NMR spectrum of [Tc(CO)$_5$PPh$_3$]OTf in CH$_2$Cl$_2$ contained a doublet at $\delta = 1958$ ppm with $J_{TcP} = 364$ Hz (Fig. 2). The chemical shift is typical for technetium pentacarbonyl complexes with soft ligands (cf. above data for pentacarbonyl iodide and isonitrile complexes). This spin–spin coupling constant is somewhat lower than that of some tricarbonyl complexes with other phosphine ligands, probably due to lower s-electron density at the technetium nucleus [23]. The reaction of [^{99m}TcI(CO)$_5$] (after treatment with silver triflate) with triphenylphosphine was studied. In contrast to TBI, the yield of the target product was nearly quantitative. Its HPLC pattern is shown in Fig. 3; the retention time (13.6 min) is close to that of [^{99}Tc(CO)$_5$PPh$_3$]OTf given in the figure for comparison.
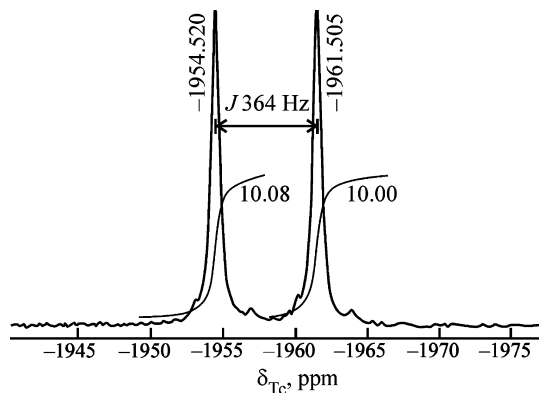

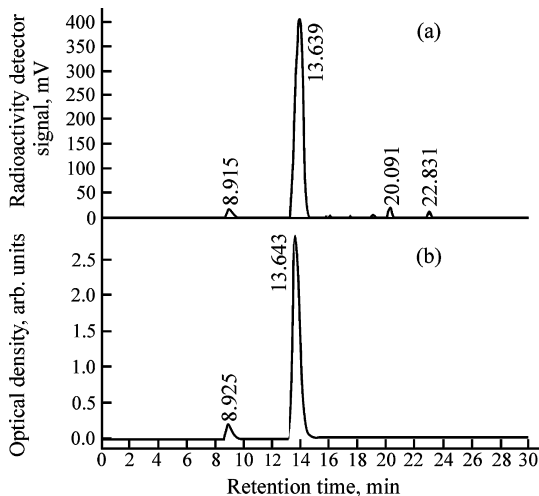Fig. 2. The ^{99}Tc NMR spectrum of [Tc(CO)$_5$PPh$_3$]OTf in CH$_2$Cl$_2$.

Fig. 3. HPLC patterns of (a) and (b) [^{99}Tc(CO)$_5$PPh$_3$]OTf.

3.3. Molecular structures of [Tc(CO)$_5$L]$^+$ derivatives

Colorless plates suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a CHCl$_3$/isopropanol solution. The structures of [Tc(CO)$_5$PPh$_3$]OTf and [Tc(CO)$_5$TBI]ClO$_4$ consist of well separated cations and anions, with the technetium atom in slightly distorted octahedral coordination surroundings. The structures of the complex cations are shown in Figs. 4 and 5; selected bond lengths and angles are given in Table 1. The metal–phosphorus distance (2.491(2) Å) in [Tc(CO)$_5$PPh$_3$]OTf is slightly longer than in the related rhenium complex [Re(CO)$_5$(PPh$_2$NHPPh$_2$)][BF$_4$] (2.475(5) Å) [24], which suggests slightly better π-acceptor properties of the diphosphazane ligand Ph$_2$PNHPPh$_2$. The Tc–CO bond lengths are between 1.985(7) and 2.012(7) Å for [Tc(CO)$_5$PPh$_3$]OTf, and 1.999(5) and 2.022(6) Å for [Tc(CO)$_5$TBI]-ClO$_4$. These values are similar to those in [Tc$_2$CO$_{10}$] (1.90–2.00 Å) [25]. It is interesting that the equatorial and axial Tc–CO bond lengths in the complexes with PPh$_3$ and TBI differ insignificantly, in contrast to [TcI(CO)$_5$] studied in [26], in which the difference between the axial and equatorial (mean) Tc–CO bond lengths is about 0.1 Å. That is, neutral ligands with noticeable π-acceptor properties, whose *trans* effect, as compared to anionic ligands like I$^-$, is more similar to that of CO groups, exert a levelling effect on the Tc–CO bond lengths. A certain correlation is also seen with the IR spectra. In the spectra of pentacarbonyltechnetium halides, including iodide [27], there is a medium-intensity low-frequency band assigned to the A$_1$ vibration involving primarily the axial C=O group. In the spectra of the complexes with PPh$_3$ and
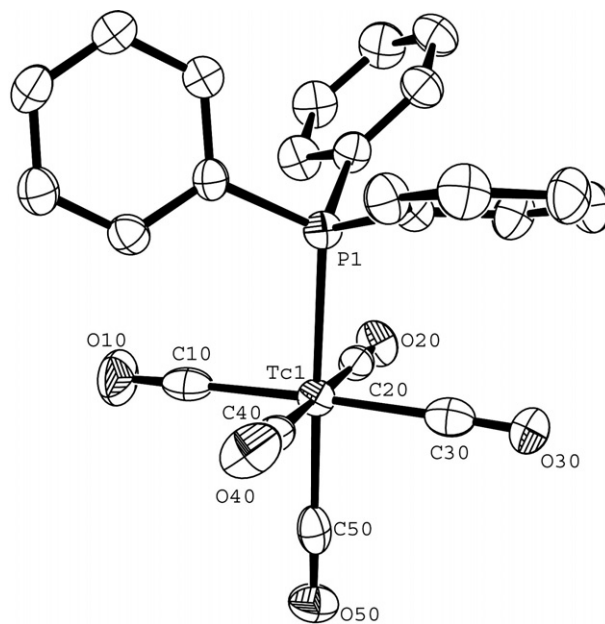

Fig. 4. Displacement ellipsoid representations of the [Tc(CO)$_5$(PPh$_3$)]$^+$ cation in [Tc(CO)$_5$(PPh$_3$)]OTf. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.
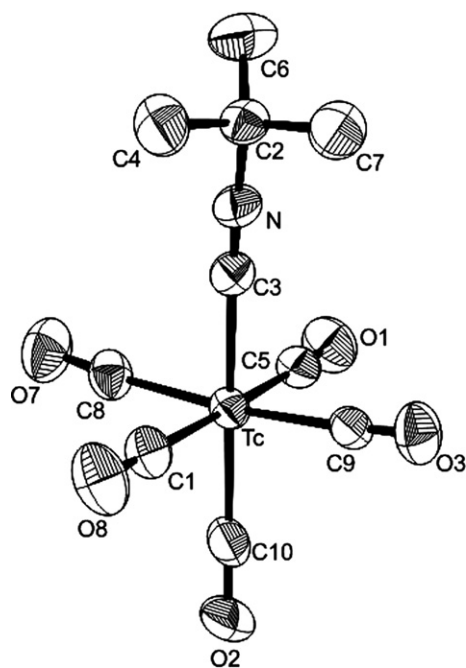
Fig. 5. Displacement ellipsoid representations of the $[Tc(CO)_5TBI]^+$ cation in $[Tc(CO)_5TBI]ClO_4$. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.

TBI, where the difference between the axial and equatorial CO groups is levelled off, bands in this region are ill-defined or lacking at all.

4. Conclusion

The procedure developed for preparing carrier-free $[^{99m}TcX(CO)_5]$ opens new prospects for synthesis of novel radiopharmaceuticals. It should be noted that the resulting complexes are stable in solutions for several hours, but in longer storage they gradually decompose to give the tricarbonyl species However, the possibility of transferring $[^{99m}TcX(CO)_5]$ from the aqueous reaction mixture through the gas phase to a nonaqueous solvent makes it possible to perform syntheses that require inert solvents. Also, it becomes possible to prepare bioconjugates containing $[Tc(CO)_5]^+$ moiety as alternatives to $[Tc(CO)_3]^+$-based bioconjugates. It was found that π-acceptor ligands (triphenylphosphine and *tert*-butyl isocyanide) form stable complexes with the pentacarbonyltechnetium core. The crystal structures of $[Tc(CO)_5(PPh_3)]OTf$ and $[Tc(CO)_5(CNC(CH_3)_3)]ClO_4$ were solved. The complex $[^{99m}Tc(CO)_5(PPh_3)]OTf$ was prepared in a reasonable yield. Thus, the possibility of replacing bulky tridentate chelators (or combinations of bidentate and monodentate ligands) with monodentate ligands as units for binding technetium carbonyl moiety to biomolecules does exist (see Table 2).

Table 1
Selected bond lengths (Å) and angles (°) in $[Tc(CO)_5(PPh_3)]OTf$ and $[Tc(CO)_5(CNC(CH_3)_3)]ClO_4$

[Tc(CO)₅(PPh₃)]OTf			
Tc–C10	2.012(7)	C10–O10	1.134(8)
Tc–C20	1.992(7)	C20–O20	1.144(7)
Tc–C30	1.985(7)	C30–O30	1.154(8)
Tc–C40	2.019(7)	C40–O40	1.125(7)
Tc–C50	2.005(7)	C50–O50	1.121(7)
Tc–P	2.491(2)		
P–Tc–C10	93.0(2)	P–Tc–C20	92.2(2)
P–Tc–C30	90.1(2)	P–Tc–C40	86.6(2)
P–Tc–C50	177.2(2)	C10–Tc–C20	87.1(2)
C10–Tc–C30	176.1(2)	C10–Tc–C40	94.3(2)
C10–Tc–C50	89.1(2)	C20–Tc–C30	90.5(2)
C20–Tc–C40	178.2(2)	C20–Tc–C50	89.7(2)
C30–Tc–C40	88.2(2)	C30–Tc–C50	87.8(2)
C40–Tc–C50	91.5(2)		
[Tc(CO)₅(CNC(CH₃)₃)]ClO₄			
Tc–C10	1.999(6)	C10–O2	1.118(6)
Tc–C8	2.008(5)	C8–O7	1.116(5)
Tc–C5	2.011(5)	C5–O1	1.112(5)
Tc–C9	2.015(5)	C9–O3	1.115(5)
Tc–C1	2.022(5)	C1–O8	1.115(5)
Tc–C3	2.095(5)	C3–N	1.131(5)
C3–Tc–C10	173.98(18)	C3–Tc–C8	89.91(19)
C3–Tc–C5	93.18(18)	C3–Tc–C9	84.69(18)
C3–Tc–C1	89.32(19)	C10–Tc–C8	94.09(19)
C10–Tc–C5	91.55(19)	C10–Tc–C9	91.44(18)
C10–Tc–C1	86.3(2)	C8–Tc–C5	86.53(19)
C8–Tc–C9	174.26(18)	C8–Tc–C1	88.24(19)
C5–Tc–C9	91.79(18)	C5–Tc–C1	174.20(18)
C9–Tc–C1	93.65(19)		

Table 2
X-ray structure data collection and refinement parameters for $[Tc(CO)_5(PPh_3)]OTf$ and $[Tc(CO)_5(CNC(CH_3)_3)]ClO_4$

Formula	$C_{24}H_{15}F_3O_8PSTc$	$C_{10}H_9ClNO_9Tc$
M (g mol^{-1})	649.39	420.63
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
Temperature (K)	183	100
Unit cell dimensions		
a (Å)	11.6336(7)	12.0022(7)
b (Å)	14.5348(8)	11.4127(7)
c (Å)	15.052(1)	23.2639(17)
α (°)	90	90
β (°)	91.57(1)	90
γ (°)	90	90
V (Å^3)	2544.2(3)	3186.6(4)
Z	4	8
D_c (g cm^{-3})	1.695	1.754
Linear absorption coefficient (mm^{-1})	0.780	1.112
Absorption correction	Numerical	Semiempirical
trans$_{min}$/trans$_{max}$	0.8846/0.9671	0.215/0.272
Measured reflections	27626	13405
Unique reflections/R_{int}	5006/0.1015	1554/0.0715
Refined parameters	343	199
R_1(F)/wR_2 (F^2) ($I > 2\sigma(I)$)[a]	0.057/0.132	0.0283/0.0527
GooF	0.887	0.871
Instrument	IPDS	Bruker Smart Apex

[a] $R_1 = |F_o - F_c|/|F_o|$; $wR_2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

5. Supplementary material

CCDC 637712 and 641395 contain the supplementary crystallographic data for $[Tc(CO)_5PPh_3]OTf$ and $[Tc(CO)_5\text{-}TBI]ClO_4$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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