Some new cationic di- and tricarbonyl complexes of technetium(I)

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Abstract. Some new low-valent, cationic complexes of technetium-99 have been prepared. Oxidation of \( \text{Tc}_2(\text{CO})_6 \) \((1)\) with \( \text{NOPF}_5 \) in acetonitrile gave \( [\text{Tc}(\text{CH}_3\text{CN})(\text{CO})_5]^{\text{PF}_6} \) \((2)\) quantitatively. This complex constitutes a useful precursor for cationic carbonyl complexes, as exemplified by a variety of reactions with bi- and tridentate ligands from which air-stable, water-soluble complexes of type \( [\text{LTc}(\text{CO})_5]^{\text{X}^+} \) \((L = 1,4,7\text{-triazacyclononane}, 1,4,7\text{-trimethyl-1,4,7-triazacyclononane} and 1,7,4\text{-trithiaplicyclononane})\) have been isolated and characterized. A series of mixed complexes of technetium(I) of general formula \( [\text{Tc}(\text{N,N})\text{[P(OR)}_3]_2(\text{CO})_3]^{\text{PF}_6} \) \((\text{N,N} = 2,2\text{-bipyridine}, 4,4\text{-dime}-\text{thyl-2,2\text{-bipyrriyde and R = methyl, isopropyl}) have also been prepared.

Introduction

The intensive use of \( ^{99m}\text{Tc} \) in diagnostic nuclear medicine has prompted several inorganic chemists to study the basic chemistry of technetium. Excellent reviews covering this subject have been published\(^1\)–\(^2\), and these clearly present the role of technetium in radiopharmaceuticals. \( \text{Deutsch} et al.\)\(^1\), reported, in 1981, the significant myocardial uptake of the cationic \( \text{Tc(C)}(\text{CO})_5 \) \((3)\) \((\text{CO})_5 \)] complexes of formula \([\text{Tc(DIARS)}_2\text{X}]^+\) \((\text{DIARS} = 1,2\text{-phenylenebis(dimethylarsine)}; \text{X} = \text{Cl, Br})\). Since then, several other unipositive technetium complexes have been synthesized and tested in animals\(^3\)–\(^9\). However, human heart delineation of the most promising candidates has been less convincing than expected, except in the case of \( [\text{Tc(TBIN)}]^{\text{Cl}^-} \) \((\text{TBIN} = \text{tert-butyl isonitrile})\), the only cationic \( ^{99m}\text{Tc} \) complex for which animal data has been usefully predictive of human biodistribution\(^10\). A systematic comparison covering the results obtained up to 1984 together with some interesting observations on this subject have been presented by \( \text{Münze et al.}\)\(^11\). All \( \text{Tc(I)} \) and \( \text{Tc(II)} \) unipositive complexes have, more or less, effect on the heart, depending on their lipophilicity and reactivity rather than on their stereochemical properties. Despite the fact that \( \text{Tc(I)} \) complexes are relatively easy to prepare, especially when compared to the metastable \( \text{Tc(II)} \) intermediates, only a few cationic carbonyl complexes of \( \text{Tc(I)} \) are known, probably due to the lack of effective preparative methods for the starting materials. \( \text{Hieber et al.}\)\(^12\) reported the synthesis of \([\text{Tc}(\text{CO})_5\text{X}]\text{[AlCl}_4\) \( \) \([\text{n = 0, 2; L = P(\text{C}_3\text{H}_5)}_3\text{]}^{-}\), \( \text{Biagini Cingi et al.}\)\(^13\) prepared cis- and trans-\([\text{Tc}(\text{CO})_5\text{P(\text{OEt})_3\text{Ph})_3]\text{[ClO}_4\] while studying the change of reactivity as a function of halogen in complexes \([\text{TcX}_3\text{P(\text{OEt})_3\text{Ph})_3]\text{[ClO}_4\] \((\text{X} = \text{Cl, Br, I})\). An interesting starting material for cationic carbonyl complexes, \([\text{Tc}(\text{CH}_3\text{CN})(\text{CO})_2]\text{[PF}_6\] \), has been reported by \( \text{Kaden et al.}\)\(^14\), as well as four other derivatives from its reactions with different phenylphosphines \( \text{PhPL}_2 \) \((\text{L} = \text{Me, Ph, NaO,SCH}_3\)\).

Experimental

Technetium-99 was supplied by Mallinkrodt Diagnostica (Holland) laboratories in the form of dry \( \text{NH}_3\text{[TcO}_3\) \( \) \( \). This isotope is a low energy \((0.3 \text{MeV})\) \( \beta \) particle emitter with a half-life of 2.12 10\(^7\) years, which does not present a serious health hazard when handled in milligram amounts, since the \( \beta \) rays are absorbed by the glassware and there is no associated \( \gamma \) radiation. When larger quantities are used \((> 250 \text{mg})\), a distance of 30 cm must be maintained from the working area to avoid the effect of very soft X-rays produced by the action of the \( \beta \) particles on the glass. \( \text{Tc}_2(\text{CO})_6 \) \((1)\) was prepared according to a procedure previously reported\(^15\). The ligands 1,4,7-triazacyclononane \((\text{[9]aneN}_3\) \), 1,4,7-trimethyl-1,4,7-triazacyclononane \((\text{Me}_3[9]aneN}_3\) and 1,7,4-trithiaplicyclononane \((\text{[9]aneS}_3\) were obtained from Aldrich. Reactions were carried out under nitrogen in Schlenk glassware. Solvents were dried by conventional methods, distilled under nitrogen and used immediately. Infrared spectra were measured by using a Pye Unicam model SP3-300 spectrophotometer in NaCl cells \((\text{CH}_3\text{CN})\). \(^1\)H NMR spectra were recorded on a Bruker WH-90. Chemical shifts are reported in parts per million \((\text{ppm})\) and are referenced to residual protons in deuterated solvents \((\text{acetoni-trile-d}_3\) \((1.93), \text{acetone-d}_6\) \((2.05))\).

\( [\text{Tc}(\text{CH}_3\text{CN})(\text{CO})_2]\text{[PF}_6\] \((2)\)

227 mg \((1.3 \text{mmol})\) \( \text{NOPF}_5\) were added to a solution of 300 mg \((0.63 \text{mmol})\) \( \text{Tc}_2(\text{CO})_6 \) in 10 ml acetonitrile. A vigorous reaction took place with evolution of NO gas. After stirring of the reaction mixture for an additional 5 min, the solution was concentrated in
vacuum and the product precipitated by addition of 70 ml of diethyl ether. After washing three times with small portions of ether and drying in vacuum, 0.51 g (96% yield) of white \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6}\) was obtained. IR (CH\(_3\)CN): \(\nu(CO)\) 2169 w, 2069 vs, 2040 s, \(\nu(PF_6)\) 840 vs cm\(^{-1}\). \(^{1}H\) NMR (acetone-\(d_{6}\)): \(\delta 2.65\) (s, CH\(_3\)).

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

200 mg (0.47 mmol) \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\) were refluxed in 20 ml acetonitrile for 1 h. After concentration to 5 ml addition of diethyl ether yielded 220 mg (98% yield) of colourless product. IR (CH\(_3\)CN): \(\nu(CO)\) 2060 s, 1950 vs br; \(\nu(CH)\) 2300 m, 2280 w [these bands are proportionally much weaker than the \(\nu(CH)\) bands]; \(\nu(PF_6)\) 840 cm\(^{-1}\). \(^{1}H\) NMR (acetone-\(d_{6}\)): \(\delta 2.65\) (s, CH\(_3\)).

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

200 mg (0.47 mmol) \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\) dissolved in 15 ml acetonitrile were stirred under nitrogen and 60.6 mg (0.47 mmol) 1,4,7-triazacyclononane were added to the solution, producing an instantaneous change of colour from pale- to dark-yellow. The reaction solution was stirred for an additional 1/2 h. After concentration to 5 ml and addition of diethyl ether, 118 mg (55% yield) of yellow microcrystalline product precipitated. IR (CH\(_3\)CN): \(\nu(CO)\) 2025 m, 1918 s; \(\nu(PF_6)\) 840 cm\(^{-1}\). \(^{1}H\) NMR (acetone-\(d_{6}\)): \(\delta 2.17\) (s, 3 H, 3 CH\(_3\)); 3.0 (m, 12 H, 6 CH\(_2\)).

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

To 200 mg (0.47 mmol) \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\) in 15 ml acetonitrile 85 mg (0.47 mmol) 1,4,7-triazacyclononane were added. The reaction mixture was stirred at 60°C for 2 h and, by that time, some of the product had precipitated. The solution was allowed to cool until precipitation was complete and the solids were then collected by filtration, washed with ether and dried under reduced pressure. Addition of ether to the mother liquor improved the yield to 73% (174.3 mg). IR (CH\(_3\)CN): \(\nu(CO)\) 2045 m, 1965 s; \(\nu(PF_6)\) 840 cm\(^{-1}\). \(^{1}H\) NMR (acetone-\(d_{6}\)): \(\delta 3.05\) (broad s, 6 CH\(_3\)).

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

80 mg (0.5 mmol) 2,2'-bipyridine were added to a solution of 200 mg (0.47 mmol) \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\) in 10 ml acetonitrile and the mixture was stirred at 60-65°C under nitrogen for 4 h. The solvent was removed under reduced pressure and the residue washed three times with diethyl ether to give 176 mg (71.5% yield) of pale yellow microcrystalline product \(\text{[Tc(H}_{2}O)_{6}]PF_6}\) was obtained. IR (CH\(_3\)CN): \(\nu(CO)\) 2045 m, 1945 s; \(\nu(PF_6)\) 840 cm\(^{-1}\). \(^{1}H\) NMR (acetone-\(d_{6}\)): \(\delta 2.08\) (s, 3 H, CH\(_3\)); 7.62-7.77 (m, 2 H, 2 CH ring), 8.13-8.33 (m, 2 H, 2 CH ring), 8.40-8.49 (m, 2 H, 2 CH ring). 8.97-9.02 (m, 2 H, 2 CH ring).

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

Following the procedure described above, 200 mg (0.36 mmol) \(\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\) were treated with excess of P(O\(_{2}\)Pr\(_{3}\)) and refluxed for 2 h. 5 mg (20% yield) of product \(\text{[Tc}((CH\(_3\)CN)_{3}P(O\(_{2}\)Pr\(_{3}\))_{2}]PF_6\) was obtained.

\[\text{[Tc(CH}_{3}CN)_{2}(CO)_{3}]PF_6\]

The compound was prepared as described above using, in this case, a two-molar excess of P(O\(_{2}\)Pr\(_{3}\)). The reaction mixture was refluxed for 24 h; the yield was 70%.

Results and discussion

We have reported elsewhere \(^{15}\) a novel, high-field synthetic route to \(\text{Tc}_{2}(CO)_{10}\) (1), based on the reductive character of sodium amalgam in THF. This procedure starts from \(\text{NH}_{3}\text{TcO}_{2}\) and gives the decacarbonyl dimer in 70-80% yields when working at 100 atm of carbon monoxide and 120°C for three days. The scope and potential diversity of NOPF\(_6\) in acetonitrile for the preparation of new metal-acetonitrile complexes was first studied by Connelly and Dahl in 1970\(^{16}\). It was found that the decacarbonyls of rhenium and manganese react with NOPF\(_6\) in acetonitrile to form \([\text{M(CO)}_{5}(\text{CH}_{3}\text{CN})]^{+}\) species. These white crystalline complexes are air-stable, diamagnetic and soluble in polar solvents to give solutions unstable in air. We found that \(\text{Tc}_{2}(CO)_{10}\) was able to react in the same way giving the \(\text{Tc(I)}\) pentacarbonyl cation \(\text{[Tc}_{2}(CO)_{5}(\text{CH}_{3}\text{CN})]PF_6}\) in almost quantitatively yield in a few minutes under the same reaction conditions. Further solvolysis of 2 takes place in refluxing acetonitrile without the aid of other reagent to give \(\text{fac-[Tc(CH}_{3}CN)_{5}(CO)_{2}]PF_6}\). The fac configuration of the
carbonyl ligands has been inferred from the v(CO) bands in the infrared spectra. The facility with which the labile nitrite groups can be replaced by other types of ligands makes the pentacarbonyl an excellent starting material for the preparation of cationic technetium complexes.

During the preparation of the same type of unipositive carbonyls of manganese, Drew et al. observed that quantitative displacement of CH₃CN from [Mn(CH₃CN)₃(CO)₅]⁺ by Lewis bases was only possible when the reaction was carried out in a solvent other than acetonitrile. Complexes 2 reacts readily with macrocyclic ligands such as 1,4,7-triazacyclononane ([9]aneN₃), 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃[9]aneN₃), or 1,4,7-trithiacyclononane ([9]aneS₃) in acetonitrile at 60°C to give cationic tricarbonyl complexes of general formula [Tc(L)(CO)₃]PF₆ (Scheme 1). Cyclic triamines are known to form metal complexes of unusually high thermodynamic and kinetic stability due to the rather rigid steric constraints that these ligands impose to the metal. Complexes 3-5 are not air-sensitive in the solid state or in solution and they are soluble in acetonitrile, water and other polar organic solvents.

Reactions between 2 and bipyridines also take place in acetonitrile when kept at 60-65°C for 4 hours, probably via initial formation of [Tc(CH₃CN)₃(CO)₅][PF₆] followed by replacement of two acetonitrile ligands by the bipyridine. We also found that, in fact, no reaction would take place between the bipyridine complexes and phosphine as long as excess of acetonitrile was present, even at reflux temperature. It was necessary to use another solvent, e.g., acetone, in order to achieve conversion to the mixed complexes [Tc(N,N)₃][P(OR)₃]₂(CO)₂]PF₆ (6-9). Scheme 2 shows this synthetic route starting from 2. A widely used method of identification for metal carbonyls involves IR spectroscopy. The C-O stretching mode is sufficiently affected by the kind of metal present and the symmetry properties of the molecule, which permits rather easy identification of most compounds. In general, they all show at least one absorption maximum in the 2000-cm⁻¹ region as a reflection of the metal-CO interaction.

The spectrum of the pentacarbonyl shows the three-band pattern of carbonyl stretching modes (2A₁ + E) characteristic of C₅₃₉₅₄mm symmetry. Complexes 3-5 show the well known two-band spectral pattern of carbonyl stretching modes (A₁ + E) characteristic of C₃ᵥ symmetry for these simple tricarboxyls cations. From the two intense v(CO) bands observed in every case, we conclude that the dicarboxylic derivatives 6-9 must have a cis configuration. This is in agreement with the assumption that the reaction takes place via initial formation of [ac-Tc(CH₃CN)₃(CO)₅][PF₆] because, in that case, the cis strong labilizing effect of both N atoms of bipyridine would cause the second entering phosphite ligand to replace the CO trans to the first phosphite. This means that from the two possible isomers: cis,trans and cis,cis (Figure 2), only the first one is formed. Unfortunately, due to the same local symmetry (C₃ᵥ) of the carbonyl groups in these two isomers it is not possible to corroborate this assumption on basis of their v(CO) absorptions.

![Scheme 2](image)

**Scheme 2**

**Figure 1.** cis,trans and cis,cis isomers of complexes 6-9.

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References


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