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Preparation and Characterization of $TcCl_3(PPh_3)_2(MeCN)$ and Its Reactions with Small π-Accepting Ligands

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The preparation and characterization of (acetonitrile)trichlorobis(triphenylphosphine)technetium(III) from (n-Bu_4N)[$TcOCl_4$] with triphenylphosphine in acetonitrile solvent is described. The potentially rich reaction chemistry of this complex is discussed in relation to $ReCl_3(PPh)_2(MeCN)$. Reactions of $TcCl_3(PPh_3)_2(MeCN)$ with CO and NO are described. Characterization of the products, carbonyltrichlorobis(triphenylphosphine)technetium(III) and trichloronitrosylbis(triphenylphosphine)technetium(II), is also described. The carbonyl complex, $C_{37}H_{30}Cl_3OP_2Tc$, which crystallizes in space group $C2/c$ with a = 24.649 (9) Å, b = 9.530 (3) Å, c = 15.870 Å, β = 116.40 (3)°, V = 3339 (4) Å^3, and Z = 4, was structurally characterized. The Tc—C bond distance of 1.985 (9) Å as well as the C≡O stretching frequency of 2054 cm^{-1} is indicative of the absence of significant π-back-bonding in this complex.

Introduction

There has been a great deal of study of technetium complexes with tertiary phosphine ligands that was due, in part, to the prospects[2] of a ^{99m}Tc–phosphine myocardial imaging agent. A limitation in this research was imposed by the lack of suitable technetium phosphine starting materials that could readily be prepared in good yields. The most notable starting materials,[3] $TcCl_4P_2$ (P = PPh_3, PMe_2Ph) and $TcCl_3(PMe_2Ph)_3$ have some drawbacks. The former is a complex of technetium(IV) that often undergoes unpredictable redox changes in addition to ligand substitution. The latter complex cannot be prepared with triphenylphosphine, presumably due to the large steric requirement of this ligand, which inhibits cis-octahedral coordination.

Trop[4] noted that the oxotetrachlorotechnetate ion reacted with triphenylphosphine in acetonitrile to give an unidentified orange material. We now report an improved preparation of this material and its identification as $TcCl_3(PPh_3)_2(MeCN)$. Since the analogous rhenium complex,[5] $ReCl_3(PPh_3)_2(MeCN)$, has been shown to be a useful synthetic reagent, some reactions of the technetium complex were performed to explore its utility.

Experimental Section

Instrumentation. Fourier transform IR spectra were measured from 4800 to 400 cm^{-1} on an IBM IR/30S spectrometer with a DTGS detector and a 2-cm^{-1} bandwidth. ^{1}H NMR spectra were recorded at 300 MHz on a Varian XL-300 spectrometer. X-Band ESR spectra were recorded on a Varian E-line spectrometer or on a Bruker ESP 300 spectrometer equipped with a variable-temperature accessory.

Fast atom bombardment mass spectra were measured on samples dissolved in a 3-nitrobenzyl alcohol matrix by using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV. The source was equipped with an Ion Tech B11N FAB gun producing a beam with 6–8-keV xenon neutrals.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8451A photodiode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses. *Caution*! ^{99}Tc is a β^- emitter ($t_{1/2}$ = 2.1 × 10^5 years). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes with precautions outlined elsewhere.[6]

All solvents were of at least reagent grade and were used as received, except for toluene, which was distilled under N_2 from sodium. The complex (n-Bu_4N)[$TcOCl_4$] was prepared[7] by literature methods.

Preparation of $TcCl_3(PPh_3)_2(MeCN)$. To 103.97 mg of (n-Bu_4N)[$TcOCl_4$] (0.208 mmol) in a disposable vial was added with stirring 256 mg of triphenylphosphine dissolved in 12 mL of MeCN. The solution rapidly became very dark, but within 1 min it was bright orange. Precipitation was then induced by adding a glass bead, which was agitated by the magnetic stirbar. The solution was stirred for an additional 10 min while the bright orange solid precipitated. The precipitate was collected on a medium-porosity fritted glass funnel and rinsed with 10 mL of MeCN followed by 2 mL of hexane. After drying in vacuo overnight, the product weighed 98.75 mg (62% yield). This material is slightly soluble with slow decomposition in MeCN, acetone, and toluene. It decomposes more rapidly in CH_2Cl_2.

Anal. Calcd for $C_{38}H_{33}Cl_3NP_2Tc$: C, 59.21; H, 4.31; Cl, 13.79; N, 1.82. Found: C, 58.99; H, 4.43; Cl, 13.17; N, 1.89.

IR (KBr): 3055 (w), 2928 (w), 2917 (w), 1481 (m), 1433 (s), 1400 (w), 1385 (w), 1367 (w), 1316 (w), 1189 (w), 1163 (w), 1120 (w), 1091 (m), 1072 (w), 1027 (w), 998 (w), 753 (w), 747 (m), 742 (m), 696 (s), 521 (s), 511 (s), 496 (m), 479 (w), 454 (w) cm^{-1}. FABMS(+), m/z [ion, abundance]: 769 [M$^+$, 19%], 728 [(M – MeCN)$^+$, 91%], 693 [(M – MeCN – Cl)$^+$, 100%].

Preparation of $TcCl_3(PPh_3)_2(NO)$. To 35.24 mg of $TcCl_3(PPh_3)_2$(MeCN) (0.046 mmol) in a nitrogen-purged 50-mL round-bottomed flask with a sidearm was added 15 mL of toluene. Nitric oxide (Matheson) was then bubbled through the resulting suspension warmed with a water bath. The acetonitrile starting material dissolved as it reacted, forming a green solution. The reaction was allowed to proceed for a total of 35 min. An aliquot of the reaction mixture gave an electron spin resonance spectrum consisting of a three-line pattern ($\langle g\rangle \sim 2.0$, $\langle a\rangle \sim$ 12 G) due to NO superimposed on a ten-line pattern ($\langle g\rangle \sim 2.0$, $\langle a\rangle$ $\sim$ 130 G) due to the technetium(II) complex. The remaining green solution was filtered, and the solvent was evaporated under reduced pressure. The residue was recyrstallized from CH_2Cl_2/MeOH, yielding a dark green microcrystalline solid.

IR (KBr): ν(NO) 1805 cm^{-1} (vs). FABMS(+), m/z [ion, abundance]: 723 [(M – Cl)$^+$, 89%], 688 [(M – 2Cl)$^+$, 100%].

Preparation of $TcCl_3(PPh_3)_2(CO)$. To 28.38 mg of $TcCl_3(PPh_3)_2$(MeCN) (0.037 mmol) in a nitrogen-purged 100-mL round-bottomed flask was added 20 mL of toluene. Carbon monoxide (Matheson) was then bubbled through the resulting suspension, which was warmed to 65 °C. The acetonitrile starting material dissolved as it reacted, forming a clear wine red solution within 10 min. The bubbling of CO continued for an additional 5 min to ensure complete reaction. The reaction mixture was filtered through paper, and the solvent was evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2/heptane, yielding 17.27 mg (62%) of small red prisms.

Anal. Calcd for $C_{37}H_{30}Cl_3OP_2Tc$: C, 58.64; H, 3.99; Cl, 14.03. Found: C, 57.58; H, 3.98; Cl, 14.19. A separate preparation gives the following: C, 57.51; H, 3.94.

IR (KBr): ν(CO) 2054 cm^{-1} (vs). ^{1}H NMR ($CDCl_3$): δ 9.9 (broad, 12 H), 7.5 (broad with shoulder, 18 H). Visible (CH_2Cl_2), λ_{max} (ϵ): 562 nm (770 l·mol^{-1}·cm^{-1}). FABMS(+), m/z [ion, abundance]: 693 [(M – Cl – CO)$^+$, 100%], 686 [(M – 2Cl)$^+$, 95%].

X-ray Structure Determination of $TcCl_3(PPh_3)_2(CO)$. A small red prism grown by heptane diffusion into a CH_2Cl_2 solution of $TcCl_3(PPh_3)_2(CO)$ having approximate dimensions 0.1 × 0.1 × 0.3 mm was mounted on a glass fiber. Crystal density was determined by suspension in an aqueous CsCl solution. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. On the basis of systematic absences (hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$), a statistical analysis of intensity distribution, and the

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Table I. Crystallographic Data for $TcCl_3(PPh_3)_2(CO)$

$C_{37}H_{30}Cl_3OP_2Tc$	space group $C2/c$ (No. 15)
fw 755.95	$T = 23$ °C
$a = 24.649$ (9) Å	$\lambda = 0.71069$ Å
$b = 9.530$ (3) Å	$\rho_{obsd} = 1.52$ g cm^{-3}
$c = 15.870$ (6) Å	$\rho_{calcd} = 1.504$ g cm^{-3}
$\beta = 116.40$ (3)°	$\mu = 7.78$ cm^{-1}
$V = 3339$ (4) Å^3	$R(F_o) = 0.036$
$Z = 4$	$R_w(F_o) = 0.043$

successful solution and refinement of the structure, the monoclinic space group was determined to be $C2/c$.

The intensity data were collected by using the ω-scan technique to a maximum 2θ value of 45.0°. A total of 2402 reflections were measured, of which 2336 were unique ($R_{int} = 0.026$). Of these reflections, 1587 had $I > 3\sigma(I)$ and were used in subsequent calculations.[8] The data were corrected for Lorentz and polarization effects, but no absorption correction was made. Neutral-atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were taken from ref 9. Anomalous dispersion effects were included in structure factor calculations.[10]

The technetium atom was located by the Patterson method, and the remaining non-hydrogen atoms were found by a difference Fourier synthesis. All of the non-hydrogen atoms were refined anisotropically by using a full-matrix least-squares algorithm that minimized the function $\sum 4F_o^2(|F_o| - |F_c|)^2/\sigma^2(F_o^2)$. The hydrogen atoms were not refined but were included in the structure factor determinations in calculated positions.

Table II. Selected Bond Distances (Å) and Angles (deg) for $TcCl_3(PPh_3)_2(CO)$ (Primed Atoms Generated by 2-Fold Rotation)

Tc–C(1)	1.985 (9)	Tc–P	2.525 (2)
Tc–Cl(1)	2.322 (2)	Tc–Cl(2)	2.397 (2)
C(1)–O	1.12 (1)	P–C(11)	1.825 (6)
P–C(21)	1.829 (5)	P–C(31)	1.824 (5)
C(1)–Tc–Cl(1)	84.71 (4)	C(1)–Tc–P	89.65 (4)
Cl(1)–Tc–Cl(1)′	169.43 (8)	Cl(1)–Tc–Cl(2)	95.29 (4)
Cl(1)–Tc–P	88.14 (6)	Cl(1)–Tc–P′	91.79 (6)
Cl(2)–Tc–P	90.35 (4)	P–Tc–P′	179.3 (1)
C(31)–P–C(21)	104.6 (2)	C(31)–P–C(11)	105.6 (2)
C(31)–P–Tc	109.0 (2)	C(21)–P–Tc	116.8 (2)
C(21)–P–C(11)	101.0 (2)	C(11)–P–Tc	118.4 (2)

Table III. Positional Parameters for $TcCl_3(PPh_3)_2(CO)$

atom	x	y	z
Tc	0	0.17081 (7)	$^1/_4$
Cl(1)	−0.05375 (7)	0.1484 (2)	0.0878 (1)
Cl(2)	0	0.4223 (2)	$^1/_4$
P	0.09622 (6)	0.1692 (2)	0.2305 (1)
O	0	−0.1546 (6)	$^1/_4$
C(1)	0	−0.037 (1)	$^1/_4$
C(11)	0.1612 (2)	0.2687 (6)	0.3140 (4)
C(12)	0.1579 (2)	0.3504 (6)	0.3830 (4)
C(13)	0.2074 (3)	0.4276 (6)	0.4438 (4)
C(14)	0.2600 (3)	0.4249 (7)	0.4350 (4)
C(15)	0.2633 (3)	0.3475 (8)	0.3646 (5)
C(16)	0.2146 (3)	0.2692 (8)	0.3050 (5)
C(21)	0.0909 (2)	0.2339 (6)	0.1186 (4)
C(22)	0.0701 (3)	0.3691 (6)	0.0911 (5)
C(23)	0.0688 (3)	0.4269 (7)	0.0105 (5)
C(24)	0.0868 (3)	0.3477 (7)	−0.0449 (4)
C(25)	0.1064 (3)	0.2148 (7)	−0.0198 (4)
C(26)	0.1090 (3)	0.1575 (6)	0.0618 (4)
C(31)	0.1227 (2)	−0.0112 (6)	0.2381 (4)
C(32)	0.1733 (3)	−0.0605 (7)	0.3148 (4)
C(33)	0.1871 (4)	−0.2036 (8)	0.3218 (5)
C(34)	0.1520 (4)	−0.2944 (7)	0.2550 (6)
C(35)	0.1014 (3)	−0.2476 (7)	0.1779 (5)
C(36)	0.0872 (3)	−0.1076 (6)	0.1690 (5)

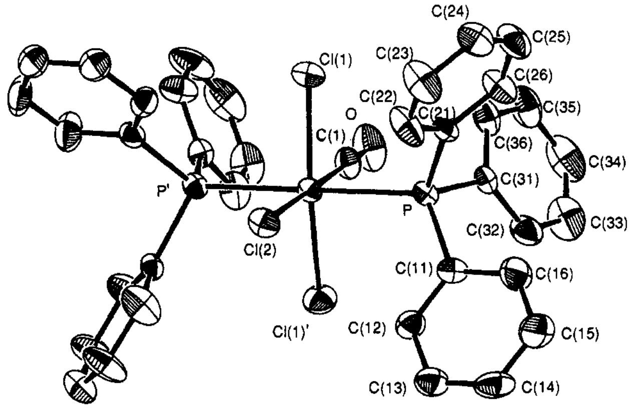

Figure 1. ORTEP representation of $TcCl_3(PPh_3)_2(CO)$ showing 50% probability ellipsoids. The primed atoms are generated by 2-fold symmetry.

Results and Discussion

The reduction of $ReOCl_3(PPh_3)_2$ with triphenylphosphine, forming $ReCl_3(PPh_3)_2(MeCN)$, was shown to require the prior coordination of acetonitrile.[5] Furthermore, oxo-transfer reactions in which oxotechnetium(V) complexes are converted to technetium(III) complexes are well established with PR_3 as the oxygen atom acceptor.[11] It is not surprising, therefore, that the reduction of the oxotetrachlorotechnetate anion with triphenylphosphine also only appears to proceed cleanly in the presence of acetonitrile. Since the product, $TcCl_3(PPh_3)_2(MeCN)$, is unstable toward aerial oxidation while in solution, its rapid precipitation from the reaction mixture is essential when the reaction is carried out in air. Induction of crystallization is conveniently provided by placing a glass bead in the stirred reaction mixture, creating nucleation sites on the walls of the reaction vessel. Solutions of this complex, however, may be safely manipulated under a nitrogen atmosphere.

The characterization of this product as (acetonitrile)trichlorobis(triphenylphosphine)technetium(III) is straightforward on the basis of analogy with the rhenium complex[5] as well as the fast atom bombardment mass spectrum showing the molecular ion and sequential losses of MeCN and Cl. The elemental analysis fits well for C, H, and N but deviates by 0.62% for Cl. No infrared band attributable to ν(CN) of the nitrile is observed; however, this phenomenon has also been noted for the rhenium analogue.[5]

Substitution reactions of $ReCl_3(PPh_3)_2(MeCN)$ follow a predictable course depending on the nature of the incoming ligands. Addition of neutral ligands displaces first the acetonitrile ligand and then the phosphine ligands.[5,12,13] In contrast, salts of anionic ligands substitute first for the chlorides via elimination of alkali-metal chlorides.[14,15] It is expected that $TcCl_3(PPh_3)_2(MeCN)$ should have substitution chemistry similar to that of its rhenium analogue. The reaction of $TcCl_3(PPh_3)_2(MeCN)$ with carbon monoxide gas in toluene cleanly replaces just the acetonitrile ligand with a carbonyl group, yielding carbonyltrichlorobis(triphenylphosphine)technetium(III). It is surprising, therefore, that this reaction has not been reported with rhenium.

A single-crystal X-ray structure determination of this carbon monoxide derivative was carried out. Pertinent crystallographic data are given in Table I, and selected bond distances and angles are given in Table II. Table III lists the positional parameters for the atoms of the asymmetric unit. The molecule, shown in Figure 1, has crystallographically imposed 2-fold rotational symmetry about the axis defined by Tc, C(1), O, and Cl(2). As expected on steric grounds, the phosphine ligands are disposed mutually trans and the chlorine atoms are meridional. The coordination geometry of the technetium atom is nearly octahedral,

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though the equatorial chlorine atoms (Cl(1)-Tc-C(1) = 84.71 (4)°) but not the equatorial phosphines (P-Tc-C(1) = 89.65°), are significantly displaced toward the axial carbonyl ligand. The equatorial Tc-Cl(1) bond lengths at 2.322 (2) Å are shorter than expected for technetium(III) complexes of this type.[16] Furthermore, the technetium-phosphorus bonds are quite long (2.525 (2) Å) when compared with those of other triphenylphosphine complexes of technetium(III) (2.44-2.52 Å).[16,17]

The technetium carbonyl complex has an intense infrared band at 2054 cm^{-1} assigned as $\nu(CO)$. The high frequency of $\nu(CO)$ in this complex is suggestive of terminal carbonyl ligation with minimal π-back-bonding.[18] This hypothesis is supported by the unusually long technetium-carbon bond length of 1.985 (9) Å, though the carbon-oxygen distance of 1.12 (1) Å is within experimental error of the norm.[16] Although *mer*-$TcCl_3(PMe_2Ph)_3$ reacts with CO to form[19] the diamagnetic C_{3v} seven-coordinate complex $TcCl_3(PMe_2Ph)_3(CO)$, there is no evidence for the formation of a seven-coordinate dicarbonyl complex in the acetonitrile substitution reaction described above. This difference in reactivity may be attributed to the greater σ-basicity of PMe_2Ph compared to PPh_3, leading to a higher affinity for π-acids (e.g. CO) in complexes of the former.

The reaction of $TcCl_3(PPh_3)_2(MeCN)$ with nitric oxide is similar to the reaction with CO, except that there is now a change in the formal oxidation state of the technetium, yielding trichloronitrosylbis(triphenylphosphine)technetium(II). The assignment of the unpaired electron onto the metal is verified by the presence of a ten-line pattern in the electron spin resonance (ESR) spectrum of the isolated complex dissolved in CH_2Cl_2 attributed to hyperfine coupling to a ^{99}Tc nucleus, which has nuclear spin $I = {}^9/_2$. No phosphorus superhyperfine coupling, however, was noted in this solution spectrum. The NO stretching mode in the infrared spectrum at 1805 cm^{-1} is consistent with a terminal linear NO^+ linkage.[20] This complex is entirely analogous to the complex $TcCl_3(PMe_2Ph)_2(NO)$, previously prepared[21] from the tris(phosphine)-trichloride starting material. Although the solution and low-temperature glass ESR spectra for these two analogues appear identical, a slight lowering of $\nu(NO)$ is noted for the PMe_2Ph derivative, which may be understood similarly to the carbonyl phosphines discussed above.

Conclusions

The complex $TcCl_3(PPh_3)_2(MeCN)$ is readily prepared in high yields. By analogy to its rhenium cogener, it promises to be a useful starting material for low-valent technetium chemistry. It reacts with the small potentially π-accepting molecules CO and NO, but they do not participate appreciably in back-bonding.

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Supplementary Material Available: For $TcCl_3(PPh_3)_2(CO)$, listings of anisotropic thermal parameters and torsion angles and, for $TcCl_3(PPh_3)_2(NO)$, a frozen-glass EPR spectrum (5 pages); for $TcCl_3(PPh_3)_2(CO)$, a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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Efficient Syntheses of Dioxorhenium(V) Complexes

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An improved general synthesis for $[ReO_2L_4]X$ complexes is presented. The amine complex $[ReO_2(en)_2]I$ can be made in 90% yield from $[ReO_2(PPh_3)_2I]$ and ethylenediamine in less than 15 min at room temperature. Refluxing methanol suspensions of $[ReO_2(PPh_3)_2I]$ with 12-50 equiv of electron-rich pyridines results in the formation of $[ReO_2L_4]I$ compounds in 50-85% yield.

Introduction

The complex $[ReO_2(py)_4]^+$ has been shown to exhibit a long-lived luminescence in aprotic solvents (τ = 10 μs) that is efficiently quenched by hydroxylic compounds[1] and by electron transfer to viologen acceptors.[2] The luminescence lifetime of this compound is highly dependent on the environment. It has been found that this complex is an effective probe of the hydrophobicity of binding regions in micelles[3] and the intracrystalline environments of complex-layered oxides.[4] For these reasons, we became interested in the tunability of ReO_2^+ species in terms of both ground-state and excited-state properties. Unfortunately, the existing synthetic methods[5] are not suitable for use with hydrophobic or high melting pyridines. We therefore sought an alternative route for smooth insertion of the ReO_2^+ unit into a variety of ligand environments.

The Re(IV) compound K_2ReCl_6 is the common starting material for the syntheses of coordination complexes containing the ReO_2^+ unit. For example, the compound $[ReO_2(py)_4]Cl$ is obtained (in 34-60% yield) by bubbling O_2 through an aqueous pyridine solution of K_2ReCl_6.[5a]

$$2K_2ReCl_6 + 14py + {}^1/_2O_2 + 7H_2O \rightarrow 2[ReO_2(py)_4]Cl\cdot 2H_2O + 6(pyH)Cl + 4KCl$$

In a similar fashion, the ethylenediamine complex $[ReO_2(en)_2]Cl$ is synthesized by reacting K_2ReCl_6 in aerated 90% ethylenediamine for a 12-h period.[5c,6]

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