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The synthesis of a technetium(V) phenylimido complex from pertechnetate. The single crystal X-ray structure of $[TcCl_3(NPh)(PPh_3)_2]\cdot CH_2Cl_2$

Terrence Nicholson[a, b] *, Alan Davison[a] and Alun G. Jones[b]

[a] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (U.S.A.)*

[b] *The Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, MA 02215 (U.S.A.)*

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Abstract

The reaction of $(NH_4)[TcO_4]$ with triphenylphosphine and the organohydrazine *N*-acetyl, *N'*-phenylhydrazine $(PhNHNHC{=}OCH_3)$ in methanol with a minimal amount of $HCl_{(aq)}$ gives the neutral Tc(V) complex $[Tc(NPh)Cl_3(PPh_3)_2]$ in very good yields. The IR spectrum of this complex displays a strong band in the 1090 cm^{-1} region which has tentatively been assigned to $\nu(Tc{\equiv}N)$. The (+)FAB mass spectrum does *not* show the peak associated with the neutral parent species $[TcCl_3(NPh)(PPh_3)_2]$. However, a prominent feature of 784 *m/z* is associated with the fragment generated from the loss of a chloride ligand, giving the cationic species $[TcCl_2(NPh)(PPh_3)_2]^+$. Other peaks present in the mass spectrum correspond to the fragments $[TcCl_2(NPh)(PPh_3)]^+$ of 522 *m/z* and $[TcCl(NPh)(PPh_3)]\cdot H^+$ of 488 *m/z*. The diamagnetic Tc(V) complex displays a ^1H NMR spectrum with the proton signals from the imido-phenyl group resolved from those of the phosphine-phenyl groups. The complex displays distorted octahedral molecular coordination geometry, with mutually *trans* triphenylphosphine ligands and equatorial phenylimido and chloride ligands. The technetium–nitrogen bond length is 1.704(4) Å with a technetium–nitrogen–carbon bond angle of 171.8(4)°, which reflects the sp hybridization of the phenylimido nitrogen atom. Bond lengths and angles involving the chloride and phosphine ligands are unexceptional for technetium in the +5 oxidation state. Crystal data for $C_{43}H_{37}NP_2Cl_5Tc$: triclinic space group $P\bar{1}$, $a=10.8651(9)$, $b=12.2236(9)$, $c=16.867(2)$ Å, $\alpha=71.998(7)°$, $\beta=74.078(7)°$, $\gamma=80.336(7)°$, $V=2040.2$ Å^3, with $D_{calc}=1.455$ g cm^{-3} to give $Z=2$. Structure solution based on 9334 reflections converged at $R=0.054$, $R_w=0.053$, $GOF=1.35$. In an analogous reaction, $[TcO_4]^-$ reacts with benzoylhydrazine $(PhC{=}ONHNH_2)$ and triphenylphosphine in methanol with HCl to give the Tc(V) nitrido complex $[TcNCl_2(PPh_3)_2]$ in excellent yields.

Introduction

The organoimido core, (M≡N–R), may prove to be of great synthetic utility in radiopharmacology, since a variety of organic substituents can be incorporated into a stable technetium–nitrogen core. This property may allow the chemical 'fine-tuning' of the complexes' biological properties by simply altering the imido group's organic substituent –R. The organoimido unit, in its linear conformation (A), is formally isoelectronic to the oxo group. It can also adopt a bent conformation, with a lone pair of electrons residing on the nitrogen atom (B), see Fig. 1. This core can ultimately be expected to form a whole new class of technetium complexes based on established technetium–oxo chemistry.

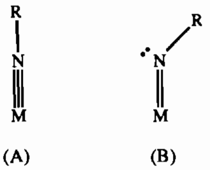

Fig. 1. Linear (A) and bent (B) coordination geometries for the organoimido core.

We have previously reported the synthesis and characterization of the first technetium complex to incorporate the organoimido core, $[TcCl(NPh)(PhNNCON_2HPh)_2]$ [1]. This neutral complex was synthesized from the reaction of $(Bu_4N)[TcOCl_4]$ and the organohydrazine phenylazo formic acid 2-phenylhydrazide, $(PhNHNHCON_2Ph)$. The phenylimido unit is incorporated into the technetium complex through the fragmentation of the disubstituted

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*Author to whom correspondence should be addressed.

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organohydrazine, in a manner analogous to that presented below.

Recently Dilworth and co-workers published the synthesis of the arylimido complex $(Bu_4N)[Tc(NC_6H_4\text{-}p\text{-}CH_3)Cl_4]$, which was made from the reaction of $(Bu_4N)[TcOCl_4]$ and ArNCO in dry toluene under nitrogen [2]. This anionic species was reported to be moisture sensitive. The more stable Tc(V) species $[TcCl_3(NAr)(PPh_3)_2]$ was synthesized from the reaction of $(Bu_4N)[TcOCl_4]$, an aromatic amine and triphenylphosphine [2]. This complex can be expected to be a very useful synthetic precursor. However, any application of these complexes toward the development of diagnostic imaging agents is of very limited scope due to the cumbersome procedures necessary to generate both $(Bu_4N)[Tc(NAr)Cl_4]$ and $(Bu_4N)[TcOCl_4]$, neither of which is practical at the tracer level with the isotope ^{99m}Tc employed in nuclear medicine.

We have now developed a simple, 'one pot' synthesis of the neutral Tc(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ from ammonium pertechnetate, triphenylphosphine, 1-acetyl,2-phenylhydrazine and HCl in methanol. The phenylimido unit is generated through the cleavage of the N–N bond in the organohydrazine.

In a similar synthetic scheme, benzoylhydrazine reacts with the pertechnetate ion in the presence of triphenylphosphine and HCl in methanol to precipitate the neutral, five-coordinate Tc(V) nitrido species $[TcNCl_2(PPh_3)_2]$. This reaction is presumed to proceed through a similar mechanism, with the benzamide ($PhCONH_2$) eliminated from the coordinated benzoylhydrazine.

Experimental

Caution: technetium-99 is a weak β^--emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [3]. The ammonium pertechnetate was supplied as a gift by DuPont-Biomedical Products. Reagents and solvents were used as received unless otherwise stated. The benzoylhydrazine was obtained from Alfa Chemicals, while the 1-acetyl,2-phenylhydrazine was obtained from Aldrich Chemicals.

Routine IR spectra were obtained on a Mattson Cygnus 100 FTIR spectrometer. Fast atom bombardment(+) spectra of samples dissolved in *p*-nitrobenzyl–alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with a Ion Tech B11N FAB gun, operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Electronic spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL-300 FTNMR spectrometer. Analytical results were obtained from Atlantic Microlab Inc., Norcross, GA.

X-ray crystallographic data collection parameters

The crystal data and experimental details of the structure determination are given in Table 1. The crystal exhibited no significant decay under X-irradiation.

A yellow-green prismatic crystal of complex **1** was isolated from the methylene chloride–methanol–diethyl ether mixture as described below. The crystals dimensions were $0.12 \times 0.10 \times 0.10$ mm. The diffractometer employed was a CAD-4 with the data set collected at room temperature. The scan mode used was ω–2θ, with a maximum 2θ of 54.9°. A total of 9334 unique reflections was collected of which 5694 were of $I > 3\sigma(I)$ and were used in the final structure refinement. The technetium atom was located using the Patterson method. Neutral atomic scattering factors were used throughout the analysis. Extinction effects were not observed. Hydrogen atoms were located and refined. All non-hydrogen atoms were refined anisotropically.

Syntheses:

$[TcCl_3(NPh)(PPh_3)_2]$ (1)

A 1 ml sample of aqueous $(NH_4)[TcO_4]$, (0.35 M), was evaporated to dryness with a rotary evaporator, and subsequently dissolved in 100 ml of methanol.

TABLE 1. X-ray data for structure determination of complex **1**

Empirical formula	$C_{43}H_{37}NP_2Cl_5Tc$
Formula weight	893.91
Crystal system	triclinic
a (Å)	10.8651(9)
b (Å)	12.2236(9)
c (Å)	16.687(2)
α (°)	71.998(7)
β (°)	74.078(7)
γ (°)	80.336(7)
V (Å^3)	2040.2(7)
Space group	$P\bar{1}$
Z	2
D_{exp} (g cm^{-3})	1.445
μ (cm^{-1})	7.76
Radiation[a] (λ, Å)	Mo Kα (0.71069)
Temperature (°C)	23
T_{max}, T_{min}	1.26, 0.78
R, R_w	0.054, 0.053
Goodness of fit	1.35

[a] Graphite monochromated.

To this solution was added 0.092 g (1.1 equiv.) of the organohydrazine $PhNHNHCOCH_3$ and 0.45 g (5 equiv.) of triphenylphosphine. The resulting solution was brought to reflux, with the color changing from colorless, to gray–green, to a dull brown. At this point, the solution was removed from heat, cooled to room temperature and ~6 drops of concentrated hydrochloric acid added, which gradually caused the desired complex to form as a yellow–brown microcrystalline precipitate from the red solution. This solution was stirred at room temperature for 15 min. The product was then isolated on a fine, fritted funnel. The complex was washed with 50 ml of methanol, dried under vacuum and recrystallized from methylene chloride layered with methanol and diethyl ether, giving yellow–green X-ray quality crystals within 24 h at room temperature. Yield 68–75%.

Analytical results for a crystalline sample of $[TcCl_3(NPh)(PPh_3)_2]$ (which contains one molecule of methylene chloride of solvation): Calc. for $[TcCl_3P_2NC_{42}H_{35}\cdot CH_2Cl_2]$: C, 56.96; H, 4.12; N, 1.55; Cl, 19.57. Found: C, 56.57*; H, 4.03; N, 1.56; Cl, 19.72%. FAB-MS(+): $[TcCl_2(NPh)(PPh_3)_2]^+$, 784 *m/z*; $[TcCl_2(NPh)(PPh_3)]^+$, 522 *m/z*; $[TcCl(NPh)(PPh_3)]\cdot H^+$, 488 *m/z*. IR (KBr): $\nu(Tc{\equiv}N)$: 1090 cm^{-1}; $\nu(C–N)$: 1320 cm^{-1}. Electronic spectroscopy ($\epsilon = 1$ mol^{-1} cm^{-1}) in methylene chloride: $\lambda_{max} = 232$ nm ($\epsilon = 4.42 \times 10^4$), $= 300$ nm ($\epsilon = 3.52 \times 10^4$), $= 364$ nm ($\epsilon = 9.40 \times 10^3$). ^1H NMR (CD_2Cl_2, 22 °C): δ 7.88–7.74 (m, 12H, ArH-PPh_3); δ 7.54–7.46 (t, 1H, N-Ph-*p*); δ 7.18–7.34 (m, 18H, ArH-PPh_3); δ 7.08–7.12 (d, 2H, N-Ph-*o*); δ 6.72–6.79 (t, 2H, N-Ph-*m*).

$[TcNCl_2(PPh_3)_2]$ (2)

A 1 ml sample of aqueous $(NH_4)[TcO_4]$ (0.39 M) was evaporated to dryness under vacuum and redissolved in 75 ml of methanol. To this was added 0.255 g triphenylphosphine and 0.132 g of benzoylhydrazine. The resulting solution was refluxed for 15 min generating a light yellow solution. To this was added 7 drops of concentrated hydrochloric acid, which caused the color to darken to orange–brown. The heat was then removed, and the solution allowed to stir at room temperature for 15 min, during which time a peach colored precipitate formed. The product was isolated on a fritted funnel, washed with dry methanol and diethyl ether, and then dried under vacuum. Yield 83–88%.

Anal. for $[TcNCl_2(PPh_3)_2]$ $TcCl_2P_2NC_{36}H_{30}$: Calc.: C, 61.03*; H, 4.27; N, 1.98; Cl, 10.01. Found: C, 59.55*; H, 4.26; N, 1.98; Cl, 9.95%. IR (KBr): $\nu(Tc{\equiv}N)$, 1100 cm^{-1}. The IR spectrum of this product is identical to that of $[TcNCl_2(PPh_3)_2]$ prepared by the literature method.

Results and discussion

The rhenium(V) oxo complex $[ReOCl_3(PPh_3)_2]$ has, since its discovery, proven to be a excellent synthetic precursor due to the facile displacement of both the chloride and phosphine ligands. It has not to date been possible to synthesize the technetium analogue $[TcOCl_3(PPh_3)_2]$, due to the ease of the oxo-group abstraction with the second row metal. However, nitrogen based cores, such as the phenylimido unit, are frequently less labile than the oxygen-based analogues, thus the phenylimido derivative $[TcCl_3(NPh)(PPh_3)_2]$ may prove to be a very useful and versatile synthetic precursor for technetium chemistry.

The analogous rhenium phenylimido complex has been synthesized from the reaction of $[ReOCl_3(PPh_3)_2]$ with a variety of reagents including $Ph_3P{=}NAr$ [5], ArNCO [6], ArNSO [7], $ArNH_2$ [8] and 1-acetyl,2-phenylhydrazine [9]. The latter reagent, the organohydrazine ($PhNHNHCOCH_3$), appears to fragment in such a manner as to allow the metal complex to incorporate the phenylimido moiety.

In a similar procedure, the technetium phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ has been synthesized, from the reaction of ammonium pertechnetate, triphenylphosphine and 1-acetyl,2-phenylhydrazine in methanol with the addition of hydrochloric acid, in good yields. The procedure represents a significant improvement from the synthesis involving the intermediate $(Bu_4N)[TcOCl_4]$, since the reaction proceeds in an alcoholic medium, at relatively mild pH, directly from pertechnetate. This synthetic protocol may prove applicable to synthesis at the tracer level. The synthesis involves refluxing the anhydrous pertechnetate, triphenylphosphine and the organohydrazine in methanol, forming an as yet unidentified intermediate, which subsequently reacts with HCl to precipitate the desired complex.

The electron releasing effect of the phenyl group on the disubstituted organohydrazine makes the α-nitrogen more basic than the β-nitrogen, whose basicity is diminished by an electron withdrawing effect of the acetyl group. Coordinated in this manner, the proton introduced as HCl can only attack at the β-nitrogen, generating the cationic species depicted below. This species can eliminate acetamide through the cleavage of the N–N bond, incorporating the

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*It has been previously reported in our laboratories that, although samples analyze extremely well for other elements, carbon analyses can be up to one carbon low [4]. A possible explanation is that an incomplete combustion results from the formation of residual technetium carbide.

phenylimido unit and subsequently yielding the complex $[TcCl_3(NPh)(PPh_3)_2]$ (see Fig. 2.).

The presence of a organohydrazine containing intermediate is supported by the fact that under the given reaction conditions, the Tc(IV) complex $[TcCl_4(PPh_3)_2]$ is formed if the organohydrazine is not coordinated in some manner prior to the addition of the HCl. No $[TcCl_4(PPh_3)_2]$ was detected in the mass spectrum of the isolated crude product unless less than one equivalent of the organohydrazine is used in the reaction. Additional evidence for the proposed organohydrazide intermediate is the fact that $[TcCl_4(PPh_3)_2]$ fails to react with the organohydrazine to form the phenylimido complex. The presence of the organohydrazide containing intermediate is also supported by the color changes observed prior to the addition of the hydrochloric acid.

The neutral, octahedral phenylimido complex is formally a technetium(V) species, with the phenylimido unit formally a dianionic ligand. The ^1H NMR spectrum of the phenylimido complex *1* shows a pair of complex multiplets at 7.82 and 7.26 ppm from the aryl protons of the triphenylphosphine ligands. The multiplets integrate 2:3, which suggests that the resonance arising from the *ortho* protons is distinguished from the *meta* and *para* protons signals on these ligands. The signals from the aryl protons from the phenylimido unit occur as a triplet at 7.50 ppm, a doublet at 7.10 ppm and a triplet at 6.76 ppm. The integration of these signals is 1:2:2, corresponding to the *para–ortho–meta* protons, respectively. These resonances show the proper integration relative to the phosphine aryl proton signals.

The IR spectrum of the phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ displays major features at 515, 690, 745, 1090, 1435 and 1480 cm^{-1}, all of which are present in the IR spectrum of the nitrido complex $[TcNCl_2(PPh_3)_2]$. The absorption band at 1090 cm^{-1} has been assigned to $\nu(Tc{\equiv}N)$, which is in the region where the absorption is reported for the rhenium analogue [5, 8a]. A relatively broad feature of medium intensity at 1320 cm^{-1} is associated with $\nu(C–N)$ [6]. The only other feature observed in the IR spectrum of $[TcCl_3(NPh)(PPh_3)_2]$ not present in the spectrum of the nitrido complex is a sharp, medium intensity band which occurs at 1575 cm^{-1}.

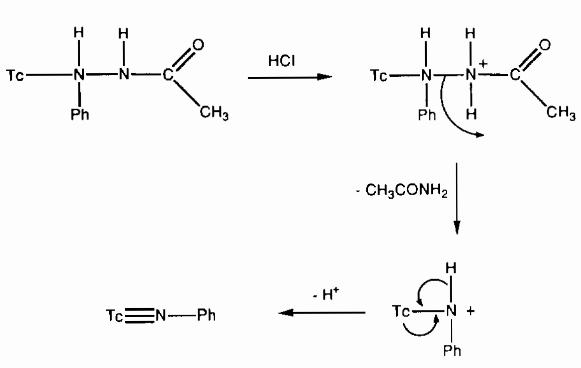


Fig. 2. Proposed mechanism for the incorporation of the phenylimido unit into $[TcCl_3(NPh)(PPh_3)_2]$.

The fast atom bombardment mass spectrum(+) of this complex does not show the signal associated with the parent ion. However, a prominent feature of 784 *m/z* units corresponds to the cationic species $[TcCl_2(NPh)(PPh_3)_2]^+$ generated from the loss of a chloride from the neutral molecule. Other features observed in the mass spectrum include $[TcCl_2(NPh)(PPh_3)]^+$ of 522 *m/z* and $[TcCl(NPh)(PPh_3)_2]\cdot H^+$ of 488 *m/z*.

A single crystal X-ray structural determination was performed to confirm the identity of the phenylimido complex. This was deemed necessary since the mass spectrum failed to show the parent ion, and the analytical results were only accurate when calculated to include a methylene chloride molecule of solvation. In addition, the previously reported tolylimido complex $[TcCl_3(NC_6H_4\text{-}p\text{-}CH_3)(PPh_3)_2]$ was only partially characterized with a ^{31}P NMR spectrum and molecular representation [2]. Table 1 lists the experimental details of the data set collection, and Table 2 lists the atomic positional parameters. The coordination geometry about the technetium consists of a slightly distorted octahedral arrangement of ligands. The steric bulk associated with the triphenylphosphine ligands results in their mutually *trans* coordination geometry. The remaining coordination sites are occupied by the three chloride ligands and the phenylimido unit. Figure 3 displays an ORTEP diagram of complex **1**. The technetium–phosphorous and technetium–chlorine bond lengths are unexceptional for technetium in this oxidation state. The average values for these interactions are 2.503 and 2.411 Å, respectively. The technetium–nitrogen bond length of complex **1** is 1.704(4) Å, which falls within the range reported for structurally analogous rhenium complexes, 1.709 Å for $[ReCl_3(NC_6H_4\text{-}p\text{-}OCH_3)(PPh_3)_2]$ and 1.690 Å for $[ReCl_3(NC_6H_4\text{-}p\text{-}COCH_3)(PPh_3)_2]$ [11]. Table 3 lists selected bond lengths and angles for complex **1**. The technetium–nitrogen–carbon bond angle of 171.8(4)° confirms the linear coordination mode of the triply-bonded phenylimido unit (see Fig. 1). The $Tc{\equiv}N$ bond length is significantly longer than the value of 1.629(4) Å reported for the octahedral Tc(V) nitrido complex $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ [12]. The difference in the $Tc{\equiv}N$ bond lengths reflects the difference between the (3–) nitrido core and the (2–) organoimido core. The technetium, three chloride and phenylimido ligands are essentially coplanar, with a slight tilt observed in the phenyl group in

TABLE 2. Atomic positional parameters for [$TcCl_3(NPh)(PPh_3)_2$]·CH_2Cl_2

Atom	x	y	z
Tc	0.12736(5)	0.15045(4)	0.25106(3)
Cl1	0.1895(1)	0.0578(1)	0.38497(9)
Cl2	0.0852(2)	0.2464(1)	0.1122(1)
Cl3	0.3419(1)	0.2077(1)	0.1825(1)
P1	0.1972(1)	−0.0372(1)	0.2123(1)
P2	0.0844(1)	0.3395(1)	0.2850(1)
N1	−0.0297(4)	0.1221(4)	0.2893(3)
C1	0.3284(5)	−0.1304(5)	0.2544(3)
C2	0.4285(6)	−0.0862(5)	0.2666(4)
C3	0.5324(6)	−0.1580(6)	0.2909(5)
C4	0.5359(7)	−0.2750(6)	0.3046(5)
C5	0.4359(6)	−0.3204(5)	0.2933(5)
C6	0.3334(6)	−0.2591(5)	0.2686(4)
C7	0.0644(5)	−0.1304(4)	0.2598(3)
C8	0.0128(6)	−0.1783(5)	0.2141(4)
C9	−0.0859(7)	−0.2502(6)	0.2544(4)
C10	−0.1295(6)	−0.2762(6)	0.3415(4)
C11	−0.0777(6)	−0.2307(5)	0.3886(4)
C12	0.0178(5)	−0.1574(5)	0.3485(4)
C13	0.2413(6)	−0.0332(5)	0.0994(4)
C14	0.3606(6)	−0.0839(6)	0.0633(4)
C15	0.3897(9)	−0.0830(8)	−0.0224(5)
C16	0.304(1)	−0.0333(9)	−0.0717(5)
C17	0.185(1)	0.0169(7)	−0.0364(5)
C18	0.1556(7)	0.0164(6)	0.0488(4)
C19	0.1758(5)	0.3683(5)	0.3519(3)
C20	0.1267(6)	0.4579(5)	0.3910(4)
C21	0.1959(6)	0.4857(6)	0.4388(4)
C22	0.3113(7)	0.4246(6)	0.4482(5)
C23	0.3599(6)	0.3378(6)	0.4101(4)
C24	0.2919(6)	0.3096(5)	0.3614(4)
C25	−0.0798(5)	0.3472(4)	0.3516(3)
C26	−0.1028(6)	0.2655(5)	0.4304(4)
C27	−0.2251(6)	0.2601(6)	0.4851(4)
C28	−0.3248(6)	0.3348(6)	0.4605(4)
C29	−0.3042(6)	0.4147(6)	0.3832(5)
C30	−0.1817(6)	0.4232(5)	0.3283(4)
C31	0.1017(6)	0.4680(5)	0.1927(4)
C32	0.0164(7)	0.4986(6)	0.1395(4)
C33	0.035(1)	0.5952(7)	0.0691(5)
C34	0.137(1)	0.6584(7)	0.0500(5)
C35	0.221(1)	0.6272(7)	0.1007(5)
C36	0.2055(7)	0.5302(6)	0.1732(4)
C37	−0.1583(6)	0.1120(5)	0.3099(4)
C38	−0.2167(6)	0.0461(6)	0.3914(4)
C39	−0.3465(7)	0.0338(7)	0.4109(5)
C40	−0.4171(7)	0.0874(7)	0.3518(6)
C41	−0.3612(7)	0.1529(7)	0.2723(6)
C42	−0.2313(6)	0.1670(6)	0.2490(4)
Cl1(s)	0.3424(4)	0.3177(4)	0.9086(3)
Cl2(s)	0.4013(6)	0.5397(4)	0.8898(3)
Cl(s)	0.342(1)	0.420(1)	0.9611(7)

the imido unit. Table 4 lists the least-square planes calculation for these ligands. As can be seen from this calculation, the principal deviation from coplanarity is introduced by the phenyl ring. Steric interactions with the triphenylphosphine group's phenyl rings may be responsible for the tilt observed in the imido group's phenyl ring, although there are no unusually close intramolecular contacts between any of the aryl-carbon atoms of these phenyl rings.

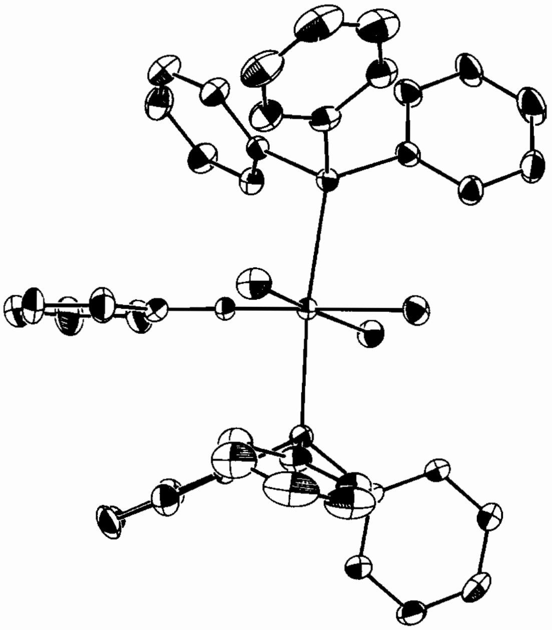


Fig. 3. ORTEP diagram of [$TcCl_3(NPh)(PPh_3)_2$] (**1**) showing 15% probability ellipsoids.

TABLE 3. Selected bond lengths and angles for [$TcCl_3(NPh)(PPh_3)_2$]·CH_2Cl_2

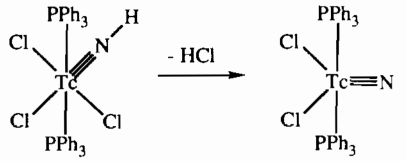
Tc–Cl1	2.416(2)	Tc–Cl2	2.404(2)
Tc–Cl3	2.414(2)	Tc–P1	2.517(2)
Tc–P2	2.489(2)	Tc–N1	1.704(4)
Cl1–Tc–Cl2	174.88(6)	Cl1–Tc–Cl3	90.70(5)
Cl1–Tc–P1	88.04(5)	Cl1–Tc–P2	90.58(5)
Cl1–Tc–N1	95.9(1)	Cl2–Tc–Cl3	84.19(6)
Cl2–Tc–P1	91.54(6)	Cl2–Tc–P2	89.27(6)
Cl2–Tc–N1	89.2(1)	Cl3–Tc–P1	88.78(5)
Cl3–Tc–P2	84.95(5)	Cl3–Tc–N1	173.1(1)
P1–Tc–P2	173.56(5)	P1–Tc–N1	93.4(1)
P2–Tc–N1	93.0(1)	Tc–N1–C37	171.8(4)

When benzoylhydrazine ($PhC{\equiv}ONHNH_2$) is substituted for the N,N′ disubstituted organohydrazine, the neutral Tc(V) nitrido complex [$TcNCl_2(PPh_3)_2$] is synthesized in excellent yields. The reaction involves refluxing ammonium pertechnetate, benzoylhydrazine and triphenylphosphine in methanol followed by the addition of a few drops of aqueous hydrochloric acid. The mechanism likely involves the elimination of benzamide from the coordinated organohydrazide species, analogous to the mechanism proposed above. And if this is the case, the unsubstituted imido complex [$TcCl_3(NH)(PPh_3)_2$] is probably an inter-

TABLE 4. Least-squares plane for $[TcCl_3(NPh)(PPh_3)_2]\cdot CH_2Cl_2$

Atoms defining plane	Distance	e.s.d.
Tc	0.0074	0.0005
Cl1	−0.0025	0.0015
Cl2	0.0230	0.0017
Cl3	−0.0681	0.0016
N1	0.0022	0.0042
C37	−0.0670	0.0056
C38	0.0245	0.0068
C39	−0.0097	0.0080
C40	−0.1588	0.0076
C41	−0.2623	0.0078
C42	−0.2184	0.0072

Mean deviation from plane is 0.0767 Å. Chi-squared = 5323.8.



Tc(V) imido complex Tc(V) nitrido complex

Fig. 4. Structure of proposed intermediate in the synthesis of the Tc(V) nitrido complex $]TcNCl_2(PPh_3)_2]$. The Tc(V) imido complex $[TcCl_3(NH)(PPh_3)_2]$ loses the N–H proton and a chloride to form the neutral five-coordinate nitrido complex.

mediate which subsequently loses the N–H proton as HCl, generating the five-coordinate nitrido species (see Fig. 4). Apparently the five-coordinate, 16-electron nitrido complex is more thermodynamically stable than the six-coordinate, 18-electron imido complex. The presence of the nitrogen–aryl-carbon bond in the 1-acetyl,2-phenylhydrazine reaction prevents the phenylimido species from reorganizing to form the five-coordinate nitrido complex. The IR spectrum of the nitrido complex prepared in this manner is identical to that of an authentic sample of $[TcNCl_2(PPh_3)_2]$ prepared by the literature method [10]. The IR spectrum contains no sign of an N–H absorption from the proposed intermediate.

The technetium nitrido core has recently received considerable attention as applied towards nuclear medicine [13] and the synthesis of new diagnostic imaging agents. Duatti *et al.* [14] have recently presented an improved synthesis of the technetium–nitrido core at the tracer level using the diagnostic isotope ^{99m}Tc and the reagent $(H_2NNRC{=}SSCH_3)$. The reaction conditions employed in this procedure are remarkably similar to the reaction conditions reported here. The authors react pertechnetate with hydrochloric acid, the nitrogen donating reagent and triphenylphosphine. The reaction probably proceeds along a mechanism similar to that proposed above, with the organohydrazine eliminating $HNRCS_2CH_3$. Under the acidic reaction conditions employed, the thioester leaving group is probably hydrolyzed to the dithio acid $(HNRCS_2H)$, which is itself an excellent ligand. This might explain the lack of radiochemical purity at this stage of their synthetic procedure. In the analogous reaction with benzoylhydrazine, the benzamide leaving group, at best a very poor ligand, is easily displaced by the excess of chloride ions in solution.

Conclusions

We have developed simple syntheses of the technetium(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ and the Tc(V) nitrido complex $[TcNCl_2(PPh_3)_2]$ directly from pertechnetate under relatively mild reaction conditions. The neutral Tc(V) phenylimido complex is proving to be a very useful synthetic precursor in synthesizing technetium complexes with the new nitrogen based core. The results of this chemistry and the analogous chemistry with the metastable isotope ^{99m}Tc will be presented elsewhere.

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