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The synthesis and characterization of $[TcCl_3(NPh)(Ph_2PCH_2CH_2PPh_2)]$ and $[TcCl_3(NPh)(PPh_3)_2]$. The single crystal X-ray structure of $[TcCl_3(NPh)(Ph_2PCH_2CH_2PPh_2)]$

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Abstract

The reaction of $(Bu_4N)[TcOCl_4]$ in methanol with 1-acetyl-2-phenylhydrazine, followed by 1,2-bis(diphenylphosphino)ethane (DPPE) gives the green technetium(V) phenylimido complex $[TcCl_3(NPh)(DPPE)]$. The IR spectrum of this complex shows a characteristic peak at 1110 cm^{-1} which is assigned to $\nu(Tc{\equiv}N)$ from the linearly coordinated phenylimido unit. The ^1H NMR spectrum shows a pair of coupled multiplets at 3.1 and 3.6 ppm from the aliphatic protons plus a series of six multiplets between 6.5 and 8.1 ppm from the aromatic protons of the bidentate phosphine ligand and imido–phenyl groups. The positive mode fast atom bombardment mass spectrum displays a peak at 695 *m*/*z* which corresponds to the protonated parent molecule. Also, a peak at 658 *m*/*z* corresponds to the fragment generated from the loss of one chloride from the neutral parent molecule. The X-ray crystal structure shows a facial arrangement of chloride ligands, with a Tc≡N bond length of 1.687 Å and a Tc–N–C bond angle of 175.7° indicative of sp hybridization of the linearly coordinated phenylimido unit. Crystal data for $TcCl_3P_2NC_{32}H_{29}$: monoclinic space group *Pc* (No. 7), $a=11.177(2)$, $b=10.912(2)$, $c=14.056(2)$ Å, $\beta=108.34(1)°$, $V=1627.3(5)$ Å^3, with $D_{calc}=1.414$ g cm^{-3} to give $Z=2$. Structure solution based on 3069 reflections converged at $R=0.051$, $R_w=0.072$, $GOF=2.32$. The analogous reaction with triphenylphosphine gives the previously reported Tc(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$. This Tc(V) phenylimido complex reacts with pyridine in methanol to give the mixed ligand complex $[TcCl_3(NPh)(PPh_3)(NC_5H_5)]$. The positive mode FAB mass spectrum of this complex shows fragments which correspond to the sodium adducts of the neutral molecule minus one chloride ligand, $(Na)[TcCl_2(NPh)(PPh_3)(C_5H_5N)]^+$ at 624 *m*/*z*, and the molecule minus two chloride ligands, $(Na)[TcCl(NPh)(PPh_3)(C_5H_5N)]^+$ at 589 *m*/*z*. Also present in the mass spectrum are peaks which correspond to the fragments $[TcCl_3(PPh_3)(C_5H_5N)]^+$ at 545 *m*/*z* and $[TcCl_2(PPh_3)(C_5H_5N)]^+$ at 510 *m*/*z*. The IR spectrum of this complex shows an absorption at 1090 cm^{-1} which is assigned to $\nu(Tc{\equiv}N)$ from the linearly coordinated phenylimido unit.

Introduction

We have been examining the reaction chemistry of technetium with the chelating, the potentially chelating and the non-chelating organohydrazines ($RNH\text{-}NH_2$). While the chemistry of this class of ligands with rhenium, technetium's third row congener, has been thoroughly examined, the chemistry with the second row metal is just now beginning to emerge. These ligands are extremely versatile geometrically and are capable of adopting numerous coordination geometries with varying degrees of protonation and modes of protonation [1]. This chemistry is also complicated by the inherent redox activity of the ligand's hydrazine moiety, which allows complexes of differing oxidation states than their precursors to be isolated. In addition, they display a tendency to fracture at the nitrogen–nitrogen bond to generate nitrido (M≡N), imido (M≡N–R), amido ($M{=}NR_2$) and/or amine ($M\text{–}NH_3$) containing complexes. All of these factors lead to an appreciation for the complexity of studying the chemistry of the organohydrazines with transition metals.

The redox activity of these ligands makes them attractive for technetium chemistry, in that diagnostic imaging agent pharmaceutical kit formulations generally require the addition of a reducing agent to facilitate the reduction of the pertechnetate ion. In the chemistry presented here, the organohydrazine serves not only as a ligand, but as the reducing agent as well. Pertechnetate is the chemical species (of ^{99m}Tc) routinely

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available in radiopharmacies which is employed in diagnostic imaging procedures.

Experimental

Caution. Technetium-99 is a weak β^--emitter ($E=0.292$ MeV, $t_{1/2}=2.12\times10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [2]. Reagents and solvents were used as received unless otherwise stated. 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. Analytical results were obtained from Atlantic Microlab Inc., Norcross, GA. 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 in CD_2Cl_2 at room temperature.

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 green prismatic crystal of complex **2** was isolated from the methylene chloride–methanol mixture as described below. The crystals dimensions were $0.15\times0.090\times0.220$ mm. The diffractometer employed was a Rigaku AFC6R with the data set collected at room temperature. The scan mode used was ω–2θ, with a maximum 2θ of 55.1°. A total of 3955 unique reflections was collected of which 3069 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. Final hydrogen atom positions were calculated. All non-hydrogen atoms were refined anisotropically except carbon atoms C(14), C(15) and C(16). These three phenyl ring carbon atoms displayed a site disorder. Each of the three atoms and their 'shadows' were refined for both position and population. The two sets of carbon atoms showed optimal refinement with a 60–40% occupation for the two sites listed in the positional parameters as C14, C14′; C15, C15′; C16 and C16′. The molecule was checked for chirality and both stereoisomers were found present in the crystallographic solution.

TABLE 1. X-ray data for structure determination of complex **2**

Empirical formula	$C_{32}H_{29}NP_2Cl_3Tc$
Formula weight	692.89
Crystal system	monoclinic
a (Å)	11.177(2)
b (Å)	10.912(2)
c (Å)	14.056(2)
β (°)	108.34(1)
V (Å^3)	1627.3(5)
Space group	*Pc* (No. 7)
Z	2
D_{exp} (g cm^{-3})	1.414
μ (cm^{-1})	7.9
Radiation[a] (λ, Å)	Mo Kα (0.71073)
Temperature (°C)	23
T_{max}, T_{min}	1.15, 0.77
R, R_w	0.051, 0.072
Goodness of fit	2.32

[a] Graphite monochromated.

Syntheses

[TcCl$_3$(NPh)(PPh$_3$)$_2$] (1)

To a methanolic solution of $(Bu_4N)[TcOCl_4]$ (435 mg in 200 ml) was added dropwise 1-acetyl-2-phenylhydrazine (260 mg/1.1 equiv.) dissolved in 10 ml of methanol, which results in the rapid generation of dark red–brown color. This solution was stirred at room temperature for 30 min under air. Solid triphenylphosphine (0.92 g) was added and the reaction mixture refluxed for 30 min, during which time the dark red solution lightened in color and a yellow precipitate appeared. The resulting dull yellow–brown solid was isolated and washed with methanol (50 ml) and diethyl ether (50 ml). The product was then dried under vacuum. Yield 50–55%. The isolated product is spectroscopically identical to a sample of $[TcCl_3(NPh)(PPh_3)_2]$ prepared from $[TcO_4]^-$. Analytical results are for a crude sample. *Anal.* Calc. for $[TcCl_3P_2NC_{42}H_{35}]$: C, 61.44; H, 4.30; N, 1.71; Cl, 12.95. Found: C, 61.38; H, 4.39; N, 1.71; Cl, 12.93%. IR (KBr): 1090 cm^{-1}; ν(Tc≡N).

[TcCl$_3$(NPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] (2)

To a methanolic solution of 317 mg of $(Bu_4N)[TcOCl_4]$ were added 114 mg (1.2 equiv.) of 1-acetyl-2-phenylhydrazine in methanol to give a red–brown solution of total volume 70 ml. To this was added 506 mg of DPPE (2 equiv), and the resulting solution was refluxed for 40 min. The resulting yellow–brown suspension was cooled to room temperature and filtered on a fritted funnel. The isolated bright yellow–green precipitate was washed with 50 ml of methanol and dried under vacuum. Bright green, X-ray quality crystals were grown from a methylene chloride solution of complex **2** layered with methanol. Yield 23–30%. IR

(KBR): 1110 cm^{-1}; $\nu(Tc{\equiv}N)$. FAB-MS(+): 695 *m/z*, $[TcCl_3(NPh)(DPPE)]\cdot H^+$; 658 *m/z*, $[TcCl_2(NPh)(DPPE)]^+$. Electronic spectroscopy in methylene chloride: λ_{max} (ϵ (1 mol^{-1} cm^{-1})) 236 (4.22×10^4), 336 (1.04×10^4) nm. ^1H NMR (CD_2Cl_2, 22 °C): δ 3.0–3.7 (2m, 4H, CH_2–CH_2); δ 6.5–8.1 (6m, 25H, N–Ph and P–Ph). *Anal.* Calc. for $[TcCl_3P_2NC_{32}H_{29}]$: C, 55.31; H, 4.21; N, 2.02; Cl, 15.31. Found: C, 55.04; H, 4.18; N, 2.05; Cl, 14.82%.

$[TcCl_3(NPh)(PPh_3)(C_5H_5N)]$ (3)

A 100 mg sample of complex **1** was suspended in 50 ml of methanol, and 2 ml of pyridine were added. The resulting suspension was brought to reflux and heated until the complex solubilized, giving a red–brown solution. This solution was allowed to evaporate at room temperature, gradually yielding red–brown crystals of complex **3**. Yield 80–85%. *Anal.* Calc. for $[TcCl_3PN_2C_{29}H_{25}]$: C, 54.61; H, 3.95; N, 4.39; Cl, 16.67. Found: C, 53.74*; H, 4.07; N, 4.39; Cl, 16.43%. FAB-MS(+): 624 *m/z*, $(Na)[TcCl_3(NPh)(PPh_3)(C_5H_5N)]^+$; 589 *m/z*, $(Na)[TcCl_2(NPh)(PPh_3)(C_5H_5N)]^+$; 545 *m/z*, $[TcCl_3(PPh_3)(C_5H_5N)]^+$; 510 *m/z*, $[TcCl_2(PPh_3)(C_5H_5N)]^+$. IR (KBR): 1090 cm^{-1}; $\nu(Tc{\equiv}N)$.

Conclusions

The synthesis and characterization of the technetium(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ was recently reported [4]. This complex was obtained from the reaction of ammonium pertechnetate and 1-acetyl-2-phenylhydrazine ($CH_3CONHNHPh$) with triphenylphosphine and HCl in methanol. The phenylimido unit (Tc≡N–Ph) is generated through the acid mediated fragmentation of the coordinated organohydrazine, presumably via the elimination of acetamide.

The reaction of $(Bu_4N)[TcOCl_4]$ with 1-acetyl-2-phenylhydrazine, followed by triphenylphosphine in methanol also gives the Tc(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ (**1**). The identity of this product was confirmed with analytical results, FAB(+) mass spectrometry and IR spectroscopy. The analytical results of the previously reported, structurally characterized complex, in its crystalline form, contained a molecule of methylene chloride in the lattice. The crude reaction product from the reaction with $(Bu_4N)[TcOCl_4]$ analyzes well for the non-solvated complex. The mass spectrum of complex **1** displays a signal from the cationic species generated from the loss of a chloride ligand from the neutral parent molecule, $[TcCl_2(NPh)(PPh_3)_2]^+$ at 784 *m/z*. The IR spectrum of complex **1** displays a prominent feature in the 1090–1100 cm^{-1} region which has been assigned to $\nu(Tc{\equiv}N)$. All spectroscopic data is identical to that of the complex synthesized directly from pertechnetate [4, 5].

The synthesis of $[TcCl_3(NPh)(PPh_3)_2]$ directly from pertechnetate required the addition of hydrochloric acid to facilitate nitrogen–nitrogen bond cleavage and provide the necessary chloride ions. However, in the reaction of the organohydrazine with the Tc(V) precursor, the bond fragments spontaneously, without the addition of the acid. The proton may be donated by the solvent, methanol, allowing the protonated organohydrazide ligand to cleave, with acetamide as the leaving group.

In a related synthetic procedure, $[Bu_4N][TcOCl_4]$ reacts with 1-acetyl-2-phenylhydrazine in methanol, followed by 1,2-bis(diphenylphosphino)ethane (DPPE), to give the formally Tc(V) complex $[TcCl_3(NPh)(DPPE)]$. The yields of this complex are significantly lower than the yields of the analogous bis-triphenylphosphine complex. This result was not unexpected since an excess of the phosphine is required to remove the oxo group from the precursor $[TcOCl_4]^-$ as the phosphine oxide, while too large an excess of the phosphine results in the formation of the previously reported cationic species $[TcCl(NPh)(DPPE)_2]^+$ [6]. The bis-DPPE, cationic Tc(IV) species as its tetraphenylborate salt was characterized with fast atom bombardment(+) mass spectrometry, which displayed fragments associated with $\{[TcCl(NPh)(DPPE)_2]\cdot H\}^+$ at 1022 *m/z* and $\{[TcCl(NPh)(DPPE)]\cdot H\}^+$ at 624 *m/z*. The IR spectrum of the cationic complex displayed a prominent feature associated with $\nu(Tc{\equiv}N)$ at 1097 cm^{-1}. As a consequence of using the tetrabutylammonium salt of $[TcOCl_4]^-$ as a precursor, $(Bu_4N)(BPh_4)$ co-precipitates with the bis-DPPE complex when $NaBPh_4$ is added to the reaction mixture containing the methanol soluble cationic complex as the chloride salt.

The IR spectrum of neutral complex $[TcCl_3(NPh)(DPPE)]$ displays a prominent feature at 1090 cm^{-1}, which is characteristic of the linearly coordinated phenylimido unit. The FAB(+) mass spectrum of complex **2** displays the protonated parent ion $[TcCl_3(NPh)(DPPE)]\cdot H^+$ at 695 *m/z*. Also, a fragment of 658 *m/z* is associated with the cation generated from the loss of a chloride ion from the neutral parent species. The ^1H NMR spectrum of this complex shows a pair of multiplets at 3.1 and 3.6 ppm from the aliphatic protons on the DPPE ligand. The aryl protons appear as a series of multiplets between 6.5 and 8.1 ppm. The electronic spectrum of complex **2** in CH_2Cl_2 shows two absorptions at 236 and 336 nm with extinction coefficients of 4.22×10^4 and 1.04×10^4, respectively. The neutral complex $[TcCl_3(NPh)(DPPE)]$ reacts with an

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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 upto one carbon low [3]. A possible explanation is that an incomplete combustion results from the formation of residual technetium carbide.

excess of DPPE to give the Tc(IV) bis-(DPPE) complex $[TcCl(NPh)(DPPE)_2]^+$, which can be precipitated cleanly from methanol with the addition sodium tetraphenylborate.

The X-ray crystal structure of complex **2** shows the molecule to contain distorted octahedral coordination geometry, with a facial arrangement of chloride ligands. The distortion is a result of the small bite angle imposed by the five-membered chelate ring of the bidentate phosphine ligand; see Fig. 1 for an ORTEP diagram of complex **2**. The technetium–chlorine bond lengths of 2.436, 2.426 and 2.422 Å are roughly 0.2 Å longer than those to the chlorine atoms of the bis-triphenylphosphine complex $[TcCl_3(NPh)(PPh_3)_2]$ with meridional chlorine coordination geometry. The technetium–phosphine bonds of 2.420 and 2.431 Å are significantly shorter than those in $[TcCl_3(NPh)(PPh_3)_2]$, which were 2.517 and 1.489 Å. This may reflect the diminished steric congestion around the technetium atom in complex **2** as compared to the bis-triphenylphosphine complex. The technetium–nitrogen bond length is 1.687 Å, which is in the range expected for the triply-bonded, dianionic, nitrogenous core [5]. The technetium–nitrogen–carbon bond angle of 175.7° reflects the sp hybrization of the phenylimido nitrogen atom. Table 2 lists the atomic positional parameters for complex **2**. Selected bond lengths and angles are listed in Table 3. The bond angles about the technetium atom reflect the distorted octahedral molecular geometry.

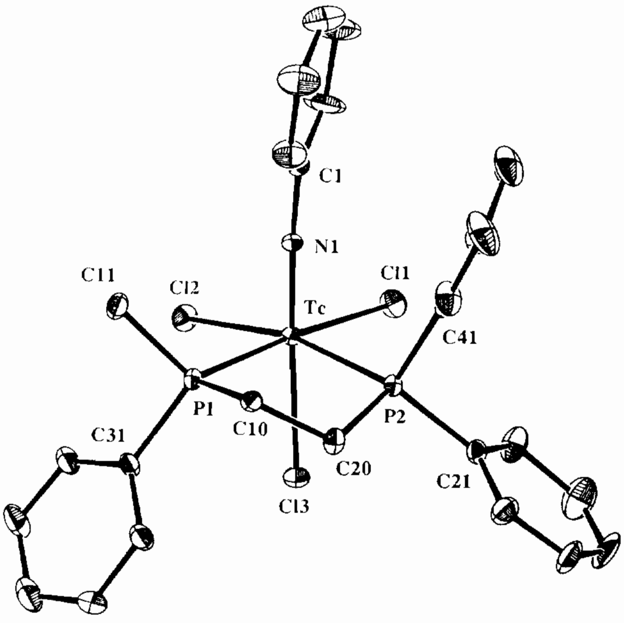

Fig. 1. ORTEP diagram of $[TcCl_3(NPh)(DPPE)]$ showing 20% probability elipsoids. The hydrogen atoms and the disordered phenyl ring off P1 have been eliminated (except for C11) for clarity.

TABLE 2. Atomic positional parameters for $[TcCl_3(NPh)(Ph_2PCH_2CH_2PPh_2)]$

Atom	*x*	*y*	*z*
Tc	0.0002	0.16925(7)	0.0001
C11	−0.1665(3)	0.2174(3)	0.0715(2)
C12	0.1508(3)	0.1947(3)	0.1661(2)
C13	−0.0118(3)	−0.0467(2)	0.0360(2)
P1	0.1634(3)	0.1037(3)	−0.0681(2)
P2	−0.1416(3)	0.1037(3)	−0.1585(2)
N1	0.0054(9)	0.3114(7)	−0.0458(2)
C1	0.000(1)	0.427(1)	−0.0874(9)
C2	0.025(2)	0.446(2)	−0.179(1)
C3	0.015(2)	0.557(2)	−0.218(1)
C4	−0.027(2)	0.650(2)	−0.182(1)
C5	−0.058(2)	0.635(2)	−0.092(2)
C6	−0.045(2)	0.521(1)	−0.045(2)
C10	0.086(1)	0.071(1)	−0.2001(8)
C11	0.283(1)	0.214(1)	−0.068(1)
C12	0.312(1)	0.314(1)	0.003(1)
C13	0.404(2)	0.397(2)	0.003(1)
C14	0.500(5)	0.347(4)	−0.035(3)
C14′	0.455(3)	0.403(3)	−0.072(2)
C15	0.429(4)	0.315(4)	−0.141(3)
C15′	0.484(6)	0.228(5)	−0.099(4)
C16	0.373(5)	0.157(4)	−0.107(4)
C16′	0.339(2)	0.212(2)	−0.139(4)
C20	−0.043(1)	0.010(1)	−0.2166(8)
C21	−0.273(1)	−0.005(1)	−0.1657(8)
C22	−0.340(2)	0.005(2)	−0.097(1)
C23	−0.441(2)	−0.076(2)	−0.108(2)
C24	−0.476(2)	−0.155(2)	−0.183(2)
C25	−0.410(1)	−0.165(2)	−0.247(1)
C26	−0.309(1)	−0.095(1)	−0.242(1)
C31	0.256(1)	−0.028(1)	−0.0142(8)
C32	0.243(1)	−0.138(1)	−0.065(1)
C33	0.315(2)	−0.238(1)	−0.020(1)
C34	0.404(1)	−0.226(2)	0.075(1)
C35	0.417(1)	−0.114(2)	0.125(1)
C36	0.343(1)	−0.022(1)	0.079(1)
C41	−0.212(1)	0.219(1)	−0.2444(8)
C42	−0.265(1)	0.316(1)	−0.207(1)
C43	−0.308(2)	0.421(2)	−0.266(2)
C44	−0.300(2)	0.430(2)	−0.357(1)
C45	−0.256(2)	0.328(2)	−0.395(1)
C46	−0.208(1)	0.229(2)	−0.338(1)

TABLE 3. Selected bond lengths and angles for $[TcCl_3(NPh)(Ph_2PCH_2CH_2PPh_2)]$

Tc–C11	2.436(3)	Tc–C12	2.426(3)
Tc–C13	2.422(3)	Tc–P1	2.420(3)
Tc–P2	2.431(3)	Tc–N1	1.687(9)
C11–Tc–C12	88.2(1)	C11–Tc–C13	91.4(1)
C11–Tc–P1	175.2(1)	C11–Tc–P2	95.0(1)
C11–Tc–N1	94.7(3)	C12–Tc–C13	88.7(1)
C12–Tc–P1	91.9(1)	C12–Tc–P2	167.2(1)
C12–Tc–N1	99.5(3)	C13–Tc–P1	83.9(1)
C13–Tc–P2	78.8(1)	C13–Tc–N1	169.9(3)
P1–Tc–P2	83.9(1)	P1–Tc–N1	90.0(3)
P2–Tc–N1	92.6(3)	Tc–N1–C1	175.7(9)

It has been previously reported that the reaction of the rhenium analogue of complex **1** with carbon monoxide under pressure gives the substitution product [ReCl$_3$(NPh)(CO)(PPh$_3$)]. In this complex one of the axial triphenylphosphine ligands has been replaced by a CO [7a]. Also reported is the reaction of the rhenium complex with pyridine at reflux to give [ReCl$_3$(NPh)(C$_5$H$_5$N)$_2$], with both phosphines replaced by pyridine ligands [7b]. However, neither of these complexes were structurally characterized. Also reported is the reaction of [Re(NPh)Cl$_2$]$_2$ with the amine Me$_3$SiNHCMe$_3$ to give [ReCl$_3$(NPh)(H$_2$NCMe$_3$)$_2$ [7c]. This Tc(V) was structurally characterized and shown to display the amine ligands in a mutually *trans* coordination geometry.

In similar reaction chemistry, the technetium(V) phenylimido complex **1** reacts with pyridine in refluxing methanol to give the neutral mono-pyridine adduct [TcCl$_3$(NPh)(PPh$_3$)(C$_5$H$_5$N)], in which only one phosphine has been replaced by a pyridine. The fact that the reaction stops with the substitution of a single phosphine ligand is probably a reflection of both the lower concentration of pyridine present in the reaction medium, as compared to the neat pyridine in which the bis-pyridine rhenium complex was synthesized, and the diminished reaction temperature. The IR spectrum of this complex shows the absorption from the Tc≡N) in the 1090–1100 cm^{-1} range, indicative of a linear conformation of this moiety. The FAB(+) mass spectrum of complex **3** fails to show the parent ion; however, a fragment at 624 *m/z* can be assigned to the sodium adduct of [TcCl$_2$(NPh)(PPh$_3$)(C$_5$H$_5$N)]. The mass spectrum also contains fragments associated with (Na)[TcCl(NPh)(PPh$_3$)(C$_5$H$_5$N)]$^+$ at 589 *m/z*, [TcCl$_3$(PPh$_3$)(C$_5$H$_5$N)]$^+$ at 545 *m/z* and [TcCl$_2$(PPh$_3$)(C$_5$H$_5$N)]$^+$ at 510 *m/z*.

The pyridine complex [TcCl$_3$(NPh)(PPh$_3$)(C$_5$H$_5$N)] likely displays an octahedral arrangement of ligands, with the pyridine and triphenylphosphine ligands in the axial sites (see Fig. 2). This structural arrangement is analogous to the structurally characterized rhenium(V) tolylimido complex [ReCl$_3$(NC$_6$H$_4$-p-Me)(PPh$_3$)(NH$_2$C$_6$H$_4$-p-Me)], which displays an octahedral arrangement of ligands, with axial tolylamine and phosphine donors [8], and the previously mentioned bis(tertiarybutyl)amine complex [ReCl$_3$(NPh)(H$_2$NCMe$_3$)$_2$] [7c].

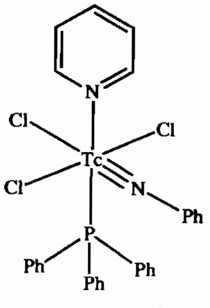

Fig. 2. Proposed structure of complex 3, with axial neutral donor ligands and equatorial chloride and phenylimido ligands.

Discussion

We recently reported the synthesis of the first example of a technetium complex to incorporate the organoimido core, (Tc=N–R) [9]. This neutral technetium(I) complex [TcCl(NPh)(PhN$_2$CON=NHPh)$_2$] was synthesized from the reaction of the chelating organohydrazine phenylazo formic acid 2-phenylhydrazide (PhNHNHCON=NPh) with the technetium(V) oxocomplex (Bu$_4$N)[TcOCl$_4$]. In this reaction, the organohydrazine not only serves as the source of the phenylimido unit, but also occupies four coordination sites; as two, bidentate organodiazene ligands, with pendant, cationic (–N=NHPh) groups. The organohydrazines, like the unsubstituted parent molecule hydrazine (H$_2$N–NH$_2$), are powerful reducing agents. Each of two organohydrazines, upon coordination, reduces the metal's oxidation state by two electrons, generating the technetium(I) product. In the process, the organohydrazine moieties (RNH–NHR′) are oxidized by two electrons, coordinating as organodiazene chelates (RN=NR′). The organodiazene ligand shows delocalization from the terminal phenyl groups, through both sets of nitrogen–nitrogen double bonds to the carbonyl group: {Ph–N(H)=N–C(=O)–N=N–Ph}; see Fig. 3 for the proposed structural representation of this complex. The representation depicts a 'bent' phenylimido moiety with a technetium–nitrogen double bond. This ligand geometry gives

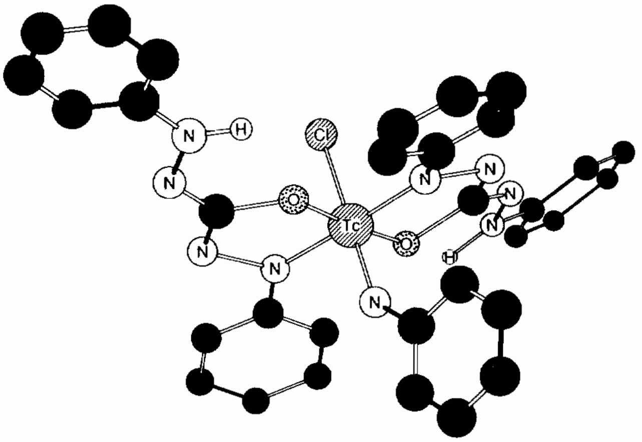

Fig. 3. Proposed structure of the Tc(I) phenylimido complex formed from the reaction of phenyl azo formic acid 2-phenylhydrazide and the Tc(V) complex [Bu$_4$N][TcOCl$_4$]. Established trends suggest an octahedral coordination geometry with the chloride ligand situated *trans* to the phenylimido unit.

the complex an electron count of eighteen. The organoimido moiety tends to adopt the bent conformation when the more frequently observed, linear conformation generates a species with an electron count of greater than eighteen [5]. The IR spectrum of this complex does not show a prominent absorption near 1100 cm^{-1}, which is the region expected for a linearly coordinated organoimido species of rhenium and technetium. Established trends in Group VII organoimido chemistry suggest that the complex displays octahedral coordination geometry with the chloride ligand situated *trans* to the phenylimido unit. The depicted arrangement of equatorial organodiazene ligands, with mutually *trans*-carbonyl groups, is arbitrary.

The precise coordination mode of the cationic, bidentate organodiazene ligands was established in a structurally characterized Tc(III) complex $[TcO(PhN_2CON{=}NHPh)(SAr)_2]$ (where $Ar{=}C_6HMe_4$) [9]. This complex was synthesized from the reaction of the Tc(V) complex $[TcO(SAr)_3(C_5H_5N)]$ and phenylazo formic acid 2-phenylhydrazide. Here, too, the coordination of one bidentate organohydrazide chelate has reduced the metal's formal oxidation state by two electrons. The bidentate organodiazene ligand was shown to contain a delocalized five-membered chelate ring, coordinating through the α-nitrogen and carbonyl oxygen atoms. The organohydrazide is thus oxidized by two electrons upon its coordination. The pendant ($-N{=}NHPh$) moiety was unambiguously determined to contain the N–H proton on the terminal nitrogen atom with an X-ray crystallographic structural determination. The exocyclic nitrogen–nitrogen bond length for this moiety was 1.315 Å, which corresponds to a double bond. The bond angles for this moiety are 114.2(3)° for C–N–N, 111.45° for N–N–H and 121.1(3)° for N–N–Ph; which reflect sp^2 hybridization and thus establishes the ligand's cationic nature.

This mode of coordination of the organodiazene ligand is also presumed present in the bis-organodiazene Tc(I) complex, $[TcCl(NPh)(PhN_2CON{=}NHPh)_2]$ with the 'bent' phenylimido group. The two (+1) charges on the molecule's periphery, from the two pendant cationic moieties, account for the formal oxidation state assignment for this species as Tc(I).

The fast atom bombardment(+) mass spectra of these two complexes support our contention that this type of organohydrazide tends to fragment in a manner which generates phenylimido containing species. The mass spectrum of the bis-diazene complex contains fragments of 520 *m/z* which corresponds to $\{[Tc(NPh)_2(PhN_2CON{=}N(H)Ph)]\cdot H\}^+$ and of 372 *m/z* which corresponds to $[Tc(NPh)_3]^+$, while the mass spectrum of the mono-diazene complex contains a fragment assigned to the species $[TcO(NPh)(SAr)]^+$ at 589 *m/z*.

The redox behavior of hydralazine $(C_8H_5N_2NHNH_2)$, another potentially chelating organohydrazine, with technetium was recently discussed in a paper describing the synthesis of the cationic Tc(I) tris-organodiazene chelate complex $[Tc(C_8H_5N_2N{=}NH)_3](BPh_4)$ from $[TcO_4]^-$ [10]. In this reaction, each of three organohydrazine molecules serves to reduce the metal by two electrons from pertechnetate, in the (VII) oxidation state, to an oxidation state of Tc(I) in the cationic tris-organodiazene chelate product. The three coordinating organohydrazine molecules are concomitantly oxidized by two electrons, coordination with nitrogen–nitrogen double bonds [11] (see Fig. 4). In this instance, however, the Tc(I) tris-chelate complex is sufficiently stable that no organohydrazide fragmentation is observed and thus no organoimido units appear in the isolated product. The increased stability of the tris-hydralazine chelate complex probably results from the increased base strength of the chelating moiety, an aromatic amine as compared to the carbonyl oxygen in the complexes with phenylazo formic acid 2-phenylhydrazide, *vide supra*.

The neutral complex $[TcCl_2(PPh_3)_2(N{=}NC_8H_5N_2)]$ was recently reported, synthesized from the reaction of $(Bu_4N)[TcOCl_4]$ and hydralazine followed by triphenylphosphine [12]. The oxidation state of the product

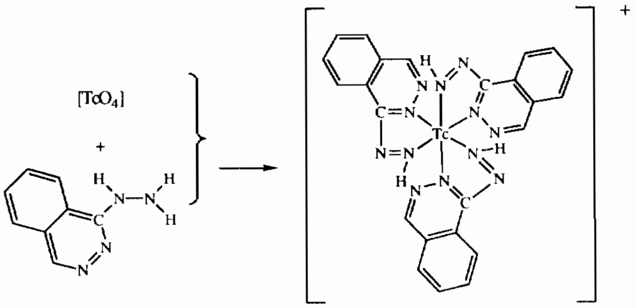

Fig. 4. Diagram depicting the redox chemistry involved in the conversion of pertechnetate into the cationic Tc(I) tris-chelate complex $[Tc(HN{=}NC_8H_5N_2)_3]^+$. The Tc(VII) precursor is reduced by six electrons by oxidizing each of the three organohydrazine molecules by two electrons, which coordinate as chelated diazene moieties with locallized nitrogen–nitrogen double bonds.

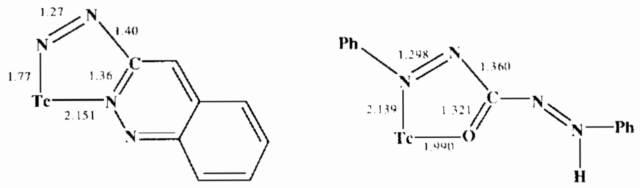

Fig. 5. Bonding parameters for the (1−) organohydrazide chelate of the Tc(III) complex $[TcCl_2(PPh_3)_2(N{=}NC_8H_5N_2)]$. The aromatic nature of the chelating moiety results in a more locallized set of bonding parameters for this species as compared to the neutral organodiazene chelate complex $[TcO(PhN_2CON{=}NHPh)(SAr)_2]$.

was reported to be Tc(V), with the organohydrazide a (3-) ligand by virtue of the loss of three protons from the parent organohydrazine. However, examination of the structural parameters of the organohydrazide show that the complex could be assigned as a Tc(III) species, with the organohydrazine chelate formally an anionic derivative of the organodiazene chelates discussed above. The reaction likely involves the incorporation of a neutral chelated organodiazene form of hydralazine, ($HN{=}NC_8H_5N_2$), which reduces the oxidation state of the technetium from Tc(V) to Tc(III) while oxidizing the organohydrazide by two electrons. The subsequent addition of the triphenylphosphine allows the isolation of the stable complex $[TcCl_2(PPh_3)_2(N{=}NC_8H_5N_2)]$, with the intermediate organodiazene N–H moiety being deprotonated and thus mono-anionic. Figure 5 displays the bonding parameters for the organohydrazide chelate in this complex, which shows a significant contraction of the five-membered chelate ring due to the anionic nature of the chelated ligand when compared to the organodiazene moiety in $[TcO(PhN_2CON{=}NHPh)(SAr)_2]$. The different nature of the chelating moieties complicates any direct assessment of the structural consequences of the (1-) charge on the chelated ligand. The technetium–(α)-nitrogen bond length, (1.77 Å), is significantly contracted as compared to the analogous bond in the carbonyl-chelated species (2.139 Å). This is likely a reflection of the anionic nature of the hydralazine chelate. However, the technetium–nitrogen bond length to the aromatic amine nitrogen atom is 2.151 Å, which falls in the range expected for a bond to a neutral nitrogen donor ligand. This bond is significantly longer than the analogous bond to the carbonyl–oxygen atom in $[TcO(PhN_2CON{=}NHPh)(SAr)_2]$, 1.990 Å, which is a reflection of the partial negative charge on the carbonyl oxygen atom that results from the delocalization extended throughout the functional portion of this ligand.

Another example of this type of redox behavior was recently reported in which the Tc(V) complex $[TcOCl_4]^-$ was shown to react with the chelating organohydrazine ($PhC{=}SNHNH_2$) to form the neutral Tc(I) bis-thiobenzoyldiazene complex $[Tc(HN{=}NCSPh)_2(S_2CPh)]$ [13]. The chelated organodiazene ligands display localized nitrogen–nitrogen double bonds and are thus considered neutral bidentate ligands. This nitrogen–nitrogen bond length contraction upon coordination is the only structural difference between the structurally characterized free ligand and the two electron oxidized form present in the structurally characterized coordination complex. The remaining two coordination sites are occupied by the anionic, bidentate dithiobenzoic acid which is present as a contaminant from the synthesis of the organohydrazine precursor.

The trend that seems to emerge from the reaction chemistry of technetium with the chelating organohydrazides is that for each bidentate organohydrazide ligand incorporated into a given metal complex, the oxidation state of the metal precursor is reduced by two electrons. This reduction is facilitated by the concomitant, two-electron oxidation of the organohydrazine (RNH–NHR), a species with a nitrogen–nitrogen single bond, to an organodiazene (RN=NR), a species with a nitrogen–nitrogen double bond (see Table 4). In addition, when the organohydrazine has a weakly binding chelating moiety or a suitable leaving group and can form a more stable complex with a multiply bonded nitrogenous core than the complex that would result if the organodiazene nitrogen–nitrogen bond remained intact, bond cleavage occurs. To date we have generated the phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ and the nitrido complex $[TcCl_2N(PPh_3)_2]$ in this manner. This chemistry is also very dependent upon the reaction conditions employed, as was recently established by Zubieta and co-workers [14]. They showed that the reaction of $(Bu_4N)[TcOCl_4]$ with hydralazine·HCl in methanol followed by triphenylphosphine yields the neutral complex $[TcCl_2(N{=}NC_8H_5N_2)(PPh_3)_2]$ when refluxed for 2 min. However, if the reaction of $(Bu_4N)[TcOCl_4]$ with hydralazine·HCl is done in methylene chloride and refluxed for 30 min followed by the addition of triphenylphosphine, the nitrido complex $[TcCl_2N(PPh_3)_2]$ is isolated as the major product, generated from the cleavage of the organohydrazine's nitrogen–nitrogen bond. These results pointedly illustrate the many complexities of organohydrazine coordination chemistry.

TABLE 4.

Precursor	Formal oxidation state	Product	Assigned oxidation state[a]
$[TcO(SAr)_3(C_5H_5N)]$	Tc(V)	$[TcO(SAr)_2(PhN_2CON{=}NHPh)]$	Tc(III)
$(Bu_4N)[TcOCl_4]$	Tc(V)	$[TcCl(NPh)(PhN_2CON{=}NHPh)_2]$	Tc(I)
$(NH_4)[TcO_4]$	Tc(VII)	$[Tc(HN{=}NC_8H_5N_2)_3](BPh_4)$	Tc(I)
$(Bu_4N)[TcOCl_4]$	Tc(V)	$[TcCl_2(N{=}NC_8H_5N_2)(PPh_3)_2]$	Tc(III)
$(Bu_4N)[TcOCl_4]$	Tc(V)	$[Tc(HN{=}NCSPh)_2(S_2CPh)]$	Tc(I)

[a] Oxidation states are assigned according to the rationale presented in the preceding discussion, which is based on structural and spectroscopic features observed in these and related complexes.

Conclusions

We have synthesized and characterized a new Tc(V) phenylimido complex [$TcCl_3(NPh)(DPPE)$] using 1-acetyl-2-phenylhydrazine, $[TcOCl_4]^-$, and bis(diphenylphosphino)ethane in methanol. The same technetium precursor reacts with the organohydrazine and triphenylphosphine in methanol to give the previously reported complex $[TcCl_3(NPh)(PPh_3)_2]$. Both of these complexes can be expected to be very useful synthetic precursors. The reaction of the bis-triphenylphosphine complex with pyridine in methanol forms the Tc(V) mixed ligand complex $[TcCl_3(NPh)(PPh_3)(C_5H_5N)]$.

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