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Synthesis, Characterization and X-ray Molecular and Crystal Structure of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ – a First Example of Mixed Phosphine/Phosphine Oxide Coordination

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Abstract

The reaction of $TcNCl_2(Me_2PhP)_3$ with excess S_2Cl_2 yields trichloro(dimethylphenylphosphine)-(dimethylphenylphosphine oxide)thionitrosyltechnetium(II), $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$, whereas an equimolar reaction mixture yields dichlorotris-(dimethylphenylphosphine)thionitrosyltechnetium-(I), $Tc(NS)Cl_2(Me_2PhP)_3$. $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ (formula weight 543.74) crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 10.513(1)$, $b = 14.274(2)$ and $c = 15.187(2)$ Å ($Z = 4$). The phosphine oxide ligand is arranged in *trans* position to the linearly coordinated thionitrosyl group.

Introduction

The exploration of the coordination chemistry of technetium is strongly connected with the demands of diagnostic nuclear medicine for new ^{99m}Tc radiopharmaceuticals for organ scintigraphy (^{99m}Tc: γ-emitter, $E_\gamma = 140$ keV, half-life $t_{1/2} = 6$ h) [1–3]. Chemical studies are commonly done with the long-lived nuclide ^{99}Tc (weak β^--emitter, $E_{max} = 0.3$ MeV, $t_{1/2} = 2.12 \times 10^5$ years) which is available in macroscopic amounts from fission products and can be handled with conventional laboratory equipment.

Transition metal thionitrosyl complexes can be prepared (a) from nitrido complexes by the reaction with S_2Cl_2, propylene sulphide or elemental sulphur, (b) from metal complexes and $(NSCl)_3$, (c) by reactions of N_4S_4 with metal halides or nitrides, (d) by halide abstraction from coordinated NSF or NSCl or (e) by reaction of NS^+ salts with transition metal complexes [4].

Technetium thionitrosyl complexes have been obtained following route (a) from the reaction of nitridotechnetium(V) compounds with S_2Cl_2 (or $SOCl_2$) [5–8]. The oxidation state of the central metal and the coordination geometry depend on the coordinating ligands and the reaction conditions used: $TcN(et_2dtc)_2$ (et_2dtc^- = diethyldithiocarbamate) yields the seven-coordinate technetium(III) complex $Tc(NS)Cl_2(et_2dtc)_2$ [5], whereas with $TcN(morphtcb)_2$ ($morphtcb^-$ = (morpholinylthiocarbonyl)benzamidinate) $Tc^{II}(NS)Cl_2(morphtcb)$ is formed [7]. Recently, we found that $TcNCl_2(Me_2PhP)_3$ (Me_2PhP = dimethylphenylphosphine) [9, 10] reacts with disulphur disulphide to yield different low-valent technetium thionitrosyl complexes depending on the conditions used [6]. The red technetium(II) product which can be isolated from the reaction of the nitrido complex with excess S_2Cl_2 was earlier described to be $Tc(NS)Cl_3(Me_2PhP)_2$ [6].

Experimental

Health Precautions

Normal glassware gives adequate protection against the weak β^--emission of ^{99}Tc; secondary X-rays (bremsstrahlung) play an important role only if working with larger amounts of technetium. All operations were carried out with gloves and in a hood.

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Preparations

All reactions were carried out under dry argon. $TcNCl_2(Me_2PhP)_3$ was prepared from $TcCl_3(Me_2PhP)_3$ and sodium azide according to ref. 10. CH_2Cl_2 and S_2Cl_2 were distilled under Ar prior to use.

$Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$

A mixture of 600 mg (1.0 mmol) of $TcNCl_2(Me_2PhP)_3$ and 1.6 ml (20 mmol) of S_2Cl_2 was refluxed in 20 ml CH_2Cl_2 for 20 h. The red solution was reduced in volume to 10 ml and filtered. Addition of 100 ml n-hexane resulted in a red precipitate which was filtered off. The material was recrystallized from CH_2Cl_2/n-hexane under anaerobic conditions to give deep red crystals. Yield: 330 mg (63% based on Tc). Melting point (m.p.) 155 °C. *Anal.* Calc. for $C_{16}H_{22}NOSP_2Cl_3Tc$: C, 35.3; H, 4.1; N, 2.6; Cl, 19.6; Tc, 18.2. Found: C, 35.2; H, 4.2; N, 2.5; Cl, 20.1; Tc, 17.1%. IR: ν(NS) 1240 cm^{-1}, ν(P=O) 1147 cm^{-1}.

$Tc(NS)Cl_2(Me_2PhP)_3$

A mixture of 200 mg (0.33 mmol) of $TcNCl_2(Me_2PhP)_3$ and 0.03 ml (0.33 mmol) of S_2Cl_2 in 40 ml CH_2Cl_2 was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the pale reddish* solid was recrystallized from CH_2Cl_2/n-hexane to give 82 mg (40% based on Tc) reddish crystals. M.p. 141–143 °C. *Anal.* Calc. for $C_{24}H_{33}NSP_3Cl_2Tc$: C, 45.7; N, 2.2; Cl, 11.2; Tc, 15.7. Found: C, 46.2; N, 2.3; Cl, 11.5; Tc, 15.9%. IR: ν(NS) 1177 cm^{-1}.

Physical Measurements

IR spectra were measured for KBr pellets on a UR 10 instrument.

Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB-HSQ spectrometer with argon as primary beam gas. The ion gun was operated at 8 kV and 100 μA. Glycerol was used as matrix.

EPR spectra were recorded in the X-band ($\nu \approx 9.3$ GHz) on an E-112 spectrometer (Varian) in chloroform solutions at $T = 295$ and 140 K.

X-ray Structure Determination of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$

Crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of a CH_2Cl_2/n-hexane solution. A crystal of approximately 0.18 × 0.23 × 0.23 mm was used for the measurements, at $T = 295$ K, using Cu Kα radiation. The unit cell dimensions were determined from the angular settings of 25 high angle reflections: $a = 10.513(1)$, $b = 14.274(2)$, $c = 15.187(2)$ Å. The space group was determined to be orthorhombic; $P2_12_12_1$. The intensity data of 6246 reflections (half a sphere up to $\theta = 70°$) were averaged to give 4309 unique reflections of which 3664 were observed ($I > 3\sigma$). Experimental details are given elsewhere [11]. Empirical absorption correction factors are in the range 0.78–1.00 (EMPABS, μ(Cu Kα) = 68.4 cm^{-1}).

The structure was solved by automated heavy-atom Patterson method (PATSYS). The isotropic R factor reduced from 0.12 to 0.07 upon application of empirical absorption corrections; correction factors are in the range 0.65–1.56 (DIFABS). The absolute configuration was established by the Bijvoet coefficient 0.872(3) for 679 selected Friedel pairs. All non-hydrogen atoms were refined with anisotropic temperature factors, phenyl groups with idealized geometry, and hydrogen atoms are included on calculated positions. The final conventional agreement factors were $R = 0.040$, $R_w = 0.048$ and $S = 1.49$ for 3664 'observed' reflections and 220 variables. The function minimized was $\Sigma w(F_o - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift over e.s.d. ratio in the last full-matrix least-squares cycle was less than 0.6 for the methyl groups and less than 0.1 Å for atomic positions. The final difference Fourier map showed maximum peaks of 0.70 e/Å^3 in the neighbourhood of Tc.

Programs used: PATSYS, BIJVOET, EMPABS, DIFABS, SHELX, PARST; see ref. 11.

Results and Discussion

Preparation and Characterization

The formation of low-valent technetium thionitrosyl complexes during the reaction of nitridotechnetium(V) complexes is not unexpected and follows a synthetic route which was successfully applied for rhenium compounds [12]. By analogy with the reaction of $ReNCl_2(Me_2PhP)_3$ [12], $TcNCl_2(Me_2PhP)_3$ reacts with equimolar amounts S_2Cl_2 to yield $Tc^I(NS)Cl_2(Me_2PhP)_3$. In the reaction with excess S_2Cl_2, however, a mixed phosphine/phosphine oxide complex is formed: $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$.

$Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ is a red crystalline solid which is stable in air and easily soluble in organic solvents such as $CHCl_3$ or benzene. The ν(NS) frequency in the infrared spectrum was found at 1240 cm^{-1}. This assignment was verified by isotope substitution. In the ^{15}N-substituted product the band is shifted bathochromically by 34 cm^{-1} [10]. The band occurring at 1147 cm^{-1} should be assigned to the P=O stretch of the coordinated Me_2PhPO ligand. Such a frequency cannot be found in the IR spectrum of the technetium(I) compound and underlines its

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*The reddish colour may be due to small amounts of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ impurities, which is indicated by a less intense room temperature EPR spectrum with the parameter set of the Tc(II) compound (see Table 1).

formulation as $Tc(NS)Cl_2(Me_2PhP)_3$, the ν(NS) frequency of which can be detected at 1177 cm^{-1} (1147 cm^{-1} for the ^{15}N-substituted complex [10].

Due to its 4 d^5 'low-spin'-configuration the Tc(II) complex $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ gives a well-resolved EPR spectrum with ten ^{99}Tc hyperfine (hfs) lines (^{99}Tc: $I = 9/2$) even at room temperature. The frozen solution spectrum shows a typically axial-symmetric pattern with ten ^{99}Tc hfs lines in the parallel and the perpendicular part. The lines in the parallel part are split into doublets due to the interaction of the unpaired electron with one ^{31}P nucleus ($I = 1/2$). The spectrum can be described by a spin Hamiltonian as given in ref. 7; the parameters are summarized in Table 1. They suggest an 'in-plane-π-type' MO for the unpaired electron. Therefore, contributions due to the axially coordinated ligands are expected to be very small and the ^{31}P splitting observed is caused by the equatorially coordinated phosphine ligand. In conclusion, it must be noted that no deviations can be observed concerning the EPR parameter set of $Tc(NS)Cl_3(Me_2PhP)_2$ and $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$. Electron nuclear double resonance studies which allow the detection of nuclei with small hyperfine couplings are in progress.

Figure 1 shows the high mass region of the FAB$^+$ mass spectrum of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$. A molecular ion peak ($m/z = 542$) could not be detected, but an intense peak at $m/z = 507$ can be assigned to a $M^+ - Cl$ fragment. Further fragmentation takes place by loss of complete ligands and by cleavage of the NS group. Scheme 1 summarizes the designation of selected metal-containing fragmentation products observed in the spectrum.

TABLE 1. EPR parameters of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)^a$ (coupling constants in 10^{-4} cm^{-1})

$\tilde{g}$	$\tilde{A}^{Tc}$	$\tilde{A}^{P}$
$g_0 = 2.032$	$a_0^{Tc} = 148.6$	$A_{\parallel}^{P} = 23.7$
$g_{\parallel} = 2.027$	$A_{\parallel}^{Tc} = 236.7$	
$g_{\perp} = 2.039$	$A_{\perp}^{Tc} = 106.3$	

^{a}The perpendicular part values $g_{\perp}$ and $A_{\perp}^{Tc}$ are derived using the relations $g_{\perp} = (3g_0 - g_{\parallel})/2$ and $A_{\perp}^{Tc} = (3a_0^{Tc} - A_{\parallel}^{Tc})/2$.

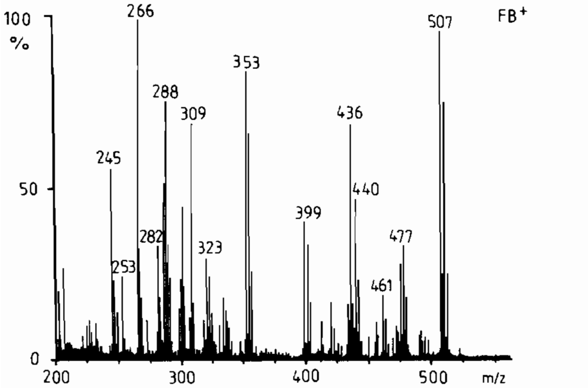


Fig. 1. FAB$^+$ mass spectrum of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$, matrix glycerol.

The title compound is the first example of a technetium complex with mixed phosphine/phosphine oxide coordination. A triphenylphosphine oxide technetium(III) complex, $TcCl_2(Ph_3PO)(HBpyz_3)$ ($HBpyz_3$ = hydrotris(1-pyrazolyl)borate), was prepared by the reaction of $TcOCl_2(HBpyz_3)$ with Ph_3P [13]. The Ph_3PO ligand in this compound was found to be very labile and could easily be replaced by other ligands. $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ does not react with excess Me_2PhP to form $Tc(NS)Cl_3(Me_2PhP)_2$ but yields by sulphur abstraction the nitridotechnetium(V) compound $TcNCl_2(Me_2PhP)_3$.

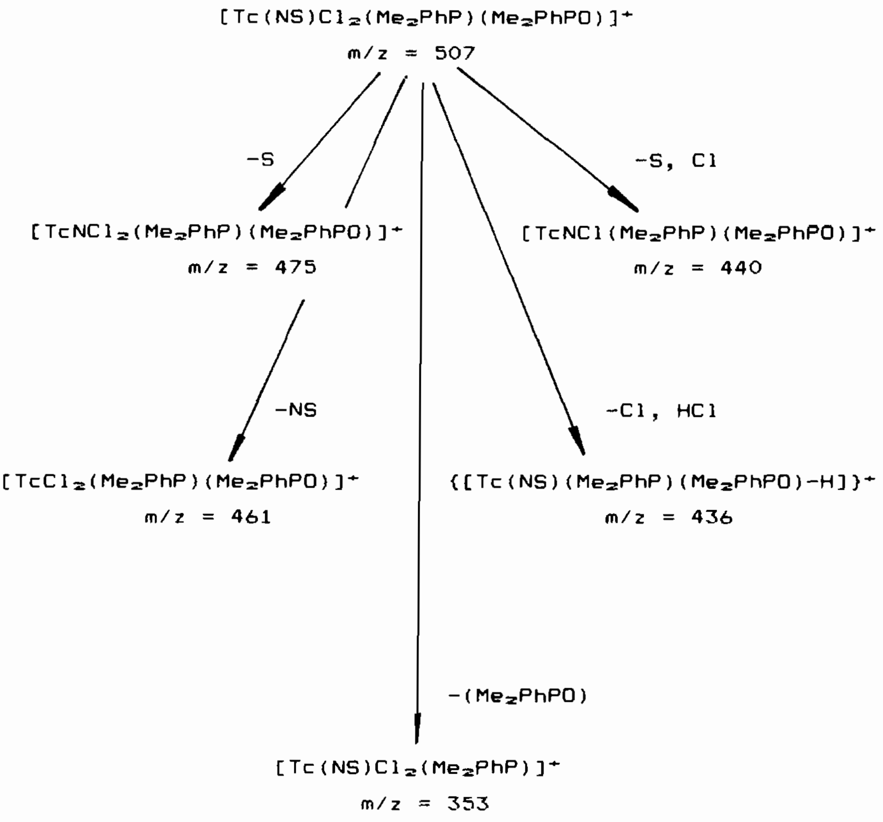
Until now, we have not been able to verify the source of oxygen which was used for the formation of the phosphine oxide. All chemicals had been purified carefully and purged with argon before use, and the reaction was performed under argon which was checked to contain no traces of oxygen.

X-ray Structure Determination of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$

The structure consists of discrete monomeric molecules. The molecular structure together with the crystallographic numbering scheme is given in Fig. 2. Table 2 contains the fractional positional parameters; selected interatomic distances and angles are collected in Table 3.

The technetium is six-coordinate, with the three chloro ligands coordinated meridionally *cis* to the thionitrosyl group. The phosphine oxide ligand is arranged in *trans* position to NS$^+$. The complex is slightly distorted from octahedral geometry, as the four ligands *cis* to the thionitrosyl bend out of the equatorial plane away from the thionitrosyl. This fact is reflected by the bond angles of 170.5(1)° (Cl1–Tc–Cl2) and 175.0(1)° (Cl3–Tc–P2).

The Tc–N–S bond is perfectly linear (Tc–N–S-angle: 179.9(1)°) and confirms the assignment of the ligand as NS$^+$ rather than NS$^-$. Similar results have been found for $Tc(NS)Cl_2(et_2dtc)_2$, the only other crystallographically characterized technetium thionitrosyl complex (Tc–N–S angle: 176° av. for two independent molecules) [5]. It comes close to the structural features in other transition metal thionitrosyl complexes [3]. The Tc–N bond length is quite short at 1.746(5) Å and compares favourably to the Tc–NS bond length in $Tc(NS)Cl_2(et_2dtc)_2$ [5] and Tc–NO bond lengths in six-coordinate nitrosyl complexes of technetium(I) and (II) (1.72–1.73 Å) [14–16]. The N–S bond length (1.521(5) Å)



Further metal containing fragments:

$[TcCl_2(Me_2PhPO)]^+$	m/z = 323
$[TcNCl(Me_2PhPO)]^+$	m/z = 302
$[TcCl(Me_2PhPO)]^+$	m/z = 288
$[Tc(NS)(Me_2PhP)]^+$	m/z = 282
$[TcN(Me_2PhPO-H)]^+$	m/z = 266
$[Tc(Me_2PhPO)]^+$	m/z = 253

Scheme 1.

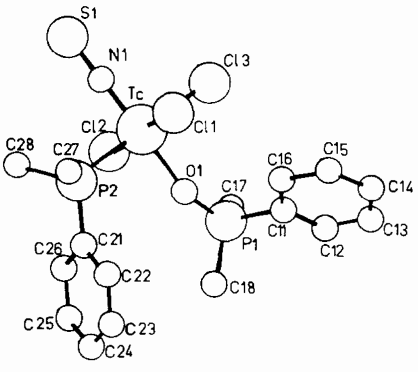


Fig. 2. Molecular structure of $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ with atomic numbering scheme.

shows no significant deviations from the values obtained for NS complexes of other metals (1.46–1.59 Å) [3]. Slight differences may occur by the different π-backbonding properties of the different coligands coordinated.

The phosphine oxide ligand is coordinated via O with a Tc–O bond length of 2.097(4) Å. This value is slightly shorter than those obtained for other axial Tc–O bonds [17] and comes in the range of the coordinated 'carbonyl' oxygen in tris(monothiodibenzoylmethanato)technetium(III) (2.01–2.09 Å) [18]. This slight lengthening could be understood by the *trans* influence of the thionitrosyl group but may also be due to steric interactions with the equatorial ligands taking into account that they are bent toward the axial phosphine oxide.

TABLE 2. Fractional positional and thermal parameters for the non-hydrogen atoms in $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$

Atom	x	y	z	$100 \times U_{eq}$ ($Å^2$)[a]
Tc	0.06451(4)	0.03127(4)	0.08722(3)	4.00(1)
Cl1	−0.04770(15)	0.09147(13)	−0.03415(12)	6.36(6)
Cl2	0.20676(14)	−0.02832(14)	0.19371(10)	5.60(5)
Cl3	−0.09018(15)	−0.09012(15)	0.11305(16)	7.84(8)
S1	−0.06410(21)	0.18216(18)	0.22217(14)	8.39(8)
N1	−0.0044(4)	0.1118(4)	0.1594(4)	5.08(17)
P1	0.18747(13)	−0.15362(12)	−0.03303(10)	4.10(5)
O1	0.1541(4)	−0.0558(3)	−0.00505(26)	4.35(13)
C11	0.0773(4)	−0.19503(27)	−0.1135(3)	4.43(18)
C12	0.0789(4)	−0.28851(27)	−0.1402(3)	6.22(25)
C13	−0.0066(4)	−0.31971(27)	−0.2041(3)	7.8(3)
C14	−0.0937(4)	−0.25742(27)	−0.2411(3)	7.8(3)
C15	−0.0953(4)	−0.16394(27)	−0.2143(3)	7.2(3)
C16	−0.0098(4)	−0.13274(27)	−0.1505(3)	5.65(24)
C17	0.1905(8)	−0.2366(5)	0.0543(5)	6.74(27)
C18	0.3397(6)	−0.1552(5)	−0.0832(6)	7.02(28)
P2	0.23596(13)	0.14465(11)	0.05745(9)	3.64(4)
C21	0.3808(4)	0.0955(3)	0.01167(23)	4.10(18)
C22	0.4755(4)	0.0613(3)	0.06746(23)	5.41(22)
C23	0.5885(4)	0.0264(3)	0.03230(23)	6.75(27)
C24	0.6070(4)	0.0258(3)	−0.05866(23)	7.4(3)
C25	0.5124(4)	0.0600(3)	−0.11445(23)	7.0(3)
C26	0.3993(4)	0.0948(3)	−0.07928(23)	5.58(22)
C27	0.1880(7)	0.2378(5)	−0.0159(5)	5.46(23)
C28	0.2806(6)	0.2065(5)	0.1553(4)	5.50(23)

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j a^*_i a^*_j a_i a_j U_{ij}$.

TABLE 3. Selected bond lengths and angles in $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ [a]

Bond lengths (Å)

Tc–N1	1.746(5)	Tc–Cl1	2.351(2)	Tc–Cl2	2.361(2)
Tc–Cl3	2.408(2)	Tc–O1	2.097(4)	N1–S1	1.521(5)
P1–O1	1.501(4)	P1–C11	1.784(5)	P1–C17	1.779(7)
P1–C18	1.773(6)	P2–C21	1.815(4)	P2–C27	1.806(6)
P2–C28	1.791(6)				

Bond angles (°)

Tc–N1–S1	179.9(1)	N1–Tc–O1	175.1(2)
Tc–O1–P1	147.7(3)	Cl1–Tc–Cl2	170.5(1)
Cl3–Tc–P2	175.0(1)	N1–Tc–P2	89.2(2)
Cl1–Tc–N1	92.5(2)	Cl2–Tc–N1	94.0(2)
Cl3–Tc–N1	95.2(2)		

[a] e.s.d.s given in parentheses.

A similar effect can be recognized for the chloro ligands with the chlorides *cis* to the phosphine having Tc–Cl bondings 0.05 Å shorter than that in *trans* position to the phosphine. This is consistent with the structural *trans* effect of the phosphine.

Table 4 contains a comparison of main structural features of the title complex with related Me_2PhP complexes of technetium: $TcNCl_2(Me_2PhP)_3$ [19] and *mer*-$TcCl_3(Me_2PhP)_3$ [20]. The Tc–N bond in the nitrido complex is significantly shorter than that in the thionitrosyl complex under study and represents a technetium–nitrogen triple bond. The Tc–P bond length in $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$ is shortened, possibly due to the lack of sterical hindrance by bulky coligands in the equatorial coordination sphere. In all compounds a slight *trans* labilizing effect of the phosphines can be found.

TABLE 4. Comparison of selected bond lengths (Å) in $Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$, $TcNCl_2(Me_2PhP)_3$ [19] and *mer*-$TcCl_3(Me_2PhP)_3$ [20]

Bond	Tc–N	Tc–P		Tc–Cl	
		trans to Cl3	*trans* to P	*trans* to Cl2	*trans* to P
$Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)$	1.746(5)	2.464(2)		2.351(1)	2.408(2)
$TcNCl_2(Me_2PhP)_3$	1.624(4)	2.444(1)	2.480(2)		2.441(1)
mer-$TcCl_3(Me_2PhP)_3$		2.42(1)	2.47(1)	2.33(1)	2.455(9)

Supplementary Material

A full list of atomic coordinates and anisotropic thermal parameters (including hydrogen atoms), and $F_0 - F_c$ tables are available from author P.T.B. (University of Nijmegen) on request.

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