

## Structure of *trans*-Tetrachlorobis(dimethylphenylphosphine)technetium(IV)

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**Abstract.** [TcCl<sub>4</sub>{P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>],  $M_r = 516.1$ , monoclinic,  $P2_1/c$ ,  $a = 9.692$  (2),  $b = 13.746$  (3),  $c = 8.339$  (2) Å,  $\beta = 106.56$  (2)°,  $V = 1064.9$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.61$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 13.1$  cm<sup>-1</sup>,  $F(000) = 259$ ,  $T = 293$  K,  $R = 0.037$  for 1703 observed reflections. The mean Tc—Cl distance is 2.324 (2) Å and the Tc—P distance is 2.531 (1) Å.

**Introduction.** Since an earlier study of  $M\text{Cl}_4(\text{PMe}_2\text{Ph})_2$  compounds with  $M = \text{W}$ , Re, Os or Ir (Aslanov, Mason, Wheeler & Whimp, 1970) revealed an interesting trend in  $M$ —P bond lengths through this horizontal series of compounds, we have studied the Tc compound to begin adding data on the vertical relationship.

**Experimental.** Crystals of this compound were provided by Professor A. Davison and Ms Anne Breikss, Department of Chemistry, Massachusetts Institute of Technology. A green crystal was mounted inside a thin-walled glass capillary and examined on a Nicolet four-circle autodiffractometer at Crystalitics Company, Lincoln, Nebraska. Crystal parameters and basic information on data collection and refinement are presented in Table 1. The structure was solved from a Patterson function followed by alternating cycles of full-matrix least-squares refinement and difference maps until all atoms had been found (Frenz, 1985). H atoms were omitted and all other atoms were refined with anisotropic displacement parameters.

**Discussion.** The positional parameters and equivalent thermal parameters are given in Table 2, and the bond distances and angles are listed in Table 3. Fig. 1 shows the structure and the atom numbering. ‡

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52863 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[TcCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] is presumably isomorphous with its previously reported Re analog although this cannot be asserted unequivocally because of the absence of crystal parameters in the earlier report. The mean  $M$ —Cl distances, 2.324 (2) and 2.331 (3) Å, are not significantly different in the Tc and Re compounds, but the Tc—P distance, 2.531 (1) Å, is slightly longer than the Re—P distance, 2.505 (3) Å. This tendency of  $M$ —P distances to be greater for the lighter  $M$  atom is already

Table 1. Crystallographic data

Systematic absences	0k0, $k \neq 2n$ $h0l$ , $l \neq 2n$
Crystal size (mm)	0.20 × 0.50 × 0.55
Orientation reflections	15, $2\theta > 20^\circ$
number, range $2\theta$ (°)	
Scan speed in $\omega$ (° min <sup>-1</sup> )	6.0 ( $2\theta \leq 43.0$ ); 3.0 ( $2\theta \geq 43.0$ )
Index ranges (data collection)	$h$ : 0–12; $k$ : 0–17; $l$ : –10–10
Scan method	$\omega$
Scan width, background measurement	1.10°; bg/scan time ratio = 0.50
Data collection range (°)	3–55
Monitor reflection, decay (stability)	6 reflections, no observed decay
Number of unique data, total	2441
with $F_o^2 > 3\sigma(F_o^2)$	1703
$R_{int}$	0.018
Number of parameters refined	106
Transmission factors	1.00, 0.73
(relative) max., min.	
$R$	0.037
$wR$ , $w = 1/\sigma^2( F_o )$	0.049
Quality-of-fit indicator	1.379
Largest shift/e.s.d., final cycle	0.01
Largest peak (e Å <sup>-3</sup> )	0.61

Table 2. Positional and equivalent isotropic displacement parameters for [TcCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]

$$B_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$B_{eq}$ (Å <sup>2</sup> )
Tc	0.000	0.000	0.000	2.360 (8)
Cl(1)	0.1283 (1)	0.06232 (9)	–0.1738 (1)	3.64 (2)
Cl(2)	0.1386 (1)	–0.14053 (9)	0.0373 (2)	3.92 (3)
P	0.1678 (1)	0.0697 (1)	0.2653 (1)	3.01 (2)
C(1)	0.3296 (5)	0.1264 (4)	0.2403 (5)	2.98 (9)
C(2)	0.4245 (5)	0.0678 (4)	0.1852 (7)	3.8 (1)
C(3)	0.5527 (6)	0.1078 (5)	0.1677 (7)	4.6 (1)
C(4)	0.5812 (6)	0.2069 (5)	0.2000 (7)	5.1 (1)
C(5)	0.4856 (7)	0.2638 (4)	0.2499 (8)	5.6 (1)
C(6)	0.3594 (6)	0.2258 (4)	0.2719 (7)	4.5 (1)
C(7)	0.2337 (7)	–0.0227 (5)	0.4248 (7)	5.1 (1)
C(8)	0.0795 (6)	0.1602 (5)	0.3629 (7)	4.8 (1)

Table 3. Bond distances (Å) and bond angles (°) for [TcCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]

Numbers in parentheses are e.s.d.'s in the least-significant digits.

Tc—Cl(1)	2.325 (1)	C(1)—C(2)	1.395 (6)
Tc—Cl(2)	2.322 (1)	C(1)—C(6)	1.405 (6)
Tc—P	2.531 (1)	C(2)—C(3)	1.404 (6)
P—C(1)	1.815 (4)	C(3)—C(4)	1.402 (8)
P—C(7)	1.817 (5)	C(4)—C(5)	1.365 (8)
P—C(8)	1.827 (5)	C(5)—C(6)	1.389 (8)
Cl(1)—Tc—Cl(2)	89.91 (4)	P—C(1)—C(2)	117.5 (3)
Cl(1)—Tc—P	94.63 (4)	P—C(1)—C(6)	122.3 (4)
Cl(2)—Tc—P	89.69 (4)	C(2)—C(1)—C(6)	120.2 (4)
Tc—P—C(1)	115.0 (1)	C(1)—C(2)—C(3)	119.7 (5)
Tc—P—C(7)	112.3 (2)	C(2)—C(3)—C(4)	119.5 (5)
Tc—P—C(8)	112.4 (2)	C(3)—C(4)—C(5)	120.1 (5)
C(1)—P—C(7)	104.5 (2)	C(4)—C(5)—C(6)	121.6 (5)
C(1)—P—C(8)	106.7 (2)	C(1)—C(6)—C(5)	118.9 (5)
C(7)—P—C(8)	105.1 (3)		

known in other compounds, such as corresponding pairs of Mo<sup>III</sup> and W<sup>III</sup> complexes, where the differences are *ca* 0.02 Å (Canich, Cotton, Daniels & Lewis, 1987). An explanation for this does not appear to have been presented. If it were a relativistic effect it might have been expected to shorten all metal–ligand distances. It may be that the heavier atom has *d* orbitals better suited for  $\pi$  bonding to the P atom.

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## Structures of Two Niobium(IV) Complexes: [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[NbCl<sub>6</sub>] and [P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)H][NbCl<sub>5</sub>{P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]

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**Abstract.** Bis(tetraethylammonium) hexachloroniobate(IV),  $M_r = 566.13$ , monoclinic,  $C2/c$ ,  $a = 14.006$  (2),  $b = 14.366$  (4),  $c = 13.206$  (3) Å,  $\beta = 90.67$  (2)°,  $V = 2657$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.415$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 9.12$  cm<sup>-1</sup>,  $F(000) = 293$ ,  $T = 295$  K,  $R = 0.055$  for 1184 observed reflections. The independent Nb—Cl distances and the average value are 2.413 (2), 2.422 (2), 2.393 (2) and 2.409 (9) Å. The Cl—Nb—Cl angles average 90° by symmetry and range from 89.36 (8) to 90.78 (8)°. Dimethylphenylphosphonium penta-

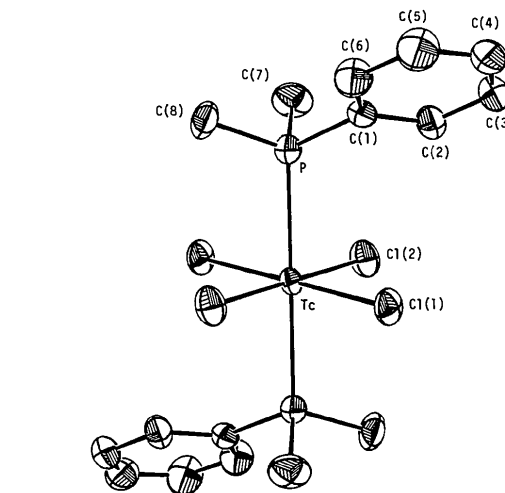


Fig. 1. ORTEP (Johnson, 1965) drawing of [TcCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]. The ellipsoids are drawn at 40% probability level.

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chloro(dimethylphenylphosphine)niobate(IV),  $M_r = 547.48$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.830$  (3),  $b = 13.633$  (6),  $c = 13.021$  (5) Å,  $V = 2277$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.597$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 12.33$  cm<sup>-1</sup>,  $F(000) = 275$ ,  $T = 295$  K,  $R = 0.0546$  for 1257 observed reflections. The quasi-octahedral anion has an Nb—P distance of 2.673 (5) Å, an Nb—Cl distance *trans* to P of 2.405 (5) Å and *cis* Nb—Cl distances of 2.366 (10), 2.362 (10), 2.360 (10) and 2.394 (10) Å, which give an average of 2.363 (2) Å, excluding the last one which is affected by hydrogen bonding. Thus, there is a *trans* influence from the phosphine ligand of 0.042 (5) Å.

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