Preparation and Crystal and Molecular Structure of *mer*-Trichlorotris(dimethylphenylphosphine)technetium(III)

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The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray diffractometer data by Fourier methods and refined by anisotropic block-diagonal least-squares to *R* 0.054 for 4 065 independent observed reflections. Crystals are monoclinic, space group $P2_1/n$, with cell parameters a = 10.935(9), b = 39.191(11), c = 13.738(7) Å, β = 107.33(7)°, and Z = 8. The two crystallographically independent molecules are stereochemically equivalent (there is only a small difference in the orientation of a benzene ring) and the metal atom has a somewhat distorted octahedral co-ordination, with two pairs of like ligands mutually *trans*. Technetium–ligand bond distances are: Tc–Cl (*trans* to P) 2.46(1), Tc–Cl (*trans* to Cl) both 2.33(1), Tc–P (*trans* to Cl) 2.42(1) and Tc–P (*trans* to P) both 2.47(1) Å. The noticeable *trans*-influence of the phosphine ligands on Tc–Cl bonds is discussed.

THE phosphine derivatives of technetium have been already studied intensively by us.[1] Since much work has been carried out on the chemistry and stereochemistry of the compounds *mer*-[MCl_3L_3] [M = Re, Os, or Ir, L = PMe_2Ph (ref. 2), M = Rh, L = PEt_2Ph (ref. 3)], we have investigated the properties of the analogous complex *mer*-[$TcCl_3(PMe_2Ph)_3$] in order to establish any connection between technetium and neighbouring atoms in the Periodic Table and to study the dependence of M–P and M–Cl bond lengths on the electronic configuration of the metal for the second-row transition-metal, as was done by Mason *et al.* for complexes of third-row transition-metals.[2]

EXPERIMENTAL

Preparation.— *mer*-Trichlorotris(dimethylphenylphosphine)technetium(III) was prepared by two different methods. (*a*) Diammonium hexachlorotechnetate(IV) (0.5 g, 1.4 mmol) and dimethylphenylphosphine (6 ml, 43 mmol) in anhydrous ethanol (40 ml) were heated under reflux under nitrogen for *ca.* 24 h, until the initial solid had completely disappeared. Reduction in volume of the orange solution followed by cooling gave yellow-orange crystals of *mer*-[$TcCl_3(PMe_2Ph)_3$] (80%). (*b*) Ammonium pertechnetate (0.5 g, 2.8 mmol), dimethylphenylphosphine (6 ml, 43 mmol), and concentrated hydrochloric acid (2.5 ml) in ethanol (60 ml) were heated under reflux for a few minutes. The resulting orange solution was then reduced in volume and yellow-orange crystals precipitated on cooling (90%). Crystals suitable for *X*-ray work were grown by keeping the ethanolic solution at 40 °C for several days and then leaving it at room temperature to evaporate.

Crystal Data.—$C_{24}H_{33}Cl_3P_3Tc$, $M = 619.8$, Monoclinic, $a = 10.935(9)$, $b = 39.191(11)$, $c = 13.738(7)$ Å, $\beta = 107.33(7)°$, $U = 5\,620.2$ Å^3, D_m (by flotation) = 1.45, $Z = 8$ (two molecules in the asymmetric unit), $D_c = 1.46$ g cm^{-3}, $F(000) = 2\,528$. Space group $P2_1/n$ (a non-standard orientation of $P2_1/c$, No. 14) from systematic absences, with the general equivalent positions: $\pm (x, y, z)$; $\pm (1/2 + x, 1/2 - y, 1/2 + z)$. Cu-$K_\alpha$ radiation, $\lambda = 1.541\,78$ Å; μ(Cu-K_α) = 86.3 cm^{-1}.

Measurements.—Intensity data were collected for a crystal *ca.* 0.45 × 0.10 × 0.31 mm, protected from air and mounted with the *a* axis nearly coincident with the ϕ-axis of a Siemens on-line automatic four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4.5°, a Ni-β filter and a Na(Tl)I scintillation counter were used. Unit-cell parameters, determined initially from *X*-ray photographs, were adjusted by a least-squares fit of the setting angles of 30 accurately centred reflections. The intensities of 4 525 independent reflections (to θ 45°) were measured by use of the θ—2θ scan technique with a five-value measuring procedure. Of these, 460 were considered unobserved, having $I \leqslant 2.5\sigma(I)$. The net count of the 212 reflection, monitored every 20 reflections, did not change noticeably during data collection (*ca.* 12 days). Data were adjusted to

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[1] G. Bandoli, D. A. Clemente, U. Mazzi, and E. Tondello, *Cryst. Struct. Comm.*, 1974, **3**, 293; U. Mazzi, D. A. Clemente, G. Bandoli, L. Magon, and A. A. Orio, *Inorg. Chem.*, to be published; M. Biagini Cingi, D. A. Clemente, L. Magon, and U. Mazzi, *Inorg. Chim. Acta*, 1975, **13**, 47.

[2] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

[3] A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1973, 1789.

a common arbitrary scale using the reference reflection, and Lorentz and polarisation corrections were applied. An absorption correction was made according to the method of ref. 4, the choice of which was justified since the present maximum μR is 3.9 (and it has been shown [4] that the approximations in the model calculation are satisfactory for $\mu R \leqslant 4.5$); also, the machine time, both on the four-circle diffractometer and on the computer, is surprisingly short. Moreover, this absorption-correction procedure has been tested by comparing the deviations of the intensities of symmetry-equivalent reflections before and after absorption correction; an R factor, defined as $R = \Sigma(F_i - F_j)/\Sigma F$ (F_i and F_j equivalent reflections), decreased from 3.4 to 1.8%.

Solution and Refinement of the Structure.—An unsharpened three-dimensional Patterson revealed the positions of the two technetium atoms, refinement of which gave R 0.46. The chlorine and the phosphorus atoms were located from the resulting difference-Fourier synthesis. Further refinement (with unit weights assigned to each reflection) including these positions reduced R to 0.24, and the positions of the remaining 48 non-hydrogen atoms were found from a subsequent difference synthesis. Three cycles of block-diagonal least-squares refinement of the positional parameters, with only the 'inner core' anisotropic, lowered R to 0.09. The function minimised in the refinement (unobserved reflections were excluded) was $\Sigma w(K|F_o| - |F_c|)^2$, where K is the overall scale factor, while the weighting scheme used was the reciprocal of the best polynomial fitting of ΔF^2 as a function of $|F_o|$, *i.e.* $w^{-1} = a_i|F_o|^i$. The best fitting was not achieved *via* the usual least-squares method but, with better results, *via* orthogonal polynomials. The number and value of the a_i parameters were adjusted by our own computer program, PESO, during refinement so as to give approximately constant average of $w\Delta F^2$ for equally populated ranges of $|F_o|$. (An analysis of the final distribution of $w\Delta F^2$ in 15 ranges of $|F_o|$ showed maximum 1.53 and minimum 0.67.) Allowance was then made for the anisotropic thermal vibrations for all non-hydrogen atoms and the application of a dispersion correction with four further cycles of refinement reduced R to 0.054. In the last cycle all parameter shifts were $<0.5\sigma$. A final difference-Fourier map was essentially featureless. Atomic scattering factors used were taken from ref. 5, with allowance for anomalous dispersion ($\Delta f'$, $\Delta f''$ for technetium, phosphorus, and chlorine from ref. 6).

Final parameters are given in Table 1 with standard deviations in parentheses. Calculated and observed structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21523 (8 pp., 1 microfiche).*

The solution and refinement of the structure were carried out by use of the X-ray '70 program system,[7] on the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6 600 computer.

RESULTS AND DISCUSSION

Preparation.—Elemental analysis, magnetic susceptibility, i.r., and ^{1}H n.m.r. measurements showed the product obtained by either method to be the same. Comparison of the first method with that for the analogous diethylphenyl phosphonite complex is of interest.[1] In fact, when an excess of PMe_2Ph is used the compound ***mer***-$[TcCl_3(PMe_2Ph)_3]$ is obtained, while in similar conditions excess of $P(OEt)_2Ph$ affords ***trans***-$[TcCl_2\{P(OEt)_2Ph\}_4]Cl$. This difference in behaviour is a result of the electronic and steric distinction between phosphine and phosphonite.[8] We suggest that in both cases the *mer*-$[TcCl_3L_3]$ complex is obtained, but owing to the larger *trans*-effect and smaller steric hindrance of the $P(OEt)_2Ph$ ligand than for the phosphine, chlorine can be displaced from the plane of the three phosphorus only by $P(OEt)_2Ph$. The larger *trans*-effect of $P(OEt)_2Ph$ appears to be quite reasonable [9] since the more electron-deficient phosphorus can behave as stronger π-acceptor.[10] The smaller steric hindrance of $P(OEt)_2Ph$ compared with PMe_2Ph is consistent with C–P–O angles being less than the corresponding C–P–C, P–O distances being less than P–C, and the oxygen van der Waals radius being less than that of $-CH_3$. Further, the phosphonites have a smaller 'Tolman cone angle' [9] than do the bulky phosphines although compounds containing the $Re(PMe_2Ph)_4$ moiety, with the four phosphorus atoms in one plane, are known.[11]

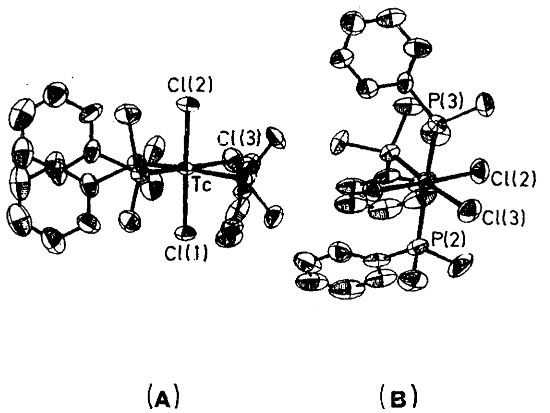

FIGURE 1 Relative orientation of the two molecules (A) and (B) in the asymmetric unit projected along [100]. Thermal vibration ellipsoids scaled to include 50% probability

Molecular Geometry.—The crystal structure of the complex *mer*-$[TcCl_3(PMe_2Ph)_3]$ is built up of two independent molecules [labelled (A) and (B)] in the asymmetric unit of a large monoclinic unit cell and completely agrees with that found in the series of complexes *mer*-$[MCl_3L_3]$ ($M = Re^{III}, Os^{III}$, or Ir^{III}, $L = PMe_2Ph$).[2] Moreover, the title compound is monomeric and the relative orientation of molecules (A) and (B) is shown in

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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[8] D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 4545.

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[11] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578; M. Mercer, *J.C.S. Dalton*, 1974, 1637; J. Chatt, G. R. Dilworth, and G. J. Leigh, *Chem. Comm.*, 1969, 687.

TABLE 1

(*a*) Final fractional co-ordinates (× 10^4), with standard deviations in parentheses

Atom	x/a	y/b	z/c
(*a*) Molecule (A)			
Tc	3 153(1)	96(0)	2 144(0)
Cl(1)	3 492(3)	99(1)	3 898(2)
Cl(2)	2 920(3)	81(1)	406(2)
Cl(3)	1 425(2)	−325(1)	1 904(2)
Ligand (1) *			
P(1)	4 855(2)	505(1)	2 277(2)
C(11)	4 460(9)	930(2)	1 697(7)
C(21)	4 852(10)	1 223(2)	2 261(8)
C(31)	4 589(11)	1 544(3)	1 760(10)
C(41)	3 945(12)	1 553(3)	714(11)
C(51)	3 540(12)	1 256(3)	165(9)
C(61)	3 815(10)	947(3)	666(7)
C(71)	5 804(11)	594(3)	3 578(8)
C(81)	6 068(11)	379(3)	1 652(10)
Ligand (2)			
P(2)	1 484(2)	533(1)	2 002(2)
C(12)	1 959(9)	953(2)	2 619(8)
C(22)	1 608(10)	1 259(2)	2 066(9)
C(32)	2 015(11)	1 567(3)	2 569(11)
C(42)	2 736(12)	1 571(3)	3 573(11)
C(52)	3 044(11)	1 270(3)	4 124(9)
C(62)	2 661(10)	959(3)	3 649(7)
C(72)	510(12)	617(3)	685(8)
C(82)	257(11)	401(3)	2 593(10)
Ligand (3)			
P(3)	4 501(2)	−424(1)	2 410(2)
C(13)	6 230(9)	−414(2)	2 743(6)
C(23)	6 878(10)	−478(2)	2 014(8)
C(33)	8 200(11)	−447(3)	2 285(9)
C(43)	8 917(11)	−367(3)	3 282(10)
C(53)	8 270(11)	−293(3)	3 996(8)
C(63)	6 940(9)	−319(2)	3 724(7)
C(73)	4 020(11)	−708(2)	1 294(8)
C(83)	4 250(10)	−690(2)	3 436(8)
(*b*) Molecule (B)			
Tc	2 478(1)	−2 052(0)	2 460(1)
Cl(1)	3 786(2)	−1 569(1)	2 710(2)
Cl(2)	1 140(2)	−2 529(1)	2 149(2)
Cl(3)	4 273(3)	−2 439(1)	3 221(2)
Ligand (1)			
P(1)	566(2)	−1 726(1)	1 666(2)
C(11)	−679(8)	−1 702(3)	2 303(6)
C(21)	−1 073(9)	−1 387(3)	2 601(7)
C(31)	−2 087(11)	−1 379(3)	3 059(8)
C(41)	−2 671(11)	−1 687(4)	3 197(8)
C(51)	−2 290(10)	−1 995(3)	2 900(8)
C(61)	−1 269(9)	−2 013(3)	2 456(7)
C(71)	843(10)	−1 276(2)	1 402(8)
C(81)	−382(10)	−1 890(3)	406(7)
Ligand (2)			
P(2)	2 394(2)	−1 978(1)	4 219(2)
C(12)	1 598(9)	−1 613(3)	4 583(6)
C(22)	662(10)	−1 649(3)	5 074(8)
C(32)	134(11)	−1 350(4)	5 386(8)
C(42)	497(12)	−1 033(4)	5 183(8)
C(52)	1 441(11)	−995(3)	4 662(8)
C(62)	1 970(10)	−1 282(3)	4 375(8)
C(72)	1 773(12)	−2 359(3)	4 700(9)
C(82)	3 989(10)	−1 932(3)	5 134(8)
Ligand (3)			
P(3)	3 083(2)	−2 143(1)	877(2)
C(13)	2 562(8)	− 1856(2)	−231(7)
C(23)	1 783(10)	−1 964(3)	−1 175(7)
C(33)	1 453(11)	−1 726(3)	−1 981(8)
C(43)	1 886(11)	−1 389(3)	−1 831(9)
C(53)	2 660(11)	−1 292(3)	−882(8)
C(63)	2 982(10)	−1 521(2)	−79(7)
C(73)	2 677(12)	−2 570(3)	342(8)
C(83)	4 835(10)	−2 133(3)	1 128(9)

* The second digit in the C atom numbering system denotes the ligand: (1)–(3).

Figure 1, which also shows the thermal vibration ellipsoids of the non-hydrogen atoms.[12]

The co-ordination about technetium is distorted octahedral and the two groups of ligands are arranged such that there are two pairs of like ligands *trans*, leaving the remaining phosphorus atom *trans* to chlorine, *i.e.* the arrangement of the phosphine ligands is meridional, giving the isomer which, of the two possibilities (*fac* or *mer*), has the last steric hindrance between

TABLE 2

(*a*) Least-squares planes with the deviations (Å) of relevant atoms in square brackets. The equation of a plane in direct space is given by $Px + Qy + Rz = S$, where x, y, and z are in fractional unit cell co-ordinates

	P	Q	R	S
Plane (1):				
Tc, P(1)—(3), Cl(3)	−1.600 *	0.728	13.570	2.426
	6.173	31.785	−0.298	−5.066

[Tc −0.01(0.0),† P(1) −0.08(−0.12), P(2) 0.09(0.13), Cl(3) −0.09(−0.14), P(3) 0.09(0.13), Cl(1) 2.31(2.34), Cl(2) −2.34(−2.33), C(71) 1.54(1.49), C(81) −1.13(−1.19), C(72) −1.53(−1.48), C(82) 1.08(1.24), C(73) −1.36(−1.46) C(83) 1.51(1.24)]

	P	Q	R	S
Plane (2):				
Tc, P(1), Cl(1)—(3)	−7.169	29.175	1.026	−1.788
	−4.686	5.046	13.482	1.103

[Tc 0.03(0.02), P(1) 0.01(0.01), Cl(1) −0.03(−0.02), Cl(2) −0.03(−0.02), Cl(3) 0.01(0.01), P(2) 2.48(2.47), P(3) −2.43(−2.45)]

	P	Q	R	S
Plane (3):				
Tc, P(2), P(3), Cl(1), Cl(2)	8.224	25.359	−1.434	2.441
	−7.615	22.744	−2.687	−7.301

[Tc 0.09(0.09), P(2) −0.16(−0.15), P(3) −0.16(−0.16), Cl(1) 0.12(0.12), Cl(2) 0.11(0.10), P(1) 2.51(2.50), Cl(3) −2.37(−2.37)]

	P	Q	R	S
Plane (4):				
C(11)—(61)	10.691	−1.661	−6.698	3.474
	4.514	−3.940	10.182	2.713

[C(11) 0.0(0.0), C(21) 0.0(0.0), C(31) 0.0(0.0), C(41) 0.01(0.0), C(51) −0.01(−0.01), C(61) 0.0(0.01), P(1) 0.11(−0.08), C(71) 0.24(−0.40)]

	P	Q	R	S
Plane (5):				
C(12)—(62)	10.546	−1.882	−7.355	−0.053
	5.228	−0.094	9.561	5.225

[C(12) 0.01(0.01), C(22) −0.01(−0.01), C(32) −0.01(0.01), C(42) 0.01(0.0), C(52) −0.01(0.0), C(62) −0.01(0.0), P(2) 0.05(0.08), C(72) −0.03(0.22)]

	P	Q	R	S
Plane (6):				
C(13)—(63)	−0.012	37.800	−3.458	−2.510
	10.195	−10.025	−7.169	4.631

[C(13) −0.01(0.01), C(23) 0.0(0.0), C(33) 0.02(0.0), C(43) −0.02(0.0), C(53) 0.01(0.01), C(63) 0.01(−0.01), P(3) 0.07 (0.03), C(73) −0.62(0.43)]

(*b*) Angles (°) between the mean planes †

(1)–(2)	89.1 (90.0)	(1)–(9) ‡	5.6 (21.8)	(5)–(8) ‡	52.5 (53.6)
(1)–(3)	88.5 (89.3)	(2)–(3)	88.4 (89.7)	(6)–(9) ‡	75.4 (63.0)
(1)–(4)	69.7 (73.1)	(2)–(4)	49.7 (51.7)	(3)–(5)	48.6 (45.1)
(1)–(5)	66.5 (66.2)	(2)–(5)	50.6 (54.5)	(3)–(6)	53.8 (46.4)
(1)–(6)	75.9 (73.8)	(2)–(6)	41.2 (48.6)	(4)–(5)	3.2 (6.9)
(1)–(7) ‡	24.7 (24.8)	(3)–(4)	47.0 (43.3)	(4)–(6)	89.3 (79.7)
(1)–(8) ‡	27.7 (23.3)	(4)–(7) ‡	55.2 (60.8)	(5)–(6)	88.8 (77.2)

* Values for molecule (A) are above those for molecule (B). † Values in parentheses are for molecule (B). ‡ Plane (7): Tc, P(1), C(11); plane (8): Tc, P(2), C(12); plane (9): Tc, P(3), C(13).

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[12] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory Report, 1965, ORNL 3974.

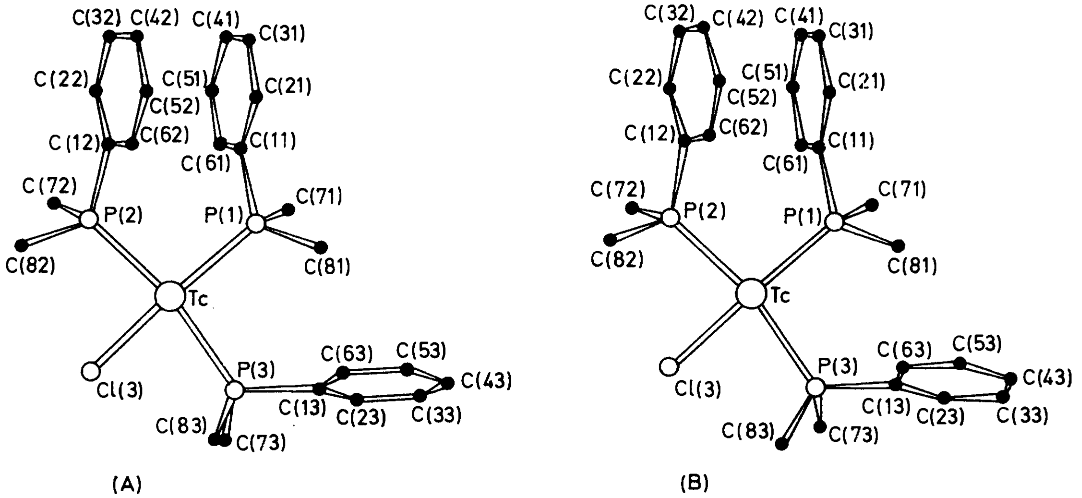

FIGURE 2 Projection of the two independent molecules (A) and (B) on the plane Tc, P(1)—(3) and Cl(3). Cl(1) and Cl(2) are omitted for clarity. The numbering system is also shown

TABLE 3

(*a*) Bond lengths (Å) with standard deviations in parentheses *

(i) In the inner co-ordination sphere of technetium

	(A)	(B)		(A)	(B)
Tc–P(1)	2.42(1)	2.42(1)	Tc–Cl(1)	2.33(1)	2.33(1)
Tc–P(2)	2.47(1)	2.46(1)	Tc–Cl(2)	2.33(1)	2.33(1)
Tc–P(3)	2.48(1)	2.48(1)	Tc–Cl(3)	2.46(1)	2.45(1)

(ii) In the phosphine ligands

	Ligand (1)		Ligand (2)		Ligand (3)	
	(A)	(B)	(A)	(B)	(A)	(B)
P–C(1)	1.84(2)	1.83(2)	1.85(2)	1.82(2)	1.81(2)	1.84(2)
P–C(7)	1.81(2)	1.84(2)	1.83(2)	1.84(2)	1.84(2)	1.83(2)
P–C(8)	1.85(2)	1.85(2)	1.84(2)	1.83(2)	1.84(2)	1.84(2)
C(1)–C(2)	1.38(2)	1.41(3)	1.41(3)	1.39(3)	1.41(2)	1.39(2)
C(2)–C(3)	1.42(3)	1.43(3)	1.40(3)	1.43(3)	1.39(3)	1.41(3)
C(3)–C(4)	1.40(3)	1.40(3)	1.37(3)	1.36(3)	1.40(3)	1.40(3)
C(4)–C(5)	1.39(3)	1.38(3)	1.39(3)	1.43(3)	1.40(3)	1.38(3)
C(5)–C(6)	1.38(3)	1.42(3)	1.39(3)	1.38(3)	1.39(3)	1.38(3)
C(6)–C(1)	1.38(2)	1.42(3)	1.39(2)	1.41(3)	1.39(2)	1.39(2)

(*b*) Bond angles (°) with standard deviations in parentheses *

(i) About technetium:

	(A)	(B)		(A)	(B)
Cl(1)–Tc–Cl(2)	177.0(2)	178.0(2)	Cl(1)–Tc–P(3)	87.0(2)	86.2(2)
P(1)–Tc–P(2)	94.6(2)	95.8(2)	Cl(2)–Tc–P(1)	86.6(2)	86.0(2)
P(2)–Tc–Cl(3)	86.2(2)	85.0(2)	Cl(2)–Tc–P(2)	94.8(2)	94.0(2)
Cl(3)–Tc–P(3)	82.4(2)	84.0(2)	Cl(2)–Tc–Cl(3)	90.0(2)	87.8(2)
P(3)–Tc–P(1)	97.1(2)	95.8(2)	Cl(2)–Tc–P(3)	90.5(2)	92.3(2)
Cl(1)–Tc–P(1)	92.1(2)	92.7(2)	P(2)–Tc–Cl(3)	176.6(2)	173.7(2)
Cl(1)–Tc–P(2)	87.9(2)	87.7(2)	P(2)–Tc–P(3)	167.4(2)	167.2(2)
Cl(1)–Tc–Cl(3)	91.2(2)	93.5(2)			

(ii) Angles about phosphorus and other angles in the phosphine ligands *:

	Ligand (1)		Ligand (2)		Ligand (3)	
	(A)	(B)	(A)	(B)	(A)	(B)
Tc–P–C(1)	119.4 (0.6)	118.6 (0.6)	118.7 (0.6)	121.5 (0.6)	123.4 (0.6)	122.6 (0.7)
Tc–P–C(7)	113.8 (0.8)	115.1 (0.7)	113.6 (0.8)	112.5 (0.8)	111.4 (0.6)	112.8 (0.9)
Tc–P–C(8)	115.4 (0.8)	114.1 (0.8)	112.9 (0.8)	112.3 (0.8)	111.2 (0.7)	111.5 (0.8)
C(1)–P–C(7)	104.1 (1.0)	103.6 (1.1)	107.0 (1.0)	106.3 (1.1)	104.0 (1.0)	104.4 (0.8)
C(1)–P–C(8)	98.6 (1.0)	100.2 (0.9)	101.0 (1.1)	99.8 (1.0)	101.7 (1.0)	101.0 (1.0)
C(7)–P–C(8)	103.3 (1.1)	103.2 (1.0)	101.6 (1.1)	102.2 (1.0)	103.0 (0.9)	102.1 (1.2)
P–C(1)–C(2)	121.1 (1.3)	121.4 (1.6)	121.0 (1.4)	122.3 (1.8)	121.7 (1.2)	122.6 (1.4)
P–C(1)–C(6)	118.0 (1.4)	117.5 (1.6)	118.3 (1.4)	118.4 (1.6)	119.4 (1.5)	116.6 (1.6)
C(2)–C(1)–C(6)	120.9 (1.7)	121.1 (1.7)	120.8 (1.7)	119.3 (2.1)	118.8 (1.8)	120.9 (1.7)
C(1)–C(2)–C(3)	118.7 (1.8)	119.5 (2.0)	118.2 (2.0)	119.0 (2.2)	119.8 (1.8)	118.3 (1.9)
C(2)–C(3)–C(4)	119.1 (2.0)	119.0 (2.2)	120.8 (2.3)	121.3 (2.4)	121.3 (2.4)	120.9 (1.8)
C(3)–C(4)–C(5)	121.3 (2.2)	121.5 (2.4)	120.9 (2.2)	119.8 (2.3)	118.7 (2.1)	119.0 (2.1)
C(4)–C(5)–C(6)	118.6 (2.0)	121.0 (2.2)	120.0 (2.0)	119.1 (2.3)	120.1 (2.4)	120.9 (2.0)
C(1)–C(6)–C(5)	121.4 (2.0)	117.9 (2.0)	119.3 (1.9)	121.4 (2.2)	121.1 (2.0)	120.0 (1.6)

* Taking into account accuracy of cell parameters.

the phosphine ligands. However, the angles between *cis*-ligands vary between 82.4 and 95.8°, while the *trans*-angles are between 167.2 and 178.0°, a departure from the ideal octahedron which is usually ascribed to the mutual repulsion of bulky phosphine ligands. The distortion can also be seen by examination of the mean planes (Table 2). The approximate non-crystallographic symmetry of the 'inner core' is C_s (m) [while for the ideal *mer*-octahedron it should be C_{2v} ($2mm$)], the mirror of symmetry being coincident with P(1), Cl(1)—(3) (maximum individual deviation 0.03 Å). Accordingly, looking along the normal to this plane, atoms P(2) and P(3) are mutually eclipsed [mean P(2)–Tc–P(3) 167.3°].

The two independent molecules (Figure 2) differ slightly, the major difference lying in the torsion angles about Tc–P(3) and P(3)–C(13) bonds (see crystal packing section). Bond lengths and bond angles are listed in Table 3.

Technetium–Ligand Bond Lengths.—The Tc–Cl bond length *trans* to the phosphine ligand is longer than the mutually *trans*-Tc–Cl bonds of 0.13 Å. Likewise, the mutually *trans* Tc–P bonds are longer than those *trans* to chlorine by 0.06 Å. These values are in the expected range,[2,3] showing the structural *trans*-influence of a co-ordinated tertiary phosphine ligand on an M–Cl or M–P bond length in an octahedral complex of *ca.* 0.1 and 0.06 Å. Moreover, in the complexes *mer*-[$\mathrm{MCl_3(PMe_2Ph)_3}$] (M = Re, Os, or Ir),[2] increasing the population of the $5d$ shell, involves a linear shortening of *ca.* 0.05 Å for unit charge of electronic configuration for the $\mathrm{M^{III}}$–P bond length. Although there are at present insufficient bond-length data, we suggest a similar trend for the $4d$ shell also; since the Rh–P distances[3] in *mer*-[$\mathrm{RhCl_3(PEt_2Ph)_3}$] are 2.40 (*trans*-P) and 2.33 Å (*trans*-Cl), in *mer*-[$\mathrm{TcCl_3(PMe_2Ph)_3}$] we would expect Tc–P distances of 2.50 (*trans*-P) and 2.43 Å (*trans*-Cl). Indeed, the agreement with the experimental values (2.48 and 2.42 Å, respectively) is good, but to support this idea a similar comparison should include structural data for [$\mathrm{RuCl_3(PMe_2Ph)_3}$] and [$\mathrm{MoCl_3(PMe_2Ph)_3}$]. An accurate molecular structure determination of the anion *mer*-[$\mathrm{RuCl_3(PEt_2Ph)_3}$]$^-$ has been made,[13] but the Ru–Cl and Ru–P distances do not fit the linear relationship for a $4d^6$ configuration, $\mathrm{Ru^{II}}$–Cl being longer and $\mathrm{Ru^{II}}$–P shorter than the corresponding expected $\mathrm{M^{III}}$–Cl and $\mathrm{M^{III}}$–P distances. Tc–Cl (*trans*-Cl) and Tc–Cl (*trans*-P) distances are nearly coincident with the corresponding ones in *mer*-[$\mathrm{M^{III}Cl_3L_3}$] complexes,[2,3] since a change in the metal has little effect on the M–Cl bond lengths.

A comparison of the Tc–P and Tc–Cl bond lengths in the present complex with those in the closely related compounds[1] *trans*-[$\mathrm{TcCl_2\{P(OEt)_2Ph\}_4}$] and *cis*-[$\mathrm{Tc(CO)_2\{P(OEt)_2Ph\}_4}$]$^+\mathrm{ClO_4}^-$ shows: (*a*) mutually *trans*-Tc–P bonds are considerably longer (0.06 Å) with a tertiary phosphine, a difference not due to the different octahedral covalent radius of technetium in valence states (I), (II), or (III) (this variation, if any, should lead to shorter distances), but to be expected since the diethylphenyl phosphonite is a better π-acceptor than the phosphine ligand,[9] and (*b*) the mutually *trans*-Tc–Cl bonds are significantly shorter (*ca.* 0.08 Å) in the $\mathrm{Tc^{III}}$ complex, since the Tc–Cl bond is substantially ionic and thus sensitive to the formal oxidation state of the metal.[2]

The Phosphine Ligand.—In tertiary-phosphine ligands the P–C(sp^2) bond lengths are usually slightly shorter than P–C(sp^3);[14] however this is not detectable in the present complex, mean P–C(sp^2) distances [1.83(2) Å] being equal to mean P–C(sp^3) [1.84(2) Å]. All Tc–P–C angles are significantly larger than the tetrahedral value and consequently all C–P–C angles smaller. Such distortions are common in transition-metal complexes of phosphine ligands and have been ascribed to the contraction of the metal–phosphorus bond.[15]

In the six-membered aromatic rings the mean C–C bond length is 1.397 Å, as expected.[16] The rings are closely planar, maximum deviation of an individual atom being 0.02 Å, phosphorus atoms are slightly but significantly out of the benzene plane (Table 2).

TABLE 4

Selected non-bonded distances (Å)

(*a*) Interphosphine contacts within the same complex

C(11) ··· C(12)	3.34 * (3.39)	C(71) ··· C(63)	3.77 (3.66)
C(81) ··· C(13)	3.43 (3.58)	C(81) ··· C(23)	3.47 (3.67)
C(31) ··· C(32)	3.32 (3.39)		

(*b*) Intraphosphine contacts

	Ligand		
	(1)	(2)	(3)
C(2) ··· C(7)	3.05 * (3.06)	3.16 (3.14)	3.12 (3.12)
C(6) ··· C(8)	3.30 (3.28)	3.39 (3.33)	3.20 (3.26)

(*c*) Chlorine–carbon contacts within the complex

Cl(1) ··· C(71)	3.32 * (3.38)	Cl(2) ··· C(72)	3.48 (3.43)
Cl(1) ··· C(82)	3.65 (3.57)	Cl(2) ··· C(73)	3.41 (3.39)
Cl(1) ··· C(83)	3.31 (3.52)	Cl(3) ··· C(82)	3.37 (3.38)
Cl(2) ··· C(61)	3.52 (3.44)	Cl(3) ··· C(83)	3.48 (3.34)
Cl(2) ··· C(81)	3.55 (3.52)	Cl(3) ··· C(73)	3.52

(*d*) Intermolecular distances (<3.7 Å)

Cl(1B) ··· C(83A)	3.58	C(31A) ··· C(53B$^{\mathrm{III}}$)	3.69
C(51B) ··· C(83B$^{\mathrm{I}}$)	3.40	C(71A) ··· C(52B$^{\mathrm{II}}$)	3.61
C(43A) ··· C(82A$^{\mathrm{I}}$)	3.60	C(32A) ··· C(33B$^{\mathrm{IV}}$)	3.69
Cl(1A) ··· C(63A$^{\mathrm{II}}$)	3.54	Cl(3B) ··· C(23B$^{\mathrm{V}}$)	3.51

Roman numeral superiors denote the following equivalent positions relative to the reference molecule at x, y, z:

I $1 + x, y, z$
II $1 - x, \bar{y}, 1 - z$
III $1 - x, \bar{y}, \bar{z}$
IV $\bar{x}, \bar{y}, \bar{z}$
V $\tfrac{1}{2} + x, -\tfrac{1}{2} - y, \tfrac{1}{2} + z$

* Values for molecule (B) are in parentheses.

However, all Tc–P–C(sp^2) angles (mean 120.7°) are considerably (*ca.* 7°) larger than Tc–P–C(sp^3) (mean 113.1°), as found in *mer*-[$\mathrm{RhCl_3(PEt_2Ph)_3}$],[3] while in other complexes, such as [$\mathrm{Ni(CN)_2(PMe_2Ph)_3}$],[17] this behaviour is reversed. Moreover, all C(sp^2)–P–C(7) angles (mean 104.9°) are significantly (*ca.* 4°) larger than C(sp^2)–P–C(8) (mean 100.4°).

Crystal Packing.—All the foregoing features are

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probably related to the intramolecular packing arrangement. The packing is controlled especially by the spatial arrangement of the two partially superimposed rings on P(1) and P(2) (Figure 3) with resulting short van der Waals separations [Table 4(*a*)], and by several contacts between the phenyl ring bonded to P(3) and the methyl group on P(1) [Table 4(*a*)]. The packing is also influenced by the peculiarity that atom C(7) for both ligands (1) and (2) is approximately contained in the plane of its adjacent benzene ring (mean deviation 0.22, maximum 0.40 Å) (Table 2), so that C(2) · · · C(7) contacts are shorter than C(2) · · · C(8) [Table 4(*b*)]. A detailed comparison of this intramolecular packing with that of *mer*-[$RhCl_3(PEt_2Ph)_3$] [3] suggests that the whole conformation of molecule (A) is almost identical with that of the rhodium complex. In particular, in this complex also the benzene rings on P(5) and P(6) are nearly parallel (angle 6.1°) and the methylene groups [*i.e.* C(51) and C(71)] are nearly contained in the benzene plane (deviation 0.24 and 0.07 Å, respectively), causing C(51) · · · C(62) and C(71) · · · C(92) short contacts (3.03 and 3.10 Å). Molecule (B) differs especially in the orientation of the benzene ring bonded on P(3) [Table 2(*b*)].

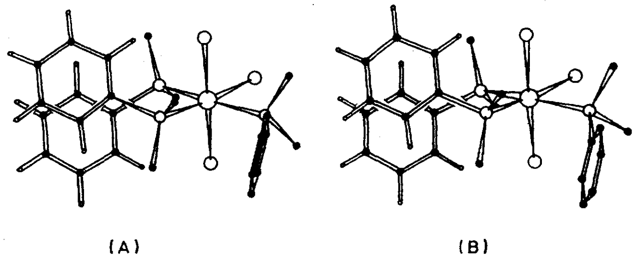

FIGURE 3 Intramolecular packing for molecules (A) and (B) showing the partial overlapping of the *cis*-phosphorus phenyl rings, with hydrogen atoms at geometrically expected positions

Some of the shorter chlorine–carbon intramolecular nonbonded distances are quoted in Table 4(*c*), while the intermolecular contacts (<3.7 Å) are given in Table 4(*d*). None of these is significantly less than the sum of appropriate van der Waals radii. The great majority are between carbon atoms, suggesting that the general mode of packing is controlled mainly by the mutual orientation of the phosphine ligands.

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