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THE STRUCTURE OF DI-μ-CHLOROBIS[BIS(2,3,5,6-TETRAFLUOROPHENYL)-(TRIPHENYLPHOSPHINE OXIDE)THALLIUM(III)]

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Summary

An X-ray crystallographic study has shown that the complex (p-$HC_6F_4)_2TlCl$-($OPPh_3$) is dimeric with unsymmetrical chlorine bridging (Tl—Cl 2.541 Å; Tl—Cl′ 2.936 Å) and five coordinate thallium atoms. The stereochemistry of each thallium is approximately trigonal bipyramidal, the equatorial positions being occupied by two carbon atoms and the more tightly held chlorine. Similar structures are likely for (p-$HC_6F_4)_2TlBr(OPPh_3)$ and $(C_6F_5)_2TlX(OPPh_3)$ (X = Br or Cl).

Introduction

Structures of a number of halogenobis(pentafluorophenyl)thallium(III) complexes have been proposed, mainly on the basis of molecular weight measurements and thallium—halogen stretching frequencies [1—4]. The proposals are interrelated, so that negation of one is likely to have a domino effect. Thus, the recent discovery that bromobis(2,3,5,6-tetrafluorophenyl)thalium(III) and chloro- and bromo-bis(pentafluorophenyl)thallium(III) are five coordinate polymers [5] rather than four coordinate dimers [1] raises the possibility that the complexes $(C_6F_5)_2TlX(L)$ (X = Br or Cl; L = Ph_3PO, 2,2′-bipyridyl, etc.) do not have the proposed monomeric structures with four and five coordinate thallium [1,2], but have associated structures with higher coordination numbers. Moreover, careful reinvestigation of the molecular weights of several of these complexes in benzene [6] reveals that some dimerization occurs in solution. Crystallographic examination of the isomorphous [2] $(C_6F_5)_2TlX(OPPh_3)$ (X = Br or Cl) complexes was precluded by lack of suitable crystals. However, the structure of the closely related $(p\text{-}HC_6F_4)_2TlCl(OPPh_3)$ has been determined. This compound is isomorphous with the corresponding bromide, and the thallium—halogen stretching frequencies of $(p\text{-}HC_6F_4)_2TlX(OPPh_3)$ (239 cm^{-1}, X = Cl; 167 cm^{-1}, X = Br [6]) are similar to those [2] of $(C_6F_5)_2TlX(OPPh_3)$ (244 cm^{-1}, X = Cl; 170 cm^{-1}, X = Br), indicative of similar stereochemistry and structures.

Experimental

Microanalyses were by the Australian Microanalytical Service, Melbourne. Molecular weights were determined at 25°C with a Hewlett Packard 302 or 301A osmometer. The compounds $(p\text{-}HC_6F_4)_2TlBr$ [7] and $[(C_6F_5)_2TlX(OPPh_3)]_2$ (X = Br or Cl) [2] were obtained by the reported methods, whilst $(p\text{-}HC_6F_4)_2TlCl$ [6] was prepared from $(p\text{-}HC_6F_4)_2TlBr$ by a procedure similar to that for $(C_6F_5)_2TlCl$ [1].

Di-μ-chlorobis[bis(2,3,5,6-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III)] (nc)

Crystallization from a solution of equimolar amounts of $(p\text{-}HC_6F_4)_2TlCl$ and triphenylphosphine oxide in methanol/water gave the compound (91%), m.p. 213—214°C (dec.) (Found: C, 43.9; H, 2.3; Cl, 4.3; F, 18.7. $C_{60}H_{34}Cl_2F_{16}O_2P_2Tl_2$ calcd.: C, 44.1; H, 2.1; Cl, 4.3; F, 18.6%). The solubility in benzene at 25°C was <0.48%.

Di-μ-bromobis[bis(2,3,5,6-tetrafluorophenyl)(triphenylphosphine oxide)thallium(III)] (nc)

A similar preparation from benzene/petroleum ether (b.p. 80—100°C) gave transparent crystals (96%), m.p. 193—195°C [Found: C, 42.1; H, 2.1; Br, 9.3; F, 17.5; Mol. wt. (benzene), 884 (1.52% w/w); 894 (2.53%). $C_{60}H_{34}Br_2F_{16}O_2P_2Tl_2$ calcd.: C, 41.9; H, 2.0; Br, 9.3; F, 17.7%; mol. wt., 1721].

Di-μ-chlorobis[bis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III)]

[Found: mol. wt., 949 (0.78%). $C_{60}H_{30}Cl_2F_{20}O_2P_2Tl_2$ calcd.: mol. wt., 1704].

Di-μ-bromobis[bis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III)]

[Found: mol. wt., 940 (1.51%); 955 (2.52%). $C_{60}H_{30}Br_2F_{20}O_2P_2Tl_2$ calcd.: mol. wt., 1793].

Crystal structure determination

Crystals of the title compound ($C_{60}H_{34}Cl_2F_{16}O_2P_2Tl_2$, M = 1632.49) are monoclinic, space group *C2/c*, a 21.899(5), b 15.403(4), c 18.367(3) Å, β 107.96(3)°, V 5893.4 $Å^3$, $Z = 4$, $F(000)$ 3120, D_c 1.839 g cm^{-3}, Mo-K_α radiation, μ = 54.5 cm^{-1}. A θ—2θ scan mode was used for data collection and reflections with $3.0 < \theta < 30.0°$ were examined. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not further examined (I_t is the count rate at the top of the reflection peak and I_b is the mean count rate from two preliminary 5 s background measurements on either side of the scan). Of the

TABLE 1

ATOMIC FRACTIONAL COORDINATES (Tl × 10^5, OTHERS × 10^4) FOR $[(p\text{-HC}_6\text{F}_4)_2\text{TlCl(OPPh}_3)]_2$ (e.s.d.'s are given in parentheses)

Atom	*x*	*y*	*z*
Tl	5116(2)	22368(3)	17582(3)
P	2322(1)	1913(2)	2096(2)
Cl	786(1)	2600(2)	3172(2)
O	1621(4)	1913(6)	1968(5)
C(11)	292(5)	880(8)	1598(7)
C(12)	602(6)	233(9)	2084(8)
C(13)	457(7)	−623(10)	1930(8)
C(14)	0(7)	−868(10)	1292(9)
C(15)	−316(7)	−266(10)	794(9)
C(16)	−175(6)	628(9)	937(8)
F(12)	1059(3)	435(5)	2749(4)
F(13)	770(4)	−1227(5)	2446(6)
F(15)	−791(5)	−461(6)	133(5)
F(16)	−501(4)	1205(6)	434(5)
C(21)	586(6)	3375(9)	1116(7)
C(22)	512(6)	4193(9)	1314(8)
C(23)	654(7)	4916(12)	901(10)
C(24)	873(7)	4760(12)	301(10)
C(25)	945(9)	3971(13)	101(11)
C(26)	781(7)	3270(12)	482(9)
F(22)	281(4)	4353(5)	1907(5)
F(23)	544(5)	5700(6)	1157(7)
F(25)	1141(6)	3822(9)	−507(7)
F(26)	878(5)	2457(7)	247(6)
C(111)	2758(6)	2020(8)	3105(7)
C(112)	3375(7)	2364(9)	3336(8)
C(113)	3710(7)	2431(9)	4150(8)
C(114)	3396(7)	2139(10)	4640(9)
C(115)	2792(7)	1805(10)	4411(9)
C(116)	2449(6)	1739(9)	3619(8)
C(121)	2562(5)	2795(8)	1604(7)
C(122)	2402(6)	3644(9)	1788(8)
C(123)	2552(7)	4339(10)	1408(9)
C(124)	2867(7)	4228(11)	878(10)
C(125)	3024(7)	3403(11)	698(9)
C(126)	2868(7)	2706(10)	1056(8)
C(131)	2548(6)	888(8)	1779(7)
C(132)	2088(6)	369(9)	1357(7)
C(133)	2262(8)	−443(11)	1115(9)
C(134)	2865(7)	−710(11)	1302(9)
C(135)	3347(7)	−172(10)	1735(9)
C(136)	3191(7)	633(10)	1973(8)
H(14)	−95	−1550	1172
H(24)	1003	5296	−1
H(112)	3596	2580	2917
H(113)	4190	2691	4364
H(114)	3641	2199	5246
H(115)	2583	1581	4838
H(116)	1971	1470	3422
H(122)	2159	3738	2213
H(123)	2429	4988	1537
H(124)	2992	4790	602
H(125)	3255	3320	260
H(126)	2994	2062	920
H(132)	1592	568	1193
H(133)	1890	−867	776
H(134)	2980	−1338	1118
H(135)	3842	−375	1893
H(136)	3563	1062	2305

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) FOR $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ [a] (e.s.d.'s are in parentheses)

Bond lengths			
Tl—Cl	2.541(3)	C(25)—C(26)	1.393(28)
Tl—O	2.391(9)	C(26)—C(21)	1.368(23)
Tl—C(11)	2.144(12)	C(22)—F(22)	1.357(20)
Tl—C(21)	2.147(14)	C(23)—F(23)	1.345(22)
O—P	1.480(9)	C(25)—F(25)	1.334(27)
Tl—Cl^{i}	2.936(3)	C(26)—F(26)	1.362(21)
Tl···Tl^{i}	4.026	C(111)—C(112)	1.390(18)
P—C(111)	1.811(12)	C(112)—C(113)	1.452(19)
P—C(121)	1.797(14)	C(113)—C(114)	1.367(26)
P—C(131)	1.804(13)	C(114)—C(115)	1.360(21)
C(11)—C(12)	1.381(17)	C(115)—C(116)	1.419(19)
C(12)—C(13)	1.351(20)	C(116)—C(111)	1.389(21)
C(13)—C(14)	1.339(19)	C(121)—C(122)	1.422(20)
C(14)—C(15)	1.336(21)	C(122)—C(123)	1.372(22)
C(15)—C(16)	1.419(21)	C(123)—C(124)	1.366(26)
C(16)—C(11)	1.380(16)	C(124)—C(125)	1.383(25)
C(12)—F(12)	1.358(14)	C(125)—C(126)	1.357(24)
C(13)—F(13)	1.354(16)	C(126)—C(121)	1.377(22)
C(15)—F(15)	1.365(16)	C(131)—C(132)	1.331(16)
C(16)—F(16)	1.322(15)	C(132)—C(133)	1.418(22)
C(21)—C(22)	1.334(20)	C(133)—C(134)	1.322(23)
C(22)—C(23)	1.435(25)	C(134)—C(135)	1.385(20)
C(23)—C(24)	1.352(28)	C(135)—C(136)	1.391(22)
C(24)—C(25)	1.292(28)	C(136)—C(131)	1.397(18)
Inter-bond angles			
O—Tl—Cl	88.5(2)	C(21)—C(22)—C(23)	121.6(16)
O—Tl—C(11)	89.6(3)	C(22)—C(23)—C(24)	118.8(17)
Cl—Tl—C(11)	109.1(4)	C(23)—C(24)—C(25)	120.2(19)
O—Tl—C(21)	90.8(4)	C(24)—C(25)—C(26)	120.9(21)
Cl—Tl—C(21)	110.3(3)	C(25)—C(26)—C(21)	122.1(17)
C(11)—Tl—C(21)	140.6(5)	F(22)—C(22)—C(21)	119.8(13)
P—O—Tl	168.0(6)	F(22)—C(22)—C(23)	118.6(13)
Cl—Tl—Cl^{i}	80.8(2)	F(23)—C(23)—C(22)	114.9(16)
O—Tl—Cl^{i}	168.7(3)	F(23)—C(23)—C(24)	126.3(17)
C(11)—Tl—Cl^{i}	90.7(4)	F(25)—C(25)—C(24)	119.9(19)
C(21)—Tl—Cl^{i}	96.1(6)	F(25)—C(25)—C(26)	119.1(18)
Tl—Cl—Tl^{i}	94.3(1)	F(26)—C(26)—C(21)	119.9(15)
O—P—C(111)	110.9(6)	F(26)—C(26)—C(25)	117.7(16)
O—P—C(121)	111.7(5)	P—C(111)—C(112)	120.2(11)
O—P—C(131)	108.9(6)	P—C(111)—C(116)	117.0(9)
C(111)—P—C(121)	107.6(6)	C(112)—C(111)—C(116)	122.8(12)
C(111)—P—C(131)	107.4(5)	C(111)—C(112)—C(113)	118.4(14)
C(121)—P—C(131)	110.3(6)	C(112)—C(113)—C(114)	117.2(13)
Tl—C(11)—C(12)	125.6(8)	C(113)—C(114)—C(115)	124.0(15)
Tl—C(11)—C(16)	117.9(9)	C(114)—C(115)—C(116)	120.1(16)
C(12)—C(11)—C(16)	116.4(12)	C(115)—C(116)—C(111)	117.4(12)
C(11)—C(12)—C(13)	122.4(11)	P—C(121)—C(122)	116.4(11)
C(12)—C(13)—C(14)	121.3(13)	P—C(121)—C(126)	125.2(11)
C(13)—C(14)—C(15)	119.6(15)	C(122)—C(121)—C(126)	118.4(13)
C(14)—C(15)—C(16)	120.5(13)	C(121)—C(122)—C(123)	118.7(15)
C(15)—C(16)—C(11)	119.8(12)	C(122)—C(123)—C(124)	121.2(15)
F(12)—C(12)—C(11)	118.9(12)	C(123)—C(124)—C(125)	120.2(17)
F(12)—C(12)—C(13)	118.8(11)	C(124)—C(125)—C(126)	119.4(17)
F(13)—C(13)—C(12)	118.7(11)	C(125)—C(126)—C(121)	121.9(15)
F(13)—C(13)—C(14)	120.0(13)	P—C(131)—C(132)	118.7(10)
F(15)—C(15)—C(14)	123.3(14)	P—C(131)—C(136)	121.2(9)
F(15)—C(15)—C(16)	116.2(12)	C(132)—C(131)—C(136)	120.1(12)
F(16)—C(16)—C(11)	121.3(12)	C(131)—C(132)—C(133)	119.0(13)
F(16)—C(16)—C(15)	118.8(11)	C(132)—C(133)—C(134)	122.4(14)
Tl—C(21)—C(22)	125.8(11)	C(133)—C(134)—C(135)	119.0(16)
Tl—C(21)—C(26)	117.8(11)	C(134)—C(135)—C(136)	119.8(14)
C(22)—C(21)—C(26)	116.1(14)	C(135)—C(136)—C(131)	119.7(12)

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[a] Atoms indicated with the superscript (i) are related by the transformation, $-x, y, 1/2 - z$.

remaining reflections, those for which the total intensity recorded in the first scan (I_i) was <500 counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a scan width of 0.74° were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 6 h during data collection and showed no significant variations in intensity. The intensities were calculated from the peak and background measurements with a program written for the PW1100 diffractometer [8]. The variance of intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04\ I)^2$, where the term in I^2 was introduced to allow for other sources of error [9]. I and $\sigma(I)$ were corrected for Lorentz and polarisation factors. Absorption corrections were applied with empirical psi-scan technique on 28 reflections, using the program X:EMPABS [10]. The merging R values before and after correction were 0.0342 and 0.0145 respectively. The maximum and minimum transmissions were 0.892 and 0.650 respectively. The final data set consisted of 2807 independent reflections of which 54 for which $I < 3\sigma(I)$ were rejected. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares calculations using the SHELX program [11]. The C—H hydrogen atom coordinates were estimated geometrically (C—H 1.08 Å) and in refinement were allowed to ride on their respective C atom coordinates. Neutral-atom scattering factors were used [12], those for Tl, P, Cl, O and F being corrected for anomalous

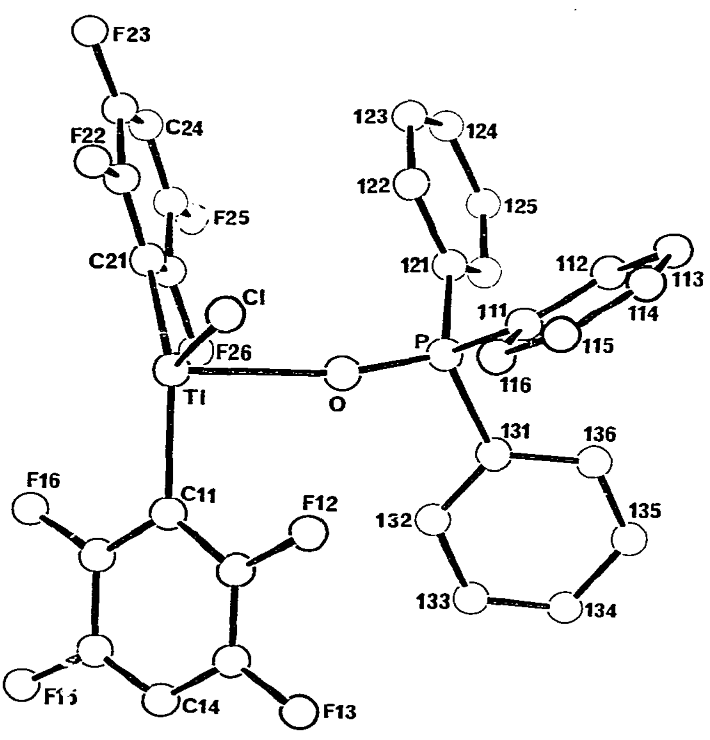

Fig. 1. The structure of the monomer unit $(p\text{-}HC_6F_4)_2TlCl(OPPh_3)$. Bonded F and C atoms have the same numbers.

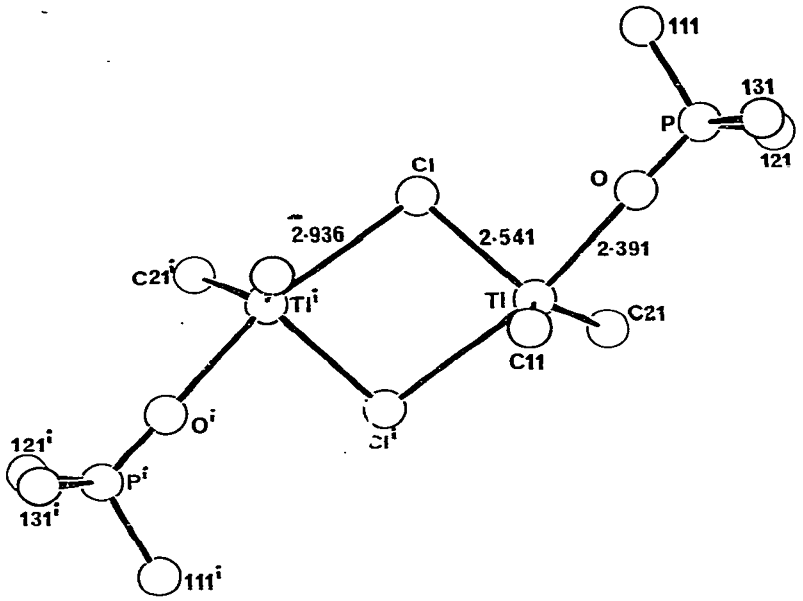

Fig. 2. The dimeric molecule $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ which has exact C_2 symmetry. Only the first carbon atom of each phenyl ring is shown. The dihedral angle between the planes TlClCl' and Tl'Cl'Cl is 148.6°.

dispersion ($\Delta f'$, $\Delta f''$). For the final stages of refinement the Tl, P, Cl, O and F atoms were assigned anisotropic thermal parameters. The final mean shift/σ was 0.011 and the maximum 0.130. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.044$ and $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.047$ where $w = 1.1658\ (\sigma^2|F_o|)^{-1}$. The final atomic parameters are listed in Table 1. Selected bond lengths and angles are presented in Table 2. Lists of structure factors, thermal parameters, and of least-squares planes are available from the authors (KH). The atom labelling scheme is shown in Figs. 1 and 2.

Discussion

The molecular structure of $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ comprises two distorted trigonal pyramidal $(p\text{-}HC_6F_4)_2TlCl(OPPh_3)$ units (Fig. 1) linked by two relatively long thallium—chlorine bridging bonds to give a discrete dimer (Fig. 2) with exact C_2 symmetry. Each thallium has distorted trigonal bipyramidal coordination geometry with two carbon atoms and the more tighly held chlorine in the equatorial positions. The structure can be derived from the halogen-bridged polymeric structure of $(p\text{-}HC_6F_4)_2TlBr$ and $(C_6F_5)_2TlX$ (X = Br or Cl) [5] by replacement of alternate pairs (the weakest) of halogen bridges by triphenylphosphine oxide (Fig. 3).

The Tl—C bond distances (Table 2) are similar to those (2.09—2.16 Å) in $(C_6F_5)_2TlOH$ [13], $(p\text{-}HC_6F_4)_2TlBr$ [5], and $[(C_6F_5)_2Tldpa]_2$ (dpa = 2,2'-dipyridylamide) [14], and lie within the range 2.01—2.20 Å for Tl—C distances

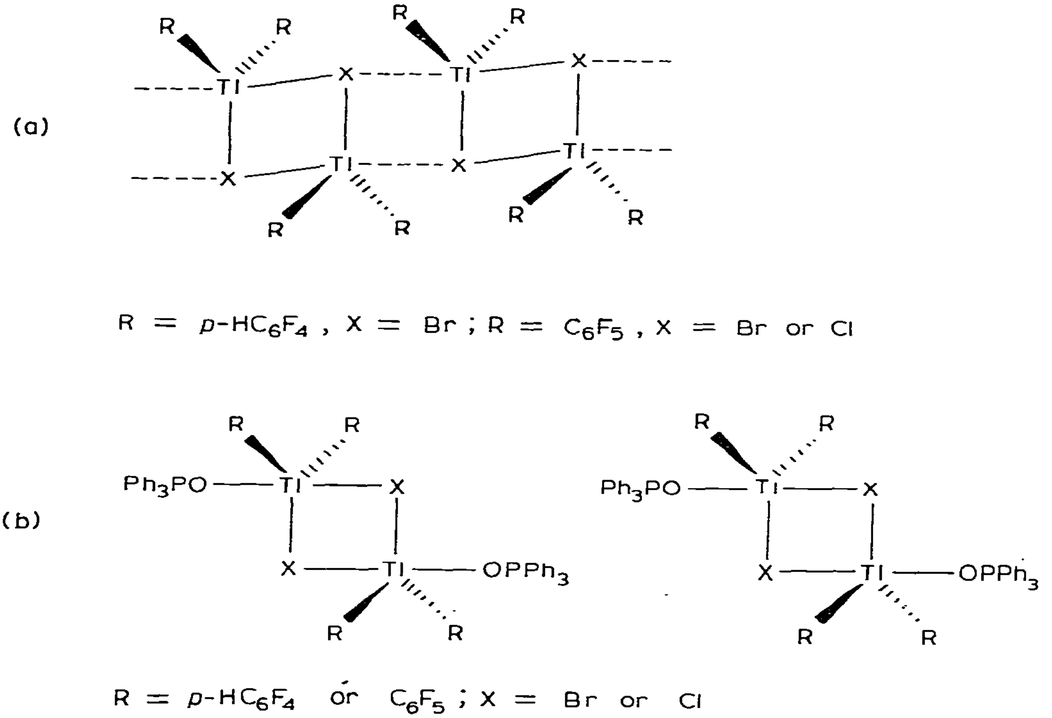

Fig. 3. The relationship between the structure of (a) R_2TlX and (b) $[R_2TlX(OPPh_3)]_2$.

in neutral dimethylthallium(III) compounds [15,16]. The Tl—Cl distance (2.541 Å) is slightly longer than reported terminal Tl—Cl distances (2.41—2.49 Å) [17—21], and the shorter bridging Tl—Cl bond (2.50 Å) in phenTlCl$_3$ [17]. The bridging distance Tl—Cl^i is shorter than the bridging Tl—Cl bonds in phenTlCl$_3$ (3.24 Å) [17] and Me$_2$TlCl (3.03 Å) [15], but is considerably longer than the equatorial Tl—Cl distance. The second axial site is occupied by the triphenylphosphine oxide oxygen. This appears to be the first structure reported for a neutral, oxygen-donor ligand coordinated to thallium.

The C—Tl—C angle (140.6°) represents the main distortion from regular trigonal bipyramidal geometry. A similar angle (138.5°) was observed in $(C_6F_5)_2$-TlOH [13], but larger (127°) and smaller (149.9 and 144.2°) angles have been found for $[(C_6F_5)_2Tldpa]_2$ [14] and $(p\text{-}HC_6F_4)_2TlBr$ [5] respectively. The very large value (168.0°) for the P—O—Tl angle cannot readily be attributed to intramolecular steric factors (see Figs. 1 and 2). On the basis of observation of two widely differing Mo—O—P angles (145.6 and 168.6°) in trichloro(oxo)bis(triphenylphosphine oxide)molybdenum(V), it was concluded that M—O—P angles are easily deformed and may be considerably affected by crystal packing factors [22].

Molecular weight measurements could not be obtained for $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ in benzene owing to insufficient solubility. The more soluble complexes $[(C_6F_5)_2TlX(OPPh_3)]_2$ (X = Br or Cl) and $[p\text{-}HC_6F_4)_2TlBr(OPPh_3)]_2$, which are considered to have a similar structure (see above), are substantially monomeric in benzene, though some dimerization persists in solution (see Experimental). The ready dissociation of the dimers on dissolution can be attributed to the presence of two weak bridging thallium—halogen bonds in each dimer.

Somewhat unexpectedly, in all reported crystal structures of bis(polyfluorophenyl)thallium(III) compounds, thallium is five coordinate with distorted trigonal bipyramidal stereochemistry and equatorial bonds relatively shorter than axial bonds.

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