1139. *The Chemistry of Organothallium Compounds. Part II.*[1] *The Complexes of Bis(pentafluorophenyl)thallium*(III) *Compounds with Some Neutral Unidentate Ligands*

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The preparations and properties of some new four- and five-co-ordinate derivatives of tervalent thallium are described. The four-co-ordinate compounds, $(C_6F_5)_2LTlX$ (L = Ph_3PO, Ph_3AsO, Ph_3P, or Ph_3As; X = Cl or Br) and $(C_6F_5)_2(Ph_3PO$ or $Ph_3AsO)TlCO_2CF_3$, have been prepared by reactions of the neutral ligands with the appropriate $(C_6F_5)_2TlX$ compounds, and $(C_6F_5)_2Ph_3AsOTlNO_3$ has been obtained from the corresponding bromide and silver nitrate. The phosphine oxide and arsine oxide complexes are monomeric in benzene, but $(C_6F_5)_2(Ph_3P$ or $Ph_3As)TlX$ complexes dissociate, losing the neutral ligand. The complexes are non-electrolytes in acetone, but dissociate extensively into L and the corresponding $(C_6F_5)_2TlX$ compounds in this solvent. The five-co-ordinate compounds, $(C_6F_5)_2L_2TlNO_3$ (L = Ph_3PO or Ph_3AsO), have been prepared similarly. They have low conductances in acetone, but dissociate extensively into $(C_6F_5)_2LTlNO_3$ and L in acetone and benzene. However, infrared data show that the crystalline compounds are not mixtures of $(C_6F_5)_2LTlNO_3$ and L, but contain five-co-ordinate thallium. The relative stabilities of the compounds, in terms of their dissociation in solution, are discussed.

THIS Paper describes the properties of new four- and five-co-ordinate thallium compounds, which have been prepared by reactions of bis(pentafluorophenyl)thallium(III) compounds with neutral unidentate ligands.* In Part I [1] the preparations and properties of three stoicheiometric classes of bis(pentafluorophenyl)thallium(III) compounds were described, *viz.*, the "simple" compounds, $(R_f)_2TlX$ ($R_f = C_6F_5$; X = Cl, Br, NO_3, etc.), four-co-ordinate anionic complexes, $Q^+ (R_f)_2TlX_2^-$ (Q = Ph_4P or Et_4N; X = Cl or Br), and five-co-ordinate complexes, $(R_f)_2$(bipy or *o*-phen)TlX (bipy = 2,2′-bipyridyl; *o*-phen = 1,10-phenanthroline; X = Cl, Br, NO_3, or $CF_3{\cdot}CO_2$—henceforth termed OAc_f).

Tervalent thallium gives rise to well-known four- and six-co-ordinate complexes, *e.g.*, $TlCl_4^-$ and $TlCl_6^{3-}$, respectively.[2] However, the organometallic derivatives of tervalent thallium, $R_2Tl^+X^-$ (R = aryl or alkyl), do not readily give co-ordination complexes, though some four-co-ordinate derivatives are known, *e.g.*, $(Me_2TlOMe)_2$ and dimethylthallium acetylacetonate.[3] Four-co-ordinate complexes of the type R_2LTlX (R, as above; L is a neutral unidentate and X an anionic unidentate ligand) have not been isolated, though the analogous R_2pyTlX species have been postulated to explain the solubility of the otherwise rather insoluble dialkylthallium compound in pyridine.[3] (The only complex of this stoicheiometry hitherto isolated, $Me_2pyTl^+ClO_4^-$, contains three-co-ordinate thallium.[4]) The aim of the present work is to establish that four-co-ordinate R_2LTlX compounds can be prepared when R is the electronegative pentafluorophenyl group. This has been accomplished using the ligands triphenylphosphine oxide, triphenylarsine oxide, triphenylphosphine, and triphenylarsine. In connexion with the possible use of these

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* The nomenclature for $(R_f)_2TlX$ and five co-ordinate thallium compounds has been changed from that in Part I,[1] in which the compounds were named by analogy with real or hypothetical dialkyl- or diaryl-thallium compounds of similar stoicheiometry. The I.U.P.A.C. nomenclature for co-ordination compounds is now used for these and for the new four-co-ordinate complexes. The $(R_f)_2TlX$ compounds are named as monomers, attention being drawn [section (1)] to those derivatives for which dimeric structures have been proposed.

[1] Part I, G. B. Deacon, J. H. S. Green, and R. S. Nyholm, *J.*, 1965, 3411.

[2] N. V. Sidgwick, "Chemical Elements and Their Compounds," Clarendon, Oxford, 1950, vol. I, pp. 472—476; A. F. Wells, "Structural Inorganic Chemistry," 3rd edn., Clarendon, Oxford, 1962, p. 366.

[3] G. E. Coates, "Organometallic Compounds," 2nd edn., Methuen, London, 1960, pp. 158—161.

[4] I. R. Beattie and P. A. Cocking, *J.*, 1965, 3860.

four-co-ordinate compounds as intermediates in the synthesis of thallium-containing metal–metal bonded derivatives, qualitative information as to the stabilities of the compounds, with respect to the dissociation of the neutral ligand, has been obtained. In addition, two further examples of the class of five-co-ordinate thallium compounds, $(R_f)_2L_2TlX$ (L and X as above), have been prepared, there being only one similar compound known,[1] *viz.*, $(R_f)_2py_2TlBr$.

RESULTS AND DISCUSSION

(1) *General Methods of Preparation.*—The four-co-ordinate complexes, $(R_f)_2LTlX$ ($L = Ph_3PO$ or Ph_3AsO; $X = Cl$, Br, or OAc_f) have been isolated from the reactions of chloro-, bromo-, and trifluoro-acetatobis(pentafluorophenyl)thallium(III) with the stoicheiometric amounts of triphenylphosphine oxide or triphenylarsine oxide in suitable polar organic solvents. In addition, $(R_f)_2Ph_3AsOTlNO_3$ has been prepared by the reaction between $(R_f)_2Ph_3AsOTlBr$ and silver nitrate in aqueous methanol. Complexes between $(R_f)_2TlX$ ($X = F$ or OAc) * and triphenylphosphine oxide could not be prepared. From the reactions of triphenylphosphine or triphenylarsine with $(R_f)_2TlX$ ($X = Cl$ or Br) * in ether, the complexes $(R_f)_2(Ph_3P$ or $Ph_3As)TlX$ have been obtained. However, $(R_f)_2Ph_3SbTlBr$ could not be prepared.

The five-co-ordinate complexes, $(R_f)_2(Ph_3PO$ or $Ph_3AsO)_2TlNO_3$, have been isolated from the reactions of $(R_f)_2TlNO_3$ with 2 moles of triphenylphosphine oxide or triphenylarsine oxide in aqueous methanol. The phosphine oxide derivative was also obtained from all attempts to prepare the four-co-ordinate complex, $(R_f)_2Ph_3POTlNO_3$. Similar five-co-ordinate complexes with anions other than nitrate (*e.g.*, Br, OAc_f) could not be prepared.

(2) *Properties of the Four-co-ordinate Complexes,* $(R_f)_2LTlX$.—(*a*) $L = Ph_3PO$ or Ph_3AsO. The halogeno-derivatives ($X = Cl$ or Br) are isostructural, as established by *X*-ray powder photography. As the compounds are monomeric in benzene (see Experimental section), they contain four-co-ordinate thallium and probably have tetrahedral stereochemistry. The Tl–Cl stretching frequencies of the chloro-complexes (Table 1) correspond closely to those of the complex ion, $(R_f)_2TlCl_2^-$, for which tetrahedral stereochemistry has been proposed,[1] *viz.*, 267 and 240 cm.$^{-1}$ (average values for Ph_4P^+ and Et_4N^+ salts [1]).

TABLE 1

Tl–Cl stretching frequencies (cm.$^{-1}$; in Nujol) of four-co-ordinate derivatives

Compounds	$(R_f)_2Ph_3POTlCl$	$(R_f)_2Ph_3AsOTlCl$	$(R_f)_2Ph_3PTlCl$	$(R_f)_2Ph_3AsTlCl$
ν(Tl–Cl)	243vs, br	242s, br	265vs	256vs

The monomeric nature of $(R_f)_2Ph_3AsOTlNO_3$ and $(R_f)_2(Ph_3PO$ or $Ph_3AsO)TlOAc_f$ in benzene establishes that both neutral and anionic ligands are co-ordinated. Probably thallium again has tetrahedral stereochemistry with unidentate nitrate or trifluoroacetate groups. However, structures with bidentate nitrate or trifluoroacetate groups [as in $Co(NO_3)_4{}^{2-}$, and probably in $Co(OAc_f)_4{}^{2-}$] [5] cannot be excluded. The nitrate absorption bands of $(R_f)_2Ph_3AsOTlNO_3$ (Table 2) confirm that the nitrate group is co-ordinated. The infrared-inactive A_1 mode of the nitrate ion appears strongly in the infrared spectrum of the compound, and the highest E' mode is split into two bands (ν_4 and ν_1), as established for nitrato-complexes.[6] Infrared spectroscopy cannot distinguish between uni- and bidentate nitrate, since both have the same symmetry. No information about the bonding of the trifluoroacetate groups in $(R_f)_2(Ph_3PO$ or $Ph_3AsO)TlOAc_f$ can be deduced from spectra. Although it is possible to relate the infrared absorption of acetate groups and their bonding [7]

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* Dimeric structures with bridging X groups have been proposed for the crystalline compounds.[1]

[5] F. A. Cotton and J. G. Bergman, *J. Amer. Chem. Soc.*, 1964, **86**, 2941.

[6] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J.*, 1957, 4222; B. M. Gatehouse and A. E. Comyns, *J.*, 1958, 3965; C. C. Addison and B. M. Gatehouse, *J.*, 1960, 613; E. Bannister and F. A. Cotton, *J.*, 1960, 2276.

[7] K. Nakamoto, "The Infra-Red Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 198.

(with certain limitations),[8] attempts to do so for trifluoroacetate groups have so far been unsuccessful, as discussed previously.[1]

TABLE 2

Vibrational assignments for nitrato-complexes *

Mode (type) ONO_2	$(R_f)_2Ph_3AsOTlNO_3$	$(R_f)_2(Ph_3PO)_2TlNO_3$	$(R_f)_2(Ph_3AsO)_2TlNO_3$	Nitrato-complexes
$\nu_4(B_1)$ NO_2 asym. str.	1481vs, br †	1486 or 1471vs †	1403vs	1531—1481
$\nu_1(A_1)$ NO_2 sym. str.	1259vs	1279vs	1307s	1290—1253
$\nu_2(A_1)$ N–O str.	1020vs	1027s	1034w	1034—970
$\nu_6(B_2)$ non-planar rock	813w	818w	825w	820—781

* Compounds examined as Nujol and hexachlorobutadiene mulls. Assignments based on those given for nitrato-complexes.[6] † Exact position uncertain owing to $(R_f)_2Tl$ absorption. ν_3 and ν_5 are obscured by absorption of other ligands.

The P=O stretching frequencies of the triphenylphosphine oxide complexes (Table 3) are lowered from the value (1195 cm.$^{-1}$) [9] for the free ligand, as expected for co-ordinated triphenylphosphine oxide.[9,10] On co-ordination, the As=O stretching frequency of triphenylarsine oxide is either raised or lowered from the value (880 cm.$^{-1}$) for the free ligand.[10] The frequencies of $(R_f)_2Ph_3AsOTlX$ compounds (Table 3) are raised when X = Cl or Br and lowered when X = NO_3 or OAc_f.

TABLE 3

P=O and As=O stretching frequencies (cm.$^{-1}$)

X =	Br	Cl	OAc_f	NO_3	NO_3 *
$(R_f)_2Ph_3POTlX$	1172vs	1172vs	1153vs †	—	1166vs ν(P=O)
$(R_f)_2Ph_3AsOTlX$	907vs	908vs	863vs	855vs	880vs, 866vs ν(As=O)

* For compounds $(R_f)_2(Ph_3PO$ or $Ph_3AsO)_2TlNO_3$. † Position uncertain, as ν(C–F) of the trifluoroacetate group also occurs here.

Molecular weights of $(R_f)_2LTlX$ compounds in acetone are less than the calculated values. As the compounds are non-electrolytes in this solvent (Table 4), the dissociation must be due to loss of the neutral ligand.

$$(R_f)_2LTlX \rightleftharpoons (R_f)_2TlX + L$$

TABLE 4

Molar conductances in acetone at *ca.* 22°

Compound	Mol. cond.	Concn. (10^3M)	Compound	Mol. cond.	Concn. (10^3M)
$(R_f)_2Ph_3POTlBr$	1·9	1·22	$(R_f)_2Ph_3AsOTlBr$	6·0	1·94
	2·1	3·75		5·9	3·43
$(R_f)_2Ph_3POTlCl$	1·4	1·37	$(R_f)_2Ph_3AsOTlCl$	4·6	1·99
	1·5	4·04		4·6	3·92
$(R_f)_2Ph_3POTlOAc_f$	3·3	0·81	$(R_f)_2Ph_3AsOTlOAc_f$	7·8	1·15
	2·7	1·25		7·7	2·08
$(R_f)_2(Ph_3PO)_2TlNO_3$	3·6	1·30	$(R_f)_2Ph_3AsOTlNO_3$	11·6	1·70
	3·9	2·72		11·5	3·59
$(R_f)_2Ph_3PTlBr$	2·3	1·36	$(R_f)_2(Ph_3AsO)_2TlNO_3$	21·5	1·00
	2·2	2·72		23·0	2·49
$(R_f)_2Ph_3PTlCl$	2·0	1·29	$(R_f)_2Ph_3AsTlBr$	4·2	1·32
			$(R_f)_2Ph_3AsTlCl$	2·2	1·25

1 : 1 electrolytes have mol. cond. (10^3M) ~100—150 in acetone.

The products $(R_f)_2TlX$ (X = Cl, Br, NO_3, or OAc_f) are monomeric in acetone, five-co-ordinate species, $(R_f)_2(Me_2CO)_2TlX$, possibly being present.[1] From the molecular-weight data, the number of particles (*n*) formed per mole of complex at various concentrations was calculated (Table 5). At similar molarities, *n* is larger for triphenylphosphine oxide complexes than for the corresponding triphenylarsine oxide derivatives, hence the Ph_3AsO

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[8] I. R. Beattie and T. Gilson, *J.*, 1961, 2585.

[9] F. A. Cotton, R. D. Barnes, and E. Bannister, *J.*, 1960, 2199.

[10] D. M. L. Goodgame and F. A. Cotton, *J.*, 1961, 2298, 3735.

complexes are more stable (in terms of the above dissociation) than the Ph_3PO complexes. A similar conclusion was reached from studies of the complexes of these ligands with stannic chloride in 1,2-dichloroethane.[11] The relative stabilities do not necessarily mean that Ph_3AsO co-ordinates more strongly to thallium than Ph_3PO, as differing solvation energies of ligands or differing entropies of formation of complexes can also cause differences in stabilities.[12]

The molar conductances of the triphenylphosphine oxide complexes in acetone (Table 4) approximate to those of the corresponding $(R_f)_2TlX$ compounds at comparable concentrations [mol. cond. (10^3M) of $(R_f)_2TlBr$, $(R_f)_2TlCl$, and $(R_f)_2TlOAc_f$ are 1·2 (1·71), 1·0 (2·16), and 3·0 (1·75), respectively],[1] which is consistent with extensive dissociation of the complexes into $(R_f)_2TlX$ compounds at these concentrations. By contrast, the conductances of the triphenylarsine oxide complexes differ significantly from those of the corresponding $(R_f)_2TlX$ compounds.

(*b*) L = Ph_3P or Ph_3As; X = Cl or Br. The four complexes are isostructural (*X*-ray powder photography). Although the compounds undergo dissociation in benzene (see Experimental section), the neutral ligands (L) are co-ordinated in the crystalline state. The bands of $(R_f)_2TlX$ at 802 and 783 cm.$^{-1}$ (average values for the chloride and bromide) [1] are shifted to 785 and 777 cm.$^{-1}$ (average values) in the spectra of the $(R_f)_2LTlX$ compounds. The ν(Tl–Cl) modes of the chloro-complexes (Table 1) are at significantly higher frequencies than ν(Tl–Cl) of $(R_f)_2TlCl$ (less than 220 cm.$^{-1}$).[1] The characteristic spectral features of co-ordinated triphenylphosphine [13] are observed in the infrared spectra of the triphenylphosphine complexes [see section (4)]. The molecular weights of the triphenylphosphine complexes in concentrated solution approach the calculated values fairly closely. This evidence, together with the fact that the compounds are isostructural, establishes that the neutral ligands are co-ordinated in the crystalline state. Thus, thallium is four-co-ordinate and the stereochemistry is probably tetrahedral. The ν(Tl–Cl) frequencies of the chloro-compounds correspond closely to those of the tetrahedral $(R_f)_2TlCl_2^-$ ion [section (2)(*a*)].[1]

TABLE 5

Number of particles (*n*) formed per mole of complex, (*a*) in acetone, (*b*) in benzene

Complex	Concn. (10^2M)	*n*	Complex	Concn. (10^2M)	*n*
(*a*) $(R_f)_2Ph_3POTlBr$ ...	1·72	1·71	(*a*) $(R_f)_2Ph_3AsOTlBr$	1·10	1·26
	4·55	1·44		4·49	1·08
$(R_f)_2Ph_3POTlCl$ ...	4·99	1·31	$(R_f)_2Ph_3AsOTlCl$	4·73	1·05
$(R_f)_2Ph_3POTlOAc_f$	1·27	1·73	$(R_f)_2Ph_3AsOTlOAc_f$ ...	1·13	1·16
$(R_f)_2(Ph_3PO)_2TlNO_3$	1·20	2·36	$(R_f)_2(Ph_3AsO)_2TlNO_3$	1·08	1·75
	7·89	1·74			
(*b*)	0·91	1·83	(*b*)	0·91	1·68 *
	3·75	1·61		1·90	1·52
$(R_f)_2Ph_3PTlBr$	1·30	1·21	$(R_f)_2Ph_3AsTlBr$	1·31	1·48
	6·04	1·09		6·42	1·29
$(R_f)_2Ph_3PTlCl$	0·60	~1·07	$(R_f)_2Ph_3AsTlCl$	0·58	~1·42 *
				0·79	~1·42

* Comparison limited by the low solubility of these compounds in benzene.

The dissociation of the compounds in benzene is due to the reaction, $2(R_f)_2LTlX \rightleftharpoons 2L + [(R_f)_2TlX]_2$. Chloro- and bromo-bis(pentafluorophenyl)thallium(III) are dimeric in benzene.[1] Dissociation is more complete for the triphenylarsine complexes; the *n* values for the compounds in dilute solution approach closely the value (1·5) for complete dissociation (Table 5). Thus, the triphenylphosphine complexes are more stable than the corresponding triphenylarsine derivatives. In general, complexes of tertiary phosphines

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[11] I. Lindqvist and M. Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

[12] G. B. Deacon, *Rev. Pure Appl. Chem.* (*Australia*), 1963, **13**, 189, and refs. therein.

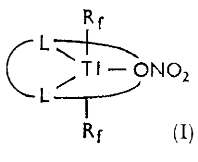
[13] G. B. Deacon and J. H. S. Green, *Chem. and Ind.*, 1965, 1031; unpublished results, 1962—1965.

with a variety of acceptors are more stable than those of the analogous arsines.[14] The failure to prepare $(R_f)_2Ph_3SbTlBr$ can be understood, as complexes of tertiary stibines are less stable than those of arsines.[14] The $(R_f)_2LTlX$ complexes are nearly completely dissociated in dilute acetone solution ($n \sim 1{\cdot}8$—$2{\cdot}0$).

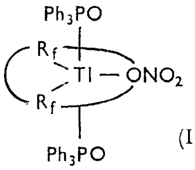
The triphenylphosphine and triphenylarsine complexes decompose on heating to *ca.* 150°, the products of the decomposition of $(R_f)_2Ph_3PTlBr$ including $(R_f)_2Ph_3POTlBr$ and thallous bromide. Prolonged heating of these complexes in solution also causes slight decomposition, the formation of $(R_f)_2Ph_3POTlBr$ being detected in the case of $(R_f)_2Ph_3PTlBr$.

(3) *Properties of the Five-co-ordinate Complexes*, $(R_f)_2L_2TlNO_3$ (L = Ph_3PO *or* Ph_3AsO).—Although the compounds dissociate considerably in benzene (see Experimental section), the crystalline complexes probably contain five-co-ordinate thallium and are not equimolar mixtures of $(R_f)_2LTlNO_3$ and L. The observed molecular weights increase with increasing concentration, whereas the apparent molecular weights of the mixtures would be approximately half the calculated values for $(R_f)_2L_2TlNO_3$ at all concentrations. Ionic structures, $(R_f)_2L_2Tl^+NO_3^-$, are unlikely as the compounds have low conductances in acetone (Table 4), and their behaviour in benzene is inconsistent with an ionic formulation. (Ionic compounds form ion-aggregates in benzene, giving apparent molecular weights greater than those of the corresponding ion-pairs.) The nitrate absorption bands of $(R_f)_2(Ph_3PO)_2TlNO_3$ (Table 2) are consistent with the presence of co-ordinated nitrate. Those of $(R_f)_2(Ph_3AsO)_2TlNO_3$ show that the symmetry of the nitrate ion is lowered from D_{3h}, though the splitting between ν_4 and ν_1 (94 cm.$^{-1}$) is not as great as is usually observed for nitrato-complexes (Table 2). However, the splitting is comparable to that observed for $(R_f)_2$bipyTlNO$_3$ and $(R_f)_2$*o*-phenTlNO$_3$ (*ca.* 118 cm.$^{-1}$),[1] which have been shown to contain co-ordinated nitrate by molecular-weight and conductance measurements.[1] The P=O stretching frequency of $(R_f)_2(Ph_3PO)_2TlNO_3$ (Table 3) is as expected for co-ordinated triphenylphosphine oxide.[9,10] This precludes the compound's being a mixture of $(R_f)_2Ph_3POTlNO_3$ and Ph_3PO, as the mixture would also have a band due to the free ligand. Two As=O stretching frequencies are observed for $(R_f)_2(Ph_3AsO)_2TlNO_3$ (Table 3), one of which corresponds to that of free triphenylarsine oxide.[10] However, evidence (additional to that above) that the compound is not a mixture of Ph_3AsO and $(R_f)_2Ph_3AsOTlNO_3$ can be given. The intense nitrate absorption at 1259 and 1020 cm.$^{-1}$ and the ν(As=O) band of $(R_f)_2Ph_3AsOTlNO_3$ are not present in the spectrum of $(R_f)_2(Ph_3AsO)_2TlNO_3$. Thus, the two ν(As=O) bands must be due either to non-equivalent Ph_3AsO ligands, or, more likely, to coupling of the As=O vibrations through thallium, leading to infrared-active symmetric and antisymmetric modes (see below).

Trigonal-bipyramidal stereochemistry has been proposed for the five-co-ordinate thallium compounds $(R_f)_2$(bipy or *o*-phen)TlX and $(R_f)_2py_2TlBr$, the structure with *trans* R_f groups being preferred.[1] By analogy, (I) is the most likely structure for



(I)



(II)

$(R_f)_2L_2TlNO_3$ compounds. The *cis* arrangement of Ph_3AsO groups is consistent with the observation of two ν(As=O) bands for $(R_f)_2(Ph_3AsO)_2TlNO_3$. The failure to observe two ν(P=O) bands for $(R_f)_2(Ph_3PO)_2TlNO_3$ does not preclude structure (I), as only one ν(P=O) or ν(As=O) frequency is observed for many tetrahedral ML_2X_2 (X = halogen) complexes of metals of the first transition series.[9,10,15] However, it also follows that structure (II)

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[14] W. C. Davies and H. W. Addis, *J.*, 1937, 1622; F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101.

[15] G. A. Rodley, D. M. L. Goodgame, and F. A. Cotton, *J.*, 1965, 1499.

with *trans* Ph_3PO ligands cannot be eliminated for $(R_f)_2(Ph_3PO)_2TlNO_3$. No clarification is provided by *X*-ray powder photography, as this compound is not isostructural with the arsine oxide analogue.

High co-ordination numbers arise with electronegative ligands of low polarisability, from which charge-transfer to acceptor metals is low.[16] Thus, the formation of five-co-ordinate derivatives $(R_f)_2L_2TlX$ when $X = NO_3$ and not when X = Br or OAc_f [section (1)] is due to the low polarisability of the nitrate ion. Other examples of high co-ordination number in nitrato-complexes are known. For example, methyldiphenylarsine oxide gives the octahedral complexes $[(Ph_2MeAsO)_4M(ONO_2)OH_2]^+NO_3^-$ with cobalt(II) and nickel(II) nitrates,[17] but tetrahedral $(Ph_2MeAsO)_2MX_2$ complexes with the corresponding metal halides.[15,17]

The dissociation of the compounds in benzene is due to the reaction (1),

$$(R_f)_2L_2TlNO_3 \overset{(1)}{\rightleftharpoons} L + (R_f)_2LTlNO_3 \overset{(2)}{\rightleftharpoons} 2L + (R_f)_2TlNO_3$$

and the stability of $(R_f)_2(Ph_3AsO)_2TlNO_3$ is greater than that of $(R_f)_2(Ph_3PO)_2TlNO_3$ (Table 5). In acetone the stability difference is still more marked. In dilute solution (*ca.* 10^{-2}M) further dissociation of $(R_f)_2(Ph_3PO)_2TlNO_3$ [reaction (2)], but not of $(R_f)_2(Ph_3AsO)_2TlNO_3$, is detectable (Table 5). In more dilute solution (*ca.* 10^{-3}M), the molar conductance of the phosphine oxide complex (Table 4) approaches that of $(R_f)_2TlNO_3$ [mol. cond. = 2·7 ($1·74 \times 10^{-3}$M)],[1] whereas the conductance of the arsine oxide complex does not.

(4) *Infrared Spectra.*—The infrared spectra of all compounds were recorded from 2000 to 200 cm.$^{-1}$. Except where bands due to other groups interfere, absorption characteristic of the $(R_f)_2Tl$ group[1] is observed at 1639—1634, 1513—1511s, 1486—1471s, 1381—1374s, 1280—1271, 1087—1079s, 1074—1067, 969—962s, 801—781, 786—774 (absent in the spectra of the five-co-ordinate complexes), 720—714, 609—601 (split into two bands in the spectra of Ph_3P and Ph_3As complexes), 370—347s [the range is so wide because it is difficult to distinguish between Ph_3AsO and $(R_f)_2Tl$ absorption in this region; the range 362—355 cm.$^{-1}$ applies for ten complexes], and 228—218 cm.$^{-1}$ in the spectra of all compounds. The most intense bands are designated "s." Vibrational assignments are being made for the $(R_f)_2Tl$ group, and will be reported later.

Bands due to Ph_3PO, Ph_3AsO, Ph_3P, and Ph_3As in the spectra of their respective complexes can be distinguished from $(R_f)_2Tl$ absorption. The following tentative assignments are based on those given for monosubstituted benzenes,[18] phenylphosphonium compounds,[19,20] phenylarsonium compounds,[20] phenylphosphine,[21] triphenylarsine and related compounds,[17,20] and for free and co-ordinated triphenylphosphine.[13,19] The X-sensitive modes involve stretching or bending of the P–C or As–C bonds coupled with aromatic-ring vibrations, the nomenclature being that of Whiffen.[18] The most intense bands are designated "s." In the spectra of the triphenylphosphine oxide complexes, bands at 1595—1590 (ν_{CC}), 1453—1449 (ν_{CC}), 1445—1439s (ν_{CC}), 1121s (X-sensitive mode *q*), 1029—1027 (β CH), 1002—998 [ring breathing; $(R_f)_2Tl$ absorption is also observed near this region[1]], 760 (γ CH), 751—749s (γ CH), 729—725s (X-sensitive mode *r*), 697—695s (ϕ CC), 544—539s (X-sensitive mode *y*), 446—441 (X-sensitive mode *t*), and 311—294 cm.$^{-1}$ (two bands, P=O def.) are characteristic of triphenylphosphine oxide. The P=O stretching frequencies are given separately in Table 3. In the spectra of the triphenylarsine oxide complexes, bands at 1462—1449 (ν_{CC}), 1445—1439s (ν_{CC}), 1183 (β CH), 1164—1160 (β CH), 1089—1087s (X-sensitive mode *q*), 1028—1025 (β CH), 1000 (ring breathing),

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755—749s (γ CH), 746—737s (γ CH, sometimes split), 695—690s (ϕ CC), 477—455s (two or three bands; X-sensitive mode *y*), and 373—347s cm.$^{-1}$ [X-sensitive mode *t*, coincident with $(R_f)_2Tl$ absorption; see above] are characteristic of triphenylarsine oxide. The As=O stretching frequencies are given in Table 3. Characteristic bands of triphenylphosphine in $(R_f)_2Ph_3PTl$(Cl or Br) * are at 1450 (ν_{CC}), 1439s (ν_{CC}), 1185 (β CH), 1171 (β CH), 1099s (X-sensitive mode *q*), 1030 (β CH), 1000 (ring breathing), 754s (γ CH), 743s (γ CH), 709 (X-sensitive mode *r*), 694s (ϕ CC), 517—490s (three bands; X-sensitive mode *y*), and 436—431 cm.$^{-1}$ (two bands; X-sensitive mode *t*). The appearance of the X-sensitive mode *r*, coincident with (ϕ CC) in the free ligand,[13, 19] and the shift of the X-sensitive mode *q* from its position (1089 cm.$^{-1}$) for free triphenylphosphine, are characteristic of co-ordinated triphenylphosphine.[13] Characteristic bands of triphenylarsine in $(R_f)_2Ph_3AsTl$(Cl or Br) * are at 1587 (ν_{CC}), 1452 (ν_{CC}), 1439s (ν_{CC}), 1190 (β CH), 1027 (β CH), 1002 (ring breathing), 746s (γ CH), 738s (γ CH), 694s (ϕ CC), 476—459s (three bands; X-sensitive mode *y*), and 325—318s cm.$^{-1}$ (two bands; X-sensitive mode *t*). The X-sensitive mode *q* is obscured by $(R_f)_2Tl$ absorption near 1080 cm.$^{-1}$, while the X-sensitive mode *r* may be obscured by the intense absorption of the ring deformation at 694 cm.$^{-1}$.

Metal–oxygen stretching frequencies of triphenylarsine oxide complexes of metals [in oxidation state (II)] of the first transition series are found [15] in the region 440—370 cm.$^{-1}$. The spectra of $(R_f)_2Ph_3AsOTlX$ complexes and of $(R_f)_2(Ph_3AsO)_2TlNO_3$ have no absorption bands from 455 to 373 cm.$^{-1}$, and are too complex from 373 to 200 cm.$^{-1}$ for definite assignments to be made of the Tl–O stretching frequencies. Similarly, the Tl–O stretching frequencies of the $(R_f)_2Ph_3POTlX$ complexes and of $(R_f)_2(Ph_3PO)_2TlNO_3$ cannot be located owing to the complexity of the spectra. Metal–oxygen frequencies of triphenylphosphine oxide complexes have not yet been assigned.

Bands due to the trifluoroacetate group in the spectra of the trifluoroacetato-complexes are not readily distinguishable from absorption due to other ligands. However, the antisymmetric $-CO_2^-$ stretching mode near 1640 cm.$^{-1}$, C–F stretching frequencies (three or four) between 1212 and 1153 cm.$^{-1}$, and a trifluoromethyl rocking frequency at *ca.* 283 cm.$^{-1}$ can be located. The assignments follow from those given for $(R_f)_2TlOAc_f$ and $(R_f)_2bipyTlOAc_f$.[1]

EXPERIMENTAL

Melting points are corrected. Molecular weights (concentrations given as % solution, w/v) and conductivities were obtained as described in Part I.[1] Infrared spectra of the compounds as Nujol and hexachlorobutadiene mulls were recorded using Grubb–Parsons GS2A (2000—700 cm.$^{-1}$) and DM2 (400—200 cm.$^{-1}$) and Unicam S.P. 100/130 (700—400 cm.$^{-1}$) instruments. The spectra of hexachlorobutadiene mulls of nitrato-complexes were examined between silver chloride plates, as exchange of nitrate between these mulls and polystyrene-covered potassium bromide plates occurred. The covered plates were satisfactory, however, for examination of Nujol mulls of these complexes.

For preparations of their complex derivatives, solutions of $(R_f)_2TlNO_3$ and $(R_f)_2TlOAc_f$ were obtained from the bromide and the appropriate silver salt, as previously described.[1]

The Complexes $(R_f)_2(Ph_3PO$ *or* $Ph_3AsO)TlX$.—*Bromobis(pentafluorophenyl)(triphenylphosphine oxide)thallium*(III). A solution of bromobis(pentafluorophenyl)thallium(III) (0·31 g., 0·50 mmole) and triphenylphosphine oxide (0·14 g., 0·50 mmole) in ether–methanol (20 ml.) was evaporated to dryness. Crystallisation of the residue from aqueous methanol gave the required *compound* as very fine white needles, which, when dried at 100° (0·33 g., 0·37 mmole, 74%), had m. p. 199·5—201·5° [Found: C, 40·2; H, 1·8; Br, 8·9; F, 21·05; P, 3·6%; *M* (in benzene), 845 (1·81%), 887 (3·00%); *M* (in acetone), 525 (1·54%), 623 (4·08%), 662 (7·77%). $C_{30}H_{15}BrF_{10}OPTl$ requires C, 40·2; H, 1·7; Br, 8·9; F, 21·2; P, 3·5%; *M*, 896]. The complex was also readily prepared by reaction of the stoicheiometric amounts of $(R_f)_2TlBr$ and Ph_3PO in the minimum amount of boiling benzene needed for complete solution. On cooling, the required compound crystallised. It was very soluble in acetone, methanol, ethanol, and ether, soluble in benzene, and insoluble in water.

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* Average values for the chloride and bromide are given; the spectra are very similar.

The following four compounds were similarly prepared and purified.

Chlorobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). This *complex* was obtained as small white tablets (75%), m. p. 216—218° (with preliminary softening) [Found: C, 42·3; H, 2·0; Cl, 4·1; F, 22·15; P, 3·8%; *M* (in benzene), *ca.* 860 (0·61%), *ca.* 894 (0·89%; limit of solubility; solution slightly cloudy); *M* (in acetone), 519 (1·79%), 648 (4·25%; near solubility limit). $C_{30}H_{15}ClF_{10}OPTl$ requires C, 42·3; H, 1·8; Cl, 4·2; F, 22·3; P, 3·6%; *M*, 852]. The chloride had solubility properties similar to those of the bromo-compound but was less soluble in benzene and acetone.

Trifluoroacetatobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). This *compound* was obtained as white microcrystals (47%), m. p. 172—174° [Found: C, 41·4; H, 1·7; F, 26·5; P, 3·3%; *M* (in benzene), 907 (1·02%), 975 (2·23%); *M* (in acetone), 536 (1·18%). $C_{32}H_{15}F_{13}O_3PTl$ requires C, 41·3; H, 1·6; F, 26·6; P, 3·3%; *M*, 929]. The solubility properties were similar to those of the bromo-compound.

Bromobis(pentafluorophenyl)(triphenylarsine oxide)thallium(III). This *complex* was obtained as very fine white needles (64%), m. p. 146—147° [Found: C, 38·4; H, 2·0; As, 8·0; Br, 8·4; F, 20·3%; *M* (in benzene), 887 (2·54%), 935 (5·27%); *M* (in acetone), 748 (1·03%), 869 (4·22%). $C_{30}H_{15}AsBrF_{10}OTl$ requires C, 38·3; H, 1·6; As, 7·9; Br, 8·5; F, 20·2%; *M*, 940]. The compound had solubility properties similar to those of the corresponding phosphine oxide complex, but was more soluble in benzene.

Chlorobis(pentafluorophenyl)(triphenylarsine oxide)thallium(III). This *compound* was obtained as white tablets (80%), m. p. 176—177° [Found: C, 40·1; H, 1·9; As, 8·5; Cl, 3·75; F, 21·3%; *M* (in benzene), 829 (1·50%), 844 (2·53%), 890 (3·26%); *M* (in acetone), 782 (2·26%), 857 (4·24%). $C_{30}H_{15}AsClF_{10}OTl$ requires C, 40·2; H, 1·7; As, 8·4; Cl, 4·0; F, 21·2%; *M*, 896]. The solubility properties were similar to those of the bromo-derivative, but the chloro-compound was less soluble in benzene.

Trifluoroacetatobis(pentafluorophenyl)(triphenylarsine oxide)thallium(III). On addition of water to a solution of trifluoroacetatobis(pentafluorophenyl)thallium(III) (0·65 g., 1·00 mmole) and triphenylarsine oxide (0·32 g., 1·00 mmole) in boiling methanol (20 ml.), the required *compound* crystallised out. After two recrystallisations from acetone–di-isopropyl ether, white microcrystals were obtained and dried at 100° (0·30 g., 0·31 mmole, 31%), m. p. 173·5—174·5° [Found: C, 39·9; H, 1·8; As, 8·5; F, 25·55%; *M* (in benzene), 922 (1·69%), 944 (3·27%), 977 (5·15%); *M* (in acetone), 836 (1·10%), 909 (3·39%). $C_{32}H_{15}AsF_{13}O_3Tl$ requires C, 39·5; H, 1·5; As, 7·7; F, 25·4%; *M*, 973]. While the high arsenic analysis may suggest the presence of free triphenylarsine oxide in the recrystallised compound, none could be detected by infrared spectroscopy. Free oxide was, however, clearly present in the crude product obtained from aqueous methanol. The complex was readily soluble in ether, ethanol, methanol, acetone, and benzene, sparingly soluble in di-isopropyl ether, and insoluble in water.

Nitratobis(pentafluorophenyl)(triphenylarsine oxide)thallium(III). To a solution of bromobis-(pentafluorophenyl)(triphenylarsine oxide)thallium(III) (0·94 g., 1·00 mmole) in methanol (15 ml.) was added a solution of silver nitrate (0·17 g., 1·00 mmole) in aqueous methanol (10 ml.). Silver bromide was filtered off, and the filtrate was allowed to evaporate overnight. The residue was crystallised from acetone–di-isopropyl ether, giving the required *compound* as white microcrystals, which were dried at 60° (0·57 g., 0·62 mmole, 62%), m. p. 116—118° [Found: C, 39·0; H, 1·9; As, 8·5; F, 21·2; N, 1·7%; *M* (in benzene), 930 (1·27%), 970 (2·99%); *M* (in acetone), 760 (1·08%), 896 (5·45%). $C_{30}H_{15}AsF_{10}NO_4Tl$ requires C, 39·0; H, 1·6; As, 8·1; F, 20·6; N, 1·5%; *M*, 922]. The solubility properties were similar to those of the trifluoroacetate.

Other preparations investigated:

Fluorobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). The stoicheiometric amounts of fluorobis(pentafluorophenyl)thallium(III) and triphenylphosphine oxide were dissolved in methanol. On addition of benzene and evaporation to crystallisation, $(R_f)_2TlF$ was obtained (identified by its infrared spectrum).

Acetatobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). Reaction of the stoicheiometric amounts of $(R_f)_2TlOAc$ and Ph_3PO in methanol, followed by addition of water and crystallisation, gave white crystals, identified as acetatobis(pentafluorophenyl)thallium(III) (infrared spectrum).

Nitratobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III). From all attempts to prepare this compound, nitratobis(pentafluorophenyl)bis(triphenylphosphine oxide)thallium(III) was obtained, *e.g.*, to a methanol solution (15 ml.) of bromobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III) (0·90 g., 1·00 mmole) was added a solution of silver nitrate (0·17 g., 1·00 mmole) in aqueous methanol (10 ml.). Silver bromide was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in acetone–di-isopropyl ether and allowed to evaporate slowly. Large crystalline plates were first deposited, followed by powdery microcrystals. The former were separated and recrystallised from acetone–di-isopropyl ether, yielding $(R_f)_2(Ph_3PO)_2TlNO_3$ (0·41 g., 0·35 mmole, 71%), m. p. 178—182° (with preliminary softening), with a spectrum identical with that of the authentic compound (for preparation, see below).

The Complexes $(R_f)_2(Ph_3PO$ or $Ph_3AsO)_2TlNO_3$.—*Nitratobis(pentafluorophenyl)bis(triphenylphosphine oxide)thallium*(III). On addition of water to a solution of nitratobis(pentafluorophenyl)thallium(III) (0·60 g., 1·00 mmole) and triphenylphosphine oxide (0·56 g., 2·00 mmoles) in boiling methanol (30 ml.), crystals were deposited. Crystallisation from acetone–di-isopropyl ether gave the required *compound* as small white plates which were dried at 100° (0·50 g., 0·43 mmole, 43%), m. p. 181—183° (with preliminary softening) [Found: C, 49·9; H, 2·9; F, 16·0; N, 1·1; P, 5·2%; *M* (in benzene), 633 (1·05%), 716 (3·75%), 780 (6·24%), 831 (8·35%), 914 (16·22%); *M* (in acetone), 489 (1·39%), 666 (9·12%). $C_{48}H_{30}F_{10}NO_5P_2Tl$ requires C, 49·7; H, 2·6; F, 16·4; N, 1·2; P, 5·4%; *M*, 1156]. The compound was readily soluble in methanol, ethanol, acetone, and benzene, sparingly soluble in di-isopropyl ether, and insoluble in water. As dissociation of the complex into free triphenylphosphine oxide and nitratobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III) occurs in benzene [Discussion, section (3)], a solution in benzene was slowly evaporated in an attempt to isolate the dissociation products. However, only $(R_f)_2(Ph_3PO)_2TlNO_3$, m. p. 179—181°, was obtained.

Nitratobis(pentafluorophenyl)bis(triphenylarsine oxide)thallium(III). The preparation was essentially similar to that of the previous compound. The *complex* was obtained as very small white plates (44%), m. p. 152·5—153·5° [Found: C, 46·0; H, 2·1; As, 12·1; F, 15·3; N, 1·1%; *M* (in benzene), 739 (1·13%), 820 (2·37%); *M* (in acetone), 711 (1·34%), 983 (11·2%). $C_{48}H_{30}As_2F_{10}NO_5Tl$ requires C, 46·3; H, 2·4; As, 12·0; F, 14·6; N, 1·1%; *M*, 1244]. The compound had solubility properties similar to those of the previous compound, but was less soluble in benzene (solubility limit *ca.* 3·5%). It was also apparently less soluble than the mono(triphenylarsine oxide) analogue, since, if even a very slight excess of Ph_3AsO was used in preparing $(R_f)_2Ph_3AsOTlNO_3$ from $(R_f)_2TlNO_3$ and the arsine oxide, $(R_f)_2(Ph_3AsO)_2TlNO_3$ was detected in the product (infrared spectroscopy), and could not be removed by recrystallisation.

Other preparations investigated:

Bromobis(pentafluorophenyl)bis(triphenylphosphine oxide)thallium(III). A solution of bromobis(pentafluorophenyl)thallium(III) (0·31 g., 0·50 mmole) and triphenylphosphine oxide (0·28 g., 1·00 mmole) in ether–ethanol (20 ml.) was evaporated to dryness, giving an oil. Addition of hexane caused crystallisation. The solid product was crystallised from acetone–di-isopropyl ether–hexane, giving bromobis(pentafluorophenyl)(triphenylphosphine oxide)thallium(III) (0·20 g., 0·22 mmole, 44%), m. p. 200·5—204° (identified by its infrared spectrum). Some triphenylphosphine oxide was recovered from the hexane used in crystallisation of the product.

Trifluoroacetatobis(pentafluorophenyl)bis(triphenylarsine oxide)thallium(III). A solution of the stoicheiometric amounts of triphenylarsine oxide and trifluoroacetatobis(pentafluorophenyl)thallium(III) in ether–methanol was evaporated to dryness. Recrystallisation of the residue from acetone–di-isopropyl ether gave triphenylarsine oxide as the first fraction (infrared identification). Thus, the four-co-ordinate $(R_f)_2Ph_3AsOTlOAc_f$ was formed.

The Complexes $(R_f)_2(Ph_3P$ *or* $Ph_3As)TlX$.—*Bromobis(pentafluorophenyl)triphenylphosphinethallium*(III). Difficulty was experienced in crystallising this compound when the stoicheiometric amounts of reactants were used in the preparation. However, when excess of ligand was used, the complex crystallised readily, and this procedure was adopted for the preparations of similar compounds. A solution of bromobis(pentafluorophenyl)thallium(III) (0·31 g., 0·50 mmole) and triphenylphosphine (0·26 g., 1·00 mmole) in ether (20 ml.) was evaporated to dryness. The residue was rapidly recrystallised from di-isopropyl ether–hexane, giving the required *compound* as white microcrystals, which were washed with hexane to remove excess triphenylphosphine and dried at 60° (0·20 g., 0·23 mmole, 45%) [Found: C, 41·0; H, 1·8; Br, 8·9; F, 21·5; P, 3·5%; *M* (in benzene), 727 (1·14%), 756 (3·00%), 805 (5·32%); *M* (in acetone), 476 (1·64%). $C_{30}H_{15}BrF_{10}PTl$ requires C, 40·9; H, 1·7; Br, 9·1; F, 21·6; P, 3·5%; *M*, 880].

On heating, the compound softened with decomposition at 140—160°, and at 190—200° decomposition was severe. To investigate the nature of the decomposition the compound was heated for 10 min. at 140—180°. The product was extracted with ether, and a pale brown solid was obtained on evaporation of the solvent. The spectrum of this substance (2000—667 cm.$^{-1}$) indicated that it contained $(R_f)_2Ph_3PTlBr$ and $(R_f)_2Ph_3POTlBr$. The ether-insoluble residue was a white powder having no infrared absorption from 2000 to 667 cm.$^{-1}$ and was probably thallous bromide. $(R_f)_2Ph_3PTlBr$ was very soluble in ether, ethanol, methanol, benzene, and acetone, soluble in di-isopropyl ether, and insoluble in hexane and water. Solutions of the compound became cloudy on prolonged heating, probably owing to the formation of thallous bromide. Slow oxidation to $(R_f)_2Ph_3POTlBr$ also occurred.

Chlorobis(pentafluorophenyl)triphenylphosphinethallium(III). The *chloride* was similarly prepared and obtained as white microcrystals (53%) [Found: C, 43·3; H, 1·7; Cl, 4·0; F, 22·7; P, 3·6%; *M* (in benzene), *ca.* 780 (0·50%), 784 (1·03%), 794 (2·39%), 809 (3·88%; near solubility limit); *M* (in acetone), *ca.* 467 (0·54%). $C_{30}H_{15}ClF_{10}PTl$ requires C, 43·1; H, 1·8; Cl, 4·2; F, 22·7; P, 3·7%; *M*, 836]. The behaviour of the compound on heating depended on the crystallinity of the sample. When powdered it softened at *ca.* 155—160° (decomp.) and partly melted at *ca.* 165—170° (decomp.). The chloro-compound was less soluble than the bromo-derivative in benzene; otherwise the solubility properties were similar.

Bromobis(pentafluorophenyl)triphenylarsinethallium(III). To a solution of bromobis(pentafluorophenyl)thallium(III) (0·31 g., 0·50 mmole) and triphenylarsine (0·31 g., 1·00 mmole) in boiling ether (10 ml.) was added boiling hexane (15 ml.). After most of the ether had evaporated, the solution was filtered, cooled, and the required *compound* crystallised. It was filtered off, washed with hexane and light petroleum (b. p. 30—40°) to remove unreacted ligand, dried at 60°, and obtained as white microcrystals (0·23 g., 0·25 mmole, 50%), decomp. *ca.* 130° (with softening) [Found: C, 39·1; H, 1·5; As, 8·3; Br, 8·8; F, 20·7%; *M* (in benzene), 625 (1·21%), 717 (5·93%). $C_{30}H_{15}AsBrF_{10}Tl$ requires C, 39·0; H, 1·6; As, 8·1; Br, 8·6; F, 20·6%; *M*, 924]. The compound had solubility properties similar to those of the phosphine analogue.

Chlorobis(pentafluorophenyl)triphenylarsinethallium(III). The *chloride* was similarly prepared, and obtained as white microcrystals (59%), m. p. 149·5° (decomp.) [Found: C, 40·8; H, 1·7; As, 8·45; Cl, 4·2; F, 21·7%; *M* (in benzene), *ca.* 621 (0·51%); *ca.* 618 (0·79%; solubility limit); *M* (in acetone), 430 (1·50%). $C_{30}H_{15}AsClF_{10}Tl$ requires C, 40·9; H, 1·7; As, 8·5; Cl, 4·0; F, 21·6%; *M*, 880]. The solubility properties were similar to those of the bromo-compound except in benzene.

An attempt to make bromobis(pentafluorophenyl)triphenylstibinethallium(III) by a method similar to that used for the triphenylarsine complex was unsuccessful. On cooling the hexane–ether solution of $(R_f)_2TlBr$ and Ph_3Sb, the former compound crystallised (infrared identification).

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