

Organothallium Chemistry

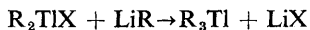
By A. G. Lee

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THE element thallium was discovered in 1861 by William Crookes, and very soon after, in 1870, the first organothallium compound was prepared.¹ This compound, diethylthallium chloride, was found to be remarkably stable, being unaffected by air and water. A large number of such dialkylthallium compounds were prepared around the turn of the century, and found to be similarly stable. The substitution of the third group on thallium by an alkyl group, however, had to wait until 1930, when it was found that the reaction of diethylthallium chloride and ethyl-lithium gave triethylthallium.² Since that time, there have been sporadic forays into organothallium chemistry, but few concerted attacks. Most of the work has, predictably, concentrated on the air stable diorganothallium derivatives, although with the advent of vacuum and dry-box techniques, methods of handling the very air-sensitive triorganothallium compounds have been developed.

1 Triorganothallium Compounds

A. Preparation.—Triorganothallium compounds are usually prepared by the reaction between a dialkyl- or diaryl-thallium halide and an organolithium compound.^{2,3}



The reaction between thallium(III) chloride and a Grignard reagent in diethyl ether stops after the introduction of two organic groups: the third group can be substituted by carrying out the Grignard reaction in tetrahydrofuran as solvent.⁴ The most convenient preparation of trimethylthallium, however, is by the reaction between thallium(I) iodide and methyl-lithium in the presence of methyl iodide.^{5a,b} The overall reaction is:



The first step of the reaction is considered to be the formation of monomethylthallium(I), followed either by disproportionation or by reaction with methyl iodide:

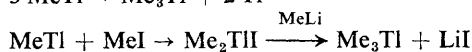
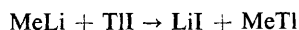
¹ C. Hansen, *Chem. Ber.*, 1870, 3, 9.

² H. P. A. Groll, *J. Amer. Chem. Soc.*, 1930, 52, 2998.

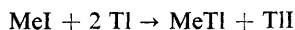
³ E. G. Rochow and L. M. Dennis, *J. Amer. Chem. Soc.*, 1935, 57, 486.

⁴ O. Ya. Okhlobystin, K. A. Bilevitch, and L. I. Zakharkin, *J. Organometallic Chem.*, 1964, 2, 281.

⁵(a) H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1946, 68, 517; (b) H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1950, 72, 1760.

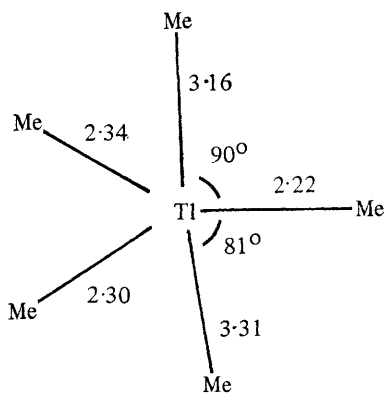


The thallium metal formed (in a finely divided state) can then react with methyl iodide:



Although methyl iodide does not react with massive thallium or with a thallium-sodium alloy,³ ethyl chloride and a thallium-sodium alloy react to give low yields of triethylthallium² and thallium reacts with phenyl iodide to give thallium(i) iodide and, possibly, phenylthallium derivatives.⁶

B. Properties.—The first point of interest concerning triorganothallium compounds is their state of association. Freezing point measurements show that trimethyl-, triethyl-, and triphenyl-thallium are monomeric in benzene solution.^{5a,7} I.r. and Raman studies of trimethylthallium also suggest that it is monomeric in benzene solution and in the vapour phase, but that it is associated in the crystal.⁸ This has now been confirmed by a single crystal *X*-ray study.⁹ In the crystal, the three nearest neighbours of each thallium are three methyl groups in a plane (1), so that little rearrangement takes place when the crystal vaporises as monomer. Association to give a polymeric three-dimensional network occurs through unsymmetrical Me-Tl-Me bridges, the co-ordination about thallium being a distorted trigonal bipyramid with three short equatorial and two long axial bonds.



(1)

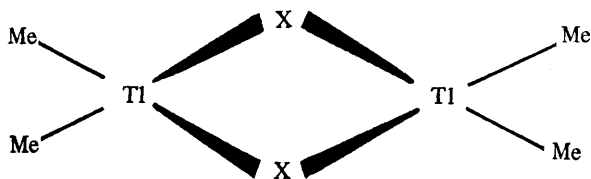
⁶ J. F. Spencer and M. L. Wallace, *J. Chem. Soc.*, 1908, 1827.

⁷ W. Strohmeier, K. Humpfner, K. Miltenberger, and F. Seifert, *Z. Elektrochem.*, 1959, **63**, 527.

⁸ A. J. Downs and A. G. Lee, to be published.

⁹ G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. (A)*, 1970, 28.

The methyl bridges are long ($\sim 3.2 \text{ \AA}$) and must clearly be weak in comparison to those in the trimethylaluminium dimer. Although no stable methyl-bridged dimer is formed by trimethylthallium, such a dimer has been postulated to be the transition state for intermolecular exchange of methyl groups in solution: this rapid intermolecular exchange is evidenced by the collapse of the $^{205}\text{Tl-H}$ and $^{203}\text{Tl-H}$ doublets in the n.m.r. spectrum. The exchange is concentration and solvent dependent, and, being second order in the concentration of trimethylthallium, has been postulated to proceed *via* a methyl-bridged dimer (2, X = Me).¹⁰ The energy of activation for the exchange is $6 \pm 1 \text{ kcal mole}^{-1}$ in solution in dichloromethane. At low temperatures ($\sim -70^\circ$) the exchange could be stopped, but all the methyl groups were equivalent in the n.m.r. spectrum, so that (2) can only be a transition state, higher in energy than the monomeric trimethylthallium molecules. Dimerisation of trimethylaluminium is favoured by low inner shell repulsion between the two aluminium atoms when separated by the internuclear distances demanded by the geometry of the dimer, and also by strong electronic configurational interaction between the aluminium atoms. For thallium, the first factor will probably be greater and the second smaller (Tl-Tl bonds are expected to be weak), so that dimerisation will be less favourable for thallium than for aluminium. A number of organothallium compounds seem to have trigonal-bipyramidal structures (see later), so that a basic D_{3h} symmetry for thallium in trimethylthallium is not so surprising; distortion from the idealised geometry is demanded by the requirements of crystal packing coupled with the requirement that the basic TlC_3 planar skeleton should be maintained. The structure adopted by trimethylthallium is closely analogous to that found for trimethylindium.¹¹



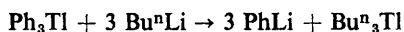
As well as undergoing intermolecular exchange of methyl groups, trimethylthallium undergoes rapid methyl exchange with dimethyl zinc.¹² Between triphenylthallium and n-butyl-lithium, however, there is a rapid redistribution of groups.¹³

¹⁰ J. P. Maher and D. R. Evans, *J. Chem. Soc.*, 1963, 5543.

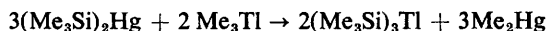
¹¹ E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, 1958, **80**, 4141.

¹² A. G. Lee, to be published.

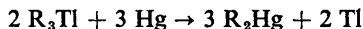
¹³ H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 2357.



Similarly, in the reaction between bis(trimethylsilyl)mercury and trimethylthallium there is a rapid redistribution to form tris(trimethylsilyl)thallium.¹⁴



Little work has yet been done on reactions of triorganothallium compounds with metal halides, but it is known that both trimethyl- and triphenyl-thallium will react with mercury:^{5a,12}



This is of interest in view of the fact that both gallium and indium react with dimethylmercury to give the corresponding metal trialkyls.

Although trimethylthallium is a much weaker acceptor than trimethylindium or trimethylgallium, it will form 1 : 1 complexes with Lewis bases. Thus with trimethylamine, trimethylthallium forms a crystalline complex $\text{Me}_3\text{Tl} \cdot \text{NMe}_3$ which is, however, extensively dissociated in the vapour phase:¹⁵ the adduct formed between trimethylamine and triphenylthallium is much less readily dissociated.¹⁰

The decidedly weak acceptor properties of triorganothallium compounds have important consequences for their chemistries. Many reactions of organo-aluminium compounds, for example, are postulated to proceed *via* preliminary adduct formation. Thus trimethylaluminium first forms a 1 : 1 adduct with acetonitrile and then reacts to form $(\text{Me}_2\text{C}:\text{NAlMe}_2)_2$,¹⁶ whereas trimethylthallium fails to form an adduct with acetonitrile and does not react.¹⁷

The two most important factors in the chemistry of these compounds are probably, however, the weakness of the Tl-C bond and the great stability of diorganothallium derivatives. Although no value for the mean Tl-C bond dissociation energy has yet been measured, the dissociation energy of the first Tl-C bond, $\text{D}(\text{Me}_2\text{Tl}-\text{CH}_3)$ has been calculated as 27.4 kcal mol⁻¹ from kinetic data for the pyrolysis of trimethylthallium.¹⁸ This compares with bond dissociation energies (D_1) of 59.5 and 47.2 kcal mol⁻¹ for trimethylgallium and trimethylindium respectively.^{19a, b}

The reactivity of triorganothallium compounds has been attributed to their ability to ionise to $\text{R}_2\text{Tl}^+\text{R}^-$.²⁰ Thus, hydrolysis to give R_2TlOH and RH has been considered a unimolecular electrophilic substitution ($\text{S}_{\text{E}}1$). However, the only experimental evidence reported to support this mechanism²⁰ has been shown to be incorrect.²¹ In the absence of any evidence to the contrary, it seems

¹⁴ E. A. V. Ebsworth, A. G. Lee, and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1969, 1052.

¹⁵ G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 1956, 3351.

¹⁶ J. R. Jennings, J. E. Lloyd, and K. Wade, *J. Chem. Soc.*, 1965, 5083.

¹⁷ A. G. Lee and G. M. Sheldrick, *J. Organometallic Chem.*, 1969, 17, 481.

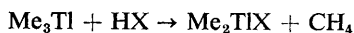
¹⁸ M. G. Jacko and S. J. W. Price, *Canad. J. Chem.*, 1965, 43, 1961.

¹⁹ (a) M. G. Jacko and S. J. W. Price, *Canad. J. Chem.*, 1963, 41, 1560; (b) M. G. Jacko and S. J. W. Price, *Canad. J. Chem.*, 1964, 42, 1198.

²⁰ C. R. Hart and C. K. Ingold, *J. Chem. Soc.*, 1964, 4372.

²¹ F. R. Jensen and D. Heyman, *J. Amer. Chem. Soc.*, 1966, 88, 3438.

most likely that the mechanism adopted is a concerted displacement of the leaving group by the entering group (often loosely referred to as an S_N2 mechanism), as is found for reactions of many other organometallic compounds. But whatever the mechanism, trimethylthallium has been shown to react with a wide variety of compounds containing an acidic hydrogen, to give methane and the corresponding dimethylthallium derivative.¹⁷



The reaction proceeds not only with such obvious acids as the hydrogen halides, alcohols, and thiols, but also with less obvious acids such as cyclopentadiene²² and $\text{HMn}(\text{CO})_5$.¹² With halogenomethanes, the corresponding dimethylthallium halide is formed:^{12,17} thus with chloroform, Me_2TlCl is formed. The order of reactivity of the halogenocarbons, $\text{I} > \text{Br} > \text{Cl} > \text{F}$ and $\text{CHX}_3 > \text{CH}_2\text{X}_2 > \text{CH}_3\text{X}$ is similar to that found for the basic hydrolysis of the halogenocarbons, involving intermediate halogenocarbon anions. If any CX_3 derivatives of thallium are first formed in these reactions, then they must be very unstable. Thus dimethylthallium ethoxide reacts with chloroform to give Me_2TlCl whereas mercury alkoxides and chloroform react to give compounds of the type RHgCCl_3 .²³ The compound $\text{Ph}_2\text{Tl}[\text{C}(\text{CN})_3]$ can, however, be made by the reaction between Ph_2TlF and $\text{K}[\text{C}(\text{CN})_3]$.²⁴ There is no reaction between trimethylthallium and dimethylamine or diethylamine,^{15,17} or between triethylthallium and ammonia.³

In a variety of other reactions of triorganothallium compounds, a diorganothallium derivative is formed:



It requires reagents such as the halogens or interhalogen compounds to cleave the final two bonds.²⁷ Even in oxidation reactions, diorganothallium species can be formed. Thus phenol, biphenyl, and diphenylthallium oxide have all been found in the products of the slow reaction of a benzene solution of triphenylthallium with dry air.^{28a,b} The reason for the great stability of the diorganothallium group is unclear.

2 Diorganothallium(III) Derivatives

A. Preparation.—The most versatile routes to diorganothallium derivatives are by reactions of triorganothallium compounds of the type detailed above. Starting from thallium(III) halides, however, dialkylthallium halides can be prepared by

²² A. G. Lee and G. M. Sheldrick, *Chem. Comm.*, 1969, 441.

²³ G. Holan, *Tetrahedron Letters*, 1966, 1985; and references therein.

²⁴ W. Beck, H. S. Smedal, and H. Kohler, *Z. anorg. Chem.*, 1967, **354**, 69.

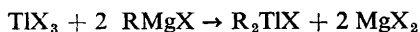
²⁵ J. Muller and K. Dehnicke, *J. Organometallic Chem.*, 1968, **12**, 37.

²⁶ A. G. Lee, *Chem. Comm.*, 1968, 1614.

²⁷ A. E. Goddard, *J. Chem. Soc.*, 1923, 1161.

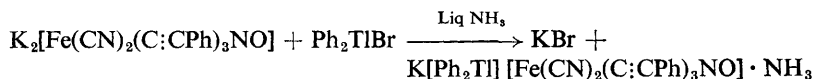
²⁸ (a) S. F. Birch, *J. Chem. Soc.*, 1934, 1132; (b) H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1939, **61**, 1513.

the Grignard reaction,^{29a,b} although yields are often poor owing to oxidation of the Grignard reagents by the thallium(III) halides:



Diarylthallium halides can be very conveniently prepared by the reaction between thallium(III) halides and arylboronic acids,^{29b,30}

Starting from the diorganothallium halides, a wide variety of other diorganothallium derivatives can be prepared by anion exchange with silver salts, alkali-metal salts, and thallium(I) salts. Thus halide can be exchanged for anions such as nitrate, chromate, thiocyanate, trichloroacetate, and even more exotic groups:³¹



Another much used procedure is to convert the diorganothallium halide to the hydroxide (using aqueous silver oxide) and then to neutralise with the appropriate acid.

In the same way that triorganothallium compounds with substituents in the alkyl chain are unstable, so are the analogous diorganothallium compounds. Electrolysis of $\text{ICH}_2\text{CH}_2\text{CN}$ using a sacrificial cathode of thallium produces the unstable compound $(\text{CNCN}_2\text{CH}_2)_2\text{TlI}$.³² Reaction of thallium(III) chloride with diazomethane produces $(\text{ClCH}_2)_2\text{TlCl}$ as an explosive solid: with diazoethane the product was too unstable to isolate.³³

B. Properties.—Dialkyl- and diaryl-thallium(III) derivatives are amongst the most stable and least reactive organometallic compounds known. They are unaffected by water and oxygen and in many ways resemble both the iso-electronic diorganomercury compounds and the corresponding thallium(I) derivatives. They can thus be used as a 'pseudo-Tl^I' cation. Vibrational and ¹H n.m.r. spectra of the organic group can be used as a probe to study the interactions of the thallium with the other ligands. This is particularly useful since the thallium(I) cation itself has relatively few easily measured properties which are sensitive to the nature of the interaction of the thallium with ligands.

Most of the thallium compounds of this type give highly conducting solutions in water. Conductance measurements indicate a high degree of dissociation for the hydroxide Me_2TlOH ³⁴ with the formation of $\text{Me}_2\text{Tl}(\text{H}_2\text{O})_x^+$ and OH^- ions. In 0.2 molar aqueous solution, about 10% of the thallium is present as the dimer

²⁹ (a) R. J. Meyer and A. Bertheim, *Chem. Ber.*, 1904, **37**, 2051; (b) F. Challenger and B. Parker, *J. Chem. Soc.*, 1931, 1462.

³⁰ F. Challenger and O. V. Richards, *J. Chem. Soc.*, 1934, 405.

³¹ R. Nast, K. W. Kruger, and G. Beck, *Z. anorg. Chem.*, 1967, **350**, 177.

³² A. P. Tomilov, Yu. D. Smirnov, and S. L. Varsharskii, *Zhur. obschei Khim.*, 1965, **35**, 391.

³³ A. Yu. Yakubovich and V. A. Ginsburg, *Doklady Akad. Nauk, S.S.S.R.*, 1950, **73**, 957.

³⁴ F. Hein and H. Meininger, *Z. anorg. Chem.*, 1925, **145**, 95.

(2, X = OH), 36% as Me_2TlOH , and 54% as $\text{Me}_2\text{Tl}(\text{H}_2\text{O})_x^+$.³⁵ The n.m.r. spectra of aqueous solutions of a wide variety of dimethylthallium derivatives suggest that the same thallium-containing species is present in all solutions,³⁶ presumably $\text{Me}_2\text{Tl}(\text{H}_2\text{O})_x^+$. Water, having a high dielectric constant and being a good electron donor, is almost an ideal solvent for the production of solutions of organometallic cations:³⁷ dimethylformamide is a less ideal solvent, and conductivity measurements suggest that Me_2TlI is incompletely dissociated in this solvent.³⁸

The Raman spectra of aqueous solutions of dimethylthallium perchlorate and nitrate show that the C-Tl-C skeleton in the dimethylthallium hydrate $[\text{Me}_2\text{Tl}(\text{H}_2\text{O})_x^+]$ ion is linear.³⁹ No information regarding the number of solvent molecules co-ordinated to the metal atom is available, but it seems probable that there will be four, producing an overall octahedral configuration for the thallium.

The dimethylthallium ion is only a very weak aquo-acid, indicating that the bonds to water molecules in the first co-ordination sphere are very weak.^{34,35,40} Supporting evidence for weak polar bonds to the water molecules comes from the Raman spectra of aqueous solutions of the dimethylthallium ion, which show no lines attributable to stretching of Tl-O bonds. Even the spectrum of 2.3 M Me_2TlOH shows no lines attributable to Tl-O bond stretching.³⁹

The dimethylthallium halides were investigated by X-ray crystallography in 1935;⁴¹ the structure consists of layers in which a linear Me_2Tl group is surrounded by four halogen atoms and each halogen is surrounded by four Me_2Tl groups (3). It is a moot point whether the structure should be described in terms of an ionic lattice or in terms of bridging halogen atoms and thallium-halogen bonds with a reasonable degree of covalency. I.r. studies of the dimethylthallium derivatives of CN^- , ClO_4^- , and NO_3^- in the solid state are all consistent with structures containing free linear Me_2Tl cations and free anions.^{42a, b} The i.r. spectrum of Me_2TlNO_3 , for example, shows only a small degree of splitting of the doubly degenerate ν_3 ionic nitrate mode, indicating that the nitrate ion is only weakly perturbed. Furthermore, the spectrum shows only one band in the Tl-C stretching region at 557 cm^{-1} , assignable to the antisymmetric stretching mode in a linear Me_2Tl group.^{42b}

For these dimethylthallium derivatives, therefore, in aqueous solution or in the solid state, there can be distinguished two distinct types of bond from the central thallium to the ligands: the kinetically inert and relatively non-polar

³⁵ J. K. Lawrence and J. E. Prue, Internat. Conference on Co-ordination Chem., London, 1959, *Chem. Soc. Special Publ.* No. 13., p. 186.

³⁶ J. V. Hatton, *J. Chem. Phys.*, 1964, **40**, 933.

³⁷ R. S. Tobias, *Organometallic Chem. Rev.*, 1966, **1**, 93.

³⁸ J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, 1961, **57**, 1795.

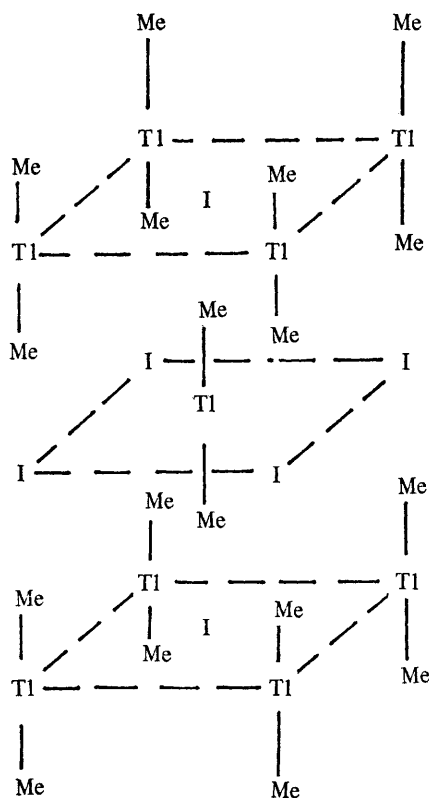
³⁹ P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1960, **56**, 1591.

⁴⁰ A. J. Berry and T. M. Lowry, *J. Chem. Soc.*, 1928, 1748.

⁴¹ H. M. Powell and D. M. Crowfoot, *Z. Krist.*, 1934, **87**, 370.

⁴² (a) G. D. Shier and R. S. Drago, *J. Organometallic Chem.*, 1966, **5**, 330; (b) G. B. Deacon, J. H. S. Green, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 3411.

bonds to carbon in the alkyl groups, and the kinetically labile and highly polar bonds to the electronegative group. It is unlikely, in the case of the halides at least, that these latter bonds can be regarded as purely 'hard-sphere' Coulomb



(3)

interactions and there will be a certain amount of covalent character to them. The example of aluminium trichloride comes to mind: although the solid has a largely ionic, distorted chromyl chloride layer-structure, it is present in the vapour phase as dimeric molecules.⁴³ Although the structures of the dialkylthallium halides in the vapour phase are unknown, the mass spectra of both Me_2TlCl and Me_2TlCN show the presence of dimeric molecules in the vapour phase: for Me_2TlBr and Me_2TlI parent ions are observed, but no dimeric species.⁴⁴ Little is known about the structures of the dialkylthallium fluorides,

⁴³ A. F. Wells, 'Structural Inorganic Chemistry', Oxford University Press, 1962.

⁴⁴ A. G. Lee, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, 3, 239.

which, by comparison with other organometallic fluorides, might well be expected to adopt fluorine-bridged structures. Di-isobutyl-, di-isoamyl-, and di-n-hexylthallium fluorides have been shown to be highly associated in benzene solution,⁴⁵ and the i.r. spectrum of Me_2TlF shows both a symmetric and an antisymmetric $\text{Tl}-\text{C}$ stretch, so that, unlike the other dimethylthallium halides, the $\text{C}-\text{Tl}-\text{C}$ skeleton must be non-linear.⁴⁶

A number of dimethylthallium compounds are known which are dimeric in solution. Molecular weight measurements show that Me_2TlOEt is largely dimeric in benzene solution,⁴⁷ although n.m.r. spectroscopy suggests that some monomer is also present in toluene solution.⁴⁸ Similarly, such groups as OPh , SMe , NMe_2 , and SO_2Me are good bridging groups.^{44,49} As already mentioned, the methyl group would seem to have little capacity for bridge formation. Thus n.m.r. spectra of mixtures of Me_3Tl and Me_2TlOEt show no evidence for the formation of mixed dimers with methyl bridges.⁴⁸ In solutions of $(\text{Me}_3\text{Si})_3\text{Tl}$, intermolecular exchange of trimethylsilyl groups occurs, and in this case a dimeric transition state with trimethylsilyl bridges was invoked.⁵⁰ Rapid exchange of alkyl groups occurs in mixtures of Me_3Tl and Et_3Tl at room temperature: at -85° additional lines are seen in the n.m.r. spectrum due to the mixed alkyls TlMe_2Et and TlMeEt_2 , but again there was no evidence for the formation of dimeric species.¹⁰ The exchange of vinyl groups on thallium is faster than that of methyl groups, and it has been suggested that this is due to stabilisation of the dimeric transition state by bridging vinyl groups; the non-bonding molecular orbital for the three-centre bridging system has the appropriate symmetry to interact with the π -orbitals of the vinyl group. With $\text{Me}_2\text{TlC}:\text{CPh}$ and $\text{Me}_2\text{TlC}_5\text{H}_5$, however, the situation is rather different. Here no redistribution of groups occurs on the thallium in solution; furthermore, there is no exchange of methyl groups between them and trimethylthallium,^{22,51} They resemble dimeric dimethylthallium compounds such as Me_2TlOEt rather than 'dimethyl-alkylthallium' compounds such as Me_2TlEt . N.m.r. results suggest that both $\text{Me}_2\text{TlC}:\text{CPh}$ and $\text{Me}_2\text{TlC}_5\text{H}_5$ exist in solution as a mixture of monomer and dimer,⁵¹ although molecular weight measurements suggest that $\text{Me}_2\text{TlC}:\text{CPh}$ is largely monomeric in aniline solution.⁵² The properties of dimethylthallium compounds of the type Me_2TlX are obviously very sensitive to the nature of the group X.

Unfortunately, no crystal structure determinations have been reported for those diorganothallium compounds, which have been shown to be dimeric in solution, so that little can be said about solid-state structures. I.r. spectroscopy suggests that the $\text{C}-\text{Tl}-\text{C}$ skeleton in a number of these derivatives is bent, but

⁴⁵ E. Krause and P. Dittmar, *Chem. Ber.*, 1930, **63B**, 1953.

⁴⁶ W. Beck and E. Schuierer, *J. Organometallic Chem.*, 1965, **3**, 55.

⁴⁷ R. C. Menzies and A. R. P. Walker, *J. Chem. Soc.*, 1934, 1131.

⁴⁸ A. G. Lee and G. M. Sheldrick, to be published.

⁴⁹ H. Kurosawa, K. Yasuda, and R. Okawara, *Bull. Chem. Soc. Japan*, 1967, **40**, 861.

⁵⁰ A. G. Lee and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1969, 1055.

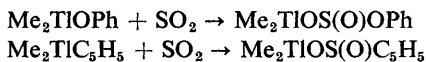
⁵¹ A. G. Lee, *J. Chem. Soc. (A)*, in the press.

⁵² R. Nast and K. Kab, *J. Organometallic Chem.*, 1966, **6**, 456.

cannot distinguish the degree of association. Thus, i.r. measurements indicate that the acetate group in $\text{Me}_2\text{TlO}_2\text{CMe}$ is probably bidentate but cannot distinguish between a dimeric structure and a polymeric structure.⁵³ In such a case, where the substituent attached to thallium has the possibility of chelating, three structural possibilities must be considered; (i) the compound is largely ionic, (ii) the compound is chelated, and (iii) it is bridged to give a dimer or polymer.

The very weakly polarising effect of the weak acid Me_2Tl^+ is indicated by its slight tendency to hydrolyse. Stability constants for complex formation with β -diketone ligands in aqueous solution are small, only one β -diketone being co-ordinated.⁵⁴ I.r. spectra of solid dimethylthallium acetylacetonate suggest that the C-Tl-C skeleton is linear and thus presumably only weakly chelated.⁵⁵ This is also consistent with the observation that very rapid exchange of acetylacetonate occurs between dimethylthallium acetylacetonate and free acetylacetonate.⁵⁶ In benzene solution, although some dialkylthallium β -diketonates (including dimethylthallium hexafluoroacetylacetonate) are monomeric, others consist of a mixture of monomer and dimer.^{57a,b} Again, i.r. spectra suggest that $\text{Me}_2\text{TlSSPMe}_2$ is ionic in the solid, $[\text{Me}_2\text{Tl}]^+ + [\text{SSPMe}_2]^-$,⁵⁸ whereas $\text{Me}_2\text{TlSSP(OR)}_2$ is monomeric in solution⁵⁹ and may well have a chelated structure, and $\text{Me}_2\text{Tl(SSPEt}_2)$ is a mixture of monomer and dimer in chloroform solution.⁶⁰ Finally, diethylthallium salicylaldehyde is monomeric in chloroform solution, but an X-ray crystallographic study⁶¹ has shown that in the solid state it has polymeric structure. Monomer units such as (4) are associated by phenolic (at 1) and aldehydic (at 2) bridges to form infinite chains of nearly coplanar Tl-O-Tl-O rings (5). Each thallium is thus six-co-ordinate, with two ethyl groups and four oxygen atoms.

Unlike many of the corresponding dialkylaluminium compounds, there is no tendency for dialkylthallium compounds to disproportionate to give monoalkylthallium(III) derivatives. The dimethylthallium group would seem to be kinetically very inert: it is possible to ring many changes with the anionic group, while leaving the diorganothallium group unchanged. Thus it is possible to insert into the thallium-substituent bond, leaving the dialkylthallium group unchanged,⁶²



No intermolecular exchange of alkyl groups occurs in solutions of dialkyl-

⁵³ G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 1968, **24**, A, 885.

⁵⁴ J. R. Cook and D. F. Martin, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1249.

⁵⁵ H. Kurosawa, K. Yasuda, and R. Okawara, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 131.

⁵⁶ G. E. Glass and R. S. Tobias, *J. Organometallic Chem.*, 1968, **15**, 481.

⁵⁷ (a) E. R. Wiltshire and R. C. Menzies, *J. Chem. Soc.*, 1932, 2734; (b) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 143.

⁵⁸ G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1964, 1295.

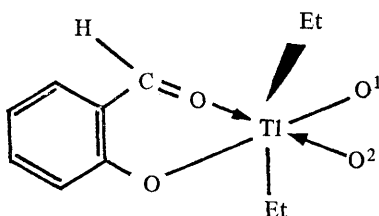
⁵⁹ F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, 1969, **3**, 161.

⁶⁰ F. Bonati, S. Cenini, and R. Ugo, *J. Organometallic Chem.*, 1967, **9**, 395

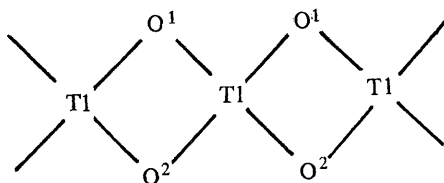
⁶¹ G. H. N. Milbam and M. R. Truter, *J. Chem. Soc. (A)*, 1967, 648.

⁶² A. G. Lee, *J. Chem. Soc. (A)*, 1970, 467.

thallium derivatives, and mixed dialkylthallium cations $R^1R^2Tl^+$ have been prepared and found to be stable towards disproportionation to $R_2^1Tl^+$ and $R_2^2Tl^+$ ⁶³

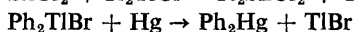
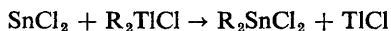


(4)



(5)

The thallium-carbon bonds in dialkylthallium groups can be cleaved by halogens, and diorganothallium derivatives will also act as alkylating and arylating agents. Dialkylthallium chloride reacts with tin(II) halides to form a tin(IV) derivative,⁶⁴ and diphenylthallium bromide reacts with mercury to give diphenylmercury:^{28b}

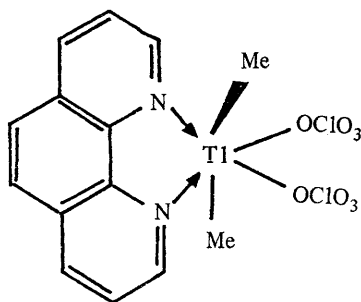


The Lewis acidity of diorganothallium derivatives has received only slight attention. For those dialkylthallium compounds which are associated, complex formation with Lewis bases must be preceded by dissociation of the dimer or polymer, or the latter process must at least occur simultaneously. As thallium compounds are in general weak Lewis acids anyway, it is not surprising that dimeric dimethylthallium derivatives [Me_2TlX , $X = OMe, SMe, SeMe$,¹⁶ or C_6H_5 ⁵¹] do not form stable complexes with trimethylamine. Dimethylthallium perchlorate and pyridine, however, react to give $Me_2TlClO_4 \cdot py$, which, on the basis of i.r. evidence, has been formulated as $[Me_2Tl py]^+ ClO_4^-$, in which the

⁶³ M. Tanaka, H. Kurosawa, and R. Okawara, *Inorg. Nuclear Chem. Letters*, 1967, 3, 565.

⁶⁴ A. N. Nesmeyanov, A. E. Borsiov, and N. V. Novikova, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim Nauk*, 1959, 644.

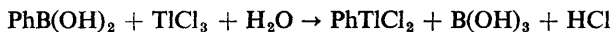
cation has a slightly distorted T-shape, the Me_2Tl portion being not quite linear.⁶⁵ An X-ray crystallographic analysis of dimethylthallium(1,10-phenanthroline) perchlorate has been performed⁶⁶ and the structure has been shown to consist of a distorted pentagonal bipyramid with one equatorial position vacant (6). The two covalent C-Tl bonds and four other bonds definitely do not form the usual octahedral configuration expected for six-co-ordination. There is a 12° departure from linearity for the Me_2Tl group.



(6)

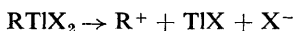
3 Mono-organothallium(III) Derivatives

In contrast to the readily prepared diorganothallium(III) derivatives, much controversy has surrounded mono-organothallium(III) derivatives until very recently. Early claims to have prepared monoalkylthallium dihalides by reaction between dialkylthallium halides and thallium(III) halides must now be discounted. Hot aqueous solutions of Me_2TlCl and TlCl_3 give impure Tl_3TlCl_6 and various organic compounds.⁶⁷ Monophenylthallium dichloride can, however, be readily prepared by reaction of phenylboronic acid and excess thallium(III) chloride.^{29b, 30}



Phenylthallium dibromide can similarly be prepared from thallium(III) bromide, but PhTlI_2 is unknown: addition of KI to either the dichloride or dibromide results in the rapid formation of iodobenzene. Pseudohalogen derivatives such as PhTl(CN)_2 and $\text{PhTl(N}_3)_2$ can be made from PhTlCl_2 and the corresponding alkali-metal salt.

It would seem that mono-organothallium(III) derivatives have a survival problem in solution. Successive ionisation of a mono-organothallium salt RTIX_2 would produce the cation RTl^{2+} , which could then fragment to produce R^+ and thallos salts:

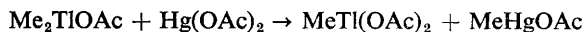


⁶⁵ I. R. Beattie and P. A. Cocking, *J. Chem. Soc.*, 1965, 3860.

⁶⁶ T. L. Blundell and H. M. Powell, *Chem. Comm.*, 1967, 54.

⁶⁷ D. Sarrach, *Z. anorg. Chem.*, 1962, 319, 16.

To stabilise a mono-organothallium(III) derivative, therefore, the charge density on thallium must be reduced. Thus monophenylthallium(III) derivatives will be more stable than monoalkylthallium(III) derivatives, and an appreciably covalent thallium-substituent bond will also serve to stabilise the species. Thus the first monoalkylthallium(III) derivatives to be isolated were diacetates. Methylthallium diacetate was prepared by the exchange reaction:⁶⁸

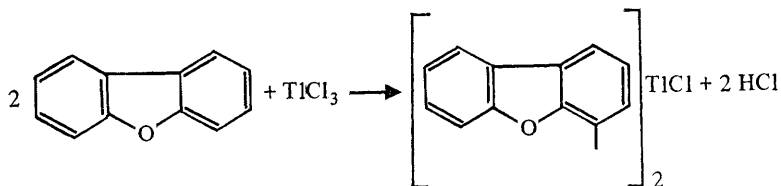


Methylthallium diacetate reacts with Me_3SnCN to form $\text{MeTl}(\text{CN})(\text{O}_2\text{CMe})$: this compound, having a covalently bound CN group, contains a C-Tl-C group and thus shows the stability associated with such a group.⁶⁹ This compound can also be prepared by the reaction of $\text{Tl}(\text{O}_2\text{CMe})_3$ and ammonium methylpentafluorosilicate in aqueous solution in the presence of cyanide ion. In the absence of the cyanide ion, the monomethylthallium(III) species formed reacts further to give a dimethylthallium species.⁷⁰ Methylthallium diacetate reacts with halide ions to produce a thallium(I) halide and methyl halides.⁶⁸ Clearly, if a methylthallium dihalide is first formed in these reactions, then it must be too unstable, under these conditions, to be isolated.

Mono-organothallium(III) derivatives can also be formed by the so called 'thallation' and 'oxythallation' reactions. In the thallation reaction a thallium-group replaces a hydrogen attached to carbon to form a thallium-carbon bond. Thus heating thallium(III) isobutyrate with benzene produces phenylthallium di-isobutyrate in high yield (90%): thallium(III) trifluoroacetate reacts in an exactly analogous manner, but under milder conditions:^{71a, b}



Similarly, thallium(III) isobutyrate reacts with dibenzofuran to give dibenzofuryl thallium di-isobutyrate.⁷² When thallium(III) chloride reacts with dibenzofuran, however, bis(4-dibenzofuryl) thallium chloride is formed.⁷³



⁶⁸ H. Kurosawa and R. Okawara, *J. Organometallic Chem.*, 1967, **10**, 211.

⁶⁹ H. Kurosawa, M. Tanaka, and R. Okawara, *J. Organometallic Chem.*, 1968, **12**, 241.

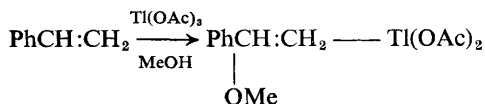
⁷⁰ H. Kurosawa, T. Fukumoto, and R. Okawara, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 473.

⁷¹ (a) V. P. Glushkova and K. A. Kocheshkov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1957, 1186; (b) A. McKillip, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Letters*, 1969, 2423.

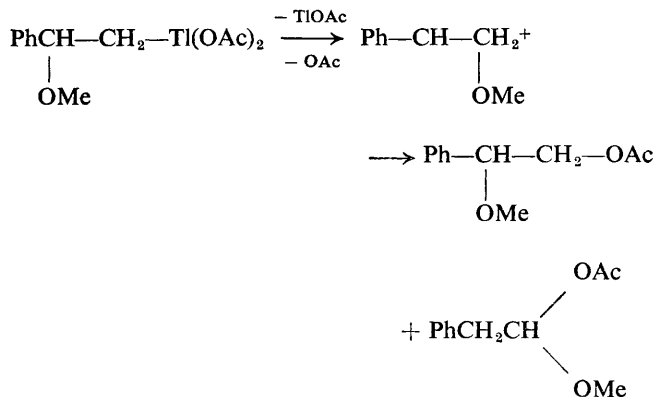
⁷² V. P. Glushkova and K. A. Kocheshkov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1957, 1391.

⁷³ H. Gilman and R. K. Abbott, *J. Amer. Chem. Soc.*, 1943, **65**, 122.

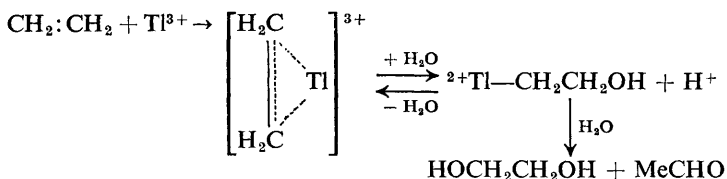
Organothallium derivatives of the type $\text{RTl}(\text{O}_2\text{CMe})_2$ have also been prepared by oxythallation reactions of styrene, *o*-allylphenol, norbornadiene, and norbornene.^{74a, b} For example, with styrene



These organothallium compounds dethallate rapidly in acetic acid to yield both normal and rearranged products, consistent with the intervention of carbonium ion intermediates,⁷⁵ e.g.



Monoalkylthallium(III) species also appear to be involved in the oxidation of olefins by thallium(III) salts. The kinetics of the oxidation of ethylene under aqueous conditions has been studied in detail, and the following mechanism suggested:⁷⁶



A number of other reactions of this type are known and agree with the above scheme: they have been the subject of a recent review.⁷⁷ A derivative similar to the postulated π -intermediate may possibly be formed in the reaction between

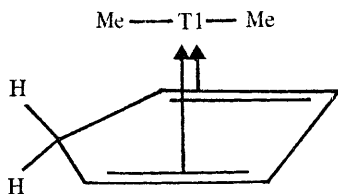
⁷⁴ (a) H. J. Kabbe, *Annalen*, 1962, **656**, 204; (b) K. C. Pandé and S. Winstein, *Tetrahedron Letters*, 1964, 3393.

⁷⁵ R. Criegee, *Angew. Chem.*, 1958, **70**, 173.

⁷⁶ P. H. Henry, *J. Amer. Chem. Soc.*, 1965, **87**, 4423.

⁷⁷ W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61.

$M_2TiC_5H_8$ and hydrogen halides. The highly coloured compounds formed have been postulated to be π -complexes (7) on the basis of n.m.r. evidence.



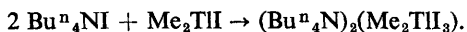
(7)

Many of these monoalkylthallium(III) derivatives appear to be associated in solution. Methylthallium di-isobutyrate is dimeric in chloroform solution and it has been suggested that both chelating and bridging butyrate groups are present.⁶⁸ Methylthallium dioxinate is monomeric in solution, and the thallium is probably five-co-ordinate.⁶⁸

The monoarylthallium dihalides are stronger Lewis acids than the corresponding diarylthallium halides. Pyridine and triphenylphosphine both form 1 : 1 adducts with phenylthallium dihalides, although no adduct is formed with the diphenylthallium halides.^{30, 78}

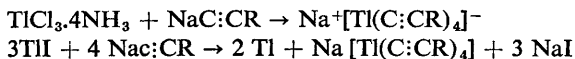
4 Cationic organothallium compounds

Halide anions, being Lewis bases, can act as donors to give complex organothallium salts $M^+[R_2TiX_2]^-$, $M^+_2[R_2TiX_3]^{2-}$, $M^+[RTiX_3]^-$, and $M^+_2[RTiX_4]^{2-}$.^{79a, b} These derivatives can be prepared by direct union of the components, thus:



In acetone solvent $[Me_2TlI_3]^{2-}$ ions are present, but n.m.r. spectra of solutions in pyridine suggest that disproportionation to the starting materials has occurred.

A preliminary report has appeared of the preparation of the $[TlMe_4]^-$ ion⁸⁰ and cationic species containing the $Tl(C:CPh)_4^-$ ion have also been prepared.⁵²



5 Vinyl and Acetylenic Derivatives

Trivinylthallium itself has not yet been reported; there is no reaction between

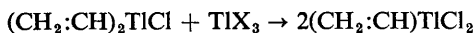
⁷⁸ J. M. Davidson and G. Dyer, *J. Chem. Soc. (A)*, 1968, 1616.

⁷⁹ (a) G. Faraglia, L. R. Fiorani, B. L. Pepe, and R. Barbieri, *J. Organometallic Chem.*, 1967, 10, 363; (b) G. Faraglia, L. R. Fiorani, B. L. Pepe, and R. Barbieri, *Inorg. Nuclear Chem. Letters*, 1966, 2, 277.

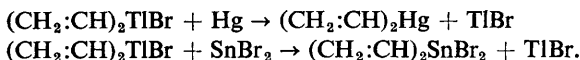
⁸⁰ C. A. Wilkie and J. P. Oliver, quoted in 'Organometallic Compounds' vol. 1. G. E. Coates and K. Wade, Methuen, 1967, p. 373.

divinylthallium chloride and vinyl-lithium. Divinylthallium halides can be prepared by treatment of thallium(III) halides either with a vinyl Grignard reagent or with divinylmercury.⁸¹ The reaction of di-1-alkenylmercurials and thallium(III) halides in ether has also been used to prepare di-*cis* and di-*trans*-propenylthallium bromide in high yield.^{82a,b} Cleavage of tetravinyltin by thallium(III) chloride gave a mixture of divinylthallium chloride and vinylthallium dichloride.⁸³

Redistribution of vinyl groups between divinylthallium halides and thallium(III) halides in aqueous solution gave vinylthallium dibromide and dichloride.⁸¹



The reductive cleavage of divinyl- and di-1-alkenyl-thallium halides by metallic mercury (at 40°) and by tin(II) bromide (at 200°) have been reported:

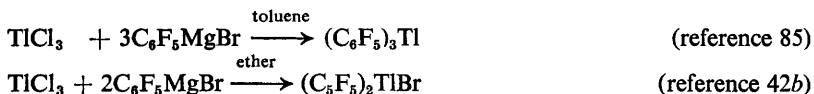


The divinyl derivatives are probably stronger Lewis acids than the corresponding dialkylthallium derivatives. Thus $(\text{ClCH}:\text{CH})_2\text{TlCl}$ forms a stable 1 : 1 adduct with pyridine and piperidine.⁸⁴

The only acetylenic thallium derivatives reported are $\text{Me}_2\text{TlC}:\text{CR}$ and $\text{Me}_2\text{TlC}:\text{CTiMe}_2$, and the salts of the $[\text{Tl}(\text{C}:\text{CR})_4]^-$ ion, which have already been discussed.

6 Pentafluorophenyl Derivatives

Pentafluorophenyl derivatives of thallium can be prepared from the Grignard reagent in an analogous manner to that employed for the alkyl derivatives:



Reaction between $(\text{C}_6\text{F}_5)_2\text{TlBr}$ and silver or sodium salts allows the preparation of a variety of bis(pentafluorophenyl)thallium derivatives.^{42b,86}

Because of the greater 'electronegativity' of the pentafluorophenyl group as compared to those of the alkyl groups, pentafluorophenyl derivatives of thallium

⁸¹ A. N. Nesmeyanov, A. E. Borisov, I. S. Savel'eva, and E. I. Golubeva, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1958, 1490.

⁸² (a) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1959, 1216; (b) A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova, and E. I. Fedin, *J. Organometallic Chem.*, 1968, **15**, 279.

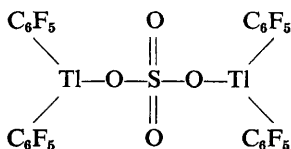
⁸³ A. E. Borisov and N. V. Novikova, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1959, 1670.

⁸⁴ R. Kh. Freidlina, A. K. Kochetkov, and A. N. Nesmeyanov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1948, 445.

⁸⁵ J. L. W. Pohlmann and F. E. Brinckmann, *Z. Naturforsch.*, 1965, **20b**, 5.

⁸⁶ G. B. Deacon, *Austral J. Chem.*, 1967, **20**, 459.

would be expected to be stronger Lewis acids than the corresponding alkyl derivatives. This is reflected in dimerisation and adduct formation. Tris(pentafluorophenyl)thallium is monomeric in benzene solution. It does however form a 1 : 1 adduct with ether, which is stable at room temperature, although it is completely dissociated at 80°. ⁸⁵ Both (C₆F₅)₂TlCl and (C₆F₅)₂TlBr are dimeric in benzene, presumably with bridging halogen atoms. ^{42b,87} Bis(pentafluorophenyl)thallium sulphate is thought to have the structure:



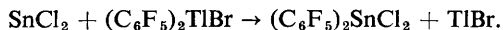
although dimethylthallium sulphate seems (on the basis of i.r. evidence) to be largely ionic, ^{42b} 2[Me₂Tl]⁺ SO₄²⁻.

A series of 1 : 1 complexes of (C₆F₅)₂TlCl and (C₆F₅)₂TlBr with Ph₃PO, Ph₃AsO, Ph₃P, and Ph₃As have been prepared. ^{88a, b} They are monomeric in benzene solution, and presumably contain four-co-ordinate thallium. Bis(pentafluorophenyl)thallium bromide dissolves in pyridine, and the complex (C₆F₅)₂Tl py₂Br can be isolated. The five-co-ordinate complexes (C₆F₅)₂L₂TlNO₃ (L = Ph₃PO or Ph₃AsO) dissociate extensively in solution to (C₆F₅)₂TlNO₃ and L. ^{88a}

Cationic complexes containing four-co-ordinate thallium, [Ph₄P⁺ or Et₄N⁺] [(C₆F₅)₂TlX₂]⁻ (X = Cl, or Br), can readily be prepared, ^{42b} although the corresponding iodide [(C₆F₅)₂TlI₂]⁻ could not be formed. ⁸⁹ Furthermore, (C₆F₅)₂TlI is less stable towards decomposition to thallium(I) halide than are the other bis(pentafluorophenyl) compounds. ⁸⁹

Presumably as a result of the 'electronegativity' of the pentafluorophenyl group, exchange will occur with other metal phenyl derivatives. Thus (C₆F₅)₂TlBr reacts with both Ph₂Hg and NaBPh₄ to produce Ph₂TlBr. ^{42b} There is no exchange of organic groups between dimethylthallium halides and NaBPh₄, and indeed the compound Me₂TlBPh₄ can be isolated.

As with other organothallium derivatives, (C₆F₅)₂TlBr will react with a variety of metal halides to give thallium(I) bromide and the pentafluorophenyl derivative of an oxidation state which is two higher than that of the metal in the original compound. ⁹⁰ Thus with tin(II) chloride:



⁸⁷ G. B. Deacon, J. H. S. Green, and W. Kynaston, *J. Chem. Soc. (A)*, 1967, 158.

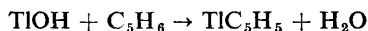
⁸⁸ (a) G. B. Deacon and R. S. Nyholm, *J. Chem. Soc.*, 1965, 6107; (b) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 1969, 25A, 355.

⁸⁹ G. B. Deacon and J. C. Parrott, *J. Organometallic Chem.*, 1968, 15, 11.

⁹⁰ R. S. Nyholm and P. Royo, *Chem. Comm.*, 1969, 421.

7 Organothallium(I) Derivatives

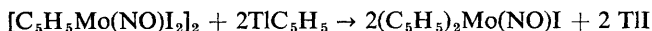
A. Cyclopentadienylthallium(I).—Cyclopentadienylthallium(I) is precipitated when aqueous thallium(I) hydroxide is shaken with cyclopentadiene.⁹¹



The methyl and higher-alkyl cyclopentadienyls, hydropentalenide, and isocyclopentadienide derivatives can similarly be prepared from thallium(I) hydroxide, but unlike TIC_5H_5 these products are air sensitive.^{92a, b}

The i.r. spectrum of TIC_5H_5 in the vapour phase suggests a highly symmetric molecule,⁹¹ and the microwave spectrum has been interpreted in terms of a symmetric-top model with a planar C_5H_5 ring, the distance from the thallium to the centre of the ring being 2.4 Å.⁹³ This relatively large distance suggests that the compound has considerable ionic character. In the solid state TIC_5H_5 consists of an infinite lattice containing zig-zag chains of $-\text{TI}-\text{C}_5\text{H}_5-\text{TI}-$,⁹⁴ and is thus quite similar to the low-temperature form of thallium(I) iodide.⁹⁵ The standard free energy of formation of TIC_5H_5 has been measured as $\Delta G_f^\circ(298) = 42.3 \pm 0.5$ kcal mol⁻¹.⁹⁶ The unexpected stability of cyclopentadienylthallium toward water is merely a reflection of the low affinity of thallium for oxygen and the solubility of TIOH in water.

Cyclopentadienylthallium(I) has recently been finding favour as a very mild reagent for the synthesis of π -cyclopentadienyl-transition-metal derivatives.⁹⁷ Thus:



B. Other Organothallium(I) Derivatives.—Although monoalkyl- and monoaryl-thallium(I) derivatives have been postulated as reaction intermediates, they have never been isolated. The reaction of thallium(I) iodide and methyl-lithium in the presence of methyl iodide, to form trimethylthallium, has been postulated to proceed via methylthallium(I). The reaction of thallium(I) chloride with phenyl-lithium gives triphenylthallium and thallium metal even at -70° .¹³ With ethylmagnesium bromide, thallium(I) chloride produces ethane + ethylene + thallium, or alternatively diethylthallium bromide, depending on the conditions employed.^{98a, b, c} Reaction of aryl- and s-alkyl-magnesium bromides with thallium(I) bromide produces biphenyls and dialkyls respectively. With

⁹¹ F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.

⁹² (a) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86; (b) T. J. Katz and J. J. Mrowca, *J. Amer. Chem. Soc.*, 1967, **89**, 1105.

⁹³ J. K. Taylor, A. P. Cox, and J. Sheridan, *Nature*, 1959, **183**, 1182.

⁹⁴ E. Frasson, E. Menegus, and C. Panattoni, *Nature*, 1963, **199**, 1087.

⁹⁵ G. Wyckhoff, 'Crystal Structures' vol. 1, 2nd edn., 1965.

⁹⁶ H. Hull and A. G. Turnbull, *Inorg. Chem.*, 1967, **6**, 2020.

⁹⁷ R. B. King, *Inorg. Chem.*, 1968, **7**, 90.

⁹⁸ (a) R. C. Menzies and I. S. Cope, *J. Chem. Soc.*, 1932, 2862; (b) H. Gilman, R. G. Jones, and L. A. Woods, *J. Amer. Chem. Soc.*, 1954, **76**, 3615; (c) A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Organometallic Chem.*, 1968, **15**, 500.

ortho-substituted aryl Grignard reagents, however, the dialkylthallium bromide is formed rather than the coupled product.⁹⁹

When triphenyl-thallium is heated above its melting point, or when refluxed in xylene, decomposition occurs to give metallic thallium and biphenyl.¹⁰⁰ When carbon dioxide is passed into a boiling solution of Ph₃Tl in xylene, benzoic acid and biphenyl are formed in equivalent amounts. It has been suggested that phenylthallium(i) is first formed, and then immediately carbonated:



No reaction occurred with carbon dioxide at room temperature, and no biphenyl was formed when diphenylthallium benzoate (a possible alternative intermediate) was refluxed with carbon dioxide.¹³ Phenylthallium(i) has also been postulated as an intermediate in the reaction between Ph₃Tl and benzophenone or benzonitrile.

Electro-reduction of both dialkyl- and diaryl-thallium cations at the dropping mercury electrode gives bivalent and monovalent organothallium species, but these undergo metallation reactions to give diorganomercury compounds and thallium amalgam.^{101a, b}

The failure to isolate monoalkyl- and monoaryl-thallium(i) species is not so surprising. The stability of TIC₅H₅ is clearly associated with the stability of the cyclopentadienyl anion, and TIC₅H₅ is largely ionic. An alkyl derivative of thallium(i), on the other hand, would be expected to have a largely covalent Tl-C bond, because of the lower stability of the alkyl anion. Covalent thallium(i) compounds, however, are always stabilised by use of the empty *p* orbitals on thallium for intermolecular bonding (or conceivably for intramolecular bonding). Thus the thallium(i) alkoxides are tetrameric with bridging alkoxide groups. It has already been seen that the methyl group has little ability for bridging thallium atoms in thallium(iii) derivatives, and it is reasonable to postulate that the same will be true for thallium(i) derivatives. If then the thallium(i) alkyls are going to be unstable, three modes of decomposition must be considered: (i) polymerisation to a thallium-thallium metal-bonded polymer, (RTl)_x, (ii) decomposition to thallium metal and trialkylthallium, and (iii) decomposition to thallium metal and decomposition products of the alkyl group. The first possibility is ruled out by the expected weakness of the Tl-Tl bond (although one compound containing such a bond, K[Tl₂Me₆], has been the subject of a preliminary report),⁸³ leaving the second and third possibilities, both of which have been observed.

8 Concluding Remarks

In this Review I have tried to put together some of the scattered observations

⁹⁹ A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 2423.

¹⁰⁰ H. Gilman and I. Haiduc, *J. Amer. Chem. Soc.*, 1968, **90**, 5912.

¹⁰¹ (a) G. Costa, *Ann. Chim. (Italy)*, 1950, **40**, 559; (b) J. S. DiGregorio and M. D. Morris, *Analyt. Chem.*, 1968, **40**, 1286.

that have been made on organothallium chemistry, to see whether any coherent picture can be made to emerge. It is obvious that, even allowing for the recent increase in publications, a great deal of structural work must yet be done before a completely satisfying description of organothallium chemistry can be achieved. Further, at the present time the only organothallium derivatives to have been studied in any detail are the methyl and pentafluorophenyl. Studies of a wider range of organothallium compounds would be very worthwhile.

Although a firm foundation for a study of organothallium chemistry has by now been laid, much is still unaccountable. As Williams James said, 'round about the accredited and orderly facts of every science there ever floats a sort of dust-cloud of exceptional observations', and in organothallium chemistry the light is only just beginning to break through the clouds.