CHAPTER II

PRELIMINARY WORKS

The most stable diorganothallium derivatives are synthesized from many other organometallic compounds ie.organolithium, organoboron, organomercury, organomagnesium etc.,[1] and the most versatile route is made by reactions of triorganothallium compounds.[8] However, diphenylthallium bromide can be conveniently prepared via the Grignard reaction, although yields are often poor because of oxidation of the Grignard reagent by the thallium (III) halide.

$$TlX_3 + 2RMgX \longrightarrow R_2TlX + 2MgX_2$$

The solubilities of the lower dialkylthallium compounds are very similar to those of the corresponding thallium (I) salts, and since a mixture of R_2TlX and TlX is almost invariably formed by the Grignard method, separation requires the use of solvents such as pyridine, concentrated aqueous ammonia of liquid ammonia, in which the organic derivatives are more soluble. The studies on the structure and some properties of diorganothallium derivatives are summerized below

Diorganothallium Cations.

Most alkylthallium derivatives give highly conducting

solution in water. Conductance measurement indicates a high degree of dissociation for the hydroxide Me_2TlOH[9] with the formation of $[Me_2Tl(H_2O)_x]^+$ and OH^- ion. In 0.2 $mol l^{-1}$ aqueous solution, about 10 % of the thallium is present as a dimer $[Me_2TlOH_2]^+$, 36 % as Me_2TlOH and 54 % as $[Me_2Tl(H_2O)_x]^+$.[10]

The NMR spectra of aqueous solutions of a wide variety of dimethylthallium derivatives suggest that the same thallium-containing species is present in all solution,[11] presumably $[Me_2Tl(H_2O)_x]^+$. Water has a high dielectric constant ($\Sigma = 78.2$) and is a good electron donor: it therefore is an almost ideal solvent for the production of solutions of organometallic compounds.[12] Dimethylformamide ($\Sigma = 36.7$) is less ideal solvent than water, and conductivity measurement suggests that Me_2TlI imcompletely dissociate in this solvent.[13]

The Raman spectra of aqueous solutions of dimethylthallium perchlorate and nitrate show that the C-Tl-C skeleton in the dimethylthallium $[Me_2Tl(H_2O)_x]^+$ ion is linear.[14, 15] The dimethylthallium ion is only a very weak aquo-acid, indicating that the bonds to the water molecules in the first coordination sphere are very weak.[9, 10, 16] Supporting evidence for weak polar bonds to the water molecules comes from Raman spectra of aqueous solution of the dimethylthallium ion, which show no lines attributable to stretching of Tl-O bonds, even in an as high as 2.3 $mol l^{-1}$ of Me_2TlOH solution.[14]

No information is yet available regarding the number of solvent molecules coordinated to the thallium in the $[Me_2Tl(H_2O)_x]^+$ ion,

but it seems probable that there will be four, producing an overall octahedral coordination for the thallium.

The weakly polarizing effect of the weak acid $\left[Me_2Tl\right]^+$ is indicated not only by its slight tendency to be hydrolyzed but also by the small stability constants for complex formation with β - diketonates in aqueous solution.[17] There was no indication of the formation of any six-coordinate species of the type $R_2Tl(RCOCHCOR')_2$. For the given ligand, the order of stability of the organothallium ion is $\left[Me_2Tl\right]^+ < \left[Et_2Tl\right]^+ < \left[n\text{-}Pr_2Tl\right]^+ < \left[(4\text{-}CH_3C_6H_4)PhTl\right]^+ < \left[Ph_2Tl\right]^+$. This order cannot be rationalized purely in terms of inductive effect of the organic group. The inductive effect will satisfactorily explain the increased stability of $\left[Ph_2Tl\right]^+$ over $\left[(4CH_3C_6H_4)PhTl\right]^+$, but it would predict the reverse order for the alkyl group. Steric effect would also presumably cause a decrease in formation constant in going from $\left[Me_2Tl\right]^+$ to $\left[n\text{-}Pr_2Tl\right]^+$ ion, and so displacement of water by the ligand will become easier as the hydrocarbon chain length increases.[17]

Diorganothallium Halides.

For the diorganothallium ion in aqueous solution, there is an impression that the two distinct types of bond from the central thallium to the ligands exist i.e, the kinetically inert, relatively non polar bonds to carbon in the organic groups, and the kinetically labile and highly polar bonds to the solvent molecules. This picture also seems to be correct for the dialkyl-

thallium (III) halides. The structure of the dimethylthallium

iodide consists of layers in which a linear Me_2Tl group is

surrounded by four iodine atoms, and each iodine is surrounded by

four Me_2Tl groups.[18] It is a doubtful point whether the structure

should be described in term of bridging iodine atoms and thallium-

iodine bonds with a reasonable degree of covalency. The latter

picture is probably nearer the truth. Thus, although the

structures of the dialkylthallium chloride in the vapor phase are

unknown, the mass spectrum of dimethylthallium chloride shows the

presence of dimeric molecules in the vapor phase: for the

corresponding bromide and iodide, the parent ions are observed, but

no dimeric species.[19] Because of the greater "electronegativity"

of the C_6F_5-group, as compared to those of the alkyl groups,

pentafluorophenyl derivatives of thallium would be expected to be

stronger Lewis acids than the coresponding alkyl derivatives. This

is reflected in dimerization. Both bis (pentafluorophenyl)

thallium chloride and bromide are dimeric in benzene solution and

(probably) in the solid, with bridging halogen atoms.[20, 21, 22]

A structure containing tetrahedrally co-ordinated thallium

was suggested:

Little is known about the structures of diorganothallium fluorides, which, by comparison with other organometallic fluorides, might well be expected to adopt fluorine-bridged structures. Such structure would be consistent with the observed solubilities of dimethylthallium- and diethylthallium fluorides in methanol, in which solvent the corresponding chlorides are relatively insoluble.[23] The infrared spectrum of dimethylthallium fluoride shows both a symmetric and antisymmetric Tl-C stretch, so that, unlike the other dimethylthallium halides, the C-Tl-C skeleton must be non-linear.[24]

Co-ordination Compounds of Diorganothallium Derivatives.

The Lewis acidity of diorganothallium derivatives have not yet recieved a great deal of attention. For those dialkyl-thallium (III) compounds that are associated, complex formation with Lewis bases must be preceded by dissociation of the dimer or polymer, or the latter process must at least occurs 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,[25] C_5H_5[26]) do not form stable complexes with pyridine or ethylenediamine.[27] Diethylthallium perchlorate and pyridine, however, react to give $Me_2Tl py ClO_4$. Based on infrared evidence this compound has been formulated as $[Me_2Tl py]^+[ClO_4]^-$, in which the cation has a slightly distorted T-shape, the Me_2Tl portion being not quite linear.[28] An X-ray crystallographic analysis

of dimethylthallium (1, 10-phenanthroline) perchlorate has been performed[29] and the structure has been shown to consist of a distorted pentagonal bipyramid with one equatorial position vacant.
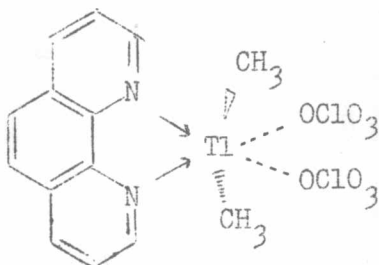

The two covalent C-Tl bonds and the four other bonds definitely do not form the usual octahedral configuration expected for the six- coordination. There is a 12° departure from linearity for the Me_2Tl group.

The diphenyl- and divinylthallium halides are evidently stronger Lewis acid than the corresponding dialkylthallium halides, and a variety 1:1 complexes with oxygen and nitrogen donor ligands can be prepared. The acidities of various thallium cation toward the chloride ion have been studied by electrophoretic methods and found to be Tl (III)>Ph_2Tl (III)>Me_2Tl (III)> Tl(I).[30] A number of derivatives with the halide anion as Lewis base has been isolated.[31] They are prepared by direct union of the components thus:

$$2\ n\text{-Bu}_4NI + Me_2TlI \longrightarrow n\text{-Bu}_4N_2\ Me_2TlI_3$$

In acetone solvent, $Me_2TlI_3{}^{2-}$ ions are present, but NMR spectra
of the solution in pyridine suggest that disproportionation to the
strating material has occurred.[33]

A series of 1:1 complexes of bis-(pentafluorophenyl)
thallium chloride and bromide have been prepared with triphenyl-
phosphine oxide, triphenylarsine oxide, triphenylphosphine and
triphenylarsine.[33] They are monomeric in benzene solution and
presumably contain four-coordinate thallium atom. The five-coor-
dinate complexes $(C_6F_5)_2Tl(L)_2No_3$ (L=R_3PO or R_3AsO) dissociate
extensively in benzene solution to $(C_6F_5)_2TlLNO_3$.
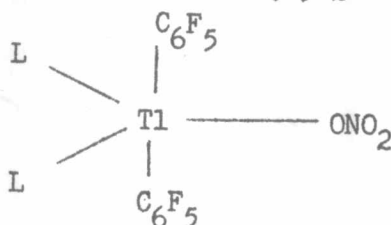
Attempts failed to prepared similar five-coordinate
complexes of the bis-(pentafluorophenyl) thallium halides. The
complex $(C_6F_5)_2Tl(py)_2Br$ can be isolated from pyridine solution,[33]
but with 1, 10-phenanthroline and 2, 2'-bipyridyl, only 1:1 complexes
are formed. All β-diketonates and 8-hydroxyquinolinate of the
bis-(pentafluoropheny) thallium group form 1:1 complexes with
1,10-phenanthroline. Only the derivatives of $MeCOCH_2COMe$,
CF_3COCH_2COMe and $CF_3COCH_2COCF_3$ give such complexes with 2,2'-bipyridyl.
The derivative of $PhCOCH_2COPh$ and 8-hydroxyquinoline give no complexes

with 2, 2' - bipyridyl, while the derivative of $PhCOCH_2COMe$ (bzac)

reacts with excess 2, 2' - bipyridyl to give a compound

$(C_6F_5)_2Tl(bipy)(bzac)_2$. With Ph_3PO and Ph_3AsO, 1:1 complexes are also

generally formed.[34] The 1:1 complexes have low conductances in $CHCl_3$

and monomeric in chloroform and benzene solutions. The infrared

spectra of the solid complexes are consistent with chelated

β-diacetonate groups, and structures were suggested with five- and

six- coordinate thallium as can be seen in $(C_6F_5)_2$ $(Ph_3AsO)Tl \cdot Y$

and $(C_6F_5)_2$ (phen or bipy)$Tl \cdot Y$ respectively.[34]
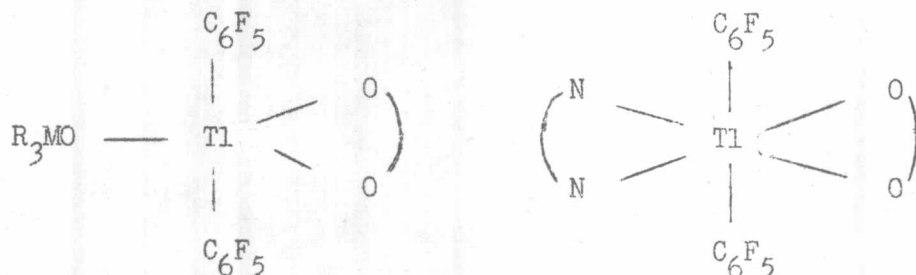
The presence of a bridging 2, 2' - bipyridyl group was suggested in

$(C_6F_5)_2 Tl$ (bipy) $(bzac)_2$.[34]
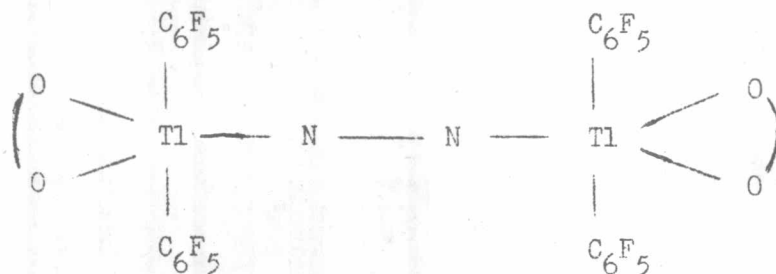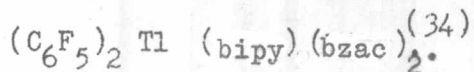
Organomercury Compounds

Studies of crystal structure,[35] electric dipole moments,[36] and spectra[37] of mercuric derivatives have all indicated that two covalencies of mercury atom are oppositely directed a linear configuration. In addition, a number of such substances has been studied by electron diffraction.[38] When the attached atom are heavy, as in mercury (II) iodide, the linear configuration can be approximately established from the patterns, but it has normally been necessary to assume linearity in interpreting these, on account of the reduction in precision caused by the excessive mercury scattering. It was found that the pure rotation spectra of methylmercury chloride and bromide are characterized as the symmetric-top spectra which shows unquestionably that C-Hg-X configuration is strictly linear. It has also been possible to dertermine the C-Hg and Hg-X distances with a good precision and to obtain a value for the effective covalent radius of divalent mercury. The nuclear quadrupole coupling of the halogens obtained from an analysis of the hyperfine structure yields a value for the electronegativity of divalent mercury.

The X-ray investigation of the structure of solid RHgX compounds has been taken[39] as to indicate the expected axial symmetry of the molecule and a C-Hg bond length in a good agreement with the microwave spectra result.[40] From the microwave spectra nuclear quadrupole coupling studies of different isotopic species of CH_3HgX indicate ioni character of 62% for HgCl and 55% for HgBr bonds in these

molecules, and lead to a value of 1.7 to 1.8 for the electronegativity of divalent mercury. The properties of the crystalline solids of RHgX compounds depend on the nature of X, when X is an atom or a group that can form covalent bond to mercury, for example Cl^-, Br^-, I^-, CN^-, SCN^-, or OH^-. The compound is a covalent non-polar substance and is more soluble in organic liquid than in water. When X is ClO_4^-, NO_3^-, the substances are saltlike and presumably quite ionic. The Raman spectra of a concentrated aqueous solution of methylmercuric perchlorate[41] indicates complete dissociation of this salt into perchlorate ion and the cation $[CH_3Hg-OH_2]^+$ in which there is a covalent bond between the mercury and oxygen atoms. The spectra of the nitrate solutions show that in benzene only undissociated molecules $CH_3-Hg-ONO_2$ are present, whereas in water there is an equilibrium between these molecules and the ion $[CH_3Hg-OH_2]^+$ and NO_3^-. The spectra of methylmercuric hydroxide in aqueous solution[14] also showed the presence of undissociated molecule CH_3Hg-OH with covalent bonding between Hg and O atoms. Several methylmercury derivatives of oxyacid in solution were studied and it was shown that these compounds behave as weak electrolytes[41].

The thermochemistry of the mercury compounds were investigated[42]. The heat of reaction of diphenylmercury with hydrogen chloride in organic solutions has been measured at $25^\circ C$. From the heat of reaction, the heat of formation of phenylmercury chloride has been derived as ΔH_f^0 (PhHgCl, cryst.) = -0.55 ± 2 kcal per mole.

Hence it can be concluded that the structures of RHgX and R$_2$Hg compounds have linear bonds, but deviation from linearity has been found in a few cases, and in solution in particular, solvation effect may contribute to this non-linearity.

Co-ordination complexes of diorganomercury derivatives are not presented here due to the non-existence of the publications involving the study of that type of the complexes of mercury.