CHAPTER 1

(General Introduction)

(i) Introduction

(ii) Scope of Work

(iii) References
The organometallic chemistry of the IIIA group of metals gallium, Indium and thallium has not been as extensively studied as that of boron and aluminium, the main reasons being the relative scarcity and the high cost of these elements. However, during the last few years, the organic chemistry of these elements has developed rapidly to a considerable extent and their organometallic compounds have found useful applications in the production of metal carbynols\(^1\), metal cyclopentadienyls\(^2\)-\(^4\), and ultrapure metals\(^5\)-\(^6\). Other important applications of organometallic compounds of the metals are their use as lubricants\(^7\), antiknock reagents\(^8\), and as polymerisation catalysts for olefins\(^9\)-\(^11\). Poisoned food technique has recently been employed to determine the fungicidal activity of these compounds.

Preliminary evaluation of biocidal activity of some of the compounds, against tomato seedlings has indicated that organometallic compounds of these elements are potential fungicides\(^12\). In view of many applications mentioned above, the organometallic compounds of gallium, Indium and thallium have received considerable attention by workers in this field during the recent years and this investigation was undertaken with a view to extend such studies.

The trends in certain physical constants of group IIIA elements which may be helpful for an understanding of the organometallic chemistry of the elements of this group are given in Table-1.

The electronegativity data indicate that its magnitude for the metals, gallium, indium and thallium are not very different from one another. Similarly the value of the first ionisation

[1]
potential of the three metals are close to each other and do not follow a regular decreasing trend, commonly met in other groups of the periodic table.

Since the metals of group IIIA are less electronegative than carbon and other electronegative element such as nitrogen, oxygen, phosphorous, sulphur and halogens with which they are linked, the bonds acquire a polar character and are easily attacked by nucleophilic reagents. The data in Table-1 indicate a general trend of increasing radius with increasing in the atomic number of the elements. With increasing radius the steric shielding by equally large substituents decreases and the bond energy diminishes as a consequence of the increasing inter atomic distance on which depends the relative polarity of the bonds.
<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic Number</th>
<th>Electronic Configuration</th>
<th>Atomic Weight (C=12)</th>
<th>Density</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>Covalent Radius (°A)</th>
<th>I.P. (eV)</th>
<th>Electro negativity (Pauling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>5</td>
<td>(He)2s²2p¹</td>
<td>10.8</td>
<td>2.40</td>
<td>2300</td>
<td>2250</td>
<td>0.80</td>
<td>8.30</td>
<td>2.0</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>(Ne)3s²3p¹</td>
<td>26.9</td>
<td>2.70</td>
<td>659.7</td>
<td>2500</td>
<td>1.25</td>
<td>5.98</td>
<td>1.5</td>
</tr>
<tr>
<td>Ga</td>
<td>31</td>
<td>(Ar)3d¹⁰4s²4p¹</td>
<td>69.7</td>
<td>5.93</td>
<td>29.7</td>
<td>2350</td>
<td>1.25</td>
<td>6.00</td>
<td>1.6</td>
</tr>
<tr>
<td>In</td>
<td>49</td>
<td>(Kr)4d¹⁰5s²5p¹</td>
<td>114.8</td>
<td>7.29</td>
<td>155</td>
<td>2100</td>
<td>1.50</td>
<td>5.79</td>
<td>1.7</td>
</tr>
<tr>
<td>Tl</td>
<td>81</td>
<td>(Xe)4f¹⁴5d¹⁰6s²6p¹</td>
<td>204.3</td>
<td>11.85</td>
<td>449</td>
<td>1390</td>
<td>1.55</td>
<td>6.11</td>
<td>1.8</td>
</tr>
</tbody>
</table>
The increasing atomic radius also decreases the mutual interference among the organic groups in the organometallic compounds, making the central metal atom less shielded and more liable to attack by the reagents.

The melting point of boron is extremely high owing to strong bonding between individual atoms in the solid state. The melting points of the other elements are markedly lower indicating less stronger bonding of atoms in the metallic lattice.

On going down from boron to thallium, the density of the elements increases, whereas the boiling point shows a gradual decreases, Slightly irregular trend exhibited by a few physical contents on possesing from aluminium to thallium may be attributed to the intervention of the d-orbitals between aluminium, gallium and indium, and also the f-orbitals between indium and thallium.
ELECTRONIC CONFIGURATION AND HYBRIDISATION:

An examination of the electronic configuration of these elements shows that they may be sub-divided into two classes one consisting of boron and aluminium with an inert gas Kernel, and the other of gallium indium and thallium possessing pseudoinert gas kernel of completed s, p and d-orbitals.

All the elements of group IIIA have three electrons in their outermost orbit, out of which the s-subshell contains two paired electrons while the p-subshell has one unpaired electron. Thus, in the ground state only one electron is available for bond formation, and gives rise to univalency, the s-electron pair remaining unaffected.

Since energy required to promote an electron from the s-orbital to Py orbital is not very large particularly for gallium and indium, mostly three electron are involved in bonding giving rise to sp² hybridisation and the elements generally show a group valency of three. The compounds therefore, posses a trigonal arrangement with three equivalent bonds around the central metal atom having an angle of 120°.

In case of thallium, however, due to polar screening effect of the intervening d and f-orbitals, a larger amount of energy is required for promotion of an electron from 6s to 6p level: with the result that univalent thallium is more stable than its trivalent oxidation state and a large number of ionic thallous salts are known.

Sidgwick ²⁴ was the first of recognize this tendency with the ascribed to the presence of the inert, s-electron pair.
The tendency to exhibit univalency is far less apparent in case of gallium and indium. A few compounds of disputed structure, apparently containing univalent metals are given below:

\[ \text{Ga}_2\text{O}, \text{Ga}_2\text{S}, \text{GaX}, \text{Ga(GaCl}_4\text{)}, \text{In}_2\text{O} \]
\[ \text{In}_2\text{S}, \text{InX}, \text{In(}\text{InCl}_4\text{)}, \text{In}_3\text{(InCl}_6\text{)} \]

**ROLE OF d-ORBITALS:**

The elements of group IIIA except boron have empty d-orbitals capable of accepting electrons to form additional bonds which results in an increases in the coordination number greater than three. Such complexes are assumed to be formed by the hybridisation of s, p and vacant d-orbitals of the metals. In tetra coordinated compounds one s and three p orbitals are hybridised to give four equivalent sp\(^3\)d and sp\(^3\)d\(^2\) type of hybridisation is assumed to occur respectively.

The type of hybridisation and resulting shape of the molecules with their coordination number are summarised in Table 2:

**TABLE – 2**

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Hybridisation</th>
<th>Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>sp(^2)</td>
<td>Trigonal</td>
<td>R(_3)M</td>
</tr>
<tr>
<td>4</td>
<td>sp(^3)</td>
<td>Tetrahedral</td>
<td>R(_3)M.PY</td>
</tr>
<tr>
<td>5</td>
<td>sp(^3)d</td>
<td>Trigonal bipyramidal</td>
<td>R(_2)MX (Phen)</td>
</tr>
<tr>
<td>6</td>
<td>sp(^3)d(^2)</td>
<td>Octahedral</td>
<td>(C(_6)F(_5))(_2) (Phen), Tl (acac)(_3), K(_3)(In Cl(_6)) Ga (acac)(_3)</td>
</tr>
</tbody>
</table>

(M = Ga, In or Tl, Py = Pyridine
Phen = 1, 10 Phenanthroline and
Acac = acetylacetonate)
ACCEPTIVE $d\sigma$ AND $d\pi$ BONDING:

The ability of aluminium, gallium, indium and thallium to accept electrons in their empty $d$-orbitals and thus establish additional bonds is of fundamental importance in their chemistry.

These bond relations may be of two types:

1. $d\sigma$ - BONDING:

The elements of the group IIIA except boron may enter into bond relations of $\sigma$ symmetry with approaching electron donors by accepting electrons in an empty $d$-orbital. If the donor atom belongs to a different molecules adducts of the type $A \leftarrow D$ ($A$ = acceptor, $D$ = donor) are formed. In the formation of $\sigma$ bonds the coordination number of the acceptor is increased.

2. $d\pi$— BONDING:

Bonds of $\pi$ — character can be formed by suitable overlap of $d$-orbitals of group IIIA elements and $p$-orbitals of the adjacent atom of the donor molecules, which contain free electron pairs. This is called $d\pi$ - $P\pi$ bonding which gives an overall double bond character. As atomic number of the metal ion increases, lateral overlap of orbitals is less effective and tendency towards $d\pi$ — $P\pi$ bonding decreases.

Another possibility, in which electrons from filled $d$-orbitals of group IIIA elements may be donated to the vacant $d$ -orbitals of the ligand atom, is sometimes called back bonding. This generally occurs between elements having filled $d$-orbitals (gallium, indium and thallium) and second row elements of group V, VI and VII which possess empty $d$-orbitals.

ORGANOMETALLIC COMPOUNDS:

The organometallic compound of these metals generally fall into three types denoted by the general formulae $R_3M$, $R_2 MX$ and $RMX_2$ ($R$-alkyl or aryl group, $X$ = an electronegative group $M$ = Ga, In or Tl).
Among the alkyl groups, a good number of methyl derivatives have been synthesised.

The main important feature of the Organometallic chemistry of this group of elements, which have attracted the attention of numerous workers in this field could be outlined as follows:

a) The bulk of the investigation deal with the search for typical methods of preparation capable of giving organometallics of the formulae $R_3M$, $R_2MX$ and $RMX_2$ in good yield.

b) A study of characteristic reactions of these compounds involving cleavage of the organic groups, displacement of the substituent negative groups, decomposition reaction and certain insertion reactions, particularly those of sulphur dioxide, have been made. The insertion reactions have greatly helped in the characterisation of the parent compounds and in the synthesis of new derivatives varying structure.

c) The most important feature of the organometallic chemistry of this group has been a study of the molecular addition compounds of the organometal moieties with coordination numbers greater than three. The unidentate bases have generally yielded tetrahedral adducts through $sp^3$ hybridisation containing four coordinated metal atoms. On the other hand bidentate bases yield comparatively less commonly met penta coordinated adducts by utilising one of the vacant d-orbitals of the metal atom.

The $sp^3d$ hybridisation so formed leads to trigonal bipyramidal geometry. The second d-orbital of the metals are much less commonly used for a type coordination and only a few hexa coordinated complexes of $sp^3d^2$ hybridisation have been reported. They are expected to be octahedral but the actual shape seldom agrees with ibis geometry due to considerable distortion.
A few physicochemical studies such as potentiometric, conductometric and spectrophotometric have also been frequently employed to determine the nature of the complex species in solution.

Due to poor reactivity of dialkyl and diaryl thallium (III) derivatives, Deacon and Nyhdlm\textsuperscript{13} have synthesised penta fluorophenyl derivatives of thallium by the Grignard reagent in an analogous manner to that employed for the alkyl derivatives. Because of the greater electronegativity of the pentafluorophenyl group as compared to those of the alkyl groups, penta fluorophenyl, derivatives of thallium are stronger lewis acids than the corresponding alkyl derivatives.

This is reflected in dimerisation and adduct formation.

A series of 1:1 complexes of $(C_6F_5)_2TlCl$ and $(C_6H_5)TlBr$ with $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$, $(C_6H_5)_3P$, $(C_6H_5)_3As 1,10-$ Phen 2,2-bipy have been prepared\textsuperscript{14}.

Less commonly met hexa coordinated hetero chelates of bis penta fluorophenyl thallium (III) of the formulae $(C_6H_5)_2$ PhenTl.acac, $(C_6F_5)_2$ bipy. Tl, acac, and $(C_6F_5)_2$ PhenTl.Bzac (acac-acetyl acetonate), bzac-benzoylacetonate) have also been synthesised by the above workers\textsuperscript{13,14}. These are monomeric in benzene and chloroform and possess the following structure (Fig. 1).

\begin{center}
\includegraphics[width=0.3\textwidth]{fig1.png}
\end{center}

(Fig. 1)
A few complexes of indium containing penta fluoro-phenyl groups have also been reported\textsuperscript{15}. Typical complexes are formulat\textsuperscript{es} below:

\[(\text{C}_6\text{F}_5)_2\text{In. O-As(}\text{C}_6\text{F}_5)_3\text{]}, [(\text{C}_6\text{F}_5)_3\text{In}_2]\text{bipy.}\]

Corresponding complexes with gallium, metal have not yet been reported and there is ample scope for further studies in this field.

d) Attention has largely been centered around the study of the structure of such complexes. Several physicochemical measurements such as dipole moment, X-ray diffraction, Nuclear magnetic resonance, Raman and Infrared spectroscopy have been largely used to establish the structure these compounds.

e) The practical utility of these organometallic has been determined and their use mainly as polymerisation, catalyst, antiknock reagents and lubricants has been suggested\textsuperscript{7-11}. T.N. Srivastava et al. have been done a considerable amount of work on the fungicidal and bactericidal activity of these compound and derivatives of the formula \(R_2MX\) have been found to be extraordinarily active against variety of fungi and bacteria\textsuperscript{12}.

Further work in progress on the activity of several newly synthesised thiocarbamates of organometallic moieties of this group may lead to the isolation of certain products of superbiocidal activity possessing enormous practical utility\textsuperscript{16}.

The organometallic chemistry of these elements has been the subject of two reviews published in 1970\textsuperscript{17,18} and two brief, general reviews by coates and wade\textsuperscript{19} and Yasuda and Okawara\textsuperscript{20}.

An exhaustive survey of preparative work has been presented by Nesmeyanov and Kocheshkov\textsuperscript{21} and Kitching has described a series of thallium and oxythallium reaction\textsuperscript{22}.

Subsequent developments can be traced through annual survey on the three metals\textsuperscript{23}.  

[10]
(I) MONOORGANOThALLIUM COMPOUNDS:

**Preparation and properties:**

Aryl- and vinyl-thallium dichlorides are usually prepared by the reaction of aryl- and vinyl-boronic acids with excess TlCl₃ in aqueous solution\(^{25}\). Aryl and vinyl derivatives of mercury(II) and tin(IV) also transfer the organic group to TlY₃ (Y = halogen, O₂CR) to give the corresponding monoorganothallium compounds. Various arylthallium dicarboxylates can be obtained very conveniently through thallation of aromatic hydrocarbons with Tl(O₂CCF₃)\(^{26}\).

\[
\text{RB(OH)}₂ + \text{TlCl}_3 \rightleftharpoons \text{RTlCl}_2 + \text{B(OH)}₃ + \text{HCl}
\]

The monoalkyls are best prepared from the dialkylide derivatives through following equations:

\[
\text{R}_2\text{TlOAc} + \text{Hg (OAc)}₂ \rightleftharpoons \text{RTl (OAc)}₂ + \text{RHgOAc}
\]

(R = Me, Ph)

\[
(\text{Me}_₂\text{YCH}_₂)₂\text{TlCl} + \text{Br}_₂ \rightleftharpoons \text{Me}_₃\text{YCH}_₂\text{TlClBr} + \text{Me}_₃\text{YCH}_₂\text{Br}
\]

\(Y = \text{C}, \text{Si}\)

Another method of preparing methyl and ethylthallium compounds of the type RTl(CN)(OAc) (R = Me, Et) is the reaction of Tl(OAc)₃ with the alkyltin compounds or \([(\text{NH}_4)_2(\text{MeSiF}_₅)]\) in the presence of cyanide\(^{25}\). In the absence of cyanide ion the monoalkyl species react further with the alkyltin compounds to give dialkylthallium compounds. The pyridiniumethyldithallium chloride is obtained by the reaction of TlCl₃ with the organochromium(III) ion in aqueous solution\(^{25}\).

\[
\text{[HN}⁺-\text{N} \text{-CH₂Cr (H₂O)}₃]^{2⁺} + \text{TlCl}_3 \rightarrow \\
\text{HN}⁺-\text{N} \text{-CH₂TlCl}_2 + [\text{Cr(H₂O)}₃]^{3⁺}
\]
Another unique route to the monoalkyl derivatives is Oxythallation of alkenes and alkynes. Unlike the corresponding organomercury counterparts, the number of isolable oxythallation products is rather limited. Typical examples include adducts from Tl(OAc)$_3$ and bicyclic alkenes e.g., fig.2 and fig.3$^{25,27}$ or alkoxythallates of terminal alkenes or allenes fig. 4 and fig.5$^{25,28}$. Some alkynes also give stable adducts, such as fig.6-fimg.$^{29,30}$. However, a different type of reaction between terminal alkynes and Tl(OAc)$_3$ to give a formal diorganothallium compound fig. 9$^{31}$.

The stereochemistry of the oxythallation of the bicyclic alkenes is cis-exo for figs. 2., and trans for fig.3, as has been revealed by proton NMR spectroscopy$^{27,32}$. A proton NMR spectral study has also indicated the confirmation of fig.4 obtained from trans-PhCH=CHD as fig. 10, thus confirming the trans stereochemistry in oxythallation of styrene$^{33}$.
\[ \text{R} = \text{Ph, Me, Bu}^n, \text{n-C}_6\text{H}_{13} \]

**Fig. (9)**

\[ \text{R} = \text{Ph, Me, Bu}^n, \text{n-C}_6\text{H}_{13} \]

**Fig (10)**
TABLE- 3

LIST OF REPRESENTATIVE MONOORGANOTHALLIUM COMPOUNDS

TOGETHER WITH METHODS OF PREPARATION.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M.P. (°C)</th>
<th>Prep (^a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(_3)CCH(_2)TlBr</td>
<td>-</td>
<td>A</td>
<td>24</td>
</tr>
<tr>
<td>ClHN-CH(_2)TlCl(_2)</td>
<td>98-100 dec.</td>
<td>B</td>
<td>35</td>
</tr>
<tr>
<td>PhCh(OMe) CH(_2)TlCl(_2)</td>
<td>146-147 dec.</td>
<td>C(^b)</td>
<td>36</td>
</tr>
<tr>
<td>CH(_2) = CHTlCl(_2)</td>
<td>170 dec.</td>
<td>D</td>
<td>37</td>
</tr>
<tr>
<td>PhTlCl(_2)</td>
<td>235 dec.</td>
<td>D</td>
<td>25</td>
</tr>
<tr>
<td>PhTlBr(_2)</td>
<td>149</td>
<td>D</td>
<td>25</td>
</tr>
<tr>
<td>MeTl (O(_2)CMe(_2))</td>
<td>102-103 dec.</td>
<td>A</td>
<td>38</td>
</tr>
<tr>
<td>MeTl (CN) O(_2)CMe</td>
<td>150-160</td>
<td>E</td>
<td>39</td>
</tr>
<tr>
<td>Me(_3)SiCH(_2)Tl(O(_2)CPri(_2))</td>
<td>144</td>
<td>A</td>
<td>40</td>
</tr>
<tr>
<td>PhTl(O(_2)CCF(_3))(_2)</td>
<td>184-189</td>
<td>F</td>
<td>41</td>
</tr>
<tr>
<td>PhTl(O(_2)CMe) (ClO(_4))</td>
<td>-</td>
<td>F</td>
<td>42</td>
</tr>
<tr>
<td>TlO(_2)(CCF(_2))</td>
<td>194-196</td>
<td>F</td>
<td>41</td>
</tr>
<tr>
<td>PhCH(OMe)CH(_2)Tl(O(_2)CMe(_2))</td>
<td>27-128 dec.</td>
<td>C</td>
<td>43</td>
</tr>
<tr>
<td>Ph(O(_2)CMe)C=C(Me)Tl(O(_2)CMe(_2))</td>
<td>169-171</td>
<td>C</td>
<td>45</td>
</tr>
</tbody>
</table>

\(a\) = Method of preparation

A = dealkylation of R\(_2\)TlX

B = From the organochromium(III) compound

C = Oxythallation
D = From RB(OH)₂
E = From methylin(IV) compounds
F = Thallation
b = Followed by treatment with KCl.

Phenylthallium dihalides are more soluble in polar solvents than the diphenylthallium halides. However, the former compounds are much less stable in solution. They tend either to disproportionate into Ph₂TIX and TIX₃ (equation (1); X = Cl, Br) or to undergo reductive degradation to PhBr and TIBr. The lower alkylthallium dicarboxylates are also thermally unstable both in the solid state and in solution.

\[ 2\text{PhTIX}_2 \rightarrow \text{Ph}_2\text{TIX} + \text{TIX}_3 \] (equ.1)

The cyanides RTI(CN)OAc and the dithiocarbamates RTI(S₂CNMe₂) (R = Me, Et)⁴⁶ are much more stable than the dicarboxylates. The branched chain compounds Me₃CCH₂TlBr and Me₃SiCH₂Tl(O₂CPri)₂ do not decompose as readily as the lower alkyl analogues.

COORDINATION CHEMISTRY:

The acidity of PhTI²⁺, and possibly also (Alkyl) TI²⁺, towards base is thought to be greater than that of the diorganothallium cation. Phenylthallium dichloride is monomeric in methanol, and a non-electrolyte in acetone⁴⁵, but its structure in the solid state has not yet been determined. Some 1:1 adducts are formed on treatment of PhTICl₂ with donor molecules, such as Py, Ph₃P, Ph₃PO, phen, bipy and N,N'-bis (acetylacetonato) ethylene-diamine⁴⁵. The complex PhTICl₂Py is a non-electrolyte in acetone, and its IR spectrum in the solid state shows bands attributable to (Tl-Cl). A five-coordinate structure fig. 11 may be postulated for the complexes containing the bidentate ligands. The five-coordinate adducts fig. 12 are also formed on treating PhTICl₂ with Ni(Salen) or bis(B-mercaptoethylamine) nickel(II) complexes⁴⁷.
However, that treatment of PhTlCl₂ with sodium salts of Schiff bases in the dianion form gives a different type of compound, e.g. PhTl(Salen)⁴⁸.

Phenylthallium dichloride reacts with free chloride ion in methanol to form (PhTlCl₃) and (PhTlCl₄)², as has been suggested by vapour-pressure measurements²⁵. Isolated as solid samples are (Me₄N) (PhTlCl₃), (Me₄N)₂ (PhTlCl₄), (Ph₄As) (PhTlX₃) (X = Br, I), K (PhTl (CN))₃, and (Bu₄N) (C₆F₅TlI₃)²⁵.

The dicarboxylates RTl(O₂CPr)₂ (R = Me, Et) are dimeric in chloroform solution⁴⁹. Their IR spectra (particularly the COO⁻ stretching region) have been taken as evidence to suggest that the compounds contain both bridging and chelating carboxylate ligands in solution, giving rise to a five-coordinate thallium atom fig. 13.

![Diagram](image-url)

**Fig. (11)**
\[ Y = O \text{ or } S \]

**Fig. (12)**

\[
\begin{align*}
\text{Ph} & \quad \text{Tl} \\
& \quad \text{Cl} \\
& \quad \text{O} \\
\end{align*}
\]

***Fig. 13***
The crystal structure of (cyclo-C\textsubscript{3}H\textsubscript{3})Tl(O\textsubscript{2}CPri)\textsubscript{2} has been determined\textsuperscript{50}. It reveals a fundamental aspect for the better understanding of the structure of the mono-organothallium dicarboxylates, for all of these compounds in the solid state exhibit. Common vibrational spectral characteristics in the COO\textsuperscript{-} stretching region. The cyclo-propyl compound contains a linear polymeric chain made through the bridge by one carboxylate group which acts as a chelate ligand simultaneously. This type of intermolecular association is quitereminiscent of that found in Me\textsubscript{2}TlOAc (Fig 14). Another carboxylate group makes an unsymmetrical chelate by O(3) and O(4) shown in figure-15. The coordination for the thallium is thus approximately distorted pentagonal bipyramidal, as In Me\textsubscript{2}TlOAc. However, one coordination site which remains vacant the case of Me\textsubscript{2}TlOAc is occupied by O(3) in the dicarboxylate. It is also notable that the C-Tl-O(4) angle is 168\textdegree\textsuperscript{0} and the Tl-O(4) distance (2.125 Å) is the shortest thallium oxygen bond ever determined for organothallium compounds. Presumably the O(4) atoms can best be considered to play a role somewhat similar to that played by one methyl group in Me\textsubscript{2}TlOAc.

![Diagram](image)

Fig (14)
The structure of Me₂TIOAC. Top view along c; bottom, View along a Large atom are TI; small open atoms are O; small solid atoms are C. All atoms in molecules that are to the rare in each view are left open (from Acta Crystallogr. (B), 1975, 31, 1929.

![Diagram of Tl coordination geometry](image)

**Fig. 15:** Coordination geometry around TI in (cyclo-C₃H₅)TI (OCOPr)₂

*(From J. Organomet. Chem, 1979, 165, 21)*

The chelate compounds RTIY₂ (R = Me, Et, Ph, Y = ox, tropolonate, S₂CNMe₂, S₂PPh₂) are monomeric in solution with the coordination number of thallium being five⁴⁹,⁴⁶,⁵¹. Another interesting chelate compound having a six-coordinate thallium can be prepared from RTI(OAc)₂ (R=Me,Et) and 2, 6 bis-(2-methyl 2- benzothiazolinyl) pyridine through rearrangement and deprotonation of the ligand (equation 2)⁵². An X-ray crystal study of fig.16 has shown that it has a highly
distorted pentagonal-pyramidal geometry with the methyl group occupying the apical position (Fig. 17) for structural parameters. The crystal structural study of a related complex, $\text{MeTl(TPP)}$ ($\text{TPP} = \text{tetraphenyl-porphinate}$), has revealed a square-pyramidal geometry with thallium being displaced from the porphyrin plane by $1.11 \text{A}^{0.52}$.

(Equ. 2) 

Fig. 16
Complexes containing an eight-membered chelate ring can be obtained from the reaction of PhTlCl$_2$ or (2-C$_6$H$_4$CO$_2$H)TlCl$_2$ with two molecules of 2-amino-4, 6-di-t-butyl phenol as shown in fig. 18]$^{53}$ Measurements, of ESR spectra of the reaction mixture from PhTl(O$_2$CCF$_3$)$_2$ and the aminophenol have indicated the existence of geometry paramagnetic intermediates as fig. 19.
Fig. 19

**REACTIONS:**

Most of the reactions of the monoorgan compounds reported here are those involving Tl-C bond cleavage.

(i) **REDUCTIVE TI-C BOND CLEAVAGE:**

The monoorganothallium compounds are particularly liable to undergo reductive cleavage of the Tl-C bond. The methyl compound MeTl(OAc)$_2$ decomposes in various solvents slowly at room temperature, and rapidly when heated, to give methyl acetate and thallium (I) acetate (equation 3). The reaction rate decreases in the solvent, H$_2$O, Me(OH)$_2$, MeNO$_2$, dioxane$^{54}$. In THF and chloroform, autocatalysis due to the formation of TlOAc occurs. A kinetic analysis of the reaction based on the OAc dependency of the rate and the conductivity data is best accommodated by the SN$_2$ mechanism shown in equation 4. When pyridine is added to a methanol solution of MeTl(OAc)$_2$ more than 90% of N-methylpyridinium acetate is produced, possibly via an SN$_2$ attack of pyridine at the methyl group of the (MeTlOAc)$^+$ intermediate$^{55}$.

MeTl(OAc)$_2$ $\rightarrow$ MeOAc + TlOAc  \hspace{1cm} (equ.3)

MeTl(OAc)$_2$ $\rightarrow$ OAc$^-+[\text{Me-Tl-OAc}]^+$ $\xrightarrow{\text{Slow}}$ MeOAc + TlOAc (equ. 4)
The decomposition of the acetate fig, 4 in aqueous methanol involves phenyl migration, forming phenylacetaldehyde and its dimethyl acetal (equation 5). The reaction is again first order with respect to the alkyl thallium species, and may proceed via a reactive species, \((\text{RTIOH})^+\) and a more reactive one, \(\text{RTI}^{2+}\) under acidic conditions (equation 6). Apparently the alkyl group in the cationic intermediates must be very susceptible to attack by nucleophiles, which eventually drives a pair of electrons used in the Tl-C bond on to the thallium atom.

\[
\begin{align*}
\text{PhCH (OMe)CH}_2\text{Tl(OAc)}_2 & \xrightarrow{\text{MeOH/H}_2\text{O}} \text{PhCH}_2\text{CHO} + \text{PhCH}_2\text{CH(OMe)}_2 + \text{TIOAc} \\
\end{align*}
\]

(equ.5)

\[
\begin{align*}
\text{RTI(OAc)}_2 & \xrightleftharpoons{} (\text{RTIOAc})^+ + \text{OAc}^- \xrightarrow{\text{H}_2\text{O}} \\
\end{align*}
\]

[equ.6]

\[
\begin{align*}
\text{[RTIOH]}^+ & \xrightarrow{\text{H}^+} \text{RTI}^{2+} \text{ Products} \\
\end{align*}
\]

R = PhCH(OMe)CH\(_2\)

With the proposed mechanism for the decomposition of the monoalkylthallium compounds in mind, it is anticipated that those monoalkyl compounds which contain lesionizable and/or better electron-donating ligands exhibit higher stabilities with respect to the reductive decomposition. Also, bulkier alkyl groups would be expected to exert a barrier to the SN\(_2\) attack. These anticipations have been realized in the stable compounds RTI(CN)(OAc) and RTI(S\(_2\)CNMe\(_2\)) (R = Me, Et), and Me\(_3\)SiCH\(_2\)Tl(O\(_2\)CPri). The role of the ionic dissociation (e.g. equation 5 and 6) in promoting the reductive decomposition of the monoalkyl compounds is clearly one of the primary bases on which the broader utility of the salts TiY\(_3\) (Y = NO\(_3^-\), ClO\(_4^-\), O\(_2\)CCF\(_5^-\)) compared with Ti(OAc)\(_3\) and TiCl\(_3\) as oxidants in organic synthesis has been explored.
Methylthallium diacetate can be decomposed by the addition of chloride, bromide and iodide ions to give methyl halides and thallium (I) halides\textsuperscript{49}. The 4 - pyridi-neomethyl compound decomposes similarly in aqueous solution containing chloride ion to give 4 - pyridiniomethyl chloride (equation 7)\textsuperscript{56}. On the other hand, neopentylthallium dibromide is stable in pyridine at room temperature and decomposes only slowly at 65°C without rearrangement to give neopentyl bromide. Apparently the SN\textsuperscript{2} displacement of the thallium moiety by bromide ion would be unfavourable in the bulky alkyl compound.

\[
\begin{align*}
\text{H} & \quad \text{CH}_{2}\text{Tl}_{2}^{2+} + 2\text{Cl}^{-} \quad \rightarrow \quad \text{HN} & \quad \text{CH}_{2}\text{Cl} + \text{TlCl} \\
\text{equ. 7}
\end{align*}
\]

Addition of CuX (X = Cl, Br) to a mixture of fig.4 KX in acetonitrile facilitates formation of PhCH(OMe)CH\textsubscript{2}X\textsuperscript{57}. A mechanistic study of this reaction employing spin-trapping reagents and fig. 10 or its diastereomer has indicated occurrence of two competing pathways\textsuperscript{58}, one is an ionic path involving anchimeric assistance by the phenyl group which predominates at lower temperatures, and the other a radical path which predominates at higher temperatures (equation 8). More detail is given later concerning the radical reactions of the monoalkylthallium derivatives. The two pathways complete also in the reaction of erythro-Oc\textsuperscript{n}CH(OMe)CHDTl(OAc)\textsubscript{2} with CuCl/KCl, although the ionic path in this case results in the inversion of configuration at the α-carbon. Heating an acetonitrile solution of fig. 4 with CuX/KX (X = I, CN\textsuperscript{−}, SCN\textsuperscript{−}, SeCN\textsuperscript{−}) likewise affords PhCH(OMe)CH\textsubscript{2}X in fair yields\textsuperscript{57,59}.

[25]
Phenyl thallium dichloride is stable with respect to spontaneous reductive decomposition. The dibromide PhTlBr₂ when heated decomposes rapidly into PhBr and TIBr. Treatment of PhTIX₂ (X = Cl, O₂CCF₃) with KI results in almost immediate formation of PhI and TII (equation 9)²⁵. Although the exact mechanism is not known, the great case of equation 9 has been applied, when combined with a facile thallation of a variety of aromatic compounds with Tl(O₂CCF₃)₃ to a simple synthesis of aromatic iodides with a great orientation control³⁸.

PhTIX₂ + 2I⁻ → PhI + TII

(i) X and or CuX₂  (ii) CuX₂

(equ. 9)

(X = Cl, O₂CCF₃)
The formation of aryl chlorides, cyanides, and selenocyananates from ArTl(OAc)(ClO₄) is affected by treating the aryl compounds with the copper(II) salts, CuX₂ (X = Cl⁻, CN⁻, SCN⁻, SeCN⁻), as typically shown in equation 10⁵⁹,⁶⁰. The reaction is solvent dependent, with the best result being obtained in pyridine for the cyanide and dioxane for the other three cases. The aryl cyanides and thiocyanates can alternatively be obtained in fair yields by irradiating aqueous solution of ArTl(O₂CCF₃)₂ containing KCN and KSCN, respectively.⁶¹-⁶² Photolysis of a suspension of these arylthallium compounds in benzene results in the formation of unsymmetrical biphenyls.⁶³

PhTl(OAc)(ClO₄) + CuCl₂ → PhCl + Tl(ClO₄)₂ + Cu(OAc)Cl

(equation 10)

The monoorganothallium compounds, can also be decomposed by obvious reductants, electrochemical reduction of PhTl (ClO₄)₂, in aqueous solution at a mercury electrode gives Ph₂Hg and metallic thallium, possibly through one and two-electron processes (equation 11 and 12).⁶⁴

PhTl²⁺ + e⁻ → PhTl⁺ → Ph₂Hg + Tl⁺

(equation 11)

PhTl⁺ + e⁻ → Hg → Ph₂Hg + Tl

(equation 12)

Ascorbic acid and hydrazine react with the acetates R₆Tl(OAc)₂ (R = Me, n-C₈H₁₇, Ph) as well as fig.4 under an inert atmosphere to give R₂TlOAC and TlOAc and as shown in (equation 13)⁶⁵-⁶⁶. The spin-trapping experiment based on ESR spectroscopy suggested intervention of alkyl radical intermediates during these reductions. In the reaction of R₆Tl(OAc)₂ with ascorbic acid under O₂, the alcohols ROH (R = n-C₈H₁₇ PhCh(OMe)CH₂) can be obtained in good yields. Furthermore, extensive epimerization at the α-carbon of the alkyl group occurs during the formation of (PhCH(OMe)CHD)₂ TlOAc when the compound fig. 10 is
allowed to react with the reductants. A possible mechanism for equation 13 involving alkyl radical intermediates is shown in equation 14.

Presumably one-electron reduction of $\text{RTI}^{2+}$ to plays a key role. Homolysis of the $\text{Tl-C}$ bond in $\text{RTI}^+$ then produces the radical R which reacts with $\text{RTI}^+$ or $\text{RTI}^{2+}$ to give $\text{R}_2\text{Tl}^+$ eventually.

$$2\text{RTI(OAc)}_2 \xrightarrow{\text{Red}} \text{R}_2\text{TlOAc} + \text{TlOAc} \quad \text{(equ. 13)}$$

$$\text{RTI}^{2+} \xrightarrow{\text{Red}} \text{RTI}^+ \rightarrow \text{R}^+ + \text{Tl}^+ \rightarrow \text{R}_2\text{Tl}^+ \quad \text{(equ. 14)}$$

where, (i) $\text{RTI}^+$, (ii) $\text{RTI}^{2+}$, (iii) red

The one-electron reduction of $\text{RTI}^{2+}$ and subsequent homolysis of the $\text{Tl-C}$ bond may also be involved in hydro-dethallation of $\text{RTIX}_2$ with N-benzyl-1,4-dihydronicotinamide (BNAH) in methanol or THF (equation 15)$^{67}$. The formation of a good yield of $\text{PhCH(OMe)CH}_3$ from fig.4 and BNAH can be contrasted to a dominant formation of styrene in the reduction of fig.4 by $\text{NaBH}_4$, in aqueous alkaline methanol$^{68}$. The yield of $\text{PhCH(OMe)CH}_3$ in the latter reduction ranges only from 10 to 6%. It is also interesting that the hydrogen source for forming this either in equation 15 is mainly BNAH, but not methanol, while it is the acidic hydrogen of methanol and water in the reduction with $\text{NaBH}_4$. In connection with the latter result, effective introduction of deuterium into aromatic compounds is made possible through the reaction of $(\text{ArTlO}_2\text{CCF}_3)_2$ with $\text{NaBH}_4$ in EtOD solution (equation 16)$^{69}$.

$$\text{RTIX}_2 + \text{BNAH} \rightarrow \text{RH} + \text{TIX} + (\text{BNA})\text{X} \quad \text{(equ. 15)}$$

$\text{R} = \text{Me, n-C}_8\text{H}_{17}, \text{PhCH(OMe)CH}_2, 4-\text{MeC}_6\text{H}_4$; (BNA)$^+$, N$^\text{CH}_2\text{Ph}$
NaBH₄ → ArTl(O₂CCF₃)₂ → Ar.D (equ. 16)

Ar = 4-RC₆H₄ (R = Prⁿ, OMe), 2-RC₆H₄ (R = CO₂Me, CO₂H), CH₂ CO₂H)

These reactivity patterns in the reduction of RTIX₂ with NaBH₄ differ significantly from those in the reduction of RHgX compounds with NaBH₄. The latter reaction involving a typical radical process can serve as the Markownikov conversion of alkenes to ethers or alcohols when applied to oxymercuration adducts of alkenes, with the hydrogen source for replacing the mercury predominantly originating from NaBH₄.⁷⁰

The spontaneous disproportionation of PhTlCl₂ into Ph₂TlCl and TlCl₃ is already described in equation 1, and the dicarboxylate PhTl (O₂CCF₃) also undergoes a similar reaction in a hot acetone or aqueous solution to give Ph₂TlO₂CCF₃.⁷¹ Treatment of PhTl(O₂CCF₃)₂ with P(OMe)₃ without solvent likewise affords the diphenyl compound.⁷¹ The stoichiometry of this reaction in acetone / methanol (5:1) has been confirmed as that shown in equation (17)⁷². The methyl compound MeTl(OAc)₂ also undergoes the same reaction quite rapidly at room temperature.

2RTl (OAc)₂ + P(OMe)₃ → MeOH → R₂TlOAc + TlOAc + O = P (OMe)₃ + AcOH + AcOMe

(equ. 17)

(R = Me, Ph)

It has been assumed in considering the mechanism for such an interesting disproportionation reaction mediated by P(OMe)₃ that there is a spontaneous equilibrium reaction (equation 18) which lies far to the left,
although actual formation of $\text{R}_2\text{TIOAc}$ in the absence of $\text{P}(\text{OMe})_3$ could not be confirmed by proton NMR spectroscopy\textsuperscript{72}. The mechanism proposed is that the rate determining disproportionation, namely the forward path of equilibrium (equation 18), is followed by a rapid removal of $\text{Tl}(\text{OAc})_3$ by $\text{P}(\text{OMe})_3$, from the equilibrium. However, occurrence of this type of equilibrium, with the rate of the forward path comparable to the overall rate of equation-17, appears highly unlikely at last for $\text{MeTl(OAc)}_2$ for it has been found that there occurs no reaction at all between $\text{Me}_2\text{TIOAc}$ and $\text{Tl}(\text{OAc})_3$ under similar conditions\textsuperscript{25}. As for the mechanism of equation (17), other possibilities such as disproportionation induced by direct electron transfer to $\text{RTl(OAc)}_2$ must also be taken into serious consideration. In this connection it should be noted that the action of $\text{P}(\text{OMe})_3$ on fig-10 in THF/methanol gave 84% yield of $\text{PhCH(OMe)CHD}_2\text{TIOAc}$ which contained ca.70% of the epimerized alkyl group\textsuperscript{66}.

$$2\text{RTl(OAc)}_2 \rightarrow \text{R}_2\text{TIOAc} + \text{Tl(OAc)}_3 \quad \text{(equ. 18)}$$

**II ELECTROPHILIC TI-C BOND CLEAVAGE:**

The TI-C bond in the monooorganothallium compounds is susceptible to certain electrophiles as well. Exchange of the phenyl group occurs between $\text{PhTl}^{2+}$ and $\text{Tl}^{3+}$ in aqueous perchloric acid, as shown in equation (19), and has been examined by the use of radioactive thallium\textsuperscript{25}. Transfer of the organic group of $\text{RTIX}_2$ to mercury (II) and lead (IV) is also a facile process, with the latter acceptor having been used as a reagent for a simple phenol synthesis from $\text{ArTl(O}_2\text{CCF}_3)_2$\textsuperscript{61}.

$$\text{PhTl}^{2+} + \text{Tl}^{3+} \rightarrow \text{PhTl}^{2+} + \text{Tl}^{3+} \quad \text{(equ.19)}$$

Palladium (II) salts are also versatile reagents in synthetic reactions when reacted with $\text{ArTl(O}_2\text{CCF}_3)_2$ particularly in the presence of alkenes or carbon monoxide, as typically shown in equations (20) and(21)\textsuperscript{73-74}.
The carboxylation shown in equation (21) proceeds at room temperature under atmospheric pressure of carbon monoxide. On the other hand, in the carboxylation of PhTl(OH)(NO₃) and PhTlX₂ (X = Cl, O₂CPr⁺) in the absence of the palladium (II) salts. It requires very high temperatures and high pressures to obtain a moderate yield of benzoic acid or its derivatives⁷⁵. The alkyl compound fig.4 also reacts with PdCl₂ in methanol containing NaOAc to give acetophenone and metallic palladium⁷⁶. Perhaps an alkylpalladium (II) intermediate, PhCH(OMe)CH₂PdX, is formed initially.

\[
\text{PhTl(O₂CCF₃)} \xrightarrow{\text{LiPdCl₄/RCH=CHR}} \text{PhC(R) = CHR} \quad \text{(equ. 20)}
\]

\[
\begin{array}{c}
\text{CH₂OH} \\
\text{PhCH(OMe)CH₂PdX}
\end{array}
\xrightarrow{\text{PdCl₂/CO}}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \text{(equ. 21)}
\]

In contrast to the reduction of ArTl(O₂CCF₃)₂ with NaBH₄ (equation 16), the dicarboxylates react with BH₄⁻, in THF to give intermediates possibly containing the Ar-B bond⁷⁷. These intermediates give, on oxidation with alkaline H₂O₂ or hydrolysis by water, good yields of phenols or arylboronic acids, respectively.

(II) **DIORGANOTHALLIUM COMPOUNDS:**

**Preparation And Properties:**

Various organometallic compounds are available for the preparation of relatively inter diorganothallium derivatives. The reactions of Grignard reagents with TlCl₃ (equation 22) is the most usual way of preparing diorganothallium halides, although yield are sometimes poor owing to the oxidation of the Grignard reagents by TlCl₃⁷⁵. Some di-n-
alkylthallium bromides, $R_2TIBr$ ($R =$ normal alkyl with carbon number 1 to 10), can also be prepared in a moderate yield by a one-step reaction between RMgBr and TIBr in a 1:2 mole ratio. However, in an analogous reaction of aryl or secondary alkyl Grignard reagents, there have been obtained only coupled products in moderate yield.

$$2RMgX + TlCl_3 \rightarrow R_2TlX + MgXCl \quad (equ. 22)$$

Diaryl and divinylthallium derivatives can conveniently be obtained in aqueous solution by the reaction of the corresponding organoboronic acids with TIX₃ (equation 23; $X =$ halogen) carboxylate.²⁵ Aryl and vinyl derivatives of mercury, tin, lead and bismuth also react with TIX₃ to give the same organothallium products. On the other hand, the analogous reaction of the alkyl derivatives of these metals with TIX₃ is much less satisfactory due to the formation of TICl as the main product. The use of Tl(OAc)₃, instead of TlCl₃, in the reaction with methyl- and ethyl-tin compounds leads to the formation of good yields of dimethyl and diethyl-thallium compounds.²⁵

$$2RB(OH)_2 + TIX_3 \rightarrow R_2TlX + 2B(OH)_3 + 2HX \quad (equ. 23)$$

The organo-boron and tin compounds are also useful for obtaining mixed diorganothallium compounds as typically shown in equations-24 and-25.²⁵,⁸⁰,⁸¹ On the other hand, ethyl and cyclohexyl Grignard reagents have been shown to react with PhTlCl₂ to give only a mixture of symmetrical diorganothallium chlorides, Ph₂TlCl and R₂TlCl ($R =$ Me, cyclo-C₆H₁₁)²⁵. Methyl (phenylethynyl) thallium derivatives are obtained by the reaction of MeTlO with PhC=CH₂ in refluxing methanol in the presence of air (equation 26), followed by treatment of the resulting carbonate with appropriate anions.²⁵
MeTl(O₂CPr)₂ + Bu₃(R)Sn  
Me(R)TlO₂CPr + Bu₃SnO₂CPr (equation 24)  
(R = CH₂ = CHCH₂, C₆H₅)

PhTlCl₂ + 3-MeC₆H₄B(OH)₂  
H₂O  
Ph(4-MeC₆H₄)TlCl + B(OH)₃ + HCl (equation 25)

2MeTlO + 2PhC ≡ CH  
[Me(PhC ≡ CH)Tl]₂CO₃ + H₂O (equation 26)

Diazomethane reacts with TlCl₃ or ArTlCl₂ (Ar = Ph 4 MeC₆H₄) to give (CH₂C₁)₂C₁ or Ar (CH₃ C₁)TlC₁, respectively²⁵,⁸².

Treating the diorganothallium halides with salts of silver (I) or thallium (I) is a very convenient way of obtaining diorganothallium salt-type compounds. Furthermore, the reaction of halides with TlOH or TlOEt gives the organothallium hydroxides or ethoxides which serve, when treated with compounds containing an acidic hydrogen, as good starting materials for various organothallium salt and chelate-type derivatives.

The reaction of mesitylene- or polyfluorobenzene-sulfinate anions with Tl(OAc)₃ affords diarylthallium compounds via desulfination, as typically shown in equation-27³⁷-³⁸.

3NaO₂SR + Tl(OAc)₃  
R₂TlO₂SR + 2SO₂ + 3NaOAc (equation 27)  
(R = 2,4,6-Me₃C₆H₂)

Table-4 lists representative diorganothallium halides and their physical properties.

The lower dialkyl- (e.g. dimethyl- or diethyl-), divinyl- and diphenyl-thallium halides are stable solids of very high melting or decomposition points. These halides exceed the fluorides are not very soluble in water, alcohols or other common solvents except for pyridine or aqueous ammonia. The higher linear alkyl analogues, as well as
(Me₃YCH₂)₂TICl (Y = C) are likewise stable, and even more soluble. Other branched-chain alkyl analogues such as Pr₂¹TICl, Bu⁺₂TICl and Bu⁺₁TICl decompose more easily when heated. Bis(pentafluorophenyl) thallium halides are more soluble than the diphenyl analogues.

Salts of dimethylthallium hydroxide and inorganic acids such as nitric, sulfuric, perchloric and chromic acids are soluble in water, but much less so in organic solvents.

**TABLE 4**

**DIORGANOTHALLIUM HALIDES**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M.P. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂TICl</td>
<td>&gt;80 dec.</td>
<td>35</td>
</tr>
<tr>
<td>Me₂TIBr</td>
<td>295 dec.</td>
<td>35</td>
</tr>
<tr>
<td>Me₂TII</td>
<td>264-266 dec.</td>
<td>35</td>
</tr>
<tr>
<td>Et₂TICl</td>
<td>205 dec.</td>
<td>35</td>
</tr>
<tr>
<td>Pr⁺₂TICl</td>
<td>198-202 dec.</td>
<td>35</td>
</tr>
<tr>
<td>Bu⁺₂TICl</td>
<td>240-250 expld.</td>
<td>36</td>
</tr>
<tr>
<td>Bu⁺₅TICl</td>
<td>150 expld.</td>
<td>36</td>
</tr>
<tr>
<td>(Me₃CCH₂)₂TICl</td>
<td>&gt;340</td>
<td>37</td>
</tr>
<tr>
<td>(Me₃SiCH₂)₂TICl</td>
<td>238</td>
<td>37</td>
</tr>
<tr>
<td>(Cyclo-C₆H₁₈)₂TICl</td>
<td>210-230 expld</td>
<td>36</td>
</tr>
<tr>
<td>(trans-MeCH=CH)₂TICl</td>
<td>&gt;310</td>
<td>38</td>
</tr>
<tr>
<td>(Cis-MeCH=CH)₂TICl</td>
<td>&gt;310</td>
<td>38</td>
</tr>
<tr>
<td>Ph₂TICl</td>
<td>&gt;310</td>
<td>39</td>
</tr>
<tr>
<td>(C₆F₅)₂TICl</td>
<td>237-239</td>
<td>40</td>
</tr>
<tr>
<td>(C₆Cl₃)₂TICl</td>
<td>314</td>
<td>41</td>
</tr>
<tr>
<td>MeEtTICl</td>
<td>&gt;250</td>
<td>42</td>
</tr>
<tr>
<td>(4-MeC₆H₄)(CH₂Cl)TICl</td>
<td>265-266</td>
<td>43</td>
</tr>
</tbody>
</table>
COORDINATION CHEMISTRY:

Most of diorganothallium salt-type compounds ionize in polar solvent to form a linear, more or less solvated cation, \( R_2\text{Tl}^+ \). The ion \( \text{Me}_2\text{Tl}^+ \), being iso-electronic \( \text{Me}_2\text{Hg} \), is only a very weak aquo-acid, and the bonds to the water molecule are very weak. A Raman spectrum of even \( \text{Me}_2\text{TIOH} \) in water is very similar to those of \( \text{Me}_2\text{TlY} \) (\( Y = \text{NO}_3^- \), \( \text{ClO}_4^- \)), showing no lines attributable to \( \nu(\text{Tl-O}) \). The undissociated portion of the hydroxide may exist as ion pairs.

Other than undergoing ionic dissociation the diorgano compounds can form both intra- and inter-molecular coordination bonds. An increase of the coordination number for thallium appears to become prominent particularly in the solid state, as revealed by X-ray crystallography. In Table-5 are shown typical coordination geometries of diorganothallium compounds determined by X-ray structural studies.

It is notable that most of the C-Tl-C angles observed in the dialkyl derivatives deviate from linearity only slightly. This is the case even in discrete four-coordinate complexes where the ideal geometry around thallium may approach the tetrahedron. Furthermore, many of the observed Tl-ligand distances are much longer than the sum of the covalent radii for the thallium and donor atoms. These facts are again in line with the weakly polarizing effect of the dialkylthallium cation upon the ligands surrounding itself. On the other hand, due to the greater electronegativity of the polyfluorophenyl groups than those of the alkyl groups, cations, such as \( (\text{C}_6\text{H}_3)_2\text{Tl}^+ \) would be expected to be stronger acids than the dialkylthallium cations.
## TABLE- 5
CO-ORDINATION GEOMETRY IN DIORGANOTHALLIUM COMPOUNDS.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Geometry</th>
<th>C.N.</th>
<th>LC-Tl-O</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ph₂Tl₂S₂CNEt₂</td>
<td>TD</td>
<td>4</td>
<td>198</td>
<td>34</td>
</tr>
<tr>
<td>2.</td>
<td>Me₂TlOPh</td>
<td>TBP</td>
<td>4</td>
<td>173</td>
<td>35</td>
</tr>
<tr>
<td>3.</td>
<td>Me₂TlSPh</td>
<td>TBP</td>
<td>4</td>
<td>163.5</td>
<td>35</td>
</tr>
<tr>
<td>4.</td>
<td>(Me₃SiCH₂)₂TlOCl</td>
<td>TBP</td>
<td>4</td>
<td>168</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>(2,3,5,6-F₄C₆H₂)₂TlBr</td>
<td>TBP</td>
<td>5</td>
<td>144</td>
<td>37</td>
</tr>
<tr>
<td>6.</td>
<td>(2,3,5,6-F₄(Hg)₂TLCl(Ph₃PO)</td>
<td>TBP</td>
<td>5</td>
<td>149.9</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>TBP</td>
<td>TBP</td>
<td>5</td>
<td>118.5</td>
<td>38</td>
</tr>
<tr>
<td>8.</td>
<td>(C₆F₅)₂TlOH</td>
<td>TBP</td>
<td>5</td>
<td>117</td>
<td>39</td>
</tr>
<tr>
<td>9.</td>
<td>(C₆F₅)₂Tl[N(2-pyridyl)]</td>
<td>OH</td>
<td>5</td>
<td>165.7</td>
<td>40</td>
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<tr>
<td>10.</td>
<td>Me₂Tl(tryptophanate)</td>
<td>PBP</td>
<td>5</td>
<td>162.6</td>
<td>41</td>
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<tr>
<td>11.</td>
<td>Ph₂Tl(tropolonate)</td>
<td>PBP</td>
<td>5</td>
<td>162.6</td>
<td>41</td>
</tr>
<tr>
<td>12.</td>
<td>Me₂TlCl</td>
<td>OH</td>
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<td>180</td>
<td>34</td>
</tr>
<tr>
<td>13.</td>
<td><a href="%5BMe%E2%82%83AlNCS">Me₂Tl</a></td>
<td>OH</td>
<td>6</td>
<td>177</td>
<td>42</td>
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<tr>
<td>14.</td>
<td>Me₂TlCN</td>
<td>OH</td>
<td>6</td>
<td>180</td>
<td>43</td>
</tr>
<tr>
<td>15.</td>
<td>Me₂TlN</td>
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<td>6</td>
<td>180</td>
<td>44</td>
</tr>
<tr>
<td>16.</td>
<td>Me₂TlC(CN)₃</td>
<td>OH</td>
<td>6</td>
<td>178.7</td>
<td>44</td>
</tr>
<tr>
<td>17.</td>
<td>Me₂TlO₂CMe</td>
<td>PBP</td>
<td>6</td>
<td>171.8</td>
<td>45</td>
</tr>
<tr>
<td>18.</td>
<td>Me₂Tl(acac)</td>
<td>PBP</td>
<td>6</td>
<td>170</td>
<td>46</td>
</tr>
<tr>
<td>19.</td>
<td>Et₂Tl(Sal)</td>
<td>PBP</td>
<td>6</td>
<td>172</td>
<td>46</td>
</tr>
<tr>
<td>20.</td>
<td>[Me₂Tl(Phen)]ClO₄</td>
<td>PBP</td>
<td>6</td>
<td>168.3</td>
<td>87</td>
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<td>21.</td>
<td>Me₂Tl(1-Phenylalaninate)</td>
<td>PBP</td>
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<td>163.7</td>
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<tr>
<td>22.</td>
<td>MeTlISSCOMe</td>
<td>PBP</td>
<td>6</td>
<td>170.9</td>
<td>90</td>
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Several adducts can be isolated by the reaction of $\text{Me}_2\text{Tl}^+$ with Lewis bases such as py, phen, bipy, DMSO and en$^{25}$. The structure of $(\text{Me}_2\text{Tl} \text{ (phen) ClO}_4$ has been solved by an X-ray crystal study (Fig.20)$^{91}$. This is a distorted pentagonal-bipyramidal structure with one equatorial position vacant. The $\text{Tl}-\text{N}$ bonds are short enough to permit partial covalent character but the two oxygen atoms are located at distances appropriate for an electrostatic bond. Complexation also occurs between $\text{Me}_2\text{Tl} \text{ (crown) picrate fig.21}^{92}$. The rigidity of the complexation in fig. 21 is such that the two methyl groups can be distinguished from each other in proton NMR spectra.
Fig. 20: The structure of $[\text{Me}_2\text{Tl}(\text{phen})]\text{ClO}_4$ (From Chem. Commun., 1967, 54).

Fig. 21
Fig. 22  Unit cell of $\text{Me}_2\text{Cl}$ (From Z. Naturforsch., Teil B, 1974, 29, 269).
The crystal structure of a polymeric compound, \( \text{Me}_2\text{TlCl} \), consists of layers where a linear Me-Tl group is surrounded by four chlorines and each chlorine atom is surrounded by four \( \text{Me}_2\text{Tl} \) cations (Fig.22)\(^93\). The observed Tl-Cl distance is 3.029 Å\(^0\). The corresponding bromide and iodide have the same overall structure\(^25\). Crystals of dimethylthallium cyanide, azide, cyanate and thiocyanate have distorted sodium chloride structures similar to those of the halides, all containing the octahedral thallium atom\(^94\).

Crystals of another polymer, \((2,3,5,6-\text{C}_6\text{HF}_4)_2\text{TIBr}\), contain a thallium atom with a different type of coordination, namely a distorted trigonal bipyramid with two carbons and one bromine occupying the equatorial position, as shown in fig.23\(^95\). The TIBr interaction (3.214 and 3.172 Å\(^0\)) between the dimeric \([\text{R}_2\text{TIBr}]_2\) units gives rise to a polymeric chain. This compound, as well as \((\text{C}_6\text{F}_5)_2\text{TIX} (X = \text{Cl, Br})\), dissociates into dimers in benzene solution. These halides also form adducts with bipy, phen, py, \(\text{Ph}_3\text{E} (E = \text{P, As})\), presumably resulting in depolymerization of the polymer chains\(^96\). In fact an X-ray structural study of \((\text{C}_6\text{HF}_4)_2\text{TIC(Ph}_3\text{PO)}\) has revealed a chlorine-bridged dimeric structure with a five-coordinate thallium atom\(^97\). An overall geometry around the thallium is similar to that of \((\text{C}_6\text{HF}_3)_2\text{TIBr}\) shown in fig.23.
Occurrence of a discrete dimeric structure in the solid state of \((\text{Me}_3\text{SiCH}_2)_2\text{TICl}\) has been confirmed by an X-ray crystal study\(^9\). Molecular weight measurements indicated that \(\text{Bu}^i_2\text{TICl}\) and \((\text{Me}_2\text{CCH}_2)_2\text{TICl}\) also are dimeric in solution\(^9\). A possibility of dimerization of \(\text{Me}_2\text{TICl}\) in the vapour phase has been presented by mass spectral studies\(^10\).
Addition of halide anions to solutions of diorganothallium halides leads to isolation of solid complexes containing the anion \([R_2TlX_2] (R = \text{Ph, C}_6\text{F}_5; X = \text{Cl, Br, I, NCS})\) and \([\text{Me}_2\text{TlX}_3]^2 (X = \text{Cl, Br, I})\)\(^{25}\). It has been suggested from an electrophoretic study that the increasing order of the acidity of the cations towards \(\text{Cl}^-\) is \(\text{Tl}^+ < \text{Me}_2\text{Tl}^+ < \text{Ph}_2\text{Tl}^+ < \text{PhTl}^{2+} < \text{Tl}^{3+} < \text{Tl}^{3+}\)\(^{101}\).

Diorganothallium fluorides, \(R_2\text{TlF} (R = \text{Bu}^i, i-\text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5)\), are associated in solution\(^{25,102}\), but little is known about the nature of the thallium-fluoride interaction.

Molecular weight measurements show that inter-molecular bridging by oxygen, sulfur, selenium and nitrogen occurs in solutions of \(\text{Me}_2\text{TlY} (Y = \text{OMe, OEt, OBu}^i, \text{OSiMe}_3, \text{OPh, SME, SPh, SeMe, NMe}_2)\) to form the dimer fig. 14\(^{103-105}\). Occurrence of this type of dimerization in the solid state of \(\text{Me}_2\text{TlY} (Y = \text{OPh, SPh})\) has been confirmed by X-ray crystallography\(^{105}\). Significantly, the C-Tl-C angles in these compounds (173, 166.2, 163.5° respectively) do not deviate much from linearity. The coordination for the thallium is better envisaged as distorted trigonal bipyramidal with one equatorial site vacant. On the other hand, the crystal structure of \((\text{C}_6\text{F}_5)_2\text{TlOH}\) contains infinite chains of dimers quite similar to these of \((\text{C}_6\text{H}_4F)_2\text{TIBr}\) shown in Fig.23\(^{106}\).

Several diorganothallium sulfinates and carboxylates are also dimeric in solution through bridging- O-sulfinato and carboxylato groups fig.25\(^{49,107}\).
Intramolecular chelate bond formation occurs in some diorganothallium derivatives both in solution and in the state, $\text{A cation R}_2\text{Tl}^+$ forms a 1:1, but no 1:2, complex with $\beta$ diketonate anions, $[\text{RCOCHCORDER}']$ ($R = R' = \text{Me}; R = R' = \text{Ph}; R = \text{Me}, R' \text{ Ph}; R = \text{CH}_2\text{COPh}, R - \text{Me or Ph}$), in dioxane/water$^{108}$. The formation constant for a given $\beta$-diketonate ligand increase in the order $\text{Me}_2\text{Tl}^+ < \text{Et}_2\text{Tl}^+ < \text{Pr}_2\text{Tl}^+$. This result can be best correlated with the hydrophobic character of the organothallium cation. As the chain length of the alkyl group increases, this character would increase and this should be paralleled by an increasing case of displacement of solvent molecule by the chelate ligand.
Thallium atoms in certain chelate compounds can attain a coordination number greater than four as a result of extra intramolecular association. Rather a small number of chelate compounds have been found to be monomeric in solution. Typical examples include \( \text{R}_2\text{TlS}_2\text{CNET}_2 \) (R = Me, Ph)\(^{109}\), \( \text{R}_2\text{TlS}_2\text{PR'}_2 \) (R = Et, Ph; R' = Et, OMe)\(^{109-110}\) and \( \text{(C}_6\text{F}_5)_2\text{TI} \) (β -diketonate)\(^{111}\). An X-ray study of \( \text{Ph}_2\text{TlS}_2\text{CNET}_2 \) has revealed that the bent C-Tl-C angle (148\(^0\)) is among the smallest for non-fluoro-alkyl- and aryl-thallium-derivatives\(^{112}\). Many other diorganothallium β-diketonates, dithiophosphinates, 7-hydroxyquinolines, salicylaldehydates and tropolonates are more or less associated in solution\(^{109,110,111,113,114}\), the apparent degree of association being usually between 1 and 2. A five-coordinate structure (Fig.26) can be assigned to the dimer of \( \text{(C}_6\text{F}_5)_2\text{TI} \) (ox = 8-hydroxyquinolinate)\(^{118}\). A rigid dimerization of chelate units has been confirmed by the X-ray structural determination of dimethyl thallium tryptophanate, as schematically shown in fig.27\(^{115}\) - This is a distorted octahedral complex with a vacant equatorial site. Also determined by X-ray crystallography was a dimeric structure of \( \text{Ph}_2\text{TI} \) (tropolonate)\(^{112}\).

Even polymerization of the chelate units occurs in the solid state of \( \text{Me}_2\text{TLY} \) (Y = acac, OAc, tropolonate) and \( \text{Et}_2\text{Tl(sal)} \), as schematically shown in fig. 28. The structures of all of these compounds have been determined by X-ray studies\(^{116-117}\), a detailed geometry for \( \text{Me}_2\text{TlOAc} \) being shown in fig. 14. This is again a distorted pentagonal bipyramidal structure with one equatorial site vacant. The other compounds in fig. 28 have an almost similar overall geometry around thallium. Dimethylthallium phenylalaninate is also polymeric in the solid state where a unit similar to fig. 27, namely fig. 29, is linked via the carboxylate bridge, so that each thallium is six coordinate\(^{118}\).

A more complex intermolecular association: exists in the solid state
of $\text{Me}_2\text{TlS}_2\text{COMe}$, as shown in fig. 30. Thallium in this compound is apparently seven coordinate with two methyl groups occupying apical sites of a distorted pentagonal bipyramidal.

Fig. 26

Fig. 27

$$R = \text{CH}_2\text{Ph}$$

Fig. 28
The increase of the coordination number in the chelate compounds is made possible by not only the intermolecular association of chelate units but also coordination of a Lewis base to thallium. Thus the compounds $(C_6F_5)_2TIY$ ($Y =$ acac, hfacac, tfacac, benzoylacetonate, ox) react with $Ph_3EO$ ($E = P$, As), bipy or phen to form five- or six-coordinate adducts, $(C_6F_5)_2TIYL$ or $(C_6F_5)_2TIYL^{111}$.

Another phentafluorophenyl chelate compound having a five-coordinate thallium atom (Fig.31) has been prepared, and its structure determined by X-ray crystallography$^{120}$. This is a very distorted trigonal-bipyramidal structure with two pyridyl nitrogen atoms at apical positions.
Notable in this structure is the relatively small C-Tl-C angle (127° A-C) which, together with those of (C₆F₅)₂TlOH(C₆HF₄)₂TIBr and (C₆HF₄)₂ TICl (Ph₃PO), contrast well with the nearly C-Tl-C angles found in many five and six coordinate dialkyl-thallium compounds.

**REACTIONS:**

Although the Tl-C bonds in diorganothallium compounds are much less labile than those in the triorgano and monoorgano counterparts, several reactions of the diorgano compounds are known in which the cleavage of the Tl-C bond(s) occurs with considerable ease.
(I) REDUCTIVE TI-C BOND CLEAVAGE:

The Tl-C bonds in the diorgano compounds can undergo several types of reductive cleavage reactions. The electrochemical one-electron reduction of the cation $R_2\text{Tl}^+$ (R = Me, Et, Pr$^n$, Bu$^n$, $n$-C$_5$H$_{11}$, Ph) is thought to afford an intermediate radical $R_2\text{Tl}$ (equation 28)$^{121-122}$. This radical then either disproportionates to $R_3\text{Tl}$ and metallic thallium (equation 29), or is further reduced to give the carbanion (equation 30). The disproportionation presumably related to the finding that the action of sodium in liquid ammonia on Ph$_2\text{TlBr}$ gives Ph$_3\text{Tl}$ and metallic thallium$^{25}$. A somewhat complicated kinetic aspect would be expected in polarography of $R_2\text{Tl}$ at a mercury electrode, for Ph$_2\text{TlBr}$ readily reacts with mercury in non-electrochemical systems to give Ph$_2\text{Hg}$ and TlBr (equation 31)$^{123}$. Based on a electropotentiometric study, a plausible intermediate in equation-31 has been suggested as in equation 28-31. In pyridine and ethylenediamine such Hg/Tl exchange occurs mainly via the homogeneous reaction with dissolved mercury, while in DMSO the contribution of the homogeneous reaction is nearly the same as that of the heterogeneous reaction$^{124}$.

$$\begin{align*}
R_2\text{Tl}^+ + e^- & \rightarrow R_2\text{Tl} \quad \text{(equ.28)} \\
3R_2\text{Tl} & \rightarrow 2R_3\text{Tl} + \text{Tl} \quad \text{(equ.29)} \\
R_2\text{Tl} + 2e^- & \rightarrow 2\text{R} + \text{Tl} \quad \text{(equ.30)} \\
\text{Ph}_2\text{TlBr} + \text{Hg} & \rightarrow \text{Ph}_2\text{Hg} + \text{TlBr} \quad \text{(equ.31)} \\
[\text{Ph-Tl-Hg-Ph}]^+ & 
\end{align*}$$

Diaryl- and divinyl-thallium chlorides react with SnCl$_2$ to give the corresponding organotin compounds (e.g. equation 32)$^{25}$. The stereochemistry of the propenyl group is retained during this reaction. The polyfluoro-phenyl analogues such as (C$_4$F$_5$)$_2\text{TlBr}$ are particularly prone to undergo the aryl transfer reaction to elements (Hg, Sn, P, S, I, [48])
Br, Cl / Zn, Ge, As) and metal complexes in the reduced form$^{125-126}$. The metal complexes which accept two C₆F₅ groups include SnCl₂ M(PPh₃)₂ (M = Ni, Pt), AuXL (X = Cl, Br, I; L = PPh₃, AsPh₃, PhNC, RhCl(PPh₃)₂ and MCl(CO)PPh₃)₂ (M = Rh, Ir). A cobalt (II) Schiff base complex can accept one C₆H₅ group according to equation (33)$^{127}$.

\[(\text{MeCH} = \text{CH})₂\text{TICl} + \text{SnCl₂} \rightarrow (\text{MeCH} = \text{CH})₂\text{SnCl₂} + \text{TICl}\]  

\[(\text{C₆F₅})₂\text{TIBr} + 2\text{CoL} \rightarrow 2\text{C₆F₅CoL} + \text{TIBr}\]  

(Equation 32)  

(Equation 33)

$L = \text{salen, N,N'}-$bis (acetylacetone) ethylenediamine,  
$\text{N,N'}-$bis (salicylaldehyde) phenylenediamine

The original claim that the reaction of (C₆F₅)₂TIBr with PdCl₂(PPh₃) affords the Pd(IV) complex Pd(C₆F₅)₂Cl₂ (PPh₃)₂ has been denied by the latter study$^{128}$. In fact mixtures of Pd₅ (C₆F₅)₂ Cl₂ (PPh₃)₂ and Pd(C₆F₅)Cl(PPh₃)₂ have been confirmed to be present in the reaction products.

Irradiating diarylthallium compounds, Ar₂TlO₂CCF₃, in benzene gives unsymmetrical bi-phenyls, Ar₆C₆H₄$^{129}$. Aryl radicals may be involved as intermediates in this transformation.

(II) ALKYL EXCHANGE:

The diorganothallium compounds undergo some alkyl exchange reactions. Attempts to isolate dimethylthallium compounds, Me₂TlY [Y = Co(CO)₄, Cr(CO)₃Cp, Fe(CO)₂Cp] all failed owing to occurrence of the disproportionation shown in equation-34$^{130}$.

\[3\text{Me₂TlY} \rightarrow 2\text{Me₃Tl} + \text{TlY₃}\]  

(Equation 34)

No facile intermolecular exchange of organic groups takes place between, diorganothallium cations in aqueous solution. However, the reversible redistribution reaction (equation 33) occurs in refluxing toluene
solution when Y is SMe, SPh, ox, sal and tropolone\textsuperscript{114}. The dithiocarbamate MeEtTlS\textsubscript{2}CNMe\textsubscript{2} is quite stable under similar conditions. Proton NMR spectroscopy indicates that the n-allyl group in Me (CH\textsubscript{2}=CHCH\textsubscript{2})TlO\textsubscript{2}CPr\textsuperscript{i} undergoes neither intermolecular exchange nor intramolecular rearrangement\textsuperscript{80}. Similarly, there is no intermolecular exchange of the n\textsuperscript{1}-C\textsubscript{5}H\textsubscript{5} group in Me(C\textsubscript{5}H\textsubscript{5})TlO\textsubscript{2}CPr\textsuperscript{i}, as revealed by the observation of the spin-spin couplings between thallium and the C\textsubscript{5}H\textsubscript{5} protons\textsuperscript{81}, in marked contrast to the rapid exchange of the C\textsubscript{5}H\textsubscript{5} group in Me\textsubscript{2}(C\textsubscript{5}H\textsubscript{5})Tl\textsuperscript{87}. In the former system a rapid intramolecular shift of the Tl-C bond around the C\textsubscript{5}H\textsubscript{5} ring is evident on the NMR time scale.

\[
\text{Me}_2\text{TlY} + \text{Et}_2\text{TlY} \rightarrow 2\text{MeEtTlY} \quad \text{(equ. 35)}
\]

Exchange of organic groups proceeds not only within the thallium compounds but with other organometallic compounds. Thus a second-order phenyl exchange occurs between Ph\textsubscript{2}TlBr and Ph\textsubscript{2}Hg in pyridine (equation 36), the kinetics having been examined by the use of c-labelled Ph\textsubscript{2}TlBr\textsuperscript{131}. The transition state (Fig.32) has been proposed on the basis of activation parameters and the simultaneous exchange of all the phenyl groups. For an apparently analogous exchange between (C\textsubscript{6}F\textsubscript{5})\textsubscript{2} TlBr and Ph\textsubscript{2}Hg (equation 37) a different, stepwise mechanism may be assumed (equation 38), since it is possible to isolate the intermediate Ph (C\textsubscript{6}F\textsubscript{5}) Hg from the product mixtures\textsuperscript{102}, continuation of electrophilic attack by an organothallium cation on the phenyl mercury bond and the liberation of the most electronegative group, C\textsubscript{6}F\textsubscript{5}\textsuperscript{-1}, would ultimately give Ph\textsubscript{2}Tl\textsuperscript{+}, which is precipitated as the bromide. The insolubility of this compound would drive the reaction to completion. The bromide (C\textsubscript{6}F\textsubscript{5})\textsubscript{2}TlBr similarly reacts with NaBPh\textsubscript{4} and Ph\textsubscript{3}Bi to give Ph\textsubscript{2}TlBr.

\[
\text{Ph*}_2\text{Tl}^+ + \text{Ph}_2\text{Hg} \rightarrow \text{Ph}_2\text{Tl}^+ + \text{Ph*Hg} \quad \text{(equ. 36)}
\]
Fig. 32

\[
\begin{align*}
(C_6F_5)_2\text{TlBr} + Ph_2\text{Hg} & \rightarrow \text{Ph}_2\text{TlBr} + (C_6F_5)_2\text{Hg} \\
(C_6F_5)_2\text{Tl}^+ + Ph_2\text{Hg} & \rightarrow \text{Ph}(C_6F_5)_2\text{Tl} + \text{PhHg}^+ \\
\text{Ph}(C_6F_5)\text{Tl}^+ + C_6\text{H}_5^- & \rightarrow \text{Ph}(C_6F_5)\text{Hg} \\
\text{Ph}_2\text{Tl}^+ C_6\text{F}_5^- & \rightarrow \text{Ph}(C_4F_5)\text{Hg} \rightarrow \text{Ph}_2(C_6F_5\text{Tl}) + C_6\text{F}_3\text{Hg}^+
\end{align*}
\]

Equation 38 (a, b and c)

Tetramethyltin can replace the organic group R in MeR\text{TlO}_2\text{CP}_{\text{t}}^+ in methanol solution, as shown in equation (39)^{80-132}. The reaction occurs only when R is Ph, CH\text{\,_2} = CH, CH\text{\,_2} =CHCH\text{\,_2} and PhCH=CH\text{\,_2} but not
when it is Et. There is no reaction if the solvent is dichloromethane or chloform. The reaction may proceed via a Me/O₂CPr\(^i\) exchange, giving Me₄SnO₂CPr\(^i\) and Me₂RTl. The latter compound then reacts with methanol, preferentially losing R which is more prone to the electrophilic attack of methanol. Alternatively, the methylation by Me₄Sn and the attack by methanol may be take place in a concreted fashion.

\[
\text{MeRTlO₂CPr}^i + \text{Me₄Sn} \xrightarrow{\text{MeOH}} \text{Me₂TlY} + \text{Me₃SnY} + \text{RH} \quad (\text{equ.39})
\]

\(Y = \text{O₂CPr}^i\) and/or OMe

(III) **ELECTROPHILIC TI-C BOND CLEAVAGE:**

Electrophilic attack on the carbon in the diorgano compounds can afford either monoorganothallium or inorganic thallium derivatives. Both dialkyl- and diaryl-thallium carboxylates react with mercury (II) carboxylates at room temperature to afford monoorganothallium dicarboxylates (equation 40)\(^{25}\). This reaction is used as the most convenient way of preparing monoalkylthallium compounds. Diarylthallium compounds react with thallium (III), lead (IV) or palladium (II) which leads to phenol or olefin synthesis constitutes a class of transformations useful for organic synthesis\(^{129,73}\).

\[
\text{R₂TlOAc} + \text{Hg(OAc)}₂ \rightarrow \text{RTl(OAc)}₂ + \text{RHgOAc} \quad (\text{equ.40})
\]

\(\text{R} = \text{Me, Ph}\)

Bromination of (Me₃YCH₂)₂TICI (Y = C, Si) (equation 41) has been used to obtain the monoalkylthallium compounds possessing uniquely high stability\(^{99,133}\). The reaction of Ar₂TlO₂CCl₃ with excess iodine in a chloroform solution (equation 42) serves as a procedure for the conversion of aromatic chlorides and bromides to iodides via Grignard reagents. The reaction may proceed stepwise, as shown in equation (43 and 44).
(Me₃YCH₂)₂TlCl + Br₂  ➔ Me₃YCH₂TlClBr + Me₃YCH₂Br

Y = C, Si

Ar₂TlO₂CCF₃ + I₂  ➔ 2ArI + TlO₂CCF₃

Ar₂TlO₂CCF₃ + I₂  ➔ ArTl(O₂CCF₃) + ArI

ArTl(O₂CCF₃)  ➔ ArI + TlO₂CCF₃

(equ.41)

(equ.42)

(equ.43)

(equ.44)

Treatment of (C₆F₅)₂TlY (Y = F⁻, Cl⁻, Br⁻, NO₃⁻, CN⁻, O₂CR⁻) with iodide anion in methanol, ethanol and water results in the formation of TlI₄ (under acidic condition, and C₆F₅H as shown in equation-45¹³⁴. One possible reaction mechanism is that the nucleophilic attack of iodide anion on thallium occurs, first, followed by the electrophilic cleavage of the Tl-C₆F₅ bonds. Alternatively, the reversed order of these processes is possible.

(C₆F₅)₂Tl⁺  ➔ excess I⁻/H⁺  ➔ 2C₆F₅H + TlI₄⁻

(equ.45)

(IV) REACTIONS WITHOUT Tl-C BOND CLEAVAGE:

There are known many reactions of diorganothallium compounds in which the Tl-C bonds remain intact. Most of these are trivial metathetical or adduct formation reactions. Here emphasis is put on some reactions of basis diorganothallium derivatives such as the hydroxide, alkoxides or: amide.

The reaction of diorganothallium hydroxides with acids to give salt-type compounds has already been described. With diphenols, aminophenols and o-phenylene-diamines, R₂TlOH (R = Ph, C₆F₅, Me,Et, Buⁿ, CH₂ = CH₂) give the paramagnetic complexes (Fig.33) which have been suggested by ESR spectra to be ion pairs of R₂Tl⁺ and semi-quinones or their NH analogues¹³⁵-¹³⁶. Similarly, R₂TlOH react with ascorbic acid to show the ESR signals attributable to the ion pairs of R₂Tl⁺ and paramagnetic anions of ascorbic acid, namely fig.34¹³⁷.

[53]
In the reaction of dialkylthallium amides and alkoxides with polychloromethanes such as dichloromethane and chloroform in the presence of cyclohexene, dialkyl-thallium chlorides, and dichloronocararane are formed suggesting the formation of the CCl₂ carbene\textsuperscript{138}. In another carbene reaction the alkoxide Et₂TIOBu\textsuperscript{1} and the polyhalogen compounds (Fig.35) give the fused lactams fig.36 (equation 46)\textsuperscript{139}.

Heterocumulene molecules such as CO₂, COS, CS₂PhNCX (X = O, S) insert into the Tl-O or Tl-N bond of Me₂TlOEt or Me₂TlNMe₂ to form stable adducts as shown in equation-47\textsuperscript{140-141}. Similarly, insertion reaction of SO₂ with Me₂TlOR (R = Et, Ph) affords, Me₂TlOS(O) or\textsuperscript{140}. The Tl-P bonded compound Me₂TlPPh₂ also reacts with PhNCX (X = O, S) in a manner similar to equation (47) to give the adducts, Me₂Tl-X-C(NPh)PPh₂\textsuperscript{142}. 
$X = O, Y = O, NPh; X = S, Y = O, S, NPh$

\[ \text{Fig. 35} \]

\[ \text{Fig. 36} \]

$Y = \text{CH}_2, R = H$

$\text{Me}_2\text{TI}-E + x = C = Y \rightarrow \text{Me}_2\text{TI} - X \text{C} = Y$

(equ. 47)

$X = O, Y = O, NPh; X = S, Y = O, S, NPh$

(III) **TRIOrganothallium Compounds:**

**Preparation and properties:**

The triorganothallium compounds, $R_3\text{TI}$ ($R = \text{Me, Et, Bu}^i, \text{Ph}$) are usually prepared by the reaction between the corresponding diorganothallium, halides and the organo-lithium or the Grignard reagents in diethyl ether or THF$^{25}$. An alternative and more convenient method of preparing $\text{Me}_3\text{TI}$ is the reaction between thallium(I) iodide and methyllithium in the presence
of methyl iodide (equation 48). This reaction may proceed via the formation of methylthallium (I), which either disproportionates (equation 49) reacts with methyl iodide (equation 50). The thallium formed in equation-49 may react with methyl iodide to generate methylthallium (I) (equation 54). Tri-ferrocenylthallium can also be prepared by a reaction similar to equation 48.

\[
\begin{align*}
2\text{MeLi} + \text{MeI} + \text{TlII} & \rightarrow \text{Me}_3\text{TI} + 2\text{LiI} \quad \text{(equ.48)} \\
3\text{MeTl} & \rightarrow \text{Me}_3\text{TI} + 2\text{Tl} \quad \text{(equ.49)} \\
\text{MeTl} + \text{MeI} & \rightarrow \text{Me}_2\text{TII} \quad \text{(equ.50)} \\
2\text{Tl} + \text{MeI} & \rightarrow \text{MeTl} + \text{TII} \quad \text{(equ.51)}
\end{align*}
\]

The tris (pentafluorophenyl) and tris (polychlorophenyl) derivatives are prepared from TICI₃ and the lithium or the Grignard reagents in one step. The polyfluorophenyl derivatives, R₃Tl (R = 2,3,4,5-2,3,4,6-C₆H₄F₄ or 2,4,6-C₆H₂F₃), can be obtained, although not isolated assuch but as dioxane or bipy, adducts, from the corresponding diorganothallium compounds either through reductive symme-trization (equation 52), decarboxylation or desulphonation (equation 53).

\[
\begin{align*}
3\text{R}_2\text{TIBr} + 2\text{Cu} & \rightarrow 2\text{R}_3\text{Tl} + \text{TIBr} + 2\text{CuBr} \quad \text{(equ.52)} \\
\text{R}_2\text{TIO}_2\text{YR} & \rightarrow \text{R}_3\text{Tl} + \text{YO}_2 \quad \text{(equ.53)}
\end{align*}
\]

(Y = C, S)

Dimethyl (ethynyl) thallium compounds are prepared from RCH = CH₂ (R = H, Me, Ph) and Me₂TlNH₂ or Me₃Tl. Dimethyl (cyclopentadienyl) thallium can similarly be obtained from cyclopentadiene and Me₃Tl.

Representative triorganothallium compounds and their physical properties are shown in Table-6.

Trimethyl- and triethyl-thallium decompose, sometimes explosively, when heated above 90°C in the latter case; they are also light
sensitive. When heated above its melting point, Ph₃Tl decomposes into thallium with the formation of some biphenyl⁸⁸. The dissociation energy for the first Tl-C bond of Me₃Tl has been estimated as 152 Kj mol⁻¹ from a kinetic study of pyrolysis in a toluene gas carrier flow system⁸⁹. This is smaller than the corresponding value for Me₃Ga (249 Kj mol⁻¹) and Me₃In (197 kJ mol⁻¹).

**TABLE -6**

**TRIORGANO THALLIUM COMPOUNDS.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C) or b.p.</th>
<th>Ref. (°C/mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃Tl</td>
<td>38.5</td>
<td>34</td>
</tr>
<tr>
<td>Et₃Tl</td>
<td>43/1</td>
<td>35</td>
</tr>
<tr>
<td>Bu₃Tl</td>
<td>74–76/1.6</td>
<td>36</td>
</tr>
<tr>
<td>Ph₃Tl</td>
<td>188–189</td>
<td>36</td>
</tr>
<tr>
<td>[(C₅H₅)Fe(C₅H₄)]₃Tl(C₆F₅)</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>(C₆Cl₅)₃Tl</td>
<td>139–141</td>
<td>38</td>
</tr>
<tr>
<td>(2,3,5,6-Cl₄C₆H₃, Tl</td>
<td>280</td>
<td>39</td>
</tr>
<tr>
<td>Me₂(C₂H₅)Tl</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Me₂(MeC=C)Tl</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>Me₂(PhC=C)Tl</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>Me₂TIC=CTlMe₂</td>
<td>-</td>
<td>41</td>
</tr>
</tbody>
</table>

**COORDINATION CHEMISTRY:**

Trimethyl thallium is a crystalline solid at room temperature which contains a polymeric three-dimensional framework constructed of Tl-Me...Tl bridges (Fig.37)⁹⁰. The compound is formally isostructural with Me₃In. The co-ordination for thallium is a distorted trigonal bipyramid with the three short bonds equatorial (2.22, 2.30 and 2.34 Å) and the two long bridge bonds apical (3.16 and 3.31 Å). The polymer dissociates into monomers in benzene solution and in the vapor phase.
Some solid complexes of the formula R₃TIL₂ can be isolated, although most of these complexes dissociate rather readily into their components at higher temperatures. Typical examples are shown in Table-7. The triorganothallium compounds are apparently much weaker acceptors than the corresponding indium and gallium analogues.

Other compounds containing a four-coordinate thallium atom are atmospheric complexes of the type (R₄TI). Typical examples are also shown in Table-7. All of those in the table except (Me₄TI) can be obtained by Simply adding the corresponding carbanion to Me₃TI C₆F₅TIBr or TICl₃. Even a six-coordinate complex, [(Bu₄N)₃ (C₆F₅)₆ TI] can be isolated in a similar way¹⁴³. The reaction of Me₃TI with the double ylide Me₃-P=N-PMe₂⁺CH₂ affords an interesting complex¹⁴⁴ (Fig.38). The reaction between (Me₄TI) and Me₃SnSnMe₃ gives the mixed atmospheric complexes (Meₙ(Me₃-Sn)₄+n TI) (n = 1,2,3)¹⁴⁶.

Fig. 37: The structure of Me₃TI in projection down the z-axis full lines represent ‘short’ Tl-C bonds and broken lines ‘long’ Tl-C bonds.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>M.P. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me$_3$TlPMe$_3$</td>
<td>27-28</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_3$TlNMe$_3$</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>(C$_6$F$_3$)$_3$TlbiPy</td>
<td>202-203</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>(C$_6$Cl$_5$)$_3$Tl(Py)$_2$</td>
<td>285</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Tl Compounds" /></td>
<td>76-80</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>MeTlCH$_2$PMe$_3$</td>
<td>53-54</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>Li(Me$_4$Tl)</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>[(Bu$_4$)$_n$(C$_6$F$_5$Tl)]</td>
<td>127</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>[(Bu$_4$)$_n$(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$-Tl]</td>
<td>142</td>
<td>41</td>
</tr>
<tr>
<td>10</td>
<td>K[(MeC=C)$_4$Tl]</td>
<td>-</td>
<td>42</td>
</tr>
</tbody>
</table>

**Fig. 38**

[59]
The other type of atmospheric complexes, \([R_3TlX]\) can be obtained by adding halide ions to the triorgano compounds. Typical examples include \([Me_3TlCN]\), \([Me_3TlFTlMe_3]\)\(^{145}\) and \([(C_6F_5)_3TlCl)\)\(^{143}\).

**REACTIONS:**

Trimethyl- and triphenyl-thallium react with mercury according equation 54\(^{25}\). On the other hand, both gallium and indium metals are known to react with \(Me_2Hg\), giving \(Me_3M\) (\(M = Ga, In\)) and mercury metal. The reaction of \(Me_3Tl\) with lithium has been used for the preparation of the tetramethylthallate as shown in equation 55\(^{146}\). The analogous reaction of \(Me_3Tl\) with potassium, however, has been reported to give a thallium(III) compound, \(K_2(Me_3Tl)\).

\[
2R_3Tl + 3Hg \rightarrow 3R_2Hg + 2Tl \quad \text{(equ.54)}
\]

\((R = Me, Ph)\)

\[
4Me_3Tl + Li \rightarrow 3Li(Me_4Tl) + Tl \quad \text{(equ.55)}
\]

Intermolecular exchange of methyl groups occurs in solution of \(Me_3Tl\), as is evident from the disappearance of \(Tl-H\) spin-spin couplings in the proton NMR spectra 147.

\((Me_3Tl)\)^{103} The polarographic reduction of \(PhTl\) in DMF at \(-30^\circ C\) is assumed to produce the anion \((Ph_4Tl)^-\) as the primary product\(^{122}\).

A dimeric transition state (Fig.39) may be assumed for this reaction. The methyl exchange rates observed in dimethyl ether or trimethylamine solution are slower than in benzene. This can be attributed to a weak complex formation between \(Me_3Tl\) and those donor solvents.

A rapid exchange of alkyl groups also occurs in mixtures of \(Me_3Tl\) and \(Et_3Tl\), generating the mixed compounds \(Me_2EtTl\) and \(MeEt_2Tl\)^{148}, Vinyl groups of \(Me_n(CH_2=CH_3-n)Tl\) \((n = 1,2)\) undergo a much more rapid exchange, presumably owing to a greater stabilization of the dimeric transition state by the bridging vinyl groups as shown in fig.40. The
cyclopentadienyl ligand in $\text{Me}_2(\text{C}_5\text{H}_5)\text{Tl}$, possibly bound to thallium in an $\text{SN}^1$ fashion, also undergoes a rapid intermolecular exchange, but no redistribution reaction of the compound is evident$^{87}$.

![Diagram of a molecule with Me groups and Tl atoms](image)

Fig. 39

![Diagram of a molecule with CH$_2$ groups and Tl atoms](image)

Fig. 40

Another redistribution reaction of synthetic interest is that between $\text{Me}_3\text{Tl}$ and $\text{Tl}[\text{W(CO)}_3\text{Cp}]_3$ to give $\text{Me}_2\text{Tl}[\text{W(CO)}_3\text{Cp}]$ equation $56^{130}$.

$$2\text{Me}_3\text{Tl} + \text{Tl}[\text{W(CO)}_3\text{Cp}]_3 \rightarrow 3\text{Me}_2[\text{W(CO)}_3\text{Cp}] \quad (\text{equ.} 56)$$
Exchange of organic group occurs also with other organometallic compounds, the typical example being show in equation 57\textsuperscript{25}. Trimethylthallium reacts with Hg(SiMe\textsubscript{3})\textsubscript{2} to give a tris(silyl) thallium compounds as shown in equation 58\textsuperscript{25}.

\[ \text{Ph}_3\text{TL} + 3\text{Bu}^n\text{Li} \rightarrow \text{Bu}^n\text{3TL} + 3\text{PhLi} \quad \text{(equ. 57)} \]
\[ 2\text{Me}_3\text{TL} + 3\text{Hg}[\text{SiMe}_3]_2 \rightarrow 2\text{TL}[\text{SiMe}_3]_2 + 3\text{Me}_2\text{Hg} \quad \text{(equ.58)} \]

One of the three organic groups of triorgano-thallium is cleaved with great ease by the action, of various electrophiles, including acids and halogens, as typically shown in equations 59,61\textsuperscript{25}. Protolysis of R\textsubscript{3}TL with water or alcohols does not proceed further than the R\textsubscript{2}TIY stage (Y = OH\textsuperscript{−}, OR\textsuperscript{−}). The reaction of Me\textsubscript{3}TL with cyclopentadiene and phenylacetylene to give the interesting mixed compounds has already been reported. Similarly, the reaction between Me\textsubscript{3}Tl and diazomethane\textsuperscript{149} or that between Et\textsubscript{3}Tl and nitromethane\textsuperscript{150} gives the largely ionic compounds (Me\textsubscript{2}Tl)\textsubscript{2}CN\textsubscript{2} or Et\textsubscript{2}Tl(CH\textsubscript{2}NO\textsubscript{2}), respectively. The latter has been indicated by vibrational spectroscopy to contain Tl-O rather than Tl-C bonding, as shown in fig.41. The reaction of R\textsubscript{3}Tl(R = Me, Et) with MH(CO)\textsubscript{3}Cp, (M=Mo,W) (130), B\textsubscript{10}H\textsubscript{14} (151) or Et\textsubscript{3}MH (M = Si, Ge) (25)affords the thallium-metal bonded compounds Me\textsubscript{2}Tl[Me(CO)\textsubscript{3}], (Me\textsubscript{2}Tl) [Me\textsubscript{2}Tl(B\textsubscript{10}H\textsubscript{12})](Fig.42) or Tl(MeEt\textsubscript{3}).

\[ \text{Me}_3\text{TL} + \text{HCL} \rightarrow \text{Me}_2\text{TLCl} + \text{CH}_4 \quad \text{(equ. 59)} \]
\[ \text{R}_3\text{TL} + \text{ClN}_3 \rightarrow \text{R}_2\text{TLN}_3 + \text{RCl} \quad \text{(equ, 60)} \]
\[ (R = \text{Me, Et}) \]
\[ \text{Ph}_3\text{TL} + \text{Se(SeCN)}_2 \rightarrow \text{Ph}_2\text{TLSeCN} + \text{PhSeCN} + \text{Se} \quad \text{(equ.61)} \]
Insertion of $\text{SO}_2$ and $\text{SO}_3$ into the one Tl-C bond of MeTl occurs as shown in equation 62$^{140,152}$. The reaction of $\text{Et}_3\text{Tl}$ with oxygen in octane initially afford, $\text{Et}_2\text{TlOOEt}$, which subsequently decomposes into $\text{Et}_2\text{TlOH}$ when heated at $50^\circ\text{C}$$^{153}$. Similar, $(\text{Ph}_2\text{Tl})_2\text{O}$, phenol and biphenyl have been found in the products of a slow oxidation of $\text{Ph}_3\text{Tl}$ with dry oxygen$^{25}$. The carbene: $\text{CCl}_2$ inserts into the Tl-C bond of $\text{Et}_3\text{Tl}$ to yield stable intermediate$^{63}$, which undergoes chlorine abstraction as shown in equation 63$^{154}$.

$$\text{Me}_3\text{Tl} + \text{SO}_n \rightarrow \text{Me}_2\text{TlO}_n\text{SMMe} \quad \text{(equ. 62)}$$

(n = 2,3)

$$\text{Et}_3\text{Tl} + :\text{CCl}_2 \rightarrow \text{Et}_2\text{TlCCl}_2\text{Et} \rightarrow \text{Et}_2\text{TlCl} + \text{CHCl} = \text{CHMe} \quad \text{(equ. 63)}$$
Very recently few more triorgano, diorgano and monoorgano thallium compounds have been synthesised and characterized which are mentioned here.

\[ \text{TlCl}_3\text{L}_2 \quad (\text{L}=\text{OPPH}_3, \text{2-HMPA, Pyridine, N-oxide, 2, 3- or 4- Methyl pyridine N-oxide, 2-Mercapte Pyridine N-oxide, DMSO}) \] were prepared and characterised by elemental analysis the solids are monomers and non electrolyte in \( \text{CH}_3\text{OH} \) solution. Possible, molecular structure were deduced from \(^1\text{H} \) NMR and IR spectra, with particular attention on the (Tl-I) and (Tl-O) stretching modes.

The reaction of PhTlCl\(_2\) and P-MeC\(_6\)H\(_4\).Tl(O\(_2\)CCF\(_3\))\(_2\) with NaS\(_2\)CXR gave 40% RTl(S\(_2\)CXR)\(_2\)\(^{156}\).

Phenylthallium bis trifluoroacetate (PhTlX\(_2\)) reacts with excess of anisole at 70-80\(^\circ\) yielding mainly the three isomeric anisyl phenyl thallium(III) compounds (o-, m-, p- AnTlX\(_2\)).

Monoanisyl thallium(III) derivatives (o-, m-, p-AnTlX\(_2\)) were obtained only in the presence of excess of HX. The slow trans thallation reaction of chlorobenzene requires the presence HX leads to the o-, m-, p- ClC\(_6\)H\(_4\)TlX\(_2\) isomers rather than the diaryl thallium (III) compounds. The three isomeric anisyl phenyl thallium (III) compounds readily undergo exchange and isomerization reactions with anisole in the presence of HX. Similar processes were observed with C\(_6\)H\(_5\)Cl but only in the presence of HX (p-chlorophenyl) phenyl thallium (III) trifluoroacetate is less reactive both towards anisole and chlorobenzene\(^{157}\).

\(^{13}\text{C}\) and \(^1\text{H} \) NMR coupling constants and chemical shifts were reported for TlR\(_2\)X and TlRX\(_2\) (R = Alkyl, Cycloalkyl). The effects of solvents and anion changes were minor. The major factors influencing J(Tl-C) and J(TIH) is the number of R groups. The ratios of analogous
coupling in TlR₂X and TlRX₂ are close to the value of 1: 2.2158.

Transmetallation of RTL (O₂CCF₃)₂ (R = Aryl) with B₂H₆ in THF gave organoboron compounds\textsuperscript{159}.

Diorganothallium (III) complexes (R = Me (II), Et, Ph) were prepared by condensing the schiff base- of 2,6-diacetylpyridine with (H₂NCH₂)₂.

\textsuperscript{13}C NMR signals of the ligand C atoms were splitted by spin-spin coupling with Tl nucleus. It shows the longest \textsuperscript{1}J(Tl-Me) and \textsuperscript{2}J(Tl-Me) values among dimethylthallium (III) compounds\textsuperscript{160}.

Phenyl thallium (trifluoroacetate) forms molecular adducts with various N, O, S and P donor bases e.g., piperidine, 1, 10-piperidine, 1,10-phenanthroline. IR of the adducts suggest that both the trifluoroacetate groups are unidentate\textsuperscript{161}.

\textit{L}TlCl (\textit{L} = octaethyl and tetraphenyl propyrines) reacted with R\textit{MgBr} (R = Me, Ph, 4-MeO\textit{C₆H₄}, C\textit{₆}F\textit{₄}H, C\textit{₆}F\textit{₅}) to give metal-carbon O-bonded LTlR. Each neutral complex was characterized by \textsuperscript{1}H NMR, IR and UV - visible spectroscopy and electro-chemistry, spectroelectrochemistry and ESR were used to characterize each singly ionized and reduced complex. The singly and doubly oxidized Tl (III) complexes containing O\textsuperscript{3} bonded alkyl or aryl groups were stable\textsuperscript{162}.

TlMe\textsubscript{2}L, (L=2 (pyridine-2- yl) imidazolato, 2-(pyridine-2- yl) (benzimidazolato) and (TlMe\textsubscript{2})\textsubscript{2}L \textsuperscript{1} (L \textsuperscript{1} = 2,2\textsuperscript{1}-bi-imidazolato,2,2\textsuperscript{1} -bibenzimidazolato) are monomeric in CHCl₃). Complexes of stereochemistry (TlMe\textsubscript{2}L\textsuperscript{2})NO₃ (L\textsuperscript{2} =1,10 -phenanthroline, 4,4 -diethyl-2-2\textsuperscript{1} -bipyridine-M-methyl 2-(pyridinc-2-yl) imidazole bis (pyridine-2-yl) methane (L\textsuperscript{3}), bis (N-methyl-imidazole-2-yl) methanol, (TlMe\textsubscript{2}L\textsuperscript{4} (OH)\textsubscript{2}NO₃. (IL\textsubscript{4} = 1,2\textsuperscript{1}, 6,2\textsuperscript{- ter. pyridine) and (TlMe\textsubscript{2})\textsubscript{3} (L\textsuperscript{3})\textsubscript{2} (NO₃)\textsubscript{3} (II. L\textsuperscript{5} = 4,4\textsuperscript{1}, 4\textsuperscript{-trimethyl-2,2\textsuperscript{1}. 6\textsuperscript{1},2\textsuperscript{-ter pyridine) prepared their H\textsuperscript{1}NMR spectra in Mass indicate coordination of the N donor ligand to Tl. The
crystal and mole structure of I, II and [(TlMe₂L³₃(NO₃))₂ III were determined by single crystal X-ray diffraction, at 295K and refined by block. Diagonal least squares to R 0.061. The complexes have linear or streightly bent C-Tl-C groups, with weak Tl-N and/or Tl-O interaction in approximate equatorial planes first contains tridentate L⁴ and has a TIC₂N₂O₂ coordination environment with C-Tl-C₂ opposite L⁴. It has two TlMe₂L⁵ groups linked by a TlMe₂(NO₃)₃ groups to give the complex with a 2 fold axis TIC₂N₂O₂ and TIC₂O₆ coordination Environment III has a dimeric centrosymme. Structure with NO₃⁻ groups weakly linking. The TlMe₂L³ groups to form the molecule with TIC₂N₂O₃ co-ordination environment¹⁶³.

The compounds were prepared and spin-spin coupling constants between the Tl and H nuclei were measured. The Tl(III) ions are more strongly co-ordinated by the O atom of quasicylindrical crown ethers than by 18-crown-6. The molecular structure of (Me₂Tl₂L)ClO₄.

(L = 1, 4, 7, 18, 21, 24-henaonaperhydro) was determined by X-ray crystallography.

The Tl(III) ion was situated essentially in the centre of the crown ethers¹⁶⁴.

The complexes Me₂Tl(Me₂P₂) are formed on reaction of Me₂TlII with Ag (R₂P₂) in non-Ag-solution. The complex Me₂Tl(Me₂P₂) is dimeric in C₆H₆ but osmomembric data of Me₂Tl (Me₂P₂) in C₆H₆ show presence of a monomer dimer¹⁶⁵.

R₃TIL (R = 3,5-H₂C₆F₃, L = 1,4-dioxane) were prepared from TlCl₃ and LiR or from Bu₄M⁺,R₄Tl and BHF₄ with subsequent addition of L.L. displacement by neutral ligands gave R TIL¹ (L¹ = OPPH₃, Py (Ph₂P)₃(H₂). The complexes were characterised by elemental analysis, conductivity and IR spectral data¹⁶⁶.

RCOCH₂Tl (C₆H₄Me-p) OOCF₃, IR = PH substituted Ph,tert.but.)
were prepared and characterized by $^1$H NMR and $^{13}$C NMP serve as anion equivalent in TiCl$_4$-mediated aldol condensations. Metal-Metal exchange with iodosylbenzene or Pb(OAC)$_2$ gives $\alpha$-nucleophilic substitution derivations from the formed $\alpha$-keto carbonium ion. The corresponding p-CH$_3$C$_6$H$_4$COCH$_2$ PbC$_6$H$_4$OCH$_3$-p(OAC)$_2$ and (p-CH$_3$OC$_6$H$_4$COCH$_2$)$_2$ Hg analogous were prepared and show likely to behave as either enolate anion or $\alpha$-keto carbonium ion$^{167}$.

The complex was prepared from tridecanil-18-crown-6 and dimethyl thallium (III) perchlorate. The mole-structure has been determined by single crystal X-ray crystallography.

The O$_6$ hexagon of the crown ether is planer without 0.05 Å and the decline moiety apparently constrinct acylinder wall the linear dimethyl thallium (III) ion penetration into the centre of the O$_6$ hexagon with six equal Tl-O bonds and the decline walls are in contact with Mg-groups of the dimethyl thallium(III) ion$^{168}$.

Structural studies on highly anisotropic organo-thallium chelates of the type RTILX (where R is an alkyl, aryl or a halo atom and L is a highly mesotropic bidentate ligand) was made. The dipole moments of ligands and chelates at 30$^0$C in a nonpolar solvent like cyclohexene.

The orcelle of moments was made for a C$_2$V symmetry of ligands molecules. The geometry was found to be squareplanar of organothallium (III) chelates$^{169}$.

The reaction of heterocyclic thiolic derivative HC (Thiophenol-2-mercapto-pyridine etc.), with diethyl thallium(III) hydroxide gives Me$_2$TlCl. The structure of dimethyl (1-oxido pyridinium-2-thiolato) thallium(III) has been determined by X-ray analysis in this compound. The thallium atom is six co-ordinate if, weak bridging interaction are considered, in lattices with polymeric chains, spectroscopic data of the complexes, ($^1$H, $^{13}$C, $^{288}$Tl NMR, IR and Raman) are discussed in order to
determine possible structural spectroscopic correlation\textsuperscript{170}.

Benzyl and phenyl cyclopentesdienyl cyclopentadiene react with thallium ethoxide in EtOH to give the corresponding benzyl and phenyl cyclopentadienyl thallium compounds in excellent yield. These reagents are air stable for brief periods have extended shelf-lives and are superior stating interval for the synthesis of a variety of cyclopentadienyl metal compounds\textsuperscript{171}.

Reaction of Cd(CF\textsubscript{3})\textsubscript{2}glym with TlPhCl\textsubscript{2} gives 87\% TlPh(CF\textsubscript{3})\textsubscript{2} after 72 hrs. If TlPh(OAC)\textsubscript{2} is the thallium source, TlPh(CF\textsubscript{3})\textsubscript{2} is generated in 2 hrs. However, the isolated yield is lower. Reaction of Cd(CF\textsubscript{3})\textsubscript{2}glym with Tl(OAC)\textsubscript{3} gives 46\% T1(CF\textsubscript{3})\textsubscript{2} OAC. The possibility of utilizing (trifluoromethyl thallium(III) species in oxidation trifluoromethylation reaction was tested by using several lone valent metallic species as substrates\textsuperscript{172}.

Treating C\textsubscript{5}H\textsubscript{2}Me\textsubscript{4} (C\textsubscript{5}H\textsubscript{6}= cyclopentadiene) with B\textsubscript{4}Li in THF-benane and then with Me\textsubscript{2}SiRCl (R#Ph,CH\textsubscript{2}Ph) Gave 68-91\% C\textsubscript{5}HMe\textsubscript{4}SiMe\textsubscript{2}R(SameR),reaction of the latter compound with TlOEt, in Et\textsubscript{2}O gave 63-71\%. The structure of was determined by X-ray crystallography which showed that it exist as polymeric chains with metallocene sandwhich type structures offording greater stability\textsuperscript{173}.

Disproportionation of RC\textsubscript{6}H\textsubscript{4}T1CO\textsubscript{2} (R') (I, R = H, 4-Me, 4Et, 4-Me\textsubscript{2}CH, 4-Me\textsubscript{3}C, 4-pentyl, 4-Ph, 4-MeO, 4-EtO, 4-PhO, 4-Me\textsubscript{2}N, 4-F, 4Cl, 4-Br, 2-HOOC, R' = CF\textsubscript{3}, R' = H, R - Cl\textsubscript{3}, CH\textsubscript{2}Cl, H, Me, CHMe, Ph, RC\textsubscript{6}H\textsubscript{4}= -Naphthyl, R' = CF\textsubscript{3})in acetone at reflux gave (RC\textsubscript{6}H\textsubscript{4})\textsubscript{2}T1O\textsubscript{2}CR'. The reaction failed in the case of I (R = 4-Me\textsubscript{2}N, R' = CH\textsubscript{3} R = H, R' = Ph). The reaction occurs smoothly under aired condition when the R substituents is electron-withdrawing or moderably electron-donating the rate of reaction depends on the carboxylate group\textsuperscript{174}.

Triorganothallium reagents, easily prepared in situ form
organomagnesium derivatives react readily and chemoselectively with acid chloride to give high yield of alkyl and Ph Keton. Selective group trans, was accomplished in the case of a mixed triorganothallium derivatives. Thus treatment of Me₂TlCl: CHp with RCoCl (R = methyl) in Et₂O at 20° rapidly gave RCO; CPh in 73-77% yield.¹⁷⁵

Alkylation of TIBr with primary bromoalkanes RBr (R = Et, Pr, Bu, isopentyl, hexyl) in presence of Li and is 0° afforded (After HBr Decomp. of R₃Tl) R₂TIBr in 44-60% yields. Secondary bromoalkanes were unsuccessful alkylating agents affording only metallic Tl.¹⁷⁶

Reaction of Me₃(COPHCMMe₃) with R₃Tl (R = Et, Bu) gave Me₃CCOP(TlR₂)CMMe₃I. Reactions of I (R = Et) with (Me₃CH₃)GeCl and (Me₂CH₂)₂PCl gave unstable Me₂CP: (COR¹) Me₃ (R¹ - Ge(CHMe₂)₃ p[(CHMe₃)₂]¹⁷⁷.

The reaction of enolacetate with Tl alkoxides gave Tl alkenyl oxides e.g. Me₂C: CHOAC reacted with EtOTl and EtOTlMe₂ to give Me₂C; CHOTl(II) and MeC; CHOTlMe₂, resp. II reacted with Et₃SiCl to give Et₃SiOCH; CMe₂.

The desproportionation of PhTl(O₂CR) I (R = CF₃, CC13, CH₂Cl, H, Me, Me₂CH, Ph) to Ph₂TlO₂ II in refluxing acetone was studied. The case of disproportionation is dependent on the strength of the corresponding acid. Thus I (R = CF₃) gave and 5.6%, II (R = CF₃) in O. Sh where I (R = Me₂CH) gave 25.9%. II (R = Me₂CH) in 20hrs. Acetone also reduced Tl(III) salts to Tl(I)salts.¹⁷⁸

**AIM SCOPE OF THE PRESENT WORK:**

The organometallic chemistry of main group elements of the periodic table has attracted the attention of a large number of workers in the recent years and many such compounds have found wide industrial¹⁷⁹-¹⁸⁵ and biological importance¹⁸⁸-¹⁹¹. A large number of publications¹⁹²-²³²,
and biological importance\textsuperscript{188-191}. A large number of publications\textsuperscript{192-232}, reviews\textsuperscript{233-241} and books\textsuperscript{242-243} have appeared on the subject. The special attention has been paid to metals of group IVi.e., organosilicon,-
germanium, -tin, and lead derivatives of the general formula R\textsubscript{n}M\textsubscript{X}\textsubscript{4-n}, (where R = alkyl, aryl and X an electronegative group, n = 1 --- 4). Various aspects of the chemistry of these sp\textsuperscript{3} hybridised tetrahedral compounds are reported and in an effort to utilise the vacant d-orbitals of the metal atoms for sigma type bonding, their interaction with -N, -O, -P, -S donor bases have been examined and a large number of stable coordination complexes have been isolated. IR, NMR, Mossbauer, X-ray and several other physicochemical techniques have been utilised to establish their structure and assign a possible geometry to the products. Solution studies using dipole moment\textsuperscript{244-245}, conductometric, potentiometric and spectrophotometric techniques have been made and the composition of the complex species in the solution has been established.

Comparative less amount of work is reported on the elements of other main groups of periodic table. Recently substantial amount of work has been reported on organo-antimony\textsuperscript{229-230}, -bismuth\textsuperscript{231}, -selenium\textsuperscript{232} and -tellurium\textsuperscript{246} compounds. The chemistry of the third main group elements Al, Ga, In and Tl has been less worked out due to extreme sensitivity of organoaluminium compounds to atmospheric oxygen and moisture\textsuperscript{247}. The less availability of Ga and In compounds and their high cost forbid detailed investigation on these elements. Organothallium(III) derivatives have been comparatively studies in greater detail and a number of derivatives of the formula R\textsubscript{n}TlX\textsubscript{3-n} have been synthesised and characterised\textsuperscript{248}. Some of these are reported to possess good antimicrobial properties\textsuperscript{248}. Similar techniques IR, X-ray etc. have been employed for establishing their structure. The molecules so synthesised are sp
hybridised and are capable of interaction with Lewis bases to yield
tetrahedral sp$^3$ and trigonal bipyramidal derivatives of sp$^{3}$d hybridisation.
This aspect of this chemistry is less studied$^{248}$ specially with bidentate
and tetradeionate Schiff base ligands.

In this present thesis work the acceptor properties of PhTlCl$_2$ and
Ph$_2$TlCl with various bidentate and tetradeionate Schiff base ligands have
been studied.

The chapters in this thesis have been organised to provide an easy
access to the formation available on the topic treated. The first two
chapters deals with the general introduction of organothallium, materials
used and experimental techniques used to characterised the synthesised
complexes.

In the third and fourth and fifth chapters the reaction of PhTlCl$_2$
and Ph$_2$TlCl with various Schiff base ligands, to synthesis and
characterise various molecular adducts have been discussed.
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