

## CHAPTER I



### INTRODUCTION

Over the last few years there has been a rapid growth in the literatures of inorganic and organometallic chemistry. Organothallium chemistry, while it has undergone a considerable expansion, has received proportionally less attention than many other areas of organometallic chemistry, namely organozinc, organomagnesium, organolithium and so on. This relative lack of interest in the chemistry of organothallium compound probably stems from the fact that they have little or no industrial significance. Though situation is improving there still are many large and obvious gaps in the chemistry of organothallium compounds.<sup>(1-3)</sup>

The potential of thallium as a synthetic intermediate in organic chemistry was realised many years ago. Between 1942 and 1947 Menzies and coworkers in Bristol published a series of papers in the Journal of the Chemical Society under the title "Application of Thallium Compounds in Organic Chemistry", in which the organothallium compounds were studied intensively. Later several groups extended to include the reaction and mechanisms of such organothallium compounds.<sup>(4,5)</sup>

### Thallium and Its Isoelectronic Ions

Thallium is a non-transition element of the group IIIA in the Periodic Table. The elements of this group show an ability to a marked degree in forming stable compound in which valency of the element is two unit less than the group valency. This is often called the "inert pair" valence state because of its association with the inertness of the  $ns^2$  electrons.

The divalent mercury ion has an isoelectronic configuration ( $5d^{10}6s^2$ ) with the thallium(III)ion. The mercury atom contains one pair of s electrons and the inner orbitals with 18 electrons which completely occupy the s-, p- and d-orbitals of the atom of mercury are never used in bond formation. Hence mercury possesses two valency states different from the other transition elements.

The complete inertness of the inner orbitals of the mercury atom is a characteristic property of a non-transition element which is shown by thallium and others in the same group.

Some properties of thallium and mercury atoms <sup>(6)</sup> are listed below.

	Hg	Tl
Atomic number	80	81
Electronic configuration	$5d^{10}6s^2$	$5d^{10}6s^26p^1$
Atomic radius ( $\text{\AA}$ )	1.44	1.55
Ionic radius ( $\text{\AA}$ )	1.10 Hg(II)	0.95 Tl(III)
First ionization potential (eV)	10.43	6.11

	Hg	Tl
Second ionization potential (eV)	18.65	20.32
Third ionization potential (eV)	-	29.27

The knowledge of the **existence** of the isoelectronic pair of certain ions is useful especially when the access to the understanding of the chemistry of a certain compound is difficult to obtain. It is a common practice in such a case to carry out a comparative study of physical and chemical properties of compounds of the isoelectronic pair. Pieces of informations are collected, compared and analysed, results of which, hopefully, should explain the chemistry of the compounds **under study** to a certain extent if not the whole.

Among the compounds of the two metals, thallium and mercury, the organometallic ones, are of interest because of the usefulness and because of a large volume of informations awaits to be filled. Though, many aspects of the organometallic compounds of thallium and mercury have been the subject of interest of several groups of researchers lately, there are still **more** to be investigated. This is due to the complexity of the chemistry of the organometallic compounds itself together with the large number of compounds that can be formed from the combination of the metals with the ligands.

#### The Organometallic Compounds of Thallium and Mercury

The first four ionization potentials of thallium atoms <sup>(7)</sup> are respectively 6.11, 20.32, 29.27 and 50.50 eV. Mono-, di- and tri-valent species may therefore be expected. It can easily be

shown that divalent thallium will be unstable towards the dissociation to Tl(I) and the disproportionation to Tl(I) and Tl(III)<sup>(3)</sup>

The Tl(III) ion is quite a powerful oxidizing agent in an aqueous solution. The reduction potential of a few of known oxidizing agents are shown below.<sup>(7)</sup>



It is known that Tl(III) ion has the  $5d^{10}$  configuration, but the relatively low-lying excited configuration  $5d^9 6s^1$  exists as well. In a cubic environment, mixing of these states is not allowed, on the contrary, it is in a tetragonally distorted environment. Hence the most favorable electronic configuration can be written as  $d^{10-\delta} s^{\delta}$ . In particular, if the two electrons that are normally in a  $d^{10}$  ion, occupying the  $dz^2$  orbital are placed in a  $(1/\sqrt{2})(dz^2-s)$  hybrid orbital along the xy-plane with the  $(1/\sqrt{2})(dz^2+s)$  orbital empty, the ligand in the xy-plane will be repelled more than those along the z-axis. A regular octahedral will therefore be distorted by lengthening the bonds in the xy-plane and shortening those in z-direction. Hence a certain favoring of linear coordinate would be expected, and the linear diorganothallium ion, eg. dimethylthallium halides, is one of the least reactive organothallium species.

At present, compounds in the  $\text{RTlX}_2$ ,  $\text{R}_2\text{TlX}$ ,  $\text{R}_3\text{Tl}$  and  $\text{RTl}$  series, which R represents an alkyl or aryl groups and X represents the anion such as acetates and halides are known. Compounds

of the first two types have received the greatest attention. Known compounds of  $R_2TlX$  and  $RTlX_2$ , of which the R groups include alkyl, aryl or alkenyl have been synthesized.<sup>(1)</sup>

Among the organothallium known at present, the compounds of the type  $R_2TlX$  are the most stable. In fact, they are at one time believed to be the only stable organothallium compound. They are unaffected by water or oxygen and insoluble in organic solvents with the exception of pyridine, dimethylsulfoxide and dimethylformamide. They are difficult to identify and decompose only above  $200-300^\circ C$ . The  $R_2TlX$  compound in many ways resembles both the isoelectronic diorganomercury compounds and the corresponding thallium (I) derivatives.

As far as the organometallic compounds of the transition metals are concerned, the organomercury compounds are the most stable ones. They are inert to oxygen, oxidizing agent, water and to a certain degree to weak acid. Moreover, they do not react with most oxygen containing organic compounds and are fairly inert to alkyl halides.

These properties of mercury which are similar to those of thallium, are in sharp contrast to the organometallic compounds of sodium, lithium, magnesium, zinc, aluminium and so on. Mercury combines with a wide range of organic molecules. There are only three basic types of organomercury compounds, fully symmetric  $R_2Hg$ , the unsymmetric  $RHgR'$  and the organomercury salts  $RHgX$  in which R represents alkyl, aryl or alkenyl groups and X represents anion i.e.,

halides, acetates etc.

In the work reported in this thesis the diphenylthallium bromide and phenylmercury bromide were synthesized. As these compounds,  $\text{Ph}_2\text{TlX}$ ,  $\text{PhHgX}$ , can act as the electron acceptors, and they form complexes with amines, ether, halide ions and other carbanions. The ease of the formation of such complexes were observed via the reactions between the two organometallic compounds and 1, 10-phenanthroline and pyridine. The behavior of the resulted compounds were characterized. Conventional physical properties (IR, NMR, UV), conductivity, thermal property, molecular weight together with some chemical properties were investigated. These results are useful since they not only give the insight of the chemistry of such complexes but also make possible for a comparative study of the organothallium and organomercury compounds.