Thallium: Inorganic Chemistry

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1 INTRODUCTION

The metallic element thallium, atomic number 81 (relative atomic mass 204.38), is the heaviest member of group 13 of the periodic table. The ground-state electron configuration is $[Xe]4f^{14}5d^{10}6s^26p^1$.

Thallium chemistry was divided into two independent fields nine years after the discovery of the element, with the first preparation of diethylthallium chloride. Organothallium chemistry thus became an independent and fruitful counterpart to the inorganic chemistry of this element (*see Thallium: Organometallic Chemistry*).

The best-known property of this element to the layperson is its toxicity (*see Metal Ion Toxicity*); indeed, the use of thallium as a 'rat poison' was the most important application for decades. Thallium appeared to be merely an exotic *Trace Element*, seeming to merit little attention from the scientific community. As a result, there are only a few books[1-7] specializing in the inorganic chemistry of thallium, and most of the recent papers have been published by a small group of research workers. However, subject areas such as coordination chemistry, redox reactions with inorganic and organic substrates (*see Electron Transfer in Coordination Compounds*), solid structures and *High-Temperature Superconductivity*, metal–metal bonds (*see also Polynuclear Organometallic Cluster Complexes*) should be mentioned as examples where the inorganic chemistry of thallium is ongoing (though, some of these fields are certainly related to the organometallic chemistry of thallium). NMR spectroscopy is the primary physical method used in studies of thallium chemistry. The thallium nuclei ^{205}Tl and ^{203}Tl both have spin $I = \frac{1}{2}$ and are suitable for NMR spectroscopy, the absolute sensitivities with respect to ^{1}H NMR being 0.13 and 0.055, respectively. Furthermore, the observation of large multibond coupling constants in many thallium compounds allows structural information to be obtained from ^{1}H or ^{13}C NMR spectra, which may be recorded routinely in most laboratories.

1.1 Discovery and History

The element thallium was discovered relatively recently. In 1861, the British chemist William Crookes attributed a bright green line in the emission spectrum of some residues from a sulfuric acid plant to a new element. However, the Frenchman C. A. Lamy was the first to obtain thallium in any quantity. Crookes named his discovery after the 'Latin *thallus*, a budding twig – a word that is frequently employed to express the beautiful green tint of young vegetation'.[8] However, his original idea that thallium was a member of the sulfur family was short lived, and on the basis of its chemical and physical properties Mendeleev rightly placed it in group 13.

1.2 Occurrence and Distribution[2]

Thallium is a relatively abundant element and is widely distributed in nature. Estimates for the abundance of thallium in the earth's crust range from 0.3 to 3 ppm, though about 1 ppm is the generally accepted value. The wide distribution is due to several factors, the most important being the isomorphous replacement of K^+ in potassium feldspars and micas (silicates) by Tl^+. Additionally, thallium sulfide is found in sphalerite, galena, pyrite, and other sulfide ores. Thallium also behaves as an accessory to manganese in geological processes; for example, manganese oxides and deep-sea manganese nodules may be enriched in thallium to levels of 0.01% and 0.1% respectively. The few existing thallium-based minerals such as lorandit ($TlAsS_2$), crookesite (($Cu,Tl,Ag)_2Se$), and avicennite (Tl_2O_3) are very rare and have no commercial importance.

In the aquatic environment, thallium is present as Tl^I at a level of about 0.01 ppb in seawater. Tl^I is also strongly adsorbed by soils.

Of the total quantity of thallium mobilized by industry amounting to about 1600 tons in the United States during 1977, 70% was reemitted to the environment either in the form of air pollution (15%) or as solid waste (55%). Coal burning power plants account for the greater part of this air pollution, but the smelting of copper, zinc, and lead may also result in concentrated local emissions. The remaining 30% is incorporated in the final products, though usually at a lower level than in the raw materials.[2]

1.3 Production and Use

Thallium is manufactured commercially as a by-product from the roasting of pyrite ores, from sulfuric acid plants, and from the smelting of lead, zinc, and copper. The global

production is estimated to be in the range of only 13–16 tons per annum during the last two decades.[9-12] Volatile compounds of thallium are gaseous at the temperature of these smelting operations and are collected in the flue dust in the form of oxides or sulfates. In a typical procedure for the recovery of thallium, the flue dust is first boiled in sulfuric acid, after which the dissolved thallium in the filtrate is precipitated by the addition of zinc. Impurities such as zinc, copper, lead, cadmium, and indium may be removed by dissolving the metal in dilute sulfuric acid and precipitating the trace elements with hydrogen sulfide. Thallium is recovered from saturated solutions of Tl_2SO_4 by electrolysis at low current density. The raw product is compressed into blocks and melted at 350–400 °C under a layer of oxalic acid or in a stream of H_2 gas. The metal obtained may be protected with a coating of paraffin or stored under glycerol or petroleum.

The commercial applications of thallium are limited, and at present there are no bulk consumers. Consumption of thallium in the United States has fallen steadily from 1.4 tons in 1987 to 0.3 tons in 1998.[11] Previously, though, over a period from 1920 to 1970, several tons of thallium were used each year in the form of insecticides and rodenticides. However, many countries have terminated its use because of accidental or secondary poisoning of wild animals and birds; even children have been known to be severely poisoned as a result of ingesting thallium-containing bait.

There are several uses of thallium in the optical industry. For example, mixed TlBr–TlI crystals may be used as optical elements for IR applications. Thallium is also added in small amounts to glass to increase the density and refractive index. For example, patents have been filed for thallium-containing glasses for use as sealants or coatings for semiconductor elements.

In the field of electronics, thallium oxysulfide is used in the so-called 'Thalofide cell', which has sensitivity for low-intensity, long-wavelength light better than that of the selenium cell, and thus has important military and research applications. Thallium-activated NaI or NaCl crystals are used in the photomultiplier tubes present in some scintillation counters. Future uses of thallium in this field can be expected because of its incorporation in thallium-based high-temperature superconductors.

Some of the alloys of thallium have found applications as a result of their unique properties. For example, the Tl–Hg alloy containing 8.7% thallium forms a eutectic mixture freezing at −59 °C, and has been considered for applications in low-temperature thermometers, switches, closures, and seals. Alloys of thallium are also used in good quality bearings, having a very high resistance to corrosion and low coefficients of friction. Thallium is also used in gold plating applications.

In spite of their known toxicity, compounds of thallium have been used in medicine and as cosmetics. Thallium has been used internally in the treatment of gonorrhea, syphilis, dysentery, and tuberculosis and externally as a depilatory. Serious cases of poisoning were recorded, some of which were even fatal. At present, the only medical application of thallium is its use in the form of intravenous injections of ^{201}Tl (half-life = 12.2 days) for myocardial imaging to diagnose the distribution of regional myocardial perfusion.

Most of the thallium in circulation today is probably present in research laboratories; in 1977 this share was estimated at 50% in the United States.[2] Thallium compounds are mainly used as intermediates or catalysts in organic synthesis and 'must now be regarded as essential reagents for modern organic synthesis'.[12] Thallium-based superconducting materials are presently being prepared and characterized in material science laboratories.[13] The first large scale commercial application of $Ba_2CaCu_2Tl_2O_8$ thin films for a microwave device has recently been reported.[14] An X-ray laser using energized atoms of thallium has been developed.[15] Thallium has also found some applications in biological research;[16] for example, Tl^+ is able to mimic K^+ in certain biological reactions and can be easily detected using ^{205}Tl NMR or fluorescence methods. Metal activated enzymes such as pyruvate kinase, ATPase, and aldehyde dehydrogenase have been studied in this way. Tl^{III} has also been used as a probe to investigate the iron sites in human transferrin.

2 PROPERTIES OF THE ELEMENT

Thallium is a silver–gray, soft, heavy, and ductile metal having three forms. The normal close-packed hexagonal lattice transforms to a body-centered cubic structure above 230 °C and a face-centered cubic form is stable at high pressures. The triple point is at 110 °C and 30 kbar. Thallium vapor is essentially monatomic, but on heating to 2000 °C, the vapor emits a visible band due to Tl_2. Some properties are listed in Table 1.[9]

There are two stable isotopes of thallium, ^{203}Tl (29.5%) and ^{205}Tl (70.5%), and numerous radioactive isotopes; in the mass range 184–210, there are 41 isotopes including 16 with half-lives longer than 10 minutes.

Thallium has the stable oxidation states I and III; there are also several compounds in which thallium exists with the *Formal Oxidation State* II, though stable compounds of Tl^{II} are not known in aqueous solution. It has been proposed that Tl^{II} is present in reactions with one-electron reactants; half-lives of 0.5 ms have been measured for the Tl^{2+} intermediate by flash photolysis. It has been shown that the electron transfer in most Tl^I/Tl^{III} redox systems is a two-electron process[17] (*see Electron Transfer Reactions: Theory*). However, thallium is present as Tl^{II} in the trinuclear $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$; an unpaired electron makes the solid compound paramagnetic.[18] Isolable molecular organothallium(II) compounds, $[(Me_3Si)_3Si]_2Tl–Tl[Si(SiMe_3)_3]_2$ and $(^tBu_3Si)_2Tl–Tl(Si^tBu_3)_2$ have been reported recently; the Tl–Tl contacts (resembling the well known Hg_2^{2+}) are 2.91 and 2.97 Å, respectively.[19]

Table 1 Some properties of thallium

Atomic number	81
Relative atomic mass	204.3833
Ground-state electron configuration	$[Xe]4f^{14}5d^{10}6s^26p^1$
Radii (pm)	
atomic (α form)	170.4
Tl^I	149
Tl^{III}	105
covalent	155
Electronegativity (Pauling)	
Tl^I	1.62
Tl^{III}	2.04
Tl^I/Tl	−0.3363
Standard reduction potentials (V)	
Tl^{III}/Tl	0.72
Tl^{III}/Tl^I	1.25
$Tl \rightarrow Tl^I$	589.3
Ionization energies (kJ mol^{-1})	
$Tl^I \rightarrow Tl^{II}$	1971.0
$Tl^{II} \rightarrow Tl^{III}$	2878
$Tl^{III} \rightarrow Tl^{IV}$	(4900)
Density (g cm^{-3})	
at 293 K	11.850
liquid at mp	11.290
Melting point (K)	576.7
Boiling point (K)	1730
Electrical resistivity (Ωm) at 273 K	18.0×10^{-8}

The Tl^I–Tl^{III} relationship is therefore a dominant feature of thallium chemistry. The standard reduction potentials at $25\,^{\circ}C$ and unit activity of H^+ are: $Tl^I/Tl = -0.336$ V, $Tl^{III}/Tl = +0.72$ V, and $Tl^{III}/Tl^I = +1.25$ V.[9] Estimates have also been made for the couples $Tl^{III}/Tl^{II} = +0.33$ V and $Tl^{II}/Tl^I = 2.22$ V. The generally valid limitations concerning the use of standard electrode potentials to predict the redox chemistry of 'real' systems are especially important in the case of thallium: factors such as complex formation in the presence of coordinating anions or neutral ligands and pH dependence due to hydrolysis do affect the actual or formal redox potentials. For example, redox potentials have been measured for $TlCl/TlCl_3 = +0.77$ V in 1 M HCl and $TlOH/Tl(OH)_3 = -0.05$ V in alkaline solution.[1] These formal potentials differ from the standard value for $Tl^{III}/Tl^I = +1.25$ V. The difference can be attributed to the substantial difference between the complex forming abilities of Tl^I and Tl^{III}, which will be discussed in detail later. The Tl^{III} is thermodynamically stable in the presence of strong complexing agents, even in acidic solutions, though in the absence of these ligands Tl^+ can only be oxidized by strong oxidizing agents such as MnO_4^- or BrO_3^-. In contrast, Tl^+ is a powerful reducing agent in alkaline media.

It is interesting to note that Tl^I is more stable than the monovalent oxidation states of the other three metallic elements of group 13, Al, Ga, and In. The occurrence of an oxidation state two units below the group valence is often known as the *Inert Pair Effect* (see, e.g. Hg, Sn, Pb, and Bi). This effect implies a resistance of a pair of s electrons

(i.e. $6s^2$ for Tl) to be lost or to form covalent bonds. The reason for the stability of the lower oxidation state cannot be attributed to its unusually high ionization potential for this pair of s electrons. The sum of the second and third ionization enthalpies for Tl (4820 kJ mol^{-1}) is slightly higher than the same value for In (4501 kJ mol^{-1}), but lower when compared to Ga (4916 kJ mol^{-1}). On the other hand, the mean bond energies of the trichlorides are 242, 206, and 153 kJ mol^{-1} for Ga, In, and Tl respectively. There is a substantial decrease in the bond strengths and this is the reason why the formation of $TlCl_3$ is less favored in comparison with $GaCl_3$ or $InCl_3$. The relativistic contribution of the inert pair effect has been appreciated in recent theoretical calculations. An s^2 pair is not stereochemically active because the s orbital is spherically distributed, unlike a 'lone pair' occupying a coordination site in a molecule (see, e.g. $SnCl_3^-$).[17]

The Pauling *Electronegativity* (EN) values of the stable oxidation states of thallium are 1.62 and 2.04 for Tl^I and Tl^{III} respectively.[9] The latter value is equal to that for boron, and thus Tl and B are the most electronegative elements of group 13. It should be noted that the trend in the electronegativities is not monotonic for this main group, and the values have limited importance in predicting trends even for compounds of elements having the III oxidation state. On the other hand, the concept of 'hard' or class 'a' and 'soft' or class 'b' metal ions and ligands (*see **Coordination & Organometallic Chemistry: Principles***) is a useful guideline in the classification of bond strengths and the ionic/covalent character of bonds in thallium compounds. Thallium(III) belongs to the group of 'soft' metal ions, in contrast to Al^{III}, Ga^{III}, and In^{III}, which are classified as 'hard' ions. The 'softness' of Tl^{III} is rationalized in terms of its strong interactions with 'soft' donor ligands such as sulfur or the halides, with the exception of F^-. One can find similarities in the chemistries of Au^I, Hg^{II}, and Tl^{III}. On the other hand, Tl^I is classified as a borderline ion, having similarities both with the alkali metal ions, which have comparable ionic radii, and also with Ag^+. Thallium(I) forms ionic crystals; however, the non-Coulombic interaction increases on moving from TlF to TlI. Furthermore, complexes of Tl^I are quite weak due to the s^2 electrons, which are σ-antibonding in all stereochemistries. The greater polarizability of Tl^I in comparison with the alkali metal ions may explain its pronounced similarity to Ag^I. The geochemical diversity of thallium might also be related to this character.

The TlX_3 compounds, like their Al, Ga, and In analogs, are found to behave as Lewis acids (*see **Lewis Acids & Bases***) and accept ligands to form tetrahedral complexes. The position of Tl is uncertain in the Al > Ga > In order. The polymerization of these compounds is extensive in order to achieve coordination saturation.[17]

Before discussing the compounds of thallium in detail, the chemical behavior of the metal will be illustrated by its reactions with some common reagents.

Freshly prepared thallium readily loses its bluish-gray tinge in air. The metal is slowly oxidized by dry air or oxygen

at room temperature, forming Tl_2O, and reacts gradually with water or steam even in the absence of oxygen to form TlOH. Dissolution of thallium in hydrofluoric acid is fast. The decreased reactivity with other hydrogen halides is purely a result of the formation of a layer of insoluble thallium(I) halide. Thallium dissolves in oxidizing acids. Thallium is not soluble in sodium hydroxide, in contrast to the amphoteric metals Al and Ga. A remarkable reaction of the metal is with alcohols forming $Tl(OR)_3$ and H_2. The metal is fairly reactive with the halogens and also reacts with sulfur at elevated temperatures.

3 THALLIUM COMPOUNDS

3.1 Thallium Hydrides

The hydrides of thallium, like those of lead and bismuth, are unstable. However, the compound $LiTlH_4$ has claimed to be a relatively stable thallium hydride. Solid $LiTlH_4$ is easily prepared from $TlCl_3$ using lithium hydride[20] (equation 1):

$$TlCl_3 + 4LiH \xrightarrow[-15\,°C]{Et_2O} LiTlH_4 + 3LiCl \qquad (1)$$
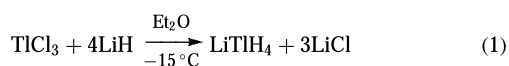
The compound readily decomposes to Tl, LiH, and H_2 above 30 °C, whereas in ether solutions a polymeric hydride is formed after a few hours at 0 °C (equation 2):

$$LiTlH_4 \xrightarrow[0\,°C,\ -LiH]{Et_2O} TlH_3{\cdot}nEt_2O \longrightarrow (TlH_3)_x \qquad (2)$$
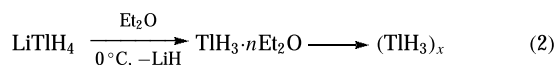
$(TlH_3)_x$ is thermally unstable and loses H_2 at 150 °C giving the stable polymeric Tl^I hydride $(TlH)_x$. This compound has also been prepared by the thermal decomposition of $TlBH_4$, or from TlOEt by addition of B_2H_6 in ether solution. The chemical properties of these compounds reported in the 1950s by Wiberg should be treated with some reservation; for example, the thermal stabilities of TlH_3 and $(TlH_3)_x$ published at that time are not in agreement with recent reports concerning other hydrides of the group 13 elements.[21] Wiberg's report on the stability of $(TlH_3)_x$ seems to be dubious on the basis of theoretical calculations also.[22] Recent ab initio calculations show the thermodynamic instability of Tl_2H_6 both in gas and solid phases, although kinetic stability has been predicted, that is, a local minimum has been found at the MP2 level. However, the isolation of $(TlH_3)_x$ still remains intricate.[23]

No experimental results appear to have been published since the late 1950s, except for the preparation of $TlHI_2$ (from TlI_3, Al, and H_2)[24] and also of HTl_2OH.[25] The latter species are hydrogen bonded and may be formed from Tl vapor with H_2O in an argon matrix by UV irradiation. TlH species have been detected and characterized by spectroscopy

in the gas phase.[26] Moreover, a large body of theoretical calculations have been published dealing with the stability and bonding of the thallium hydrides.[23] It is worth mentioning a dimeric compound, Tl_2H_2, which is often used as a model in theoretical studies dealing with the stability of the Tl–Tl bond,[22] and the monohalide-thallanes (TlH_2X) as model systems for calculation of thermodynamic stability and the role of the π-back donation of the halogeno ligand.[27]

3.2 Halides and Pseudohalides

3.2.1 Halides and Halide Complexes

The series of compounds Tl^IX and $Tl^{III}X_3$, except for $Tl^{III}I_3$, are well characterized. The relative weakness of the Tl^{III}-halide bond has been previously discussed in connection with the 'inert pair effect' (see Section 2).

The Tl^I halides are similar to the silver halides in that they are sensitive to light. The yellow compound TlI has a curious orthorhombic layer structure, which is transformed to a red metastable cubic form (CsCl type) at 4.7 kbar or 175 °C, becoming a metallic conductor at about 160 kbar.[28] If a small quantity of a Tl^I halide is added to an aqueous solution of an alkali halide, a blue **Luminescence** is emitted; furthermore, TlCl doped KCl behaves as a thallium–alkali halide phosphor. In both cases, $TlCl_2{}^-$ is believed to be the active species.[1]

Thallium(I) halides are predominantly ionic, although there is a tendency toward increasing covalent character in the series of compounds TlCl (17%), TlBr (20%), and TlI (28%). This increased degree of covalency results in decreased solubility; for example, TlF is soluble in water whilst the other Tl^I halides are only sparingly soluble. The thallium(I) halides are classical examples of 'incompletely dissociated' 1:1 electrolytes. The stability of halide complexes of Tl^I is low and follows the order TlF < TlCl < TlBr < TlI, where for the series of halides, $K_1 = -$, 0.8, 2.1, 5.0 and $K_2 = -$, 0.2, 0.7, 1.5 respectively.[1] The fluoride ion F^- is preferred to perchlorate as a 'noncomplexing' counterion. Claims have been made for $TlX_n{}^{1-n}$ species with $n = 3$ and 4; however, the formation of complexes in aqueous solution with $n > 2$ seems unlikely.

The covalent trihalides of thallium(III) are less stable than the trihalides of the lighter metals of group 13. Aqueous solutions of these compounds are acidic because of their extensive hydrolysis. The compound $TlCl_3$ is an important starting material for the preparation of Tl^{III} organometallic compounds.

The white compound TlF_3 has been prepared by the direct fluorination of Tl_2O_3 with F_2, BrF_3, or SF_4 at 300 °C. TlF_3 decomposes at 500 °C before melting, it does not form hydrates, and it hydrolyzes in water; no complexes of type Tl^{III}-F^- have been detected. The solids $MTlF_4$, where M = Li or Na, are true double salts. The complexes M_3TlF_6 (M = Na, K, Rb, Cs) have been prepared by fluorination of a mixture of $TlCl_3$ and the appropriate alkali chloride. These compounds contain discrete octahedral $TlF_6{}^{3-}$ anions.[21]

Concentrated solutions of $TlCl_3$ and $TlBr_3$ can easily be prepared by oxidation of Tl^I halides with the appropriate halogen.[29] $TlCl_3 \cdot 4H_2O$ (mp = ca. 43 °C) and $TlBr_3 \cdot 4H_2O$ (decomposes at ca. 30 °C) may be crystallized from aqueous solutions; attempts at thermal dehydration lead to the formation of TlCl or TlBr. However, $SOCl_2$ may be used to dehydrate these compounds giving, for example, anhydrous $TlCl_3$ (mp = 115 °C). Solutions of anhydrous $TlCl_3$ or $TlBr_3$ in MeCN can be prepared by simply treating the solution of the monohalide with Cl_2 or Br_2. Solid $TlCl_3$ can be prepared as shown in equation (3):[17]

$$Tl \text{ or } TlCl \text{ or } Tl_2CO_3 \xrightarrow{\text{NOCl}} TlCl_3 \cdot NOCl \xrightarrow{\text{heat}} TlCl_3 \qquad (3)$$

$TlCl_3$ is very hygroscopic and is soluble in water, acetonitrile, ether, and alcohols. In addition to $TlCl_3$, $TlCl_2^+$ and $TlCl_4^-$ species may coexist in solution. However, $TlCl_3$ reacts with ketones, yielding α-chloro ketones.[30]

As is to be expected from the 'soft' character of Tl^{III}, strong chloride and bromide complexes of type TlX_n^{3-n} are formed in solution, where n is less than or equal to 4. These species are more stable in aqueous solution than the analogous Al^{III}, Ga^{III}, and In^{III} halides. Some of these halides have been thoroughly characterized both in the solid state and in solution by means of X-ray crystallography, solution X-ray diffraction, and NMR. These complexes are among the most stable metal–halide complexes known, particular stability having been claimed for the TlX_2^+ complexes with chloride (see e.g. the overall stability constants, $\beta_n = 10^{7.16}$; $10^{12.60}$; $10^{16.15}$; $10^{18.32}$; and $\sim 10^{18.02}$; $n = 1-5$, respectively for X = Cl in 3 M $HClO_4$) and bromide ligands.[1,7] In addition, the formation of weaker species with $n > 4$ has been demonstrated.[31] In a detailed study of ligand exchange reactions between $Tl^{III}-X^-$ complexes, where X = Cl, Br, and CN, the authors claim a preference for a bimolecular reaction between the lower complexes, as opposed to a direct reaction between the complexes and the free halide, which is present only at very low concentrations. The direct path becomes dominant only for the higher complexes.[32]

There is a systematic change in the coordination geometry of the Tl^{III} complexes TlX_n^{3-n} (X = Cl, Br). The $Tl(H_2O)_6^{3+}$ cation has a regular octahedral geometry, which appears to be retained in the first and second complexes, $TlX(H_2O)_5^{2+}$ and $TlX_2(H_2O)_4^+$, the TlX_2^+ unit being linear in aqueous solution. The solids $TlCl_3 \cdot 4H_2O$ and $TlBr_3 \cdot 4H_2O$ are isomorphous, having a trigonal bipyramidal coordination around Tl^{III}. X-ray diffraction studies indicate that the three halide ligands are coordinated in a trigonal arrangement with two water molecules completing the coordination sphere. In aqueous solution, the geometry is essentially the same for $TlBr_3(H_2O)_2$, but for the chloride complex the coordination is probably a distorted tetrahedral.[7,33] In the TlX_4^- complexes where X = Cl, Br, or I, the coordination sphere is tetrahedral with no water molecules in the inner sphere, either in solution or in the solid phase.[34] The complexes $TlX_5(H_2O)^{2-}$ (X = Cl,

Br) occur in the crystal structures of $K_3TlCl_6 \cdot \frac{13}{7}H_2O$ and $Rb_3TlBr_6 \cdot \frac{13}{7}H_2O$ and also in solution for X = Cl; a distorted octahedral geometry has been found in the solids. The complexes of type TlX_6^{3-}, where X = Cl or Br, have a distorted octahedral geometry in the solid state. Numerous alkali, tetraalkyl, and arsonium salts of the tetra-, penta-, and hexahalides of thallium(III) have been prepared. $Cs_3Tl_2Cl_9$ is an example of an important structural type having the confacial bioctahedral structure.[3,21,28]

Our knowledge of the Tl^{III}–iodide complexes is relatively limited because redox reactions occur in solution. However, in the presence of a large excess of iodide, the redox reactions are avoided and a stable TlI_4^- complex has been observed; $\beta_4 = $ ca. 5×10^{35}. Derivatives of TlI_4^- with different cations have been prepared. The anion is clearly tetrahedral in the tetrabutylammonium salt[35] and probably also has the same structure in the other crystals.

Treatment of TlF with I_2, BrCl, ICl, or IBr yields $TlFI_2$, $TlFClBr$, $TlFClI$, and $TlFBrI$, respectively. These products may represent an intermediate between Tl^{III} compounds and molecular adducts of Tl^I.

No mixed Tl^I–Tl^{III} fluorides have been reported. The oxidation of TlCl and TlBr by halogens results, however, in a series of mixed-valence halides. Earlier these compounds were thought to be Tl^{II} salts, but neither magnetic susceptibility measurements nor crystal-structure determinations proved this hypothesis. For example, TlX_2 and Tl_4X_6 (X = Cl or Br) should be correctly formulated as $Tl^+ [TlX_4]^-$ and $(Tl^+)_3[TlX_6]^{3-}$. The mixed Tl^I–Tl^{III}–iodide Tl_3I_4 can be formulated with formulae $(Tl^+)_5[TlI_8]$, but another model involving $(Tl^+)_6I_5(I_3)$ with the triiodide ion cannot be ruled out.[1]

The black crystalline TlI_3 has been known since 1864 and is an intriguing compound. It is obtained by evaporating an equimolar solution of TlI and I_2 in concentrated HI. TlI_3 is isomorphous with CsI_3, and must therefore exist as $Tl^+I_3^-$ in the solid state. However, the absorption spectra of solutions of the compound in methanol do not indicate the presence of the I_3^- ion; indeed, the spectra are similar to those of $KTlI_4$, thus suggesting a tandem redox and complex formation equilibrium (equation 4):

$$4TlI_3 \rightleftharpoons Tl[TlI_4]_3 \qquad (4)$$
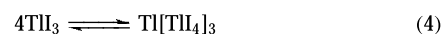
Solutions of TlI_3 yield Tl_2O_3 when shaken with sodium carbonate.[1] In order to understand these fairly complicated redox reactions in the chemistry of TlI_3, it is important to remember how the formal redox potentials vary with the experimental conditions such as solvent, pH, solubility, and complex formation (see Section 2).

The thallium(III) halides, TlX_3 (X = Cl, Br, I), form complexes with amines (L) with formulas $TlX_3 \cdot L_n$, where $n = 1-3$. Among the most studied complexes with this ligand stoichiometry are the neutral monomeric species $TlX_3 \cdot L_2$, where X = Cl or Br, the halide-bridged dimers

$L_2X_2TlX_2TlX_2L_2$, ionic monomers $[TlX_2L_2]X$, and dimer complexes of type $[TlX_2L_4][TlX_4]$.[3] Recently, $TlClBrI \cdot L_2$ complexes have also been prepared.

Our knowledge about the Lewis acid behavior of Tl^{III}-halides is scarce. A recent theoretical study claims that the π-donor ability of the halogens (X) increases with $F < Cl < Br < I$ both in TlX_3 and BX_3, and the $p(\pi)$ population at the central atom in TlX_3 is smaller than that is in BX_3. However, the hydride affinity of TlX_3 relative to TlH_3 is substantially higher compared to the hydride affinity of BX_3 relative to BH_3.[27]

3.2.2 Pseudohalides and Pseudohalide Complexes

Thallium(I) forms salts with cyanide (CN^-), cyanamide (NCN^{2-}), azide (N_3^-), cyanate (OCN^-), isocyanate (CNO^-), thiocyanate (SCN^-), and selenocyanate ($SeCN^-$); however, complexes with these ligands, like the Tl^I-halide complexes, are very weak. In contrast, the neutral $Tl^{III}X_3$ species are not well known, although the Tl^{III}-pseudohalide complexes are more or less stable.

Tl^I pseudohalides can be prepared from aqueous solutions of soluble Tl^I salts, usually the sulfate or nitrate, by adding the appropriate anion, thus precipitating the sparingly soluble Tl^I pseudohalide compounds. Thallium(I) azide has been prepared from Tl^I acetate, TlOAc, with NaN_3 in ethanol. TlN_3 is isomorphous with NaN_3 and RbN_3, but its physical properties suggest a somewhat more covalent Tl–N bond in the solid. The azide decomposes slowly at temperatures near the melting point (374 °C) and the liquid is explosive. Tl^I isocyanate, TlCNO, also explodes on heating to 105 °C.[3,21] K_1 has been determined as about 2.5 for TlN_3, but no cyano complexes of Tl^I, unlike Ag^+, have been detected. Weak complexes ($K_1 = 1.7$, $K_2 = 0.6$)[36] have been reported in the Tl^I–SCN^- system at high concentrations of the anion.

Tl^{III} azide complexes have been observed in solution, though the species are not well characterized. The solid complexes $[Ph_4As][Tl(N_3)_4Cl_2]$[1] and $H_3[Tl(N_3)_6]$ have been isolated, the latter being an explosive yellow compound.

The existence of Tl^{III} cyanide complexes has been mentioned previously; however, on the basis of the analogy with other Tl^{III}–pseudohalide redox reactions, and by analysis of the redox potentials, the existence of the $Tl(CN)_n^{3-n}$ complexes was not widely accepted for a time. However, a detailed investigation of this system using ^{205}Tl and ^{13}C NMR spectroscopy has indicated that Tl^{III} indeed forms very stable cyanide complexes (the overall formation constants, $\beta_n = 10^{13.2}$, $10^{26.5}$, $10^{35.2}$ and $10^{42.6}$ in 4 M ionic strength for $n = 1$, 2, 3 and 4 respectively).[37] These species are in fact the most stable complexes of Tl^{III} formed with monodentate ligands. The extra stability of the $Tl(CN)_2^+$ species is worth mentioning. It is certainly not a coincidence that the diorganothallium(III) compounds containing the linear C–Tl–C group (like doing the (N)C–Tl–C(N)) are also very

stable. A number of mixed cyanide-halide complexes exist in aqueous solution.[7]

The lack of success encountered by attempts to prepare Tl^{III} pseudohalides might be related to the redox reaction between Tl^{III} and reducing ligands, as in the Tl^{III}–I^- system. In the case of the Tl^{III}–SCN^- system, the reaction stoichiometry appears to be as shown in equation (5):

$$4SCN^- + 3Tl^{3+} + 4H_2O \longrightarrow 3TlSCN + HCN + SO_4^{2-} + 7H^+ \quad (5)$$

Recently, a quite stable $Tl(SCN)^{2+}$ complex was characterized by ^{205}Tl NMR, and may be the predominant intermediate in the course of the above redox reaction.[38] Stable complexes of $Tl(SCN)_3$ with 2,2'-bipyridyl and 1,10-phenanthroline have been prepared in the solid form.[1]

Mixed-valence Tl^I–Tl^{III} pseudohalides, such as $Tl(CN)_2$ and $Tl(N_3)_2$, were first prepared more than 100 years ago. Like the analogous halides, these compounds do not contain Tl^{II}, but instead can be formulated as $Tl[Tl(CN)_4]$ and $Tl[Tl(N_3)_4]$, respectively. The former compound can be isolated from both organic and aqueous solutions. As is expected, the Tl(III) is tetrahedrally coordinated.[39] The redox stability of the TlX_4^- complex might be explained in a similar manner to that of TlI_4^-.

3.3 Oxides

3.3.1 Thallium(I) and Thallium(III) Oxides and Hydroxides

The two well-defined oxides of thallium are Tl_2O and Tl_2O_3. In addition, there are some poorly defined oxides such as the Tl^IO_2 (violet), a mixed oxide Tl_4O_3 or $Tl_2O \cdot Tl_2O_3$ (black), and some nonstoichiometric oxides with formulas $TlO_{1.5}$–$TlO_{1.75}$.

Black platelets of thallium(I) oxide are formed when thallium is oxidized in air at moderate temperatures, or from TlOH or Tl_2CO_3 by heating to 100 or 700 °C, respectively, in the absence of air. Tl_2O melts at 596 °C, indicating that the solid has an ionic nature; however, it is also rather volatile and very hygroscopic, forming the yellow solid TlOH on contact with water. Solutions of TlOH are basic, its dissociation constant is about $10^{-0.3}$ at 25 °C, and its basic strength is about 10^5 times greater than that of NH_3 and 10 times greater than for $Ca(OH)_2$.[36] Chemical shift of the ^{205}Tl NMR signal, affected by the equilibrium $Tl^+ + OH^- \rightleftharpoons TlOH$, can be used to monitor the alkalinity of concentrated aluminate solutions.[40] Tl_2O dissolves in ethanol to form TlOEt.

The brown–black thallium(III) oxide can be synthesized from elemental thallium by heating it to dull redness in the presence of oxygen, but is more conveniently prepared from Tl^I salts in alkaline solution by adding hydrogen peroxide or Cl_2. Tl_2O_3 is easily precipitated and can be dried at 500 °C. It is insoluble in water but can be dissolved in acids, giving the corresponding Tl^{III} salts (see Section 3.6). The oxide has

a remarkably low electrical resistance at room temperature (about $7 \times 10^{-5} \Omega \, cm$).[28] At elevated temperatures, Tl_2O_3 vaporizes and decomposes to Tl_2O and O_2.

The appearance of the brown color of Tl_2O_3 at higher pH is very common in solutions containing inorganic Tl^{III} species. Stepwise replacement of the L ligands in $Tl^{III}L_x$ may result in mixed hydroxo complexes, such as oxohalides. Previously the aqua ion, $[Tl(H_2O)_6]^{3+}$, has been claimed to have a distorted octahedral structure in which two of the water molecules are more strongly bound than the others. However, structural investigations, both in solution and in the solid state by X-ray diffraction, indicate a regular octahedral geometry for this cation.[41] The aqua ligands of the hexaaquathallium(III) ion are quite labile; the pseudo first-order rate constant for the exchange of water ligands has been estimated to $5 \times 10^7 \, s^{-1}$.[32] The $Tl^{III} \cdot$ aq ion is very acidic, the acid constants $K_{a,1}$ and $K_{a,2}$ having values of $10^{-0.5}$ and $10^{-1.2}$ in 1 mol dm^{-3} $NaClO_4$, respectively.[36] In other words, $Tl(OH)^{2+}$ and $Tl(OH)_2^+$ are among some of the most stable metal–hydroxo species. On the other hand, in contrast to Al^{III}, Ga^{III}, and In^{III}, no polynuclear species of type $M_x(OH)_y^{(+3x-y)}$ have been characterized for Tl^{III}. Even the formation of $Tl(OH)_3$ and its hydrates is not clearly proven.

3.3.2 Ternary and More Complex Oxides

Extensive studies of these compounds are in progress as a result of their potential applications in solid-state electronics. The electrical and magnetic properties of these compounds show a particular sensitivity to their composition and even to the often 'secret' methods used for their preparation. Selected topics will be briefly discussed here (see also **Oxides: Solid-state Chemistry**).

In spite of the nonamphoteric character of thallium(I), the Tl–alkali metal oxides are often called oxythallates.[1] Red crystals, KTl^IO, and $RbTl^IO$ have been prepared by heating Tl_2O and an alkali oxide. Oxythallate(III) derivatives, $MTlO_2$ (formally metathallates), can be prepared in the same way as those of the alkali metals. The majority of these compounds have the α-$NaFeO_2$ structure: M^+ and Tl^{3+} cations lie in alternate layers in the octahedral interstices of the oxygen array. The solid-state electrolyte $Tl^I\beta$-alumina, $TlAl_{11}O_{17}$, can be prepared from sodium β-alumina by heating with a molten Tl^I salt (see **Aluminum: Inorganic Chemistry**). The Tl^I based ferrites (see **Ferrite**) have the idealized formula $TlFe_{11}O_{17}$ and are structurally closely related to ionic conductors.[42]

The recently discovered thallium-based high-temperature superconductors[13,14] received extraordinary attention because their transition temperature is above that of liquid nitrogen, 100–120 K, and these materials seem to be both stable in air and resistant to moisture. Different thallium cuprates are prepared by melting (920–950 °C) appropriate amounts of mixed powders of Tl_2O_3, BaO/SrO, CaO, and CuO.[43] The oxides have the idealized formulas $TlA_2Ca_{m-1}Cu_mO_{2m+3}$ (A = Sr, Ba) and $Tl_2Ba_2Ca_{m-1}Cu_mO_{2m+4}$. No deviation from the ideal oxygen stoichiometry, 'O_{2m+3}' and 'O_{2m+4}', has been found, and the mixed oxidation state of Cu can be explained by the thallium deficiency in the lattice. The oxidation state of Cu and Tl in these materials has been investigated since this might be important for the superconducting properties: Cu^{II} and Cu^{III} have been proposed from X-ray absorption measurements, whilst Tl^{III} is clearly dominant. Both X-ray and ^{205}Tl NMR results show the existence of some Tl^I,[44] but the 'issue of the competition between the systems Tl^I–Tl^{III} and Cu^{II}–Cu^{III} still remains open'.[45]

3.4 Chalcogenides

Chalcogenides of Tl, like those of Ga and In, are numerous and have been extensively studied since many of them are **Semiconductors** (see **Semiconductor Interfaces**), semimetals (see **Semimetal**), photoconductors (see **Photoconductivity**), or light emitters. The compounds are covalent, and the formal oxidation states can be determined by checking the overall charge balance. However, this is somewhat arbitrary in such systems: Tl has two stable oxidation states and sulfur, especially, has a great propensity for *Catenation.* Existence of Tl^{III} sesquichalcogenides, Tl_2X_3, has been tentatively proposed; Tl^{III} may be reduced to Tl^I by chalcogenides. Well-characterized compounds include, for example, the black Tl_2S (distorted CdI_2 layer lattice), Tl_4S_3 ($Tl^I_3[Tl^{III}S_3]$), the black TlS ($Tl^I[Tl^{III}S_2]$), TlS_2, the red and black forms of Tl_2S_5 and Tl_2S_9 (Tl^I polysulfides), Tl_5X_3, TlX, and Tl_2X_3, where X = Se, Te.[28]

A large number of mixed chalcogenides and ternary or more complex thallium–chalcogenide complexes have been prepared and characterized (see **Chalcogenides: Solid-state Chemistry**).

3.5 Thallium Salts with Oxoanions

Both Tl^I and Tl^{III} form salts with many oxoanions. Thallium(I) salts have no direct uses, except perhaps as starting materials for other reactions. Thallium(III) salts, however, especially thallium(III) nitrate, have been widely used in modern organic synthesis.

The following list gives some standard methods[1,3,29] for the preparation of Tl^I salts (examples shown in brackets):

1. dissolution of thallium metal in acid (Tl_2SO_4, $TlNO_3$)
2. neutralization of TlOH or Tl_2CO_3 with acid ($TlNO_3$, TlOAc, $TlClO_4$)
3. metathesis of Tl_2SO_4 with a barium salt ($TlNO_2$, $TlClO_3$, $TlBrO_3$, $TlIO_3$)
4. treatment of $TlNO_3$ with a nonvolatile acid ($TlClO_3$, Tl_3PO_4)
5. direct precipitation from aqueous solution ($TlIO_3$, Tl_2CrO_4).

Since TlOH and Tl_2CO_3 are commercially available, method 2 is a universal method for almost all salts. Thallium(I)

salts of carbonic acids can be prepared in nonaqueous solvents (ethanol or ether) by the reaction of $Tl^I OEt$ with the appropriate acid.

Some weak interactions of Tl^I with certain oxoanions have been claimed and the following stability constants (K_1) measured: $TlCO_3^-$, 3.2; TlOAc, 0.8; $TlNO_3$, 0.3–0.7; $TlSO_4^-$, 0.3; $TlClO_4$, 0.3.[1]

Oxidation of Tl^I salts by bromine may yield stable mixed Tl^I–Tl^{III} or Tl^{III} salts. $Tl_2Br_2SO_4$ has been prepared from Tl_2SO_4; it can be formulated as $Tl^I[Tl^{III}Br_2SO_4]$. The reaction of bromine with TlOAc gave $Tl(OAc)Br_2$.[1]

The preparation of Tl^{III} salts, including the nitrate, sulfate, phosphate, halogenates, acetate, and trifluoroacetate is based on the dissolution of Tl_2O_3 in the appropriate acid. Thallium(III) phosphate has also been prepared from $Tl(NO_3)_3$ by treatment with H_3PO_4. Solution of $Tl(ClO_4)_3$ can be prepared by the anodic oxidation of $TlClO_4$ in perchloric acid or by the reaction of $TlCl_3$ with $AgClO_4$.[7] Thallium(III) carboxylates are generated by the simple metathesis of $Tl(OAc)_3$ and a carboxylic acid.

Complexes of Tl^{III} with the oxoanions are much more stable than those of Tl^I. The coordination of perchlorate to Tl^{III} cannot be ruled out; however, ClO_4^- is considered to be the best noncoordinating counter anion for equilibrium studies. Related stability constant values (K_1) are: $Tl(NO_3)^{2+}$, $10^{0.9}$; $TlSO_4^+$, $10^{1.95}$; $TlHSO_4^{2+}$, $10^{1.2}$; $Tl(OAc)^{2+}$, $10^{6.2}$. The overall stability constant $\beta_3 = 10^{15.1}$ for $Tl(OAc)_3$. Some mixed hydroxo complexes have also been detected, including $Tl(OH)_2NO_3$ and $Tl(OH)(OAc)^+$. Numerous complexes have also been isolated in the solid state, such as $MTl(SO_4)_2$ (M = Li–Cs, NH_4), $K_2Tl(NO_3)_5 \cdot H_2O$, and $[NO]^+ [Tl(NO_3)_4]^-$; the last-named is produced by oxidizing $TlNO_3$ with N_2O_5. It is interesting that in the $Tl^{III}A_3 \cdot L_n$ complexes (n = 2, 3; L = bidentate N-donor ligands like 2,2'-bipyridyl or 1,10-phenanthroline), mentioned in Section 3.2.2 for A = SCN^-, A can also be NO_3^- or ClO_4^-, and the oxoanions might behave as inner-sphere ligands in the complexes.[3,21]

$Tl(OAc)_3$ is a strong Lewis acid and an effective Friedel–Crafts catalyst. The complex has been used in organic synthesis as the electrophilic agent for oxythallation reactions (see **Thallium: Organometallic Chemistry**). In fact, $Tl(OAc)_3$ is only a weak electrophile, having mild oxidizing properties, because it is a stable complex. By contrast, thallium(III) nitrate (TTN) is highly ionic and thus a good electrophile. $Tl(NO_3)_3 \cdot 3H_2O$ now has a dominant role in oxythallation reactions.[46] It is soluble in a wide range of solvents, both organic and inorganic, and can be used as a solid supported catalyst. The water of crystallization cannot be removed by heating in vacuum or by treating with $SOCl_2$; indeed, Tl^I salts are formed. Dehydration has been achieved using methyl orthoformate[46] (equation 6):

$$Tl(NO_3)_3 \cdot 3H_2O + 3HC(OMe)_3 \longrightarrow$$
$$Tl(NO_3)_3 + 6MeOH + 3HCO_2Me \qquad (6)$$
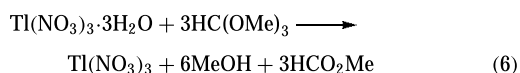
3.6 Complexes with Multidentate Organic Ligands

Thallium(I) acts as a weak Lewis acid and behaves similarly to the alkali metal ions, forming only weak complexes even with complexones such as edta and its analogs. The Macrocyclic Ligands (L), (see **Macrocyclic Ligands**) and in particular the *Crown Ethers* containing 18-membered rings, such as 18-crown-6, do however form strong complexes. As is the case for other M^+ cations, the size of the macrocyclic cavity is critical for the formation of stable complexes. Unsymmetric benzo-type crown ethers possess high thallium(I) selectivity especially against potassium and rubidium ions.[47] Thallium can be immobilized as a thallium-rich mixed-valence solid, $[\{Tl(18\text{-crown-}6)Z\}_4CuCl_4][TlCl_4]_2 \cdot nH_2O$.[48] In addition to the $Tl^I LX$ compounds, $Tl^I L_2X$ sandwich complexes (see *Sandwich Compound*) are also known.[21]

Our knowledge of Tl^{III}–organic ligand systems is rather limited. Two important 'side reactions' must be mentioned: first, that $Tl(H_2O)_6^{3+}$ is easily hydrolyzed, leading to Tl_2O_3 even at pH = 2–3, and, secondly, that it is a strong oxidant. Both these effects prevent the formation and study of many such complexes. On the other hand, the interaction of Tl^{III} with multidentate ligands can stabilize the cation against both hydrolysis and reduction. These effects are exemplified by the $[Tl^{III}(edta)]^-$ complex, which is one of the most stable metal–edta species known ($K = 10^{37.8}$); only $[Co^{III}(edta)]^-$ is more stable.[49] The Tl^{III}–edta complex is stable up to pH = 12; $Tl(edta)(OH)^{2-}$ is formed in alkaline solutions. The structure of the Tl^{III}–edta complex in the solid phase is not known, but it could well be seven coordinate with one water molecule in the inner sphere since it readily forms $Tl(edta)X^{2-}$ mixed complexes with unidentate ligands, halides, and pseudohalides (including S-bonded SCN^-) without reduction of Tl^{III}. In solid $Na_2Tl(edta)CN \cdot 3H_2O$, the thallium(III) ion is hemispherically surrounded by the hexadentate edta, and there is also one strongly bound CN^- in the inner coordination sphere.[50]

However, the coordination number of thallium(III) is found to be eight in the bis(nitrilotriacetato) complex, $[Tl^{III}(nta)_2]^{3-}$ in solid by X-ray.[51] Stepwise formation of three $[Tl(en)_n]^{3+}$ complexes (en = ethylenediamine, n = 1–3) has been established by ^{205}Tl and ^1H NMR in a pyridine solvent. The Tl^{III} is octahedrally coordinated in the $[Tl(en)_3](ClO_4)_3$ solid.[52]

Porphyrin derivatives of Tl^{III} have been prepared; the metal ion lies 0.9 Å above the N_4 plane, with an anion coordinated as the fifth ligand.[21] A $Tl^{III}L_2$ species is formed with 1,4,7-triazacyclononane; two tridentate ligands are coordinated to a Tl^{III} ion in a distorted octahedron. It is an inert species with no additional labile coordination sites, and can therefore only be reduced via an outer-sphere electron-transfer process.[53] Crown ether complexes are known only for R_2Tl salts.[21]

3.7 Metal-metal bonded Tl-complexes

Recently the metallophilic interaction between heavy elements[54] has earned considerable interest (see **Polynuclear**

Organometallic Cluster Complexes), and seems to be the most active research field of thallium coordination chemistry.

Although Tl(I) is often used as a large size counter cation in order to crystallize anionic metal complexes, its role might be more sophisticated as exemplified in the $Tl_2Pt(CN)_4$. This solid compound does not show the usual Pt–Pt 'linked' columnar structure of other $M_2Pt(CN)_4$ salts, but involves two Pt–Tl bonds with a weakly covalent character. The strong luminescence of the compound attributed to these bonds is not retained in solution.[55,56] On the contrary, the ligand supported metal–metal bond in the complex [Tl^I(crown-P_2)Pt^{II}(CN)$_2$]NO_3 (P = $-CH_2PPh_2$) is intact in solution.[57]

Recently, the formation,[58] structure,[59-61] equilibrium,[62] and kinetics[63] of a family of cyano compounds containing a direct and not supported by ligands platinum–thallium metal–metal bond have been reported. The complexes are synthesized according to the reaction:

$$mPt(CN)_4^{2-} + Tl^{3+} + nCN^- \rightleftharpoons [Pt_mTl(CN)_{4+n}]^{(n-1)-} \quad (7)$$
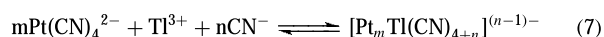
Four binuclear species represented by a general formula [$(NC)_5Pt-Tl(CN)_{n-1}$]$^{(n-1)-}$ ($n = 1-4$) and a trinuclear complex [$(NC)_5Pt-Tl-Pt(CN)_5$]$^{3-}$ are formed in aqueous solution. The complexes exist in an equilibrium, which also includes the parent complexes $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ ($n = 0-4$), and can be controlled by varying the cyanide concentration and/or pH of the solution.

Multinuclear NMR- (^{13}C, ^{195}Pt, ^{205}Tl), IR-, Raman-spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA), X-ray, and Extended X-ray Absorption Fine Structure (EXAFS) studies confirm direct, short (2.60–2.64 Å) Pt–Tl bonds. Figure 1. shows a typical ^{205}Tl NMR spectrum of [$(N^{13}C)_5Pt-Tl(^{13}CN)$]$^-$ together with the structure determined by EXAFS. The spin-spin coupling pattern is consistent with $4 + 1 + 1$ equivalent $^{13}CN^-$ ligands (I = 1/2), respectively and one ^{195}Pt nucleus (natural abundance 33.8%, I = 1/2). The spectrum has been selected to illustrate the usefulness of Tl NMR spectroscopy in studies of the inorganic chemistry of thallium. The compounds are diamagnetic, and
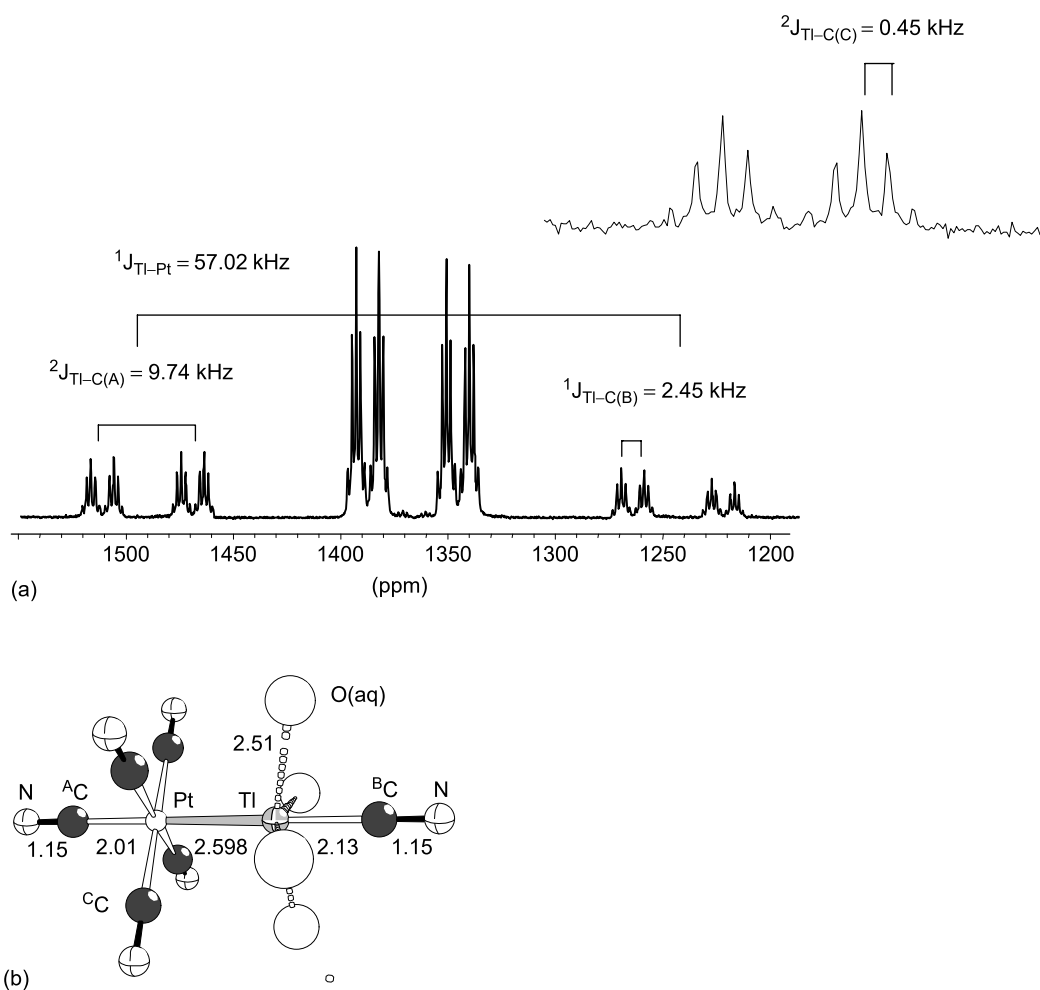

Figure 1   (a) 230.8 MHz ^{205}Tl NMR spectrum of the [(^ACN)(^CCN)$_4Pt-Tl(^BCN)$]$^-$-complex showing the spin-spin coupling schemes. The sample consists of 50 mM Tl^{3+}, 50 mM Pt(^{13}CN)$_4^{2-}$ and 150 mM Na^{13}CN, pH = 1.04. (b) Structural model based on Pt and Tl L_{III} EXAFS data

the electronic states and the nature of the Pt–Tl bonds have been elucidated by Density Function Theory (DFT) calculation.[64]

Selected crystal structures that contain platinum–thallium bonds can be divided into four groups depending on the formal oxidation states of the metal ions: Pt^0–Tl^I (2.86–3.05 Å),[65–67] Pt^{II}–Tl^I (2.88–3.15 Å),[54,57,68–73] Pt^{II}–Tl^{II} (2.70–2.71 Å),[18] and Pt^{II}–Tl^{III} (2.570–2.628 Å).[59–61,73]

4   TOXICITY[16]

The toxic effects of thallium are attributed to its ability to interfere with potassium-dependent biological reactions in a range of life forms extending from humans to plants and microorganisms.

The lethal dose of thallium is in the range of 10–50 mg kg^{-1}. In humans, 600 mg is often fatal. It should be noted that this dose is much larger than the lethal dose of many synthetic or naturally occurring organic poisons! The route of exposure and the chemical form seem to be insignificant for thallium's toxicity. Thallium is a cumulative poison that may be absorbed through the skin. Evidence of poisoning appears in 1–5 days. Acute thallium intoxication causes death by respiratory failure, preceded by paresthesia of the extremities, hypersecretion, loss of hair, uncontrolled muscle movements, convulsions, delirium, and coma. The most effective known antidote is colloidal Prussian Blue, $KFe^{III}[Fe^{II}(CN)_6]\cdot nH_2O$. Prussian Blue (prepared from $K_4[Fe^{II}(CN)_6]$) acts as an ion exchanger for Tl^+ in the intestines and accelerates the fecal elimination of Tl; 250 mg kg^{-1} body mass is administered daily. The use of activated charcoal or KCl as an antidote is recommended if Prussian Blue is not available.

5   ANALYTICAL CHEMISTRY OF THALLIUM

The qualitative detection of thallium is easily achieved by emission spectroscopy, thallium giving a green flame color. Thallium(I) iodide is a yellow precipitate that is insoluble in water, nonoxidizing acids, ammonia, and potassium cyanide, but that can be dissolved in sodium thiosulfate. Traces of thallium can be detected by dyes such as Brilliant Blue or Rhodamine B. Tl^I (or Tl^{III} after reduction by SO_2) can be determined by BrO_3^- or IO_3^- titrant. A gravimetric method uses Tl^I chromate.[3]

Instrumental analytical methods for thallium have been recently reviewed.[74] The low-detection limits of some methods allow the direct determination of thallium in environmental or biological samples, but preconcentration procedures may be necessary in order to achieve sufficient

accuracy. A detection limit of 0.1 ppb (0.1 µg dm^{-3}) has been reported for electrothermal atomic absorption spectroscopy (ET-AAS) and for neutron activation analysis. Analytical methods including pulse voltammetry, isotope dilution and field desorption mass spectroscopy, X-ray fluorescence analysis, and some flame and plasma emission spectroscopic methods have been mentioned in a recent paper related to the environmental aspects of thallium chemistry.[10] Some photometric methods exist, though the detection limits are usually much higher than those of more sophisticated instrumental methods.

6   RELATED ARTICLES

Coordination & Organometallic Chemistry: Principles; Electron Transfer Reactions: Theory; Macrocyclic Ligands; Metal Ion Toxicity; Oxides: Solid-state Chemistry; Polynuclear Organometallic Cluster Complexes; Sulfur: Organic Polysulfanes; Thallium: Organometallic Chemistry.

7   REFERENCES

1. A. G. Lee, 'The Chemistry of Thallium', Elsevier, Amsterdam, NY, 1971.

2. I. C. Smith and B. L. Carson, 'Trace Metals in the Environment, V-1-Thallium', Ann Arbor Science, Ann Arbor, MI, 1977.

3. K. Wade and A. J. Banister, in 'Comprehensive Inorganic Chemistry', ed. J. C. Bailar, Pergamon, Oxford, 1973, Vol. 1, p. 1119.

4. P. I. Fedorov, M. V. Mokhosoyev, and F. P. Alexeyev, 'Khimiya Galliya, Indiya i Talliya', Nauka, Novosibirsk, 1977.

5. A. J. Downs ed., 'Chemistry of Aluminium, Gallium, Indium and Thallium', Chapman & Hall, London, 1993.

6. V. E. Plyutser, S. B. Stepina, and P. J. Fedorov, in 'Khimiya i Tekhnologhiya Redkikh i Rasseynnikh Elementov', ed. K. A. Bol'shakowa, Visshaya Shkola, Moscow, 1976.

7. J. Glaser, in 'Advances in Inorganic Chemistry' ed. G. Sykes, Academic Press: San Diego, CA, 1995, Vol. 43, pp. 1–78.

8. W. Crookes, *Chem. News*, 1861, **3**, 303.

9. J. Emsley, 'The Elements', 2nd edn., Clarendon Press, Oxford, 1991.

10. F. H. Kemper and H. P. Bertram, in 'Metals and Their Compounds in the Environment', ed. E. Merian, VCH, Weinheim, 1991, Chap. II.29.

11. C. A. DiFrancesco and G. R. Smith, Thallium Statistics, U.S. Geological Survey, Open-File Report 01-006, 2002.

12. A. McKillop and E. C. Taylor, *Chem. Br.*, 1973, **9**, 4.

13. J. G. Bednorz and K. A. Müller eds, 'Earlier and Recent Aspects of Superconductivity', Springer-Verlag, Berlin, 1991.

14. S. C. Speller, *Mater. Sci. Technol.*, 2003, **19**, 269.

15. T. O. Llewellyn, *Ceramic Bull.*, 1990, **69**, 885.

16. K. T. Douglas, M. A. Bunni, and S. R. Baindur, *Int. J. Biochem.*, 1990, **22**, 429.

17. F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 5th edn., Wiley, New York, 1988.

18. R. Uson, J. Fornies, M. Tomas, R. Garde, and P. Alonso, *J. Am. Chem. Soc.*, 1995, **117**, 1837.

19. C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107, references therein.

20. E. Wiberg and E. Amberger, 'Hydrides of the Elements of Main Groups I–IV', Elsevier, Amsterdam, NY, 1971.

21. D. G. Tuck, in 'Comprehensive Coordination Chemistry', ed. G. Wilkinson, Pergamon, Oxford, 1987, Vol. 3, Chap. 25.2.

22. M. J. Taylor and P. J. Brothers, in 'Chemistry of Aluminium, Gallium, Indium and Thallium', ed. A. J. Downs, Chapman & Hall, London, 1993, p. 111.

23. P. Schwerdtfeger, P. D. W. Boyd, G. A. Bowmaker, H. G. Mack, and H. Oberhammer, *J. Am. Chem. Soc.*, 1989, **111**, 15; P. Hunt and P. Schwerdtfeger, *Inorg. Chem.*, 1996, **35**, 2085.

24. T. H. Pearson, *Halogen-Substituted-Metal Hydrides and Hydrocarbons*, U.S. Patent, 2,992, 248; *Chem. Abstr.*, July 11, 1962, **56**, 167e.

25. R. H. Hauge, J. W. Kauffman, and J. L. Margrave, *J. Am. Chem. Soc.*, 1980, **102**, 6005.

26. K. P. Huber and G. Herzberg, 'Molecular Spectra and Molecular Structure Constants of Diatomic Molecules', Van Nostrand, New York, 1979.

27. G. Frenking, S. Fau, C. M. Marchand, and H. Grützmacher, *J. Am. Chem. Soc.*, 1997, **119**, 6648.

28. N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', 2nd edn., Pergamon, Oxford, 1997.

29. G. Brauer, 'Handbook of Preparative Inorganic Chemistry', 2nd edn., Academic Press, New York, 1963, Vol. 1.

30. J. Glaser and I. Tóth, *J. Chem. Soc., Chem. Commun.*, 1986, 1337.

31. J. Glaser and U. Henrikson, *J. Am. Chem. Soc.*, 1981, **103**, 6642.

32. I. Bányai and J. Glaser, *J. Am. Chem. Soc.*, 1989, **111**, 3186; I. Bányai and J. Glaser, *J. Am. Chem. Soc.*, 1990, **112**, 4703; I. Bányai, J. Losonczy, and J. Glaser, *Inorg. Chem.*, 1997, **36**, 5900; I. Bányai, J. Glaser, and I. Tóth, *Eur. J. Inorg. Chem.*, 2001, 1709.

33. J. Glaser, *Acta Chem. Scand.*, 1979, **A33**, 789.

34. J. Glaser, *Acta Chem. Scand.*, 1980, **A34**, 75; J. Glaser, *Acta Chem. Scand.*, 1982, **A36**, 125; J. Glaser, *Acta Chem. Scand.*, 1982, **A36**, 451.

35. J. Glaser, P. L. Goggin, M. Sandström, and V. Lutsko, *Acta Chem. Scand.*, 1982, **A36**, 55.

36. E. Högfeldt, 'Stability Constants of Metal–Ion Complexes. Part A. Inorganic Ligands', Pergamon, Oxford, 1982.

37. J. Blixt, B. Győri, and J. Glaser, *J. Am. Chem. Soc.*, 1989, **111**, 7784.

38. J. Blixt, R. K. Dubey, and J. Glaser, *Inorg. Chem.*, 1991, **30**, 2824.

39. P. Nagy and M. Maliarik, Personal communication.

40. P. Sipos, S. G. Capewell, P. M. May, G. T. Hefter, G. Laurenczy, F. Lukács, and R. Roulet, *J. Solut. Chem.*, 1997, **26**, 419.

41. J. Glaser and G. Johansson, *Acta Chem. Scand.*, 1981, **A35**, 639.

42. S. Nariki, S. Ito, K. Uchinokura, and N. Yoneda, *Chem. Lett.*, 1989, 869.

43. S. E. Stupp and D. M. Ginsberg, in 'Physical Properties of High Temperature Superconductors', ed. D. M. Ginsberg, Word Scientific, Singapore, 1992, Vol. 3, Chap. 1.

44. M. Mehring, *Mater. Sci. Technol.*, 2003, **19**, 467.

45. B. Raveau, C. Michel, M. Hervieu, J. Provost, and F. Studer, *Mater. Sci. Technol.*, 2003, **19**, 66.

46. A. McKillop and A. Robert, *Welch Found. Conf. Chem. Res.*, 1973, 1974, **17**, 153; H. M. C. Ferraz, L. F. Silva Jr, and T. D. O. Vieira, *Synthesis*, 1999, **12**, 2001.

47. M. Ouchi and T. Hakushi, *Coord. Chem. Rev.*, 1996, **148**, 171.

48. I. A. Ishenkumba, D. Miller, M. Mitchel, F. R. Fronczek, R. G. Goodrich, D. J. Williams, C. A. O'Mahoney, A. M. Z. Slawin, S. V. Ley, and C. J. Groombridge, *Inorg. Chem.*, 1992, **31**, 3963.

49. G. Anderegg, 'Critical Survey of Stability Constants of EDTA Complexes', IUPAC Chemical Data Series 14, Pergamon, Oxford, 1977.

50. J. Blixt, J. Glaser, P. Solymosi, and I. Tóth, *Inorg. Chem.*, 1992, **31**, 5288.

51. M. A. Malyarik and A. B. Ilyukhin, *Russ. J. Inorg. Chem. (Int. Ed.)*, 1998, **43**, 865.

52. G. Ma, A. Ylyukhin, J. Glaser, I. Tóth, and L. Zékány, *Inorg. Chim. Acta*, 2001, **320**, 92.

53. K. Wieghardt, M. Kleine-Boymann, B. Nubert, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 1309.

54. P. Pyykkö, *Chem. Rev.*, 1997, **97**, 5976.

55. J. K. Nagle, A. L. Balch, and M. M. Olmstead, *J. Am. Chem. Soc.*, 1988, **110**, 319.

56. T. Ziegler, J. K. Nagle, J. G. Snijders, and E. J. Baerends, *J. Am. Chem. Soc.*, 1989, **111**, 5631.

57. A. L. Balch and S. P. Rowley, *J. Am. Chem. Soc.*, 1990, **112**, 6139.

58. M. Maliarik, K. Berg, J. Glaser, M. Sandström, and I. Tóth, *Inorg. Chem.*, 1998, **37**, 2910.

59. F. Jalilehvand, M. Maliarik, M. Sandström, J. Mink, I. Persson, P. Persson, I. Tóth, and J. Glaser, *Inorg. Chem.*, 2001, **40**, 3889.

60. G. Ma, M. Kritikos, and J. Glaser, *Eur. J. Inorg. Chem.*, 2001, 1311.

61. F. Jalilehvand, L. Erikson, J. Glaser, M. Maliarik, J. Mink, M. Sandström, I. Tóth, and J. Tóth, *Chem. Eur. J.*, 2001, 2167.

62. M. Maliarik, J. Glaser, I. Tóth, M. W. da Silva, and L. Zékány, *Eur. J, Inorg. Chem.*, 1998, 565.

63. P. Nagy, I. Tóth, I. Fábián, M. Maliarik, and J. Glaser, *Inorg. Chem.*, 2003, **42**, 6907.

64. J. Autschbach and T. Ziegler, *J. Am. Chem. Soc.*, 2001, **123**, 5320.

65. O. J. Ezomo, M. P. Mingos, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 924.

66. L. Hao, J. J. Vittal, and R. J. Puddephatt, *Inorg. Chem.*, 1996, **35**, 269.

67. V. J. Catalano, B. L. Bennett, R. L. Yson, and B. C. Noll, *J. Am. Chem. Soc.*, 2000, **122**, 10056.

68. O. Renn and B. Lippert, *Inorg. Chim. Acta*, 1993, **208**, 219.

69. R. Uson, J. Fornies, M. Tomas, R. Garde, and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 1383.

70. I. Ara, J. R. Berenguer, J. Fornies, J. Gomez, E. Lalinde, and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 6461.

71. W. Bronger and B. Bonsmann, *Z. Anorg. Allg. Chem.*, 1995, **621**, 2083.

72. K. O. Klepp, *J. Alloys Compd.*, 1993, **196**, 25.

73. K. Matsumoto, Personal communication.

74. M. Sager, 'Trace Analytical Chemistry of Thallium' (in German), Thieme, Stuttgart, 1986.

Acknowledgment

Thallium: Organometallic Chemistry

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Based in part on the article Thallium: Organometallic Chemistry by William S. Rees, Jr. & Gertrud Kräuter which appeared in the Encyclopedia of Inorganic Chemistry, First Edition.

Abbreviations

Cp = cyclopentadienyl; Cp' = substituted cyclopentadienyl; Fc = ferrocenyl; Mesityl = 2,4,6-trimethylphenyl; PPN^+ = bis(triphenylphosphoranylidene)ammonium; TPP = 5,10,15, 20-tetraphenylporphinato; OTs = *p*-toluenesulfonate.

1 INTRODUCTION

Although organothallium compounds were synthesized as early as 1870, only nine years after the discovery of the element thallium, for a long time organothallium chemistry received little attention compared to many other areas of organometallic chemistry. However, as the result of a discovery made in the late 1960s that certain thallium derivatives are remarkably efficient reagents or intermediates in organic syntheses, chemists have found an increasing interest in the organometallic chemistry of thallium. This interest has been stimulated further in recent years due to the discovery that certain thallium-containing superconducting metal oxides (SMO) possess among the highest critical temperatures identified so far (*see Superconductivity*).

Organothallium compounds are now known in oxidation states +1, +2 (silyl ligands), and +3. Several review articles dealing with the organometallic chemistry of thallium are available.[1-8] This article is essentially limited to organothallium compounds that contain at least one Tl–C bond.
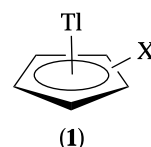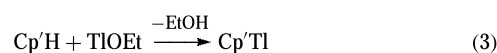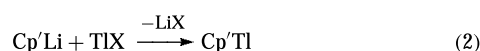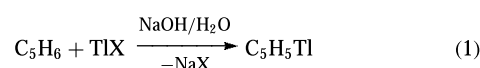
2 THALLIUM(I) COMPOUNDS

The calculated bond dissociation energy for Tl–C in the unknown MeTl is $59\,kJ\,mol^{-1}$, suggesting only limited stability for alkylthalliums (*see Bonding Energetics of Organometallic Compounds*).[9] Known organothallium(I) compounds are almost strictly limited to π bonded species such as cyclopentadienylthallium, CpTl. The most likely reason for the dearth of RTl compounds stems from the combination of weak bonding and unsaturation. In fact, even the members of the Cp'Tl series show effects of coordinative unsaturation, as indicated by polymerization and Tl$\cdots$Tl interactions commonly observed in the solid state (see Section 2.1.1). The low-valent organometallic chemistry of thallium has been reviewed.[6]

2.1 Cyclopentadienylthallium(I) Complexes

2.1.1 Preparation and Properties

Cyclopentadienylthallium (**1**, X = H) first was described by Meister in 1957.[10] It can conveniently be prepared by the reaction of cyclopentadiene with thallium(I) salts in the presence of sodium hydroxide in aqueous solution (equation 1). Since this initial synthesis, a wide variety of Cp'Tl compounds have been prepared, largely for the purpose of acting as cyclopentadienide transfer reagents in transition metal organometallic chemistry (see Section *Reactions of Cyclopentadienylthallium with Transition Metal Compounds*). The range of ring-substituted Cp'Tl compounds known and the methods used to make them have been reviewed.[6,11] Although transmetallation reactions (equation 2) are often successful, the preferred preparation method is usually the acid–base reaction (equation 3), which sidesteps the need for premetallation and produces no salt by-products.

$$C_5H_6 + TlX \xrightarrow[-NaX]{NaOH/H_2O} C_5H_5Tl \tag{1}$$

$$Cp'Li + TlX \xrightarrow{-LiX} Cp'Tl \tag{2}$$

$$Cp'H + TlOEt \xrightarrow{-EtOH} Cp'Tl \tag{3}$$

(1)

Neutral Cp'Tl species are usually polymeric in the solid state, showing a zigzag chain of alternating Tl(I) centers and bridging Cp' units (e.g. see **2**, below).[6] However, several Cp'Tl monomers[12,13] and dimers[14,15] have been identified using X-ray diffraction (*see Diffraction Methods in Inorganic Chemistry*). The compound 1,3-$(SiMe_3)_2C_5H_3Tl$[16] is a Cp'-bridged

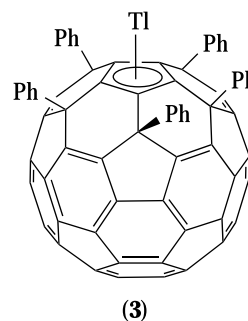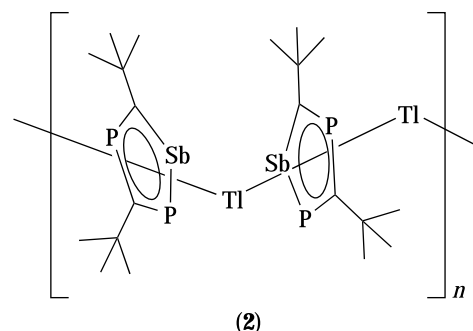**Table 1** Thallium(I) cyclopentadienide compounds characterized by X-ray diffraction

Compound	Tl–Cp^a (pm)	Cp–Tl–Cp (°)
C$_5$H$_5$Tl[20,21]	319	137
C$_5$HMe$_4$Tl[22]	268, 271	133.8
C$_5$Me$_5$Tl[23]	271	145^b
C$_5$Bz$_5$Tl^{d,}[24]	249, 488	175.7
C$_5$Bz$_5$Tl^{d,}[14]	249	–
C$_5$(CO$_2$Me)$_5$Tl[13]	296^c	–
Me$_3$SiC$_5$H$_4$Tl[16]	271, 284	149
(NC)$_2$C=C(CN)C$_5$H$_4$Tl[25]	301, 307	113.6
1,3-(Me$_3$Si)$_2$C$_5$H$_3$Tl[16]	274, 278	127, 133
1,3-Ph$_2$C$_5$H$_3$Tl(THF)[26]	283, 287	127.6, 118.7
(Me$_2$PhSi)C$_5$Me$_4$Tl[27]	263, 286	142.3
(Me$_2$BzSi)C$_5$Me$_4$Tl[27]	274	147
Ph$_2$PC$_5$Me$_4$Tl[27]	280, 288	122
8-quinolyl-C$_5$Me$_4$Tl[28]	263, 290	137.1^b
(1,4,2-P$_2$SbC$_2$Bu^t$_2$)Tl[29]	289, 291	158.8
(C$_{60}$Ph$_5$)Tl(THF)$_{2.5}$[30]	260	–
Au$_2$[(Ph$_2$PC$_5$H$_4$)$_2$Tl]$_2$(C$_6$H$_6$)$_2$[31]	271, 275	–
[CpMg(pmdeta)]$^+$ [Cp$_2$Tl]$^{-f,}$[17]	272	156.7^c
[Li(12-crown-4)$_2$]$^+$ [Cp$_3$Tl$_2$]$^-$ (THF)[18]	263, 282	134.2
[Cp$_2$Tl$_3$]$^+$ [CpMo(CO)$_3$]$^-$[19]	258, 281, 285, 262, (320)^e	114.9^b

^{a}Cp = cyclopentadienide centroid. ^{b}Tl$\cdots$Tl$\cdots$Tl. ^{c}Average value from different molecules in the asymmetric unit. ^{d}Two crystal modifications known. ^{e}Distance to Cp associated with anion unit. ^{f}pmdeta = pentamethyldiethylenetriamine.

hexamer. Also known are Cp-bridged ionic species, for example, Cp$_2$Tl$^-$, Cp$_3$Tl$_2^-$, and Cp$_2$Tl$_3^+$.[17–19] A list of structurally characterized Cp′Tl compounds is provided in Table 1.

Several oligomeric Cp′Tl species reveal weak metal–metal interactions, with Tl$\cdots$Tl distances 363–400 pm.[14–16] Similar Tl$\cdots$Tl interactions can be seen between chains in CpTl itself.[20,21] Theoretical calculations show that such short metal–metal contacts are on the borderline for weak bonding.[32–34] Homometallic interactions are expected to be weaker for thallium than for the other group 13 metals due to spin-orbit coupling and inert pair effects.[9,35]

The heteroatom cyclopentadienyl analog 1,4,2-P$_2$SbC$_2$Bu^t$_2$ has been coordinated to Tl(I) via equation (2), producing zigzag polymer (2).[29] Thallium coordination has played an important role in crystallographic characterization of metal–fullerene complexes, providing the first structurally characterized pentahapto metal complexes of C$_{60}$ (3) and C$_{70}$ (4).[30,36] The key to the formation of these monothallium(I) compounds was the arylation of the fullerenes. Methylated C$_{60}$ forms a thallium complex as well.[37]


(2)

(3)

2.1.2 Reactions of Thallium Cyclopentadienides

Cyclopentadienylthallium compounds have demonstrated tremendous preparative potential as mild reagents for the synthesis of cyclopentadienyl derivatives of *Main Group Elements, Transition Metals,* and *Rare Earth Elements.* In fact, some alkyl-substituted cyclopentadienyl metal complexes can be obtained only from the analogous Tl(I) compounds.

Reactions involving Cp′Tl compounds often are characterized by manipulative simplicity and high yields.

Reactions of Cyclopentadienylthallium with Transition Metal Compounds. Numerous *Metallocene Complexes* have been prepared using CpTl as a Cp-transfer reagent, including *Ferrocene, Cobaltocene,* and *Nickelocene,* as well

(4)
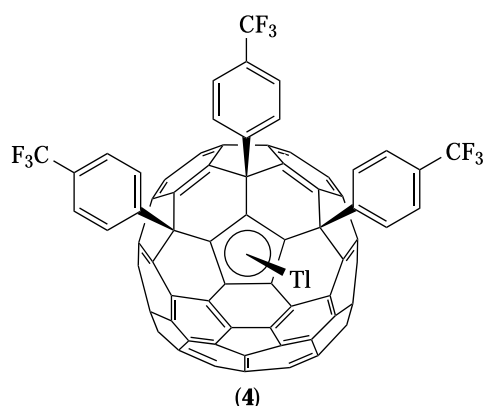
as dicyclopentadienylmercury.[1,38] The reaction of CpTl
with transition metal–halide complexes containing carbonyl
ligands gives the corresponding cyclopentadienyl metal
carbonyls.[1,38,39] Ring-substituted cyclopentadienylthallium
derivatives also have been used to prepare the corresponding
Cp′ complexes of transition metals by substitution of a halide
or Cp ligand.[40–46]

*Reactions of Cyclopentadienylthallium with Main Group
Compounds and Rare Earth Elements.* Cyclopentadi-
enylthallium has found great utility in the formation of
cyclopentadienyl derivatives of main group elements. Ger-
manium dibromide reacts with CpTl to give germanocene.[47]
Cyclopentadienylphosphines, $CpPX_2$, and dicyclopentadi-
enylphosphines, Cp_2PX, can be produced through the reaction
of X_2PCl, and $XPCl_2$ with CpTl (X = R, F).[48,49] Cyclopen-
tadienylthallium compounds react directly with rare earth
metals to produce Cp_2M and Cp_3M complexes and elemental
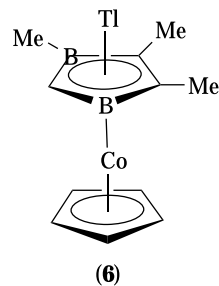thallium.[50]

2.2 Alkylthallium(I) Complexes

Only two isolable σ-bound organothallium(I) compounds
are known: $[(Me_3Si)_3C]Tl$[51] and $(2,6\text{-}Trip_2C_6H_3)Tl$ (Trip =
2,4,6-triisopropylphenyl).[52] Prepared by metathesis reaction
(equation 4), $[(Me_3Si)_3C]Tl$ is of low thermal stability. X-ray
diffraction analysis showed the compound to be tetrameric
in the solid state (structure **5**) while cryoscopy indicated
it to be monomeric in solution. The Tl···Tl distances in
$\{[(Me_3Si)_3C]Tl\}_4$ range from 332 to 364 pm, suggesting
relatively weak interactions, such as are found for Cp′Tl
oligomers. Also thermally unstable, $(2,6\text{-}Trip_2C_6H_3)Tl$ is
prepared by simple metathesis of TlCl and the aryllithium
(equation 5). X-ray diffraction reveals it to be monomeric
in the solid state. Other attempts to prepare Tl(I) σ-alkyls
and -aryls via reactions of thallium(I) halides with lithium
organyls or *Grignard Reagents* has lead to the formation of
either organothallium(III) compounds or organic products.[1]
Nevertheless, the proposed mechanism for these reactions
involves the formation of organothallium(I) compounds as

intermediates.[1,6]

$$CpTl + [(Me_3Si)_3]CLi\cdot2THF \xrightarrow{-CpLi, -2THF} [(Me_3Si)_3C]Tl \qquad (4)$$

$$(5)$$

(5)
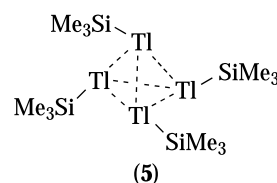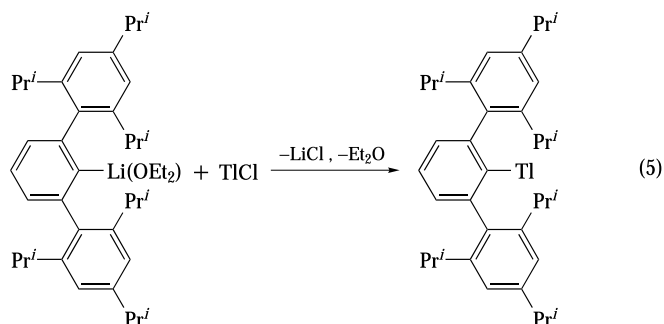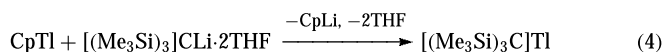
2.3 Complexes of Thallium(I) with Other Anionic Ligands

Several thallium(I) complexes with dicarbollide ligands
(*see Boron: Metallacarbaboranes*) have been prepared.[12,53]
These compounds of the general formula $Tl_2C_2RR'B_9H_9$
usually are oxygen stable, and one of the thallium atoms can
be readily replaced by a Ph_4As^+, Ph_3MeP^+, or PPN^+ cation.[54]
The crystal structures of the resulting Ph_3MeP^{+}[54] and PPN^+
salts (Figure 1)[55] have been reported. Thallium dicarbollides
react with aluminum alkyl derivatives and gallium trichloride,
forming compounds of the general formula $Tl[M(C_2B_9H_{11})_2]$
(M = Al, Ga).[56] A complex between a cobalt-containing
sandwich π-ligand and thallium(I) has been reported.[57] The
resulting compound (**6**) is a monomer in the solid state and
highly soluble in organic solvents. Thallium(I) also forms
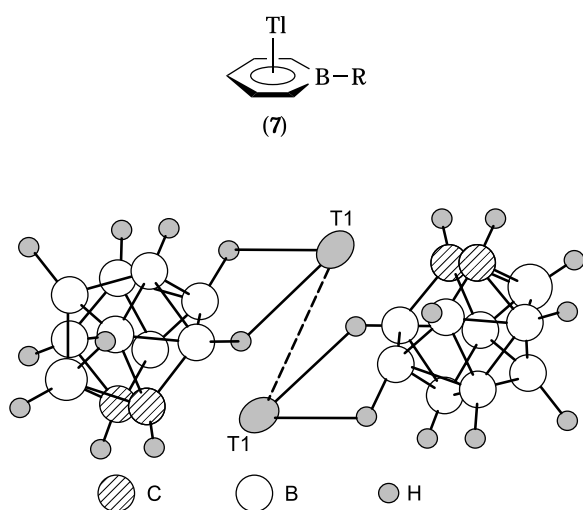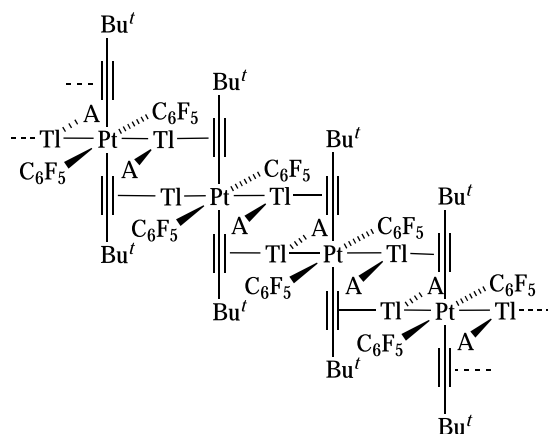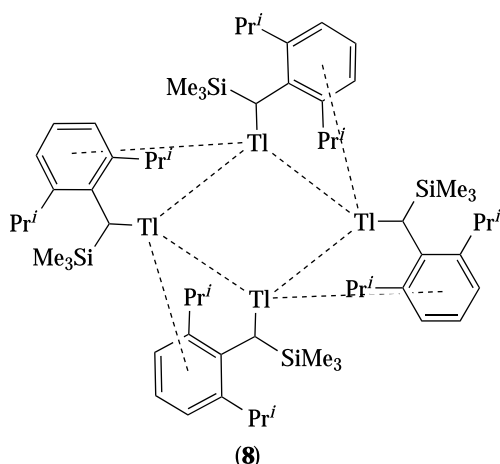a complex (**7**) with the borabenzene anion.[58] (*see Boron:
Organoboranes*).

(6)

(7)

C   B   H

Figure 1 The structure of $[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$. (Reprinted with permission from Ref. 55. © 1991 American Chemical Society)

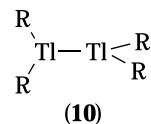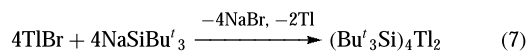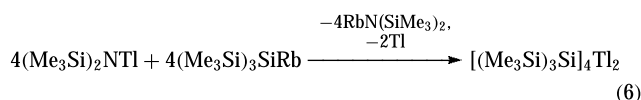## 2.4 Complexes of Thallium(I) with Neutral π-Ligands

Structurally uncharacterized π-arene Tl(I) compounds of the composition $C_6H_62\cdot TlAlCl_4$, $C_6H_6\cdot TlAlCl_4$,[59] and $[Tl\cdot 2PhMe]^+ [C_5Cl_5]^{-}$[60] were described in the literature as early as 1968. Complexes of Tl(I) with toluene, 1,2,4- and 1,3,5-trimethylbenzene, and [2.2]paracyclophane have been isolated and structurally characterized.[60-64] These (η^6-arene)Tl complexes are little more than arene solvates, the Tl cations always being additionally coordinated to halide-bearing anions. Secondary π-interactions have been noted in the structures of the two crystal modifications of $[C_5H_4CMe_2(9\text{-fluorenyl})]Tl$[65] (Figure 2). Thallium coordination to the six-membered ring in these structures showed ring slippage to η^2- and η^3-arene. Very weak (η^6-phenyl)Tl interactions result in polymerization of (3,5-diphenylpyrazoyl)Tl[66] and tetramer formation for $[2,6\text{-}Pr^i_2C_6H_3(Me_3Si)N]Tl$ (**8**).[67] Olefin coordination of Tl(I) is virtually unknown. The complex $Tl_2[Pt(C_6F_5)_2(C\equiv CBu^t)_2](acetone)_2$ (**9**) exhibits thallium–platinum bonds and Tl–η^2-alkyne interactions.[68]

3   THALLIUM(II) COMPOUNDS

True organothallium(II) compounds are unknown. Nevertheless, low-temperature disproportionation reactions (6) and (7) have produced a pair of silylthallium(II) dimers, (**10**), R = Si(SiMe₃)₃[69] and R = SiBu$^t_3$.[70] Both products were examined by X-ray crystallography, however, $(Bu^t_3Si)_4Tl_2$ underwent decomposition in the X-ray beam, yielding only limited data. True Tl–Tl bonding distances of 291.4 and 296.6 pm were found for $[(Me_3Si)_3Si]_4Tl_2$ and $(Bu^t_3Si)_4Tl_2$

(8)

(9), A = acetone; Tl···F omitted for clarity

respectively.

$$4(Me_3Si)_2NTl + 4(Me_3Si)_3SiRb \xrightarrow[-2Tl]{-4RbN(SiMe_3)_2,} [(Me_3Si)_3Si]_4Tl_2 \quad (6)$$

$$4TlBr + 4NaSiBu^t_3 \xrightarrow[]{-4NaBr, -2Tl} (Bu^t_3Si)_4Tl_2 \quad (7)$$

(10)

4   THALLIUM(III) COMPOUNDS

Thallium(III) compounds dominate the known organometallic chemistry of thallium. The structural chemistry organothallium(III) compounds has been reviewed.[7]
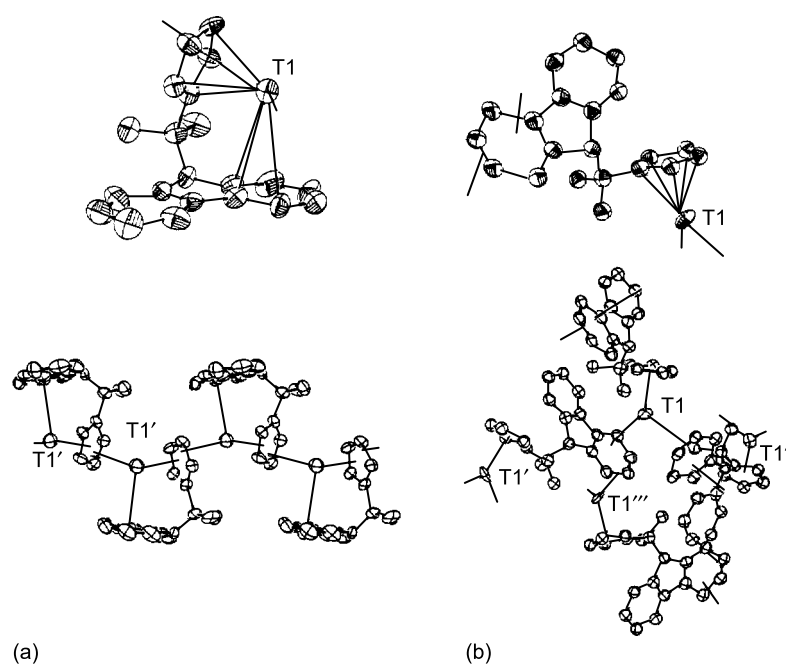
Figure 2   The structure of [C$_5$H$_4$CMe$_2$(9-fluorenyl)]Tl: (a) modification 1; (b) modification 2. (Ref. 65. Reproduced by permission of the John Wiley and Sons)

4.1   Triorgano-, tetraorgano-, and hexorganothallium Compounds

4.1.1   Preparation and Properties

Triorganothallium and the related compounds are usually prepared through the reaction of dialkyl- or diarylthallium(III) halides with organolithium compounds or, in some cases, Grignard reagents.[3] Aryllithium reagents have been used to effect conversion of TlCl$_3$, to Ar$_3$Tl.[71] Reactions involving excess carbanion source can produce peralkyl- or perarylthallium(III) anions, [R$_4$Tl]$^-$ and [R$_6$Tl]$^{3-}$.[71-74] To date, trimethylthallium and trimesitylthallium are the only structurally characterized R$_3$Tl species (see Table 2).[75-77] Trimethylthallium can be prepared conveniently by the reaction of methyllithium and thallium(I) iodide in the presence of methyl iodide (equation 8).[3] This reaction most likely involves the formation of methylthallium(I) as an intermediate. The reaction of dimethylthallium amide or trimethylthallium with R–C≡CH (R = H, Me, Ph) affords dimethyl(ethynyl)thallium compounds.[3]

$$2\text{MeLi} + \text{MeI} + \text{TlI} \xrightarrow{-2\text{LiI}} \text{Me}_3\text{Tl} \qquad (8)$$
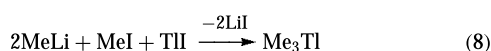
Trimethylthallium is monomeric in the gas phase, in the melt, and in solution.[78] However, it forms a polymeric framework, with weakly bridging methyls, in the solid state.[75,77] Bonded Tl–C lengths are 219.6–221.6 pm and nonbonded Tl···C distances are 324.3–336.4 pm. The dissociation energy of the first Tl–C bond in trimethylthallium

has been estimated as 152 kJ mol^{-1}.[79] The presence of this rather weak bond (compared to the corresponding values in Me$_3$Ga (249 kJ mol^{-1}) and Me$_3$In (197 kJ mol^{-1})) is the fundamental reason for the observed high reactivity of trimethylthallium and triorganothallium compounds in general. Triorganothallium compounds are oxygen and water sensitive. A word of caution is warranted about these compounds, as some have been known to decompose explosively upon heating.

Although triorganothallium compounds are much weaker electron-pair acceptors than the corresponding indium and gallium compounds, some adducts of R$_3$Tl with Lewis bases have been isolated.[3,71,74,80-86] Several such adducts have been examined using X-ray crystallography (Table 2). Two of these are chelates in which the bond lengths and angles are no doubt influenced by metallocycle formation. However, the simple Lewis base adducts (Me$_3$SiCH$_2$)$_3$TlP(SiMe$_3$)$_3$[84] and (C$_6$F$_5$)$_3$TlOPPh$_3$[74] show C-Tl-C bond angles of nearly 120°, suggesting fairly weak donor–acceptor bonding.

4.1.2   Reactions of Triorganothallium Compounds

Owing to the weakness of the Tl–C bonds, triorganothallium derivatives are highly reactive compounds. Trimethyl- and triphenylthallium react with mercury to form the corresponding diorganomercury derivatives and elemental thallium (equation 9).[2]
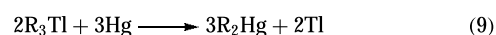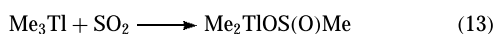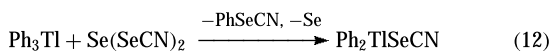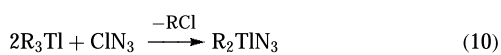
$$2\text{R}_3\text{Tl} + 3\text{Hg} \longrightarrow 3\text{R}_2\text{Hg} + 2\text{Tl} \qquad (9)$$

Table 2 Triorganothallium(III) compounds characterized by X-ray diffraction

Compound	Tl–C (pm)	C–Tl–C (°)	E, Tl–E (pm)
Me$_3$Tl[77]	219.6, 220.6, 221.6	115.1, 120.7, 124.1	–
(Mesityl)$_3$Tl[76]	222, 218, 216.9	116.9, 120.3, 122.8	–
(Me$_3$SiCH$_2$)$_3$TlP(SiMe$_3$)$_3$[84]	223, 224, 225	116.2, 116.5, 121.1	P, 292.2
(C$_6$F$_5$)$_3$TlOPPh$_3$[74]	218.0, 219.0, 219.2	116.9, 118.5, 122.2	O, 230.0
(Me$_2$NFc)$_3$Tl[85]	217.6, 218.1, 220.2	114.0, 118.5, 125.9	N, 252.3
(2-Ph$_2$PCH$_2$C$_6$H$_4$)$_3$Tl[86]	221.0, 221.4, 222.6	108.1, 122.5, 124.2	P, 279.5; P, 355.8

In the presence of acids, halogens, or pseudohalogens, one of the organic groups in R$_3$Tl is displaced and compounds of the general formula R$_2$TlX are formed (equations 10–12).[2] Insertion into the Tl–C bond occurs when trimethylthallium is reacted with either SO$_2$ or SO$_3$ (equation 13 and 14).[3]
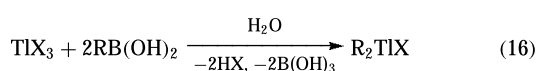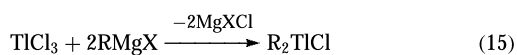
$$2R_3Tl + ClN_3 \xrightarrow{-RCl} R_2TlN_3 \quad (10)$$

$$R_3Tl + HCl \xrightarrow{-RH} R_2TlCl \quad (11)$$

$$Ph_3Tl + Se(SeCN)_2 \xrightarrow{-PhSeCN, -Se} Ph_2TlSeCN \quad (12)$$

$$Me_3Tl + SO_2 \longrightarrow Me_2TlOS(O)Me \quad (13)$$

$$Me_3Tl + SO_3 \longrightarrow Me_2TlOS(O)_2Me \quad (14)$$

The reaction of trimethyl- or triethylthallium with Et$_3$MH (M = Si, Ge), B$_{10}$H$_{14}$, or M'H(CO)$_3$Cp (M' = Mo, W) leads to the formation of the thallium–metal bonded compounds Tl(MEt$_3$), [Me$_2$Tl][Me$_2$Tl(B$_{10}$H$_{12}$)], and Me$_2$Tl(M'(CO)$_3$Cp), respectively.[3]
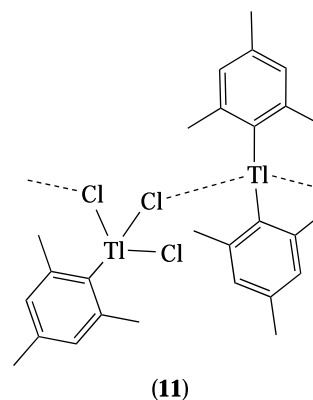
4.2 Diorganothallium Compounds

4.2.1 Preparation and Properties

Diorganothallium compounds comprise the most stable class of organothallium(III) derivatives. They usually are prepared via the reaction of TlCl$_3$ with Grignard reagents (equation 15).[2] However, the yields are rather poor, due to the oxidation of the Grignard reagent by TlCl$_3$. Some di(n-alkyl)thallium bromides have been prepared in good yields by the reaction of TlBr with RMgBr in a 2:1 molar ratio. Diaryl- and divinylthallium halides can be conveniently synthesized by the reaction of thallium(III) halides with the appropriate organoboronic acid in aqueous solution (equation 16).[2] Arylsilver derivatives (R = mesityl, 2,4,6-C$_6$F$_3$H$_2$, C$_6$F$_5$) react with TlCl$_3$ to give the corresponding diarylthallium chloride.[87]

$$TlCl_3 + 2RMgX \xrightarrow{-2MgXCl} R_2TlCl \quad (15)$$

$$TlX_3 + 2RB(OH)_2 \xrightarrow[-2HX, -2B(OH)_3]{H_2O} R_2TlX \quad (16)$$

Other methods for the preparation of diorganothallium compounds are described in Section 4.1.2. Diorganothallium halides are solids and usually are unaffected by water and atmospheric oxygen. They have high melting and decomposition points and are only sparsely soluble in typical organic solvents. Most salt-type diorganothallium(III) compounds ionize in polar solvents. The dimethylthallium cation [Me$_2$Tl$^+$], being isoelectronic with dimethylmercury, is one of the most stable methylated species in aqueous solution reported to date. Many diorganothallium compounds have been characterized by single crystal X-ray diffraction. Table 3 lists some representative diorganothallium compounds and their structural properties. A more complete list is available.[7] The thallium atom reaches coordination numbers between four and eight by both inter- and intramolecular coordination. For most dialkylthallium(III) compounds, an almost linear C–Tl–C arrangement is observed. However, significant deviations are sometimes encountered, usually owing to the steric demand of additional donor ligands and/or oligomerization. Complex (11) represents a particularly interesting combination of R$_2$Tl$^+$ and RTlCl$_3^-$ (R = mesityl).[87] The diarylthallium(III) cation and aryl(trichloro)thallium(III) anion in (11) are weakly associated through a series of long chloride bridges.

(11)

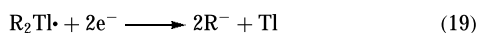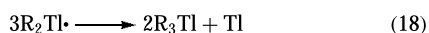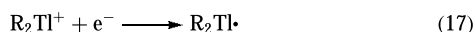### 4.2.2 Reactions of Diorganothallium Compounds

Although the Tl–C bonds in diorganothallium compounds are considerably more stable than those in either triorgano- or monoorganothallium compounds, reactions that involve the

Table 3 Representative diorganothallium(III) compounds characterized by X-ray diffraction
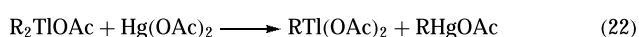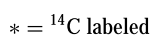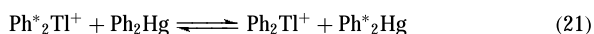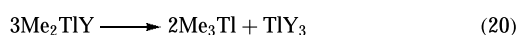
Compound	Structure type	Tl–C (pm)	Angle C–Tl–C (°)
$[Me_2TlL][ClO_4]^{a, 88}$	monomeric ion	209.9	180
$Me_2Tl(acac)^{89}$	polymer	205	171.8
$Me_2Tl(O_2CC\equiv CH)^{90}$	polymer	216	174
$Me_2Tl(S_2PEt_2)^{91}$	polymer	212.8	169.7
$Me_2Tl[S(O)CNEt_2]^{92}$	polymer	213, 214	162.5
$Me_2Tl(HDaptsc)^{b, 93}$	polymer	213.1, 214.9	152.0
$Me_2Tl(FcEtsc)^{c, 94}$	monomer	211.4, 2.123	159.2
$Me_2Tl(FcDtsc)^{d, 95}$	dimer	214.8, 215.2	158.9
$Me_2Tl(4\text{-}CF_3PymS)^{e, 95}$	polymer	212, 215.2	161.2
$[Et_4N][Me_2Tl(S_2PPh_2)_2]^{96}$	monomeric ion	212.4, 212.6	171.2
$[MePh_3P][Me_2Tl(B_{10}H_{12})]^{97}$	monomeric ion	221, 223	134.1
$Ph_2Tl(S_2PEt_2)^{91}$	polymer	214	165.6
$Ph_2TlS_2P(C_6H_{11})_2^{98}$	polymer	210.7, 211.7	160.6
$Ph_2Tl(Cptsc)^{f, 99}$	monomer	214.6, 214.8	146.6
$Ph_2Tl(5\text{-}Ph\text{-}tetrazole)(MeOH)^{100}$	polymer	213, 212	173.9
$[Et_4N][Ph_2Tl(S_2PPh_2)_2]^{101}$	monomeric ion	214.3, 214.9	159.2
$[(Mesityl)_2Tl][(Mesityl)TlCl_3]^{87}$	monomeric ion^g	212.1, 213.1^g	173.1^g
$(C_6F_5)_2TlCl(OPPh_3)^{74}$	dimer	215.6, 216.8	139.4
$(Me_3SiCH_2)_2TlCl^{102}$	dimer	217, 221	168
$(Me_2NFc)_2TlCl^{103}$	monomer	212.8	145.2

^{a}L = tridecalino-18-crown-6{1,4,15,18,29,32-hexaoxaperhydro[4.4.4](4a,8a)naphthalenophane}. ^{b}HDaptsc = 2, 6-diacteylpyridine bis(thiosemicarbazone) anion. ^{c}FcEtsc = ferrocenyl-N-ethylthiosemicarbazone. ^{d}FcDtsc = ferrocenyl-dimethylthiosemicarbazone. ^{e}4-CF$_3$PymS = 4-trifluoromethylpyrimidine-2-thionate. ^{f}Cptsc = cyclopentanone thiosemicarbazone. ^{g}Weakly polymeric through ion association, see (**11**); data for $[(Mesityl)_2Tl]^+$; see Table 4 for anion data.

cleavage of M–C bonds in diorganothallium compounds are known. Diorganothallium cations (R_2Tl^+) can be reduced electrochemically, presumably forming R_2Tl *Radicals* as intermediates (equation 17). The radicals then either form elemental Tl and R_3Tl via disproportionation (equation 18), or can be reduced further to afford the corresponding carbanion (equation 19).[3]

$$R_2Tl^+ + e^- \longrightarrow R_2Tl\cdot \tag{17}$$

$$3R_2Tl\cdot \longrightarrow 2R_3Tl + Tl \tag{18}$$

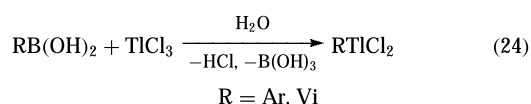$$R_2Tl\cdot + 2e^- \longrightarrow 2R^- + Tl \tag{19}$$

Diorganothallium compounds are known to undergo disproportionation and alkyl-exchange reactions, as shown in equations (20) and (21).[3] Dialkyl- and diarylthallium carboxylates react with mercury acetate to give monoorganothallium dicarboxylates (equation 22).[3]

$$3Me_2TlY \longrightarrow 2Me_3Tl + TlY_3 \tag{20}$$

$$Y = Co(CO)_4, Cr(CO)_3Cp, Fe(CO)_2Cp$$

$$Ph^*_2Tl^+ + Ph_2Hg \rightleftharpoons Ph_2Tl^+ + Ph^*_2Hg \tag{21}$$

$$* = {}^{14}C \text{ labeled}$$

$$R_2TlOAc + Hg(OAc)_2 \longrightarrow RTl(OAc)_2 + RHgOAc \tag{22}$$

4.3 Monoorganothallium Compounds

4.3.1 Preparation and Properties

Monoalkylthallium compounds are usually prepared either by the reaction of dialkylthallium carboxylates and mercury(II) carboxylates (equation 22), or by reacting dialkylthallium halides with Br_2 or I_2 (equation 23).[3,104,105] Aryl- and vinylthallium dichlorides are prepared conveniently by the reaction of aryl- and vinylboronic acid, respectively, with excess $TlCl_3$ in aqueous solution (equation 24).[2,3]

$$R_2TlX + Br_2 \xrightarrow{-RBr} RTlXBr \tag{23}$$

$$X = \text{halide, } BF_4$$

$$RB(OH)_2 + TlCl_3 \xrightarrow[-HCl, -B(OH)_3]{H_2O} RTlCl_2 \tag{24}$$

$$R = Ar, Vi$$
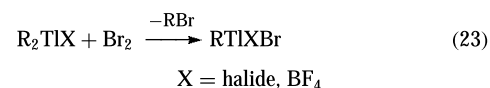
Another synthetic route to monoorganothallium compounds is the reaction of aryl or vinyl derivatives of mercury(II) or tin(IV) with TlX_3 (X = halide, carboxylate). Monoalkylthallium derivatives are intermediates in the oxidation of alkenes and alkynes by thallium(III) salts (oxythallation) (see Section 7).

Several monoorganothallium(III) compounds have been characterized by single crystal X-ray diffraction. These

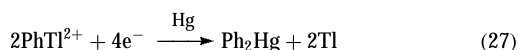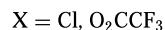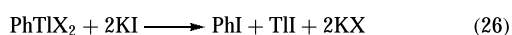**Table 4** Monoorganothallium(III) compounds characterized by X-ray diffraction

Compound	Tl Coordination sphere	Tl–C (pm)
MeTl(BtaPy)$_2$^{a,}[106]	monomer, N$_3$S$_2$C	207.3
(cyclo-C$_3$H$_5$)Tl(O$_2$CCHMe$_2$)$_2$[107]	polymer, O$_6$C	216.0
MeTl(TPP)[108]	monomer, N$_4$C	214.7
RTl(TPP)^{b,}[109]	monomer, N$_4$C	209
(4-MeC$_6$H$_4$)Tl(S$_2$CNEt$_2$)$_2$[110]	monomer, S$_4$C	215
(Me$_2$NCH$_2$-2-C$_6$H$_4$)TlCl$_2$[111]	dimer, NCl$_3$C	212.7
PhTl[S$_2$CP(C$_6$H$_{11}$)$_2$]$_2$[98]	monomer, S$_4$C	213
[(Mesityl)$_2$Tl][(Mesityl)TlCl$_3$][87]	monomeric ion, Cl$_3$C^c	214.9^c
PhTl(Daptsc)(acetone)^{d,}[93]	monomer, N$_3$S$_2$C^e	219.1
[Me$_4$N][(PhN=N-2-C$_6$H$_4$)TlCl$_3$][111]	monomeric ion, NCl$_3$C	213.8

^{a}BtaPy = 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine. ^{b}R = 2-exo-bicyclo[2.2.1]hept-exo-3-acetato-5-enyl. ^{c}Weakly polymeric through ion association, see (**11**); see Table 4 for data on [(Mesityl)TlCl$_3$]$^-$; see Table 3 for data on [(Mesityl)$_2$Tl]$^+$. ^{d}Daptsc = 2,6-diacetylpyridine bis(thiosemicarbazone) dianion. ^{e}Polymer chain formed through interligand hydrogen-bonding.

are listed in Table 4. With macrocyclic ligands, such as porphyrins, the complexes are monomeric, but with smaller readily bridging ligands, such as halide or carboxylate, oligomers can form.

4.3.2 Reactions of Monoorganothallium Compounds

Monoorganothallium compounds readily undergo reductive cleavage of the thallium–carbon bond. Methylthallium diacetate decomposes slowly in various solvents (e.g. H$_2$O, methanol, THF, chloroform) at ambient temperature to give methyl acetate and thallium acetate (equation 25).[3] Phenylthallium dichloride is more stable, but the analogous dibromide, PhTlBr$_2$, decomposes rapidly into PhBr and TlBr when heated.[3] If PhTlX$_2$ (X = Cl, O$_2$CCF$_3$) is treated with KI, the formation of PhI and TlI is observed (equation 26).[3] Cleavage of the Tl–C bond also can be achieved electrochemically (equation 27).[3] Some electrophilic reactions at the Tl–C bond of monoarylthallium compounds are of synthetic interest, for example, the bromination of arylthallium compounds that gives aryl bromides.[3]

$$\text{MeTl(OAc)}_2 \xrightarrow{-\text{MeOAc}} \text{TlOAc} \qquad (25)$$

$$\text{PhTlX}_2 + 2\text{KI} \longrightarrow \text{PhI} + \text{TlI} + 2\text{KX} \qquad (26)$$

$$X = \text{Cl, O}_2\text{CCF}_3$$

$$2\text{PhTl}^{2+} + 4e^- \xrightarrow{\text{Hg}} \text{Ph}_2\text{Hg} + 2\text{Tl} \qquad (27)$$

5 THE TOXICITY OF ORGANOTHALLIUM COMPOUNDS

Elemental thallium and its compounds are extremely toxic and must be handled with care (*see* **Metal Ion Toxicity**). The lethal dose is considered to be 10–12 mg kg^{-1} body weight. The organometallic chemistry of thallium shows similarity to that of Hg^{2+} and Pb^{2+}. Both Hg^{2+} and Pb^{2+} undergo *in vivo* biomethylation, with methylcobalamin (MeCoB$_{12}$) being the biological source of the methyl groups (*see* **Cobalt: B$_{12}$ Enzymes & Coenzymes**).[112] It has been shown that MeCoB$_{12}$ can be demethylated by Tl^{3+}, but the resulting methylated Tl species has not been isolated.[113,114] Monovalent Tl is not able to demethylate MeCoB$_{12}$, however. Bacteria from an anaerobic lake sediment have been used to convert TlO$_2$CCH$_3$ into the water-stable Me$_2$Tl$^+$ cation in an atmosphere of N$_2$ and under the exclusion of light.[115] The formation of Me$_2$Tl$^+$ is unsurprising, considering that monomethylthallium(I) compounds are unstable and Me$_3$Tl decomposes in water. Unlike the organometallic derivatives of Pb^{2+} and Hg^{2+} generated by the biological system, Me$_2$Tl$^+$ appears to be less toxic than inorganic thallium compounds and elemental thallium itself. Dimethylthallium(I) has recently been detected in Atlantic Ocean water at levels up to 3.2 ng L^{-1} using isotope dilution mass spectrometry.[116]

Although detailed data about the biological effects of organothallium compounds remain sparse, they should be considered to be extremely toxic, taking into account their chemical similarity to organomercury and -lead compounds (*see* **Mercury: Organometallic Chemistry** and **Lead: Organometallic Chemistry**), combined with the known toxicity of inorganic thallium compounds and thallium metal.

6 ORGANOTHALLIUM COMPOUNDS AS PRECURSORS FOR ELECTRONIC MATERIALS

Thallium(III) oxide is a degenerate *n*-type semiconductor (*see* **Semiconductors**) with a Band Gap of 1.4 eV, and it shows electronic and optical properties, which make it useful in applications such as solar cells and electrical contacts.[117] The interest in thallium oxide has been further stimulated by the discovery that the system Tl–Ca–Ba–Cu–O represents a

class of superconducting materials with critical temperatures as high as 125 K, coupled with the presence of very high critical current densities.[118] Superconducting metal oxides (SMO) were originally studied as bulk materials;[119] however, it is as thin films that they attract the most interest (*see Thin Film Synthesis of Solids*). One proven technique that provides high-quality films on large area substrates at mild conditions is Metal–Organic Chemical Vapor Deposition (MOCVD).[120,121] This method requires organometallic precursors that are chemically and thermally stable during their evaporation and transport to the substrate, and which decompose on the substrate to form the desired solid-state material and volatile by-products. Suitable organothallium MOCVD precursor compounds are relatively few in number, however, several have been used successfully in the preparation of thallium-containing superconductors and semiconductors by the MOCVD technique. Among them are thallium tris(β-diketonates)[122-124] and cyclopentadienylthallium.[123,125] The most promising precursors to date are CpTl and some of its derivatives. These compounds can be prepared relatively easily and come closest to possessing the necessary volatility.[126]

7 THALLIUM IN ORGANIC SYNTHESIS
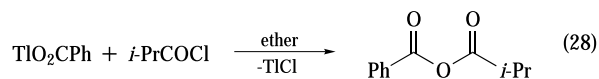
7.1 Introduction

In contrast to the other elements of group 13, thallium is considered a soft acid in Pearson's soft/hard acid classification (*see Hard & Soft Acids and Bases*).[127] This makes the element and its derivatives unique, and leads to its potentially most outstanding feature: the properties of thallium are a subtle blend of some of the most desirable properties of numerous other metals (e.g. heavy alkali metals, silver, mercury, and lead). Thallium compounds are stable in both oxidation states (+1 and +3). The trivalent cation is quite a strong oxidation reagent, since it is reduced to Tl^+ easily (standard redox potential $E°(Tl^{3+} \rightarrow Tl^+) = -1.25$ V). The ease of this reduction is utilized in certain organic reactions.

Numerous transformations in organic chemistry that occur in the presence of thallium reagents have been described. Many of these reactions are unique and are characterized by manipulative simplicity and high yields. Several review articles describe in detail the use of thallium reagents in organic synthesis.[1,127-131] Selected examples are discussed below.

7.2 Selected Examples[1,127-131]

The nonoxidative applications of thallium in organic synthesis are relatively few. Organothallium reagents act as mild nucleophiles. Thus, acid chlorides can be alkylated by R_3Tl, as can α-haloethers. Nucleophilicity is greater for R_4Tl^-. Alkyltrimethylthallate(III) is prepared from Me_3Tl and RLi, and may be used to alkylate α,β-unsaturated ketones.[130]

Symmetrical and unsymmetrical anhydrides can be prepared in quantitative yields by the reaction of Tl(I) carboxylates with carboxylic acid chlorides (equation 28).
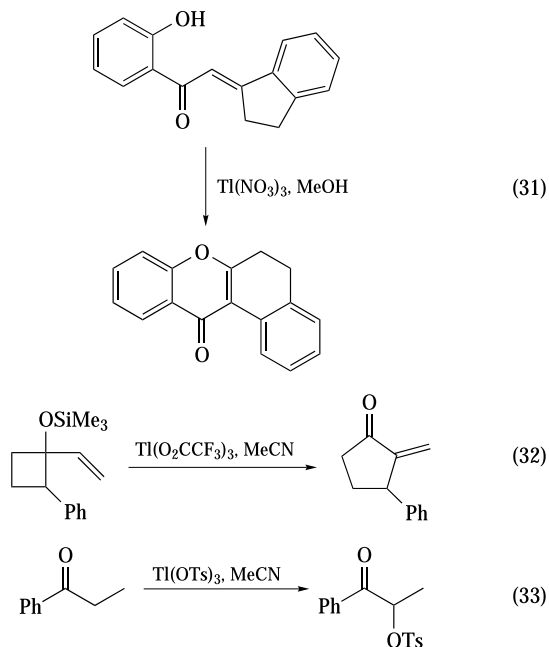
$$TlO_2CPh + \textit{i}\text{-PrCOCl} \xrightarrow[\text{-TlCl}]{\text{ether}} \underset{Ph}{\overset{O}{\parallel}}\text{O}\underset{\textit{i}\text{-Pr}}{\overset{O}{\parallel}} \tag{28}$$

Thallium(III) reagents are useful for mediating electrophilic substitutions. The resulting arylthallium dications are converted into substituted aromatic compounds easily and in high yields. The new substituent enters the aromatic ring at the position in which the TlX_2 group was attached (equation 29).

$$\tag{29}$$

$$\tag{30}$$
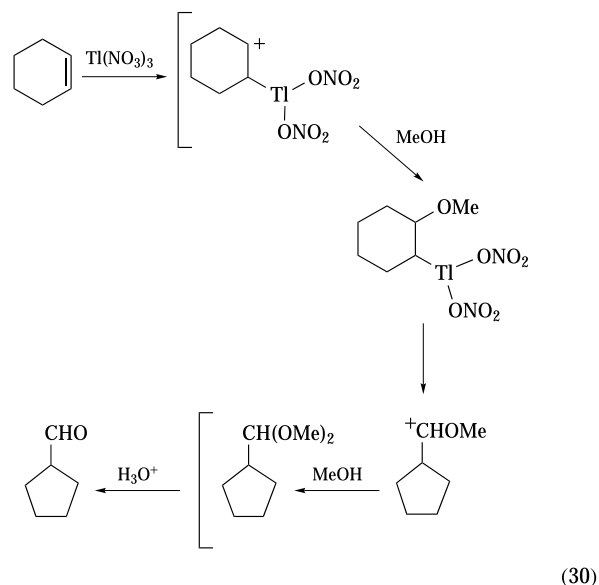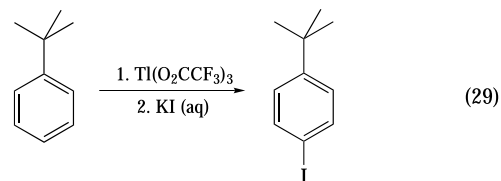
Thallium(III) salts, especially $Tl(NO_3)_3$, $Tl(O_2CCH_3)_3$, and $Tl(O_2CCF_3)_3$, are widely used as oxidizing reagents for nonaromatic unsaturated compounds.[11,130] This reaction is certainly the most important application of thallium in organic synthesis. The first step in the reaction of a thallium(III) salt with alkenes (oxythallation) takes place rapidly at ambient temperature and leads to the formation of monoalkylthallium(III) compounds. These intermediates are usually unstable under the reaction conditions, and undergo rapid decomposition to give the oxidation product of the organic substrate, while Tl^{3+} is reduced to Tl^+. Cyclic alkenes react with $Tl(NO_3)_3$ in methanol to give the ring-contracted products by oxidative rearrangement (equation 30). This reaction produces very high yields of

ring-contracted products and has been used to great advantage in the conversion of flavanones to flavones, isoflavones, and benzofurans. Similar strategy can be used for ring closures and expansions (equations 31 and 32).[130] Enolizable ketones undergo oxidation at the α position in the presence of Tl(III) salts (equation 33).[130]

$$\text{Tl(NO}_3\text{)}_3, \text{MeOH} \qquad (31)$$

$$\text{Tl(O}_2\text{CCF}_3\text{)}_3, \text{MeCN} \qquad (32)$$

$$\text{Tl(OTs)}_3, \text{MeCN} \qquad (33)$$

8   RELATED ARTICLES

Bonding Energetics of Organometallic Compounds; Diffraction Methods in Inorganic Chemistry; Gallium: Organometallic Chemistry; Indium: Organometallic Chemistry; Lead: Organometallic Chemistry; Mercury: Organometallic Chemistry; Metal Ion Toxicity; Semiconductors; Superconductivity; Thallium: Inorganic Chemistry; Thin Film Synthesis of Solids.

9   REFERENCES

1. A. McKillop and E. C. Taylor, *Adv. Organomet. Chem.*, 1973, **11**, 147.

2. A. G. Lee, in 'Organometallic Reactions', eds. E. I. Becker and M. Tsutui, Wiley, New York, 1975, Vol. 5, p. 1.

3. H. Kurosawa, in 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, Vol. 1, p. 725.

4. M. A. Paver, C. A. Russell, and D. S. Wright, in 'Comprehensive Organometallic Chemistry II', eds. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, Oxford, 1995, Vol. 1, p. 503.

5. A. McKillop and J. D. Smith, in 'Organometallic Compounds of Aluminum, Gallium, Indium, and Thallium', eds. A. McKillop, J. D. Smith, and I. J. Worall, Chapman and Hall, New York, 1985, p. 151.

6. C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107.

7. J. S. Casas, M. S. García-Tasende, and J. Sordo, *Coord. Chem. Rev.*, 1999, **193–195**, 283.

8. B. Neumüller, *Coord. Chem. Rev.*, 1997, **158**, 69.

9. P. Schwerdtfeger, P. D. W. Boyd, G. A. Bowmaker, H. G. Mack, and H. Oberhammer, *J. Am. Chem. Soc.*, 1989, **111**, 15.

10. H. Meister, *Angew. Chem.*, 1957, **69**, 533.

11. P. Jutzi, *Adv. Organomet. Chem.*, 1986, **26**, 217.

12. H. Schumann, T. Ghodsi, L. Esser, and E. Hahn, *Chem. Ber.*, 1993, **126**, 591.

13. M. I. Bruce, J. K. Walton, M. L. Williams, S. R. Hall, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2209.

14. H. Schumann, C. Janiak, J. Pickhardt, and U. Börner, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 789.

15. P. Jutzi, J. Schnittger, and M. B. Hursthouse, *Chem. Ber.*, 1991, **124**, 1693.

16. S. Harvey, C. L. Raston, B. W. Skelton, A. H. White, M. L. Lappert, and G. Srivastsva, *J. Organomet. Chem.*, 1987, **328**, C1.

17. D. R. Armstrong, R. Herbst-Irmer, A. Kuhn, D. Moncrieff, M. A. Paver, C. A. Russell, D. Stalke, A. Steiner, and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1774.

18. D. R. Armstrong, A. J. Edwards, D. Moncrieff, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell, and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1995, 927.

19. A. Dashti-Mommertz, B. Neumüller, S. Melle, D. Haase, and W. Uhl, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1828.

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

21. J. F. Berar, G. Calvarin, C. Pommier, and D. Weigel, *J. Appl. Crystallogr.*, 1975, **8**, 386.

22. H. Schumann, H. Kucht, A. Kucht, F. H. Görlitz, and A. Dietrich, *Z. Naturforsch., Teil B*, 1992, **47B**, 1241.

23. H. Werner, H. Otto, and H. J. Kraus, *J. Organomet. Chem.*, 1986, **315**, C57.

24. H. Schumann, C. Janiak, M. A. Khan, and J. J. Zuckermann, *J. Organomet. Chem.*, 1988, **354**, 7.

25. M. B. Freeman, L. G. Sneddon, and J. C. Huffman, *J. Am. Chem. Soc.*, 1977, **99**, 5194.

26. H. Schumann, A. Lentz, and R. Weimann, *J. Organomet. Chem.*, 1995, **487**, 245.

27. H. Schumann, H. Kucht, A. Dietrich, and L. Esser, *Chem. Ber.*, 1990, **123**, 1811.

28. M. Enders, J. Fink, and H. Pritzkow, *Eur. J. Inorg. Chem.*, 2000, 1923.

29. M. D. Francis, C. Jones, G. B. Deacon, E. E. Delbridge, and P. C. Junk, *Organometallics*, 1998, **17**, 3826.

30. M. Sawamura, H. Iikura, and E. Nakamura, *J. Am. Chem. Soc.*, 1996, **118**, 12850.

31. G. K. Anderson and N. P. Rath, *J. Organomet. Chem.*, 1991, **414**, 129.

32. C. Janiak and R. Hoffmann, *J. Am. Chem. Soc.*, 1990, **112**, 5924.

33. P. Pyykkö, M. Straka, and T. Tamm, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3441.

34. P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1998, 2939.

35. P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563.

36. M. Sawamura, H. Iikura, A. Hirai, and E. Nakamura, *J. Am. Chem. Soc.*, 1998, **120**, 8285.

37. M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, and E. Nakamura, *Chem. Lett.*, 2000, 270.

38. A. F. Neto, A. D. L. Borges, J. Miller, and V. A. Darin, *Synth. React. Inorg. Met.-Org. Chem.*, 1997, **27**, 1299.

39. S. Top, C. Lescop, J.-S. Lehn, and G. Jaouen, *J. Organomet. Chem.*, 2000, **593–594**, 167.

40. G. Gassman and C. H. Winter, *J. Am. Chem. Soc.*, 1986, **108**, 4228.

41. B. G. Conway and M. D. Rausch, *Organometallics*, 1985, **4**, 688.

42. M. D. Rausch, W. C. Spink, B. G. Conway, R. D. Rogers, and J. L. Atwood, *J. Organomet. Chem.*, 1990, **383**, 227.

43. T. E. Bitterwolf, *J. Organomet. Chem.*, 1986, **312**, 197.

44. S. S. Jones, M. D. Rausch, and T. E. Bitterwolf, *J. Organomet. Chem.*, 1993, **450**, 27.

45. R. P. Hughes and J. R. Lomprey, *Inorg. Chim. Acta*, 1995, **240**, 653.

46. R. Wolgramm, C. Ramos, P. Royo, M. Lanfranchi, M. A. Pellinghelli, and A. Tiripicchio, *Inorg. Chim. Acta*, 2003, **347**, 114.

47. J. V. Scibelli and M. D. Curtis, *J. Am. Chem. Soc.*, 1973, **95**, 924.

48. T. Paine, R. W. Light, and D. E. Maier, *Inorg. Chem.*, 1979, **18**, 368.

49. F. Mathey and J.-P. Lampin, *Tetrahedron*, 1975, **31**, 2685.

50. G. B. Deacon, A. J. Koplik, and T. D. Tuong, *Aust. J. Chem.*, 1984, **37**, 517.

51. W. Uhl, S. U. Keimling, K. W. Klinkhammer, and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 64.

52. M. Niemeyer and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1277.

53. P. Jutzi, D. Wegener, and M. B. Hursthouse, *Chem. Ber.*, 1991, **124**, 295.

54. H. M. Colquhoum, T. J. Greenhough, and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1977, 737.

55. M. J. Manning, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1991, **30**, 3589.

56. D. M. Schubert, M. A. Bandman, W. S. Rees, C. B. Knobler, P. Lu, W. Nam, and M. F. Hawthorne Jr, *Organometallics*, 1990, **9**, 2046.

57. K. Stumpf, H. Pritzkow, and W. Siebert, *Angew. Chem., Int. Ed. Engl.*, 1985, **25**, 71.

58. G. E. Herberich, H. J. Becker, and C. Engelke, *J. Organomet. Chem.*, 1978, **153**, 265.

59. T. Auel and E. L. Amma, *J. Am. Chem. Soc.*, 1968, **90**, 5941.

60. G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, 1972, **94**, 6069.

61. R. S. Mathur, T. Drovetskaya, and C. A. Reed, *Acta Crystallogr., Sect. C*, 1997, **53**, 881.

62. W. Frank, G. Korrell, and G. J. Reiss, *J. Organomet. Chem.*, 1996, **506**, 293.

63. H. Schmidbaur, W. Bublak, J. Riede, and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 414.

64. H. Schmidbaur, W. Bublak, B. Huber, J. Hofmann, and G. Müller, *Chem. Ber.*, 1989, **122**, 265.

65. W. Frank, D. Kuhn, S. Müller-Becker, and A. Razavi, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 90.

66. G. B. Deacon, E. E. Delbridge, C. M. Forsyth, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 745.

67. S. D. Waezsada, T. Belgardt, M. Noltemeyer, and H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1351.

68. I. Ara, J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde, and R. I. Merino, *Inorg. Chem.*, 1997, **36**, 6461.

69. S. Henkel, K. W. Klinkhammer, and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 681.

70. N. Wiberg, K. Amelunxen, H. Nöth, M. Schmidt, and H. Schwenk, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 65.

71. R. Usón, A. Laguna, J. A. Abad, and E. de Jesús, *J. Chem Soc., Dalton Trans.*, 1983, 1127.

72. R. Usón, A. Laguna, and J. A. Abad, *J. Organomet. Chem.*, 1980, **194**, 265.

73. A. T. Weibel and J. P. Oliver, *J. Organomet. Chem.*, 1974, **74**, 155.

74. A. Mendía, E. Cerrada, E. J. Fernández, A. Laguna and M. Laguna, *J. Organomet. Chem.*, 2002, **663**, 289.

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

76. J. Blümel, B. Werner, T. Kräuter, and B. Neumüller, *Z. Anorg. Allg. Chem.*, 1997, **623**, 309.

77. R. Boese, A. J. Downs, T. M. Greene, A. W. Hall, C. A. Morrison, and S. Parsons, *Organometallics*, 2003, **22**, 2450.

78. A. P. Kurbakova, S. S. Bukalov, L. A. Leites, L. M. Golubinskaya, and V. I. Bregadze, *J. Organomet. Chem.*, 1997, **536–537**, 519.

79. S. J. Price, J. P. Richard, R. C. Rumfeldt, and M. G. Jacko, *Can. J. Chem.*, 1973, **51**, 1397.

80. S. Numata, H. Kurosawa, and R. Okawara, *J. Organomet. Chem.*, 1975, **102**, 259.

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

82. J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1963, 5534.

83. G. B. Deacon and R. J. Phillips, *Aust. J. Chem.*, 1978, **31**, 1709.

84. R. A. Baldwin, R. L. Wells, and P. S. White, *Main Group Chem.*, 1997, **2**, 67.

85. K. Jacob, J. Scholz, C. Pietzsch, and F. T. Edelmann, *J. Organomet. Chem.*, 1995, **501**, 71.

86. G. Müller and J. Lachmann, *Z. Naturforsch.*, 1993, **B48**, 1544.

87. A. Laguna, E. J. Fernández, A. Mendía, M. E. Ruiz-Romero, and P. G. Jones, *J. Organomet. Chem.*, 1989, **365**, 201.

88. K. Kobiro, M. Takahashi, Y. Odaira, Y. Kawasaki, Y. Kai, and N. Kasai, *J. Chem. Soc., Dalton Trans.*, 1986, 2613.

89. Y. M. Chow and D. Britton, *Acta Crystallogr., Sect. B*, 1975, **31**, 1929.

90. M. J. Moloney and B. M. Foxman, *Inorg. Chim. Acta*, 1995, **229**, 323.

91. R. Carballo, J. S. Casas, E. E. Castellano, A. Sánchez, J. Sordo, E. M. Vázquez-López, and J. Zukerman-Schpector, *Polyhedron*, 1997, **16**, 3609.

92. J. S. Casas, A. Castiñeiras, A. Sánchez, J. Sordo, and E. M. Vázquez-López, *Main Group Met. Chem.*, 1996, **19**, 231.

93. J. S. Casas, E. E. Castellano, J. Ellena, M. S. García-Tasende, A. Sánchez, J. Sordo, E. M. Vázquez-López, and M. J. Vidarte, *Z. Anorg. Allg. Chem.*, 2003, **629**, 261.

94. J. S. Casas, M. V. Castaño, M. C. Cifuentes, A. Sánchez, and J. Sordo, *Polyhedron*, 2002, **21**, 1651.

95. A. Rodríguez, J. A. García-Vázquez, A. Sousa-Pedrares, J. Romero, and A. Sousa, *J. Organomet. Chem.*, 2004, **689**, 557.

96. G. B. Deacon, S. J. Faulks, B. M. Gatehouse, and A. J. Jozsa, *Inorg. Chim. Acta*, 1977, **21**, L1.

97. N. N. Greenwood and J. A. Howard, *J. Chem. Soc., Dalton Trans.*, 1976, 177.

98. J. S. Casas, E. E. Castellano, A. Castiñeiras, A. Sánchez, J. Sordo, E. M. Vázquez-López, and J. Zukerman-Schpector, *J. Chem. Soc., Dalton Trans.*, 1995, 1403.

99. T. S. Lobana, J. S. Casas, A. Castiñeiras, M. S. García-Tasende, A. Sánchez, and J. Sordo, *Inorg. Chim. Acta*, 2003, **347**, 23.

100. S. Bhandari, M. F. Mahon, K. C. Molloy, J. S. Palmer, and S. F. Sayers, *J. Chem. Soc., Dalton Trans.*, 2000, 1053.

101. J. S. Casas, A. Sánchez, J. Sordo, E. M. Vázquez-López, R. Carballo, and C. Maichle-Mössmer, *Polyhedron*, 1996, **15**, 861.

102. F. Brady, K. Henrick, R. W. Matthews, and D. G. Gilles, *J. Organomet. Chem.*, 1980, **193**, 21.

103. K. Jacob, J. Scholz, K. Merzweiler, and C. Pietzsch, *J. Organomet. Chem.*, 1997, **527**, 109.

104. I. F. Gun'kin and E. V. Finaevova, *Russ. Chem. Bull.*, 1997, **46**, 2130.

105. I. F. Gun'kin and K. P. Butin, *Russ. Chem. Bull.*, 1999, **48**, 448.

106. K. Henrick, R. W. Matthews, and P. A. Tasker, *Inorg. Chim. Acta*, 1977, **25**, L31.

107. F. Brady, K. Henrick, and R. W. Matthews, *J. Organomet. Chem.*, 1979, **165**, 21.

108. K. Henrick, R. W. Matthews, and P. A. Tasker, *Inorg. Chem.*, 1977, **16**, 3293.

109. F. Brady, K. Henrick, and R. W. Matthews, *J. Organomet. Chem.*, 1981, **210**, 281.

110. C. Burschka, *Z. Anorg. Allg. Chem.*, 1982, **485**, 217.

111. J. Vicente, J. A. Abad, J. F. Gutierrez-Jugo, and P. G.Jones, *J. Chem. Soc., Dalton Trans.*, 1989, 2241.

112. P. J. Craig, in 'The Handbook of Environmental Chemistry', ed. O. Hutzinger, Springer, New York, 1980, Vol. 1, p. 169.

113. G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *J. Chem. Soc., Chem. Commun.*, 1971, 850.

114. G. Agnes, H. A. O. Hill, J. M. Pratt, S. C. Ridsdale, F. S. Kennedy, and R. J. P. Williams, *Biochim. Biophys. Acta*, 1971, **252**, 207.

115. F. Huber and H. Kirchmann, *Inorg. Chim. Acta*, 1978, **29**, L249.

116. O. F. Schedlbauer and K. G. Heumann, *Anal. Chem.*, 1999, **71**, 5459.

117. R. J. Phillips, M. J. Shane, and J. A. Switzer, *J. Mater. Res.*, 1989, **4**, 923.

118. Z. Z. Zheng and A. M. Herrmann, *Nature*, 1988, **332**, 138.

119. J. G. Bednorz and K. A. Müller, *Z. Phys. (B)*, 1986, **64**, 189.

120. B. Springfellow, 'Organometallic Vapor-Phase Epitaxy: Theory and Practice', Academic Press, New York, 1989.

121. T. Sugimoto, *Mater. Sci. Forum*, 1993, **137–139**, 395.

122. K. Zhang, E. P. Boyd, B. S. Kwak, A. C. Wright, and A. Erbil, *Appl. Phys. Lett.*, 1989, **55**, 1258.

123. A. D. Berry, R. T. Holm, R. L. Mowery, N. H. Turner, and M. Fatemi, *Chem. Mater.*, 1991, **3**, 72.

124. A. Ryohei and Y. Shiokawa, *Inorg. Chim. Acta*, 1993, **203**, 9.

125. D. S. Richeson, L. M. Tonge, J. Zhao, J. Zhang, H. O. Marcy, T. J. Marks, B. W. Wessels, and C. R. Kannewurf, *Appl. Phys. Lett.*, 1989, **54**, 2154.

126. P. Zanella, G. Rosetto, S. Sitran, and D. Ferro, *Eur. J. Sol. State Inorg. Chem.*, 1992, **29**, 181.

127. E. C. Taylor and A. McKillop, *Acc. Chem. Res.*, 1970, **3**, 338.

128. A. McKillop and E. C. Taylor, *Chem. Br.*, 1973, **9**, 4.

129. A. McKillop and E. C. Taylor, in 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, Vol. 7, p. 465.

130. H. M. C. Ferraz, L. F. Silva Jr, and T. de O. Vieira, *Synthesis*, 1999, 2001.

131. I. E. Marko and C. W. Leung, in 'Comprehensive Organometallic Chemistry II', eds. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, Oxford, 1995, Vol. 11, p. 437.