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(Organo)thallium (I) and (II) chemistry: syntheses, structures, properties and applications of subvalent thallium complexes with alkyl, cyclopentadienyl, arene or hydrotris(pyrazolyl)borate ligands[1]

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Abstract

This review gives a complete coverage of all aspects of organothallium(I) chemistry. Thallium(I) compounds containing the cyclopentadienyl and electronically related ligands, most notably the hydrotris(pyrazolyl)borate ligand are described in detail. In addition, thallium(I)–arene complexes and the alkyl- and arylthallium(I) and (II) species are covered. Furthermore, molecular thallium(II) complexes are included.

List of Abbreviations (alphabetical order)

Ac	acetyl, -C(O)Me
acac	acetylacetonate
$^{n/i/s/t}$Bu	*normal/iso-/sec-/tert*-butyl
CI	configuration interaction
cod	1,5-cyclooctadiene
cot	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl, general
diglyme	diethyleneglycol dimethylether
DMAC	N,N-dimethylacetamide
DME	dimethoxyethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
Et	ethyl
Et_2O	diethyl ether
HOMO	highest occupied molecular orbital
IR	infrared (spectroscopy)
Me	methyl
MO	molecular orbital

MS	mass spectrometry
MS (EI)	mass spectrometry (electron impact)
MS (CI)	mass spectrometry (chemical ionization)
MS (FAB)	mass spectrometry (fast atom bombardment)
NMR	nuclear magnetic resonance (spectroscopy)
Ph	phenyl
pmdeta	pentamethyl-diethylene-triamine
PPN	bis(triphenylphosphoranylidene)ammonium, $(Ph_3P{=})_2N^+$
$^{n/i}$Pr	*normal*/*iso*-propyl
pz	pyrazolyl
SCF	self consistent field
THF	tetrahydrofuran
Tol	tolyl
Tp	hydro-tris(pyrazolyl)borate, general

1. Introduction

Thallium has an outer electronic configuration of $6s^26p^1$ and this element exists (mainly) in the +1 and +3 oxidation states. Both oxidation states are well known and oxidation potential data indicate that the +1 state is more stable in aqueous solution (standard reduction potentials: $Tl^{3+} + 2e^- \rightarrow Tl^+$ $E^0 = 1.25$ V; $Tl^+ + e^- \rightarrow Tl$ $E^0 = -0.336$ V; the reaction is favorable for $E^0 > 0$ [1]). In the case of organothallium agents, the more common and more stable oxidation state is +3. The only organothallium(I) compounds isolable are those with the cyclopentadienyl ligand[3] and substituted derivatives thereof, arene–thallium(I) salts, the borinates, $(C_5H_5BR)Tl$, and thallium(I) salts of dicarba-undecaborane anions $[C_2RR'B_9H_9]^{2-}$. Monoalkyl- and -aryl-thallium(I) compounds have been proposed as intermediates in various reactions, but have never been isolated. (Note added in proof: See however Section 5.2.1. *Recent results*.)

A short section in this review summarizes the known molecular thallium(II) compounds which were only recently isolated. Uncharged molecular compounds of the type $(R_2E)_2$ with E = Al, Ga and In have been known for about 10 years through the pioneering work of Uhl [2]. In these compounds the metal assumes the formal +2 oxidation state. Subsequently, the $(R_2E)_2$ complexes have a tendency towards disproportionation, which can be blocked, however, by medium bulky substituents R to give a kinetic stabilization.

Among the hard acid group 13 metals Al^{3+}, Ga^{3+} and In^{3+}, thallium is unique as Tl^+ (and Tl^{3+}) is a soft acid on the hard acid–soft base classification of Pearson [3]. Thus, thallium(I) can be expected to show properties of both Ag^+ (soft acid) and K^+ (hard acid), which is indeed the case.[4]

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[3] The unspecified term *cyclopentadienyl ligands* (Cp) or *cyclopentadienylmetal complexes* is meant to include substituted derivatives of the C_5H_5 parent ligand such as C_5R_5 and the complexes thereof. If the parent cyclopentadienyl ligand or its thallium compound is meant exclusively, it is specifically stated by giving the formula C_5H_5 or C_5H_5Tl.

[4] For the use of organic (but not organo-) thallium(I) salts such as alkoxides, carboxylates or acetyacetonates in organic syntheses, see [4].

For the major part, the interest in (organo)thallium(I) chemistry derives from one or more of the following points:

(1) the structural diversity of cyclopentadienylthallium(I) compounds in combination with Cp–Tl (Cp = cyclopentadienyl) bonding and structure and bond-theoretical aspects of the in/active lone-pair of electrons (e.g. [5–12]);
(2) as a means of isolation and characterization of a (new) cyclopentadienyl or hydrotris(pyrazolyl)borate ligand[5] [13–17];
(3) as a mild (less reducing) and often more stable ligand transfer reagent in place of alkali metal salts, for cyclopentadienyl or hydrotris(pyrazolyl)borate ligands (for more elaborate work on this topic see, for example, [13–16], [18–40]);
(4) the use of cyclopentadienylthallium(I) [and organothallium(III)] in organic synthesis [4,41–61].

These points will be focused on in the following[6]. Reviews and overviews over thallium chemistry which deal with *organo*thallium compounds cover predominantly the +III oxidation state and mostly include only a short chapter on thallium(I) complexes [62–72].[7] Furthermore, many of these reviews date back to the 1970s, yet the last 10 years have seen quite a development in organothallium(I) chemistry. For recent overviews on organothallium chemistry giving appropriate wider coverage of the +I oxidation state, see [55,73,74]. Hence, we will look here at (organo)thallium(I) complexes to point out the special features in its metal chemistry at the low valent oxidation state. To broaden the scope of this review article we have also included ligands closely related to the cyclopentadienyl group, such as hydrotris(pyrazolyl)borate (see Section 2.4). We chose a subject rather than a compound-oriented review style; hence, we summarize the compounds under the subtopics of syntheses, structures, properties (stabilities and solubilities, NMR) and applications.

It should be mentioned that thallium and its compounds are extremely toxic and must be handled with appropriate safety precautions, e.g. gloves should be worn when handling such materials. Inhalation of dust and contact with skin should be avoided. Wastes should be collected and disposed of separately as heavy-metal waste. Thallium is a cumulative poison which may be absorbed by the skin. The letal dose for a human being is 13 mg Tl(kg body weight)$^{-1}$. For further physiological properties and symptoms of thallium poisoning, see Ref. [75] and literature cited therein.

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[5] Hydrotris(pyrazolyl)borate (also abbreviated as Tp) means ligands of the general type *HB*(3-*R*-4-*R*′-5-*R*″-*pz*)$_3^-$ (pz = pyrazolyl) thereby also encompasing (indazolyl)borate ligands. The latter are sketched separately in the table headings only to illustrate the numbering scheme of the annelated six-membered ring.

[6] We have aimed here at a complete coverage of the field, but the use of CpTl or TpTl as a ligand transfer agent or in organic synthesis can be quite difficult to detect as this is sometimes neither highlighted in the title nor the abstract. Hence, we can only extend our honest apologies to the authors whose contributions we have missed, and we would very much welcome these authors to let us know about their work for example by sending us reprints or the citation so that in the future we can give adequate reference to their work.

[7] Ref. [72], a source book on organothallium compounds, has C_5H_5Tl as its only entry for thallium(I).

2. Syntheses

2.1. Alkyl- and arylthallium(I) compounds

Organothallium chemistry started with attempts to prepare alkylthallium(I) compounds, but so far they have not been isolated in substance [48,49] (see, however, Section 5.2.1). Ethylthallium(I), C_2H_5Tl, could not be obtained from TlCl and $Zn(C_2H_5)_2$ or from metallic Tl and C_2H_5I or $Zn(C_2H_5)_2$, over 100 years ago [76], soon after the discovery of the element itself (see Ref. [77]). The reactions of Grignard reagents with thallium(I) halides have been investigated several times [43,49,70]: treatment of alkylmagnesium halides with TlCl resulted in the formation of metallic thallium [78]; phenylmagnesium bromide with TlBr also gave a quantitative reduction to metallic thallium [79]. Diethylthallium bromide and thallium metal was obtained from the reaction of ethylmagnesium bromide with TlCl or TlOEt (Et = ethyl) [80]. The major portion of the Grignard reagent in this reaction, however, undergoes decomposition to a mixture of ethane and ethene [81]. Primary aliphatic Grignard reagents with an excess of thallium(I) bromide (1:2 ratio) in general gave di-n-alkylthallium(III) bromides (alkyl = methyl to decyl) in 20 to 56% yield (together with thallium metal) [82]. From a mixture of ethylmagnesium bromide and ethyl bromide with TlBr in tetrahydrofuran (THF) solution, triethylthallium can be conveniently prepared [83]. Addition of TlBr to an ethereal solution of an equimolar amount of (ortho-substituted) phenylmagnesium bromide results in a rapid reduction of the thallium halide to metallic thallium and simultaneous, high-yield formation of symmetrical biaryls. A sequence of redox reactions between Tl(I) and Tl(III) also involving arylthallium(I) was suggested [43,45].

Upon electrolysis of a solution of ethylsodium in diethylzinc (giving ethyl radicals) with a thallium electrode (anode), dissolution of the metal was observed, and it was suggested that the first reaction is the formation of ethylthallium(I), which then disproportionates into Et_3Tl and finely divided metal [84].

A report on unsuccesful attempts to prepare phenylthallium(I), PhTl (Ph = phenyl), from TlCl and PhLi at low temperature (−70 °C) has appeared. Triphenylthallium and thallium metal was obtained instead, and a disproportionation reaction with the initial formation of PhTl was suggested [85]. Similarly, trimethylthallium is produced quantitatively from thallium(I) halides, methyl lithium and methyl iodide. If an excess of MeLi (Me = methyl) or EtLi was allowed to react with TlI or TlCl in the absence of MeI, two thirds of the thallium was reduced to the metal and only one third appeared as Me_3Tl. It was again suggested that MeTl is first formed and then undergoes immediate disproportionation as outlined in Eq. (1) [86–88]:

$$3MeLi + 3TlX \rightarrow 3LiX + [3MeTl] \rightarrow 3LiX + Me_3Tl + 2Tl. \tag{1}$$

With methyl iodide present, it was proposed that the finely divided metal formed can then react in an oxidative addition with formation of Me_2TlI which can further react with MeLi under formation of Me_3Tl [86]. Triethylthallium is likewise formed in a 79–100% yield from the reaction of ethyllithium, thallium chloride and ethyl chloride, ethyl bromide or ethyl iodide. Phenyllithium, thallium(I) chloride and iodobenzene gave triphenylthallium [87]. The reaction of TlI with MeLi in the presence of C_3F_7I, however, failed to give mixed compounds of the type $Me_n(C_3F_7)_{3-n}Tl$ [89].

The transitory formation of PhTl was suggested in the reaction of Ph_3Tl with CO_2 in boiling xylene (no reaction occurred at room temperature) to give benzoic acid and biphenyl, in the reaction with benzophenone in boiling xylene, which gave Ph_3COH and biphenyl, and with benzonitrile in boiling xylene, from which metallic Tl, the trimer of benzonitrile, benzophenone, and biphenyl were obtained. In all three cases, an initial pyrolysis of Ph_3Tl to biphenyl and PhTl, and reaction of the latter *in situ* with CO_2 (to give the intermediate $PhCO_2Tl$) or with the organic compounds (benzophenone and benzonitrile), was suggested [62,65,85,90].

In the pyrolysis of Me_3Tl, which produces three methyl radicals and free thallium and which was investigated at temperatures of 452–536 K (179–263 °C), methylthallium(I) was suggested as an intermediate step in a sequence of reactions [Eqs. (2)–(4)], based on the product distribution and amount of decomposition [91,92]:

$$Me_3Tl \rightarrow Me_2Tl^{\cdot} + Me^{\cdot}, \tag{2}$$

$$Me_2Tl^{\cdot} \rightarrow MeTl + Me^{\cdot}, \tag{3}$$

$$MeTl \rightarrow Tl^{\cdot} + Me^{\cdot}. \tag{4}$$

From polarographic studies of diphenylthallium cations in aqueous solution with a dropping mercury electrode, it was proposed that reduction initially yields a strongly adsorbed diphenylthallium(II) and that at more negative potentials, the successive reduction to an adsorbed PhTl(I) occurred. PhTl would then rapidly disproportionate to give thallium metal and diphenylmercury [93]. For the polarographic reduction of monophenylthallium(III) perchlorate in aqueous solution, a three-step reaction mechanism with $(Hg\cdots)Ph\text{-}Tl^{+}$ and $(Hg\cdots)Ph\text{-}Tl$ intermediates was postulated [94]. Electron impact studies of $(RCOO)_3Tl$ (R = Me, Ph) showed RTl^{+} [95].

The instability of TlR, i.e. the driving force derived from the deposition of thallium metal, has been utilized in the reactions of magnesium, zinc and cadmium dialkyls (MR_2) with $HB(3,5\text{-}R',R''\text{-pz})_3Tl$ (pz = pyrazoyl) to give $\{HB(3,5\text{-}R',R''\text{-pz})_3\}MR$. Similarly, trimethylaluminum and $HB(3\text{-}{}^tBu\text{-pz})_3Tl$ gave $HB(3\text{-}{}^tBu\text{-pz})_3AlMe_2$ (${}^tBu$ = *tert*-butyl) (see below: Section 5.2, Eq. (27)).

The molecular properties of organothallium(I–III) compounds, including the hitherto undetected MeTl molecule have been calculated with spin-orbit averaged pseudopotential calculations. The thallium–carbon bond length was calculated as 2.233 Å, the Tl–Me dissociation energy was 59 $kJ\,mol^{-1}$, the latter indicating that MeTl is only weakly bound so that decomposition reactions may be easily possible [96].

The difficulty of isolating monoalkyl- or -arylthallium(I) species is not surprising in view of the coordinative unsaturation of such compounds. For the lighter congeners (Al, Ga or In), cluster formation is a prominent feature, as in $[Al_4(Si^tBu_3)_4]$, $[Al_4(CH_2{}^tBu)_4]$ and $[Al_6{}^tBu_6]^{-}$ [102]. The alkylgallium(I) compound $GaC(SiMe_3)_3$ was found to be monomeric in the gas phase and in dilute benzene solution, but tetrameric in the solid state with a nearly undistorted tetrahedral core of four Ga atoms [97]. The analogous indium compound $[InC(SiMe_3)_3]_4$ remained tetrameric in dilute benzene solution [98]. For the stabilization of monomeric or oligomeric organometal(I) group-13 compounds, the pentamethylcyclopentadienyl ligand or arene ligands are important [73,99–102]. The hitherto noted failure of thallium(I) alkyls to resort to a similar oligomerization, as found for aluminum through indium, has been theoretically explained by the weakness of Tl–Tl bonds. Such Tl–Tl bonds are theoretically found to be weak or not existent because of spin-orbit coupling and inert pair effects [96,103]. While relativistic effects almost always seem to result in a contraction of bond lengths for heavy elements, Tl_2 and Tl_2^- are noted as an exception: here, relativistic effects largely destroy the bond [103]

In the case of the low-valent group-14 elements (E = Ge, Sn, and Pb) the synthesis of the dialkylmetal complexes, R_2E (found monomeric or dimeric in the solid state), required the utilization of sterically demanding groups such as bis(trimethylsilyl)-methyl, $(Me_3Si)_2CH-$ [104], tris(isopropy)phenyl, C_6H_2-2,4,6-$^iPr_3$ (^iPr = *iso*-propyl) [105] or C_6H_2-2,4,6-$(CF_3)_3$ [106]. Otherwise, the isolable and kinetically stable organoelement(II) compounds of group-14 are also confined to the mono- and bis-cyclopentadienyl derivatives [107].

In organothallium chemistry, the use of bulky alkyl-type ligands such as $(Me_3Si)_3Si$ or $^tBu_3Si$ still did not allow the stabilization of the thallium(I) species. While they may be initially formed, rapid disproportionation to divalent thallium, which is then stabilized, and thallium metal occurs. The reaction of thallium(I)-bis(trimethylsilyl)amide, $TlN(SiMe_3)_2$, with rubidium tris(trimethylsilyl)silyl [hypersilylrubidium, $(Me_3Si)_3SiRb$] in a toluene–pentane mixture gave tetrakis(hypersilyl)dithallium(*Tl–Tl*) together with thallium metal between −30 and −60 °C [108]. The reaction of TlBr with supersilylsodium ($^tBu_3SiNa$) in THF at −78 °C gives tetrasupersilyldithallium(*Tl–Tl*) together with thallium metal (see below: Section 2.5) [109].

2.2. *Cyclopentadienylthallium(I) compounds*

2.2.1. *Neutral cyclopentadienylthallium compounds*

The organometallic thallium(I) compounds of any significance are those containing the cyclopentadienyl ligand and derivatives thereof. Soon after the discovery of ferrocene in 1951 and the recognition of its importance [110], cyclopentadienylthallium, C_5H_5Tl, was synthesized independently by Meister [111] and Fischer [112]. They used the reaction of cyclopentadiene with thallium(I) sulfate in aqueous potassium hydroxide, from which the product precipitated in nearly quantitative yield (method I, Eqs. (5a) and (5b)). This reaction can be viewed as a combined metathesis and acid–base reaction:

Method I:

$$2CpH + 2KOH + Tl_2SO_4 \cdot \xrightarrow{H_2O} 2CpTl\downarrow + K_2SO_4 + 2H_2O. \tag{5a}$$

$$CpH + TlOH \cdot \xrightarrow{H_2O} CpTl\downarrow + H_2O. \tag{5b}$$

The potassium hydroxide reacts with the thallium salt with formation of TlOH, which then reacts with the diene to precipitate the cyclopentadienylthallium complex, so the actual product forming reaction is given in Eq. (5b). A 10% KOH solution is usually employed. For the less reactive dihydropentalene and isodicyclopentadiene a more basic medium of 25% KOH was recommanded [9]. The preparation of C_5H_5Tl by method I and its purification has been repeatedly described in the literature [65,111–116] including an *Inorganic Synthesis* procedure [117]. Instead of the soluble sulfate, a variety of thallium salts, namely TlCl, TlBr, TlSCN, $TlNO_3$ and thallium acetylacetonate, also gave essentially quantitative yields of C_5H_5Tl. Only thallium(I)iodide was found not to react [31].

A second route which can generally be applied to the synthesis of cyclopentadienyl thallium compounds is the metathesis or salt-elimination reaction (method II, Eq. (6)):

Method II:

$$\mathrm{CpM + TlX \rightarrow CpTl + MX}, \tag{6}$$

where M = alkali metal, Li, Na, or K; X = mostly inorganic anion, e.g. Cl, $(SO_4)_{1/2}$, but also acetate, OAc (Ac = acetyl), or ethoxide, EtO.

The metathesis reaction can also proceed between the alkali metal cyclopentadienide and thallium ethoxide in ethanol, which provides a valuable route especially for functionally substituted cyclopentadienylthallium derivatives [37,118]. The metathesis reaction between $(C_5H_5)_2Hg$ and TlOH also gives C_5H_5Tl [119]. Without further details, it was reported that cyclopentadienylation of TlCl to C_5H_5Tl by $(C_5H_5)_2YbCl$ has been demonstrated [119a].

As a third alternative, direct metallation of the cyclopentadiene in an acid–base-type reaction with liquid thallium(I) ethoxide, TlOEt [or in a few cases also thallium(I) methoxide [120]] is an elegant route as it is homogeneous and free of alkali metal salt precipitates (method III, Eq. (7)). In addition, the hydrocarbon can be employed directly without the necessity of alkali metallation. Both Eqs. (6) and (7) can be carried out in ethereal or hydrocarbon solvents. A higher yield can usually be expected from method III in comparison to method II [6]:

Method III:

$$\mathrm{CpH + TlOEt \rightarrow CpTl + EtOH}. \tag{7}$$

The reaction depicted in Eq. (7) is essentially a variant of the acid–base reaction described in Eq. (5b) with thallium hydroxide for method I. Method I requires, however, water- (and usually also air-) stability of the cyclopentadienylthallium product. In cases where this prerequisite has not been fulfilled, the failure of this synthetic approach has been noted, e.g. for C_5H_4BrTl and C_5H_4ITl [20]; hence, it appears useful to discern between the use of thallium hydroxide or ethoxide as the base.

Indene and fluorene failed to give the corresponding thallium derivatives by method III, apparently due to the much smaller acidities of indene or fluorene with respect to cyclopentadiene(s) [9,121]. In the case of the perphenylated cyclopentadienyl complexes C_5HPh_4Tl, C_5Ph_5Tl and $C_5Ph_4(C_6H_4\text{-}4\text{-}^tBu)Tl$, method III had to be applied while method I and II proofed unsuccessful. This was beacuse from the latter two, the desired products could only be obtained in low yield and purification was not possible [122].

In yet another variant of the acid–base reaction, the thallium complex of pentakis (methoxycarbonyl)cyclopentadienide, $C_5(CO_2Me)_5^-$, was obtained from Tl_2CO_3 and the diene in water with evolution of CO_2 [160]. In most metal complexes with this ligand, the metal is, however, chelated by the carboxylate groups with formation of a metal–oxygen ion pair and only a few complexes contain the C_5 ring σ- or π-bonded to a metal [174]. Table 1(a) lists the known neutral and cationic cyclopentadienylthallium compounds together with their method of preparation.

Sublimation is often a preferred method of purification for cyclopentadienylthallium complexes [9,20,122]. It should be noted that occasionally, identification of the organothallium compound was performed by utilizing it in a reaction with a transition metal salt as a ligand transfer agent (see Section 5). Successful formation of the organotransition metal compound was then viewed as a proof for the existence of the organothallium reagent. Such was for example the case with isodicyclopentadienylthallium(I), $C_5H_3(C_5H_8)Tl$ [18], fluorenylthallium [123], pyrrolylthallium [123] and (trifluoromethyl)cyclopentadienylthallium [14].

2.2.1.1. Special syntheses of cyclopentadienylthallium complexes

Electrophilic Cp-ring substitution. A few reactions have been reported where the cyclopentadienyl ring of C_5H_5Tl was electrophilically substituted with retention of the Cp–Tl complex. The reaction of tetracyanoethylene $[(NC)_2C{=}C(CN)_2]$ with C_5H_5Tl results in the formation of (tricyanovinyl)cyclopentadienylthallium(I), $C_5H_4\{C(CN){=}C(CN)_2\}Tl$ and HCN [32,140]. Similarly the reaction with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene yields $C_5H_4\{C(CF_3)_2CH(CN)_2\}Tl$ [32].

With functional ring substituents present, such as aryl-thio, *S*-alkylation was performed with trimethyloxonium–tetrafluoroborate $[Me_3O]BF_4$, to give thallium alkylarylsulfonium cyclopentadienides with retention of the Cp–Tl moiety (see also Eq. (24) in Section 5.1) [53].

Transesterification of an ester-substituted cyclopentadienylthallium complex with thallium ethoxide. When solutions of $C_5H_5(CH_2CO_2Me)$ or $C_5H_5(CH_2CH_2CO_2Me)$ were reacted with $TlOEt$, a mixture of $C_5H_4(CH_2CO_2Me)Tl/C_5H_4(CH_2CO_2Et)Tl$ or $C_5H_4(CH_2CH_2CO_2Me)Tl/C_5H_4(CH_2CH_2CO_2Et)Tl$ was obtained, respectively. The reaction occurred when the excess TlOEt was given enough time to exchange the methoxide group of the substituent for an ethoxide [120].

Oxidative ligand transfer from CpIn. Cyclopentadienylindium(I), C_5H_5In, reacts with finely divided thallium metal at 50 °C. Continued heating under high vacuum leads to a sublimation of a mixture of cyclopentadienylthallium and -indium (mass

Table 1
Neutral cyclopentadienylthallium(I) compounds and their method of synthesis (ordering within each section with increasing molar mass of the Cp ligand). The table is divided into: (a) mononuclear complexes; and (b) dinuclear complexes. For cyclopentadienylthallium(I) anions, arene complexes and other compounds with Cp-related ligands, see text

Formula CpTl (name of ligand)	Method[a]	Yield (%)	Reference
Mononuclear complexes			
$50 < Cp < 100\ g\ mol^{-1}$			
C_5H_5Tl	I	95	[31,111,113]
	I	91-94	[117]
	I	61	[65,112,114,115]
	II ($Cp_2Hg + TlOH$)	30	[119]
	II ($Cp_2YbCl + TlCl$)	Not given	[119a]
	Special ($CpIn + Tl$)	Not given	[114]
	Special ($C_xH_y + Tl$)	3	[114]
C_5H_4MeTl	I	76	[124]
$C_5H_4(CN)Tl$	III	Not given	[23]
	I	40	[125,126]
$C_5H_4(CH{=}CH_2)Tl$	II ($CpLi + TlOEt$)	88	[118]
$C_5H_4(CHO)Tl$	II ($CpK + TlOAc$)	95	[19]
	II ($CpNa + TlOEt$)	Quantitative	[37]
C_5H_4EtTl	I	86	[127]
C_5H_4ClTl	III, I	72, 69	[20]
$100 < Cp < 150\ g\ mol^{-1}$			
C_8H_7Tl (hydropentalenyl) 	I	Quantitative	[18]
$C_5H_3\{\text{-}1,2/1,3\text{-}Me(CHO)\}Tl$ (mixture of isomers)	II ($CpK + TlOAc$)	ca. 75	[125]
$C_5H_4\{C(O)Me\}Tl$	II ($CpK + TlOAc$)	90	[19]
$C_5H_4(NO_2)Tl$	II ($CpNa + TlOEt$)	79	[37]
	II ($CpNa + TlOAc$)	82	[128]
$C_5H_4(SMe)Tl$	III	67	[53]
C_9H_7Tl (indenyl)	I (90 °C)	80	[129]
$C_5H_3\{\text{-}1,2\text{-}(CHO)_2\}Tl$	III	95	[54]
$C_5H_4{}^tBuTl$	I	67	[127]
C_5HMe_4Tl	III	61	[130]
$C_5H_4(PMe_2)Tl$	III	80	[131]
$C_5H_3(C_5H_8)Tl$ (isodicyclopentadienyl) 	I	not given	[18]

Table 1 (*continued*)

Formula CpTl (name of ligand)	Method[a]	Yield (%)	Reference
$C_5H_4(CF_3)Tl$	III	55–60	[14]
$C_5H_4(CO_2Me)Tl$	I	38, ca. 80	[132–134]
	II (CpNa + TlOEt)	93	[37]
C_5Me_5Tl	II (CpLi,Na + Tl_2SO_4)	70	[21,135]
$C_5H_4\{C(O)NMe_2\}Tl$	III	37	[125]
$C_5H_4(CH_2CH_2NMe_2)Tl$	III	90	[136]
$C_5H_4(CO_2Et)Tl$	I	65	[126]
	II (CpNa + TlOEt)	Quantitative	[37]
$C_5H_4\{C(O)CH_2OMe\}Tl$	I	Not given	[120]
$C_5H_4(CH_2CO_2Me)Tl$	III	Not given	[120]
	III w. TlOMe, not pure[b]	Not given	[120]
$C_5H_4(SiMe_3)Tl$	III	>80	[7]
C_5H_4PhTl	III	60, 80–90	[19,24]
C_5H_4BrTl	II	96	[20]
$C_5H_3\{\text{-}1,2\text{-}C(O)Me\}_2Tl$	III	93	[54]
$150 < Cp < 200$ g mol^{-1}			
$C_5H_4(CO_2{}^iPr)Tl$	I	60	[126]
$C_5H_4(CH_2CO_2Et)Tl$	III with transesterification	Not given	[120]
$C_5H_4(CH_2CH_2CO_2Me)Tl$	III	Not given	[120]
	III w. TlOMe, not pure[b]	Not given	[120]
$C_5H_4(CH_2CH_2O_2CMe)Tl$	III	Not given	[120]
C_5F_5Tl	Deprot. of C_5F_5H w. $TlN(SiR_3)_2$?		[137]
$C_5H_4(CH_2Ph)Tl$	III	Quantitative	[24]
$C_5H_4(C_6H_4\text{-}3\text{-}F)Tl$	I	73	[138,139]
$C_5H_4(C_6H_4\text{-}4\text{-}F)Tl$	I	74	[138,139]
$C_{13}H_9Tl$ (fluorenyl) (see also text)	II ($C_{13}H_9Na + Tl_2SO_4$)	Not given	[123]
$C_5H_4\{C(O)CO_2Et\}Tl$	II (CpNa + TlOAc)	15	[128]
$C_5H_4(CH_2CH_2CO_2Et)Tl$	III with transesterification	Not given	[120]
$C_5H_4\{C(CN){=}C(CN)_2\}Tl$	special [$C_5H_5Tl + (NC)_2C{=}C(CN)_2$]	85–90	[140]
$C_5H_4\{C^*H(Me)Ph\}Tl$	III	Not given	[138]
$C_5H_4(SPh)Tl$	III	78	[53]
$C_5H_3(\text{-}1,3\text{-}{}^tBu_2)Tl$	I	19	[127]
$C_5H_2[\text{-}1,5\text{-}\{C(O)Me\}_2\text{-}3\text{-}NO_2]Tl$	III	94	[54]
$C_5H_4(SC_6H_4\text{-}4\text{-}Me)Tl$	III	82	[53]
$[C_5H_4\{S(Me)Ph\}Tl]^+BF_4^-$	Special [Eq. (24)]	52	[53]
C_5H_4ITl	II	89	[20]
$C_5Me_4(CH_2CH_2NMe_2)Tl$	III	76	[136]
$200 < Cp < 300$ g mol^{-1}			
$[C_5H_4\{S(Me)C_6H_4\text{-}4\text{-}Me\}Tl]^+BF_4^-$	Special [Eq. (24)]	61	[53]
$C_5H_3\{\text{-}1,3\text{-}(SiMe_3)_2\}Tl$	III	>80	[7]
$C_5H_3(\text{-}1,3\text{-}Ph_2)Tl$	III	80	[141]

Table 1 (*continued*)

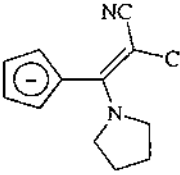
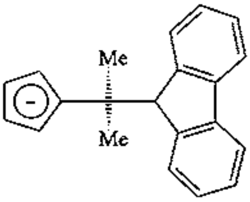
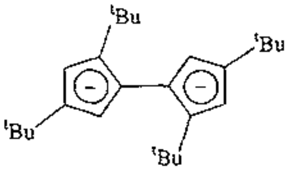
Formula CpTl (name of ligand)	Method[a]	Yield (%)	Reference
$C_5H_4[C\{N(CH_2)_5\}=C(CN)_2]Tl$ (cyclopentadienyl-methylenemalonitrile) 	II ($CpNa + Tl_2SO_4$)	Not given	[61]
$C_5H_4\{C(^iPr)=N-C_6H_4\text{-4-Me}\}Tl$	I	ca.90	[142]
C_5Cl_5Tl	III	quantitative	[150,151]
	Special, $C_5Cl_6 + Tl/Hg$	15–34	[150]
$C_5Cl_5Tl(toluene)_2$	III in toluene		[150]
$C_5H_4(PPh_2)Tl$	III	98,70	[144–146]
$C_5Me_4\{Si(Me_2)Ph\}Tl$	III	63	[147]
$C_5H_4\{SC_6H_3\text{-2,4-}(NO_2)_2\}Tl$	III	Not given	[53]
$C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$	III	71	[147]
$C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ (2 modifications[c]) (cyclopentadienyl-methylethyl-fluorene) 	II (CpLi + TlCl)	46	[6]
	or III	85	[6]
$C_5H_4\{C(CF_3)_2CH(CN)_2\}Tl$	Special [$C_5H_5Tl + (CF_3)_2C=C(CN)_2$]	Quantitative	[32]
$C_5H_2\{1,2,4\text{-}(SiMe_3)_3\}Tl$	II (CpLi + TlCl)	60	[148]
$C_5H_4(AsPh_2)Tl$	III	55	[154]
$300 < Cp < 400\ g\ mol^{-1}$			
$C_5H_3[\text{-1,2-}\{C(O)C_6H_4\text{-4-Me}\}_2]Tl$	III	93	[54]
$C_5Me_4(PPh_2)Tl$	III	82	[13]
$C_5(CO_2Me)_5Tl$ {pentakis-(methoxycarbonyl)-cyclopentadienide}	$C_5(CO_2Me)_5H + Tl_2CO_3$	90	[160]
C_5HPh_4Tl	III	92	[122]

Table 1 (*continued*)

Formula CpTl (name of ligand)	Method[a]	Yield (%)	Reference
$400 < \mathrm{Cp} < 500$ g mol^{-1}			
$Cr(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$	Special, see text	60	[149]
C_5Ph_5Tl	III	98	[122]
$Mo(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$	Special, see text	65	[149]
$500 < \mathrm{Cp} < 1100$ g mol^{-1}			
$C_5Ph_4(C_6H_4\text{-}4\text{-}{}^tBu)Tl$	III	98	[122]
$C_5(CH_2Ph)_5Tl$ (2 modifications[c])	III	75	[122]
$C_5(C_6H_4\text{-}4\text{-}Et)_5Tl$	III	78	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O)Me\}_5Tl$	III	76	[153]
$C_5(C_6H_4\text{-}4\text{-}{}^nBu)_5Tl$	III	55	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O){}^nPr\}_5Tl$	III	73	[153]
$C_5(C_6H_4\text{-}4\text{-}CO_2Et)_5Tl$	III	78	[153]
$C_5(C_6H_4\text{-}4\text{-}nC_6H_{13})_5Tl$	III	54	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O)nC_5H_{11}\}_5Tl$	III	70	[153]
$C_5(C_6H_4\text{-}4\text{-}nC_8H_{17})_5Tl$	III	59	[152]
$C_5(C_6H_4\text{-}4\text{-}CO_2\text{-}nC_5H_{11})_5Tl$	III	67	[153]
$C_5(C_6H_4\text{-}4\text{-}C(O)nC_7H_{15})_5Tl$	III	57	[153]
Dinuclear complexes			
$Tl\text{-}C_5H_4\text{–}C_5H_4\text{-}Tl$ (fulvalene–dithallium)	III	95, 87–100	[27,29]
$Tl\text{-}C_5H_3\text{-}CH_2\text{-}C_5H_3Tl$	III	60	[30]
$PhP(C_5H_4Tl)_2$	III	63	[155]a
$Tl(\text{-}1,3\text{-}{}^tBu_2)H_2C_5\text{–}C_5H_2(\text{-}1',3'\text{-}{}^tBu_2)Tl$ (tetra-*tert*-butyl-pentafulvalene)	II (CpLi + TlCl)	16	[5]
			
trans-$Cr(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	III {from $Cr(CO)_4(P\text{-}Ph_2PC_5H_5)_2$}	90	[149]
	Special, see text	90	[149]
cis-$Mo(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	III {from $Mo(CO)_4(P\text{-}Ph_2PC_5H_5)_2$}	85	[149]
	Special, see text	Quantitative	[149]
cis-$PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$	Special, see text	Not given	[155]
$Au_2[(P\text{-}Ph_2PC_5H_4)_2Tl]_2$ (see also Section2.2.2)	Special, see text	30	[156]

---

[a] Method I, formation in basic aqueous solution from CpH and TlOH [Eqs. (5a) and (5b)]; method II, metathesis reaction, see Eq. (6); method III, acid–base reaction between CpH and TlOEt [Eq. (7)].

[b] The compound contained 10–20% of C_5H_5Tl impurities, the possible source being the deprotonation reaction $2TlOMe + 2C_5H_5R \rightarrow C_5H_4RTl + MeOH + C_5H_5Tl + ROMe$, with $R = CH_2CO_2Me$ or $CH_2CH_2CO_2Me$ [120].

[c] Type of modification obtained depends on method of preparation or the work-up procedure.

spectrometry). No yield for the thallium compound has been given and because of purification problems the reaction may be of academic interest only, concerning the equilibrium reaction between thallium and indium (Eq. (8)). The displacement of the equilibrium towards the thallium complex is explained by its greater stability and the very high reactivity of the indium compound [114]:

$$\mathrm{C_5H_5In + Tl^0 \rightleftarrows C_5H_5Tl + In^0}. \tag{8}$$

Direct hydrocarbon metallation by thallium metal. At elevated temperature (500 °C) several hydrocarbons were found to give C_5H_5Tl. The following hydrocarbons which all contain the fragment structure CH–CH–CH–CH–CH_2- gave cyclopentadienylthallium: bicyclo[2,2,1]hepta-2,5-diene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, 1,4-cyclohexadiene, cycloheptratriene, cycloheptene, cyclohexene, 2-pentene, 1-octene, cyclohexane, octane and pentane. Besides the thallium compound (mass spectrometric identification), ethylene, acetylene, hydrogen, carbon, traces of benzene and polymeric material were formed, and about 60% of the starting hydrocarbon was recovered unreacted. Thallium metal can be assumed to catalyze the decomposition of the hydrocarbon then react with the cyclopentadiene formed, which is followed by trapping of the volatile cyclopentadienylthallium. Hydrocarbons not containing the above partial structure, such as benzene, cyclooctatetraene, isoprene or isobutylene failed to lead to the formation of C_5H_5Tl [114].

Ligand displacement with a functional cyclopentadienylthallium complex. When solutions of $AuCl(SMe_2)$, $PtPh_2(cod)$ (cod = 1,5-cyclooctadiene), $Cr(CO)_6$ and $Mo(CO)_6$, $C_7H_8Cr(CO)_4$, and $C_7H_8Mo(CO)_4$ are reacted with the respective equivalents of $Ph_2PC_5H_4Tl$, ligand exchange reactions take place and the dimethylsulfide, cyclooctadiene and cycloheptatriene ligands are replaced by the $Ph_2PC_5H_4Tl$ group, which coordinates through the phosphorus to the transition metal center under retention of the Cp–Tl bond [Eqs. (9a) and (9b)]. In the case of the gold compound, TlCl is also formed [see Eq. (10) in Section 2.2.2]. Hence, $Au_2^+[(P\text{-}Ph_2PC_5H_4)_2Tl]_2^-$ [156], $PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$ [155], $Cr(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$ and $Mo(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$, *trans*-$Cr(CO)_4$-$(P\text{-}Ph_2PC_5H_4Tl)_2$ and *cis*-$Mo(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$ [149] are obtained as products. The carbonyl substitution in the hexacarbonyl complexes of Cr and Mo is assisted by trimethylamine-*N*-oxide [Eq. (9a)] [149]. For the gold–thallium complex, an X-ray structure is available which suggests the ionic formulation indicated above [156] [see also under cyclopentadienylthallium(I) anions, Section 2.2.2]. For the mixed thallium–platinum, –chromium and –molybdenum compounds, no structrual data is available.

$$\mathrm{M(CO)_6 + Ph_2PC_5H_4Tl \xrightarrow{Me_3NO} M(CO)_5(\mathit{P}\text{-}Ph_2PC_5H_4Tl) + CO} \tag{9a}$$

M = Cr, Mo,

$$\mathrm{ML^1L^2_m + 2Ph_2PC_5H_4Tl \rightarrow ML^2_m(\mathit{P}\text{-}Ph_2PC_5H_4Tl)_2 + L^1}, \tag{9b}$$

The chromium and molybdenum complexes can also be prepared by a

M	L^1	L^{2m}
Pt	cod	Ph_2
Cr	C_7H_8	$(CO)_4$
Mo	C_7H_8	$(CO)_4$

different route, namely the reaction of *trans*-$Cr(CO)_4(Ph_2PC_5H_5)_2$ and *cis*-$Mo(CO)_4(Ph_2PC_5H_5)_2$, respectively, with thallium(I) ethoxide [method III, see Eq. (7) above] [149].

2.2.2. *Cyclopentadienylthallium(I) anions*

When a solution of $AuCl(SMe_2)$ is reacted with 1.5 equivalents of $C_5H_4(PPh_2)Tl$, a tetrametallic species (and TlCl) is formed, which was initially described as $[TlAu(C_5H_4PPh_2)_2]_2$ [Eq. (10)] [156]. Based on the metal–ligand arrangement shown in the X-ray structure, we would, however, suggest that the complex may be better described as being built up from gold cations and thallium anions according to the formula $Au_2^+[(P\text{-}Ph_2PC_5H_4)_2Tl]_2^-$. This complex would then represent the first synthesized organothallium(I) anion:

$$2AuCl(SMe_2)+4C_5H_4(PPh_2)Tl \rightarrow [TlAu(C_5H_4PPh_2)_2]_2+2TlCl+2SMe_2. \tag{10}$$

A similar ligand displacement reaction has been reported with $PtPh_2(cod)$ to give *cis*-$PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$ although no structural analysis has been carried out [155].

The mononuclear cyclopentadienylthallate(I) anions were obtained by reaction of C_5H_5Tl with $(C_5H_5)_2Mg$ or C_5H_5Li in tetrahydrofuran (THF) followed by addition of a chelating ligand (here, pentamethyl-diethylene-triamine, pmdeta) for the cation to allow precipitation and crystallization [157,158]. These reactions given in Eqs. (11) and (12) can be classified as a complete or partial ligand transfer or abstraction from magnesium or lithium onto thallium.

$$C_5H_5Tl+(C_5H_5)_2Mg \xrightarrow{\text{THF, pmdeta}} [C_5H_5Mg(\text{pmdeta})]^+[Tl(C_5H_5)_2]^- \tag{11}$$

$$C_5H_5Tl+C_5H_5Li \xrightarrow{\text{THF, pmdeta}} [Li(\text{pmdeta})(\mu\text{-}C_5H_5)Tl(C_5H_5)]. \tag{12}$$

When C_5H_5Li was reacted with C_5H_5Tl in a 1:2 molar ratio in THF in the presence of two equivalents 12-crown-4 a dinuclear thallium triple-decker sandwich anion is obtained [Eq. (13)]. This anion was said to be the first homometallic main group metal triple-decker sandwich. Furthermore, it is the next homologue of the thallocene anion $[(C_5H_5)_2Tl]^-$ [obtained by Eq. (11)] [158,159]:

$$2C_5H_5Tl+C_5H_5 \xrightarrow{\text{hexane-THF,2([12] crown 4)}} [Li([12]\text{-crown} \tag{13}$$

$$\text{-}4)_2]^+[(C_5H_5)Tl(\mu-C_5H_5)Tl(C_5H_5)]^-(\text{THF}).$$

2.3. Compounds with thallium(I)–arene interactions

So far, we are aware of 11 thallium(I)–arene complexes where the arene is a free molecule and not part of metal–ligand system and which could be synthesized and isolated in substance: two mono(arene)thallium(I) complexes, $(C_6H_6)[TlAlCl_4]_2$ [161] and $Tl^+(C_6H_5Me)_{2/3}$[*commo*-3,3′-$Al(3,1,2\text{-}AlC_2B_9H_{11})_2]^-$ [162,163]; one mixed mono- and bis(arene)thallium(I) complex $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ [99,164]; and seven bis(arene)thallium(I) complexes, $(C_6H_6)_2[TlAlCl_4]$ [161], $Cl_5C_5Tl(C_6H_5Me)_2$ [150], $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ [165], $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ [166], $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ [167,168] and $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ [168]. In addition, a 1:1 [2.2]paracyclophane–$Tl[GaCl_4]$ complex has been described [169].

The bis(toluene) adduct of the thallium salt of the pentachlorocyclopentadienide anion crystallized when the reaction of TlOEt with Cl_5C_5H was carried out in toluene. No structural studies have been reported, however [150,151]. In addition, the stable toluene coordinated thallium cation with the metallacarborane anion can be considered a fortuitous formation, due to the inclusion of the toluene solvate molecules [162]. The Tl(I) salt of the aluminacarborane [*commo*-3,3′-$Al(3,1,2\text{-}AlC_2B_9H_{11})_2]^-$ was prepared by addition of aluminum alkyl derivatives to a suspension of $Tl^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$ in toluene and precipitated upon addition of heptane [163]. In solution, more arene complexes are certain to be present, as thallium(I) salts like $Tl[AlCl_4]$, $Tl[AlBr_4]$, $Tl[GaCl_4]$ and $Tl[GaBr_4]$ are soluble in hot benzene, mesitylene or hexamethylbenzene. These solution–arene complexes are reported to be very unstable and difficult to access preparatively [99]. The benzene complexes $(C_6H_6)[TlAlCl_4]_2$ and $(C_6H_6)_2[TlAlCl_4]$ were reported as the first two thallium–arene complexes [161]. Their possible existence had already been proposed over a decade earlier [170]. The preparation of these complexes was not described directly, but in Ref. [161] it was referred to the synthesis of the analogous copper and silver compounds $(C_6H_6)[MAlCl_4]$ (M = Cu, Ag). These were obtained by treating a slight excess of MCl with $AlCl_3$ and benzene, followed by heating for 2 h at 40 °C [171]. Furthermore, $(C_6H_6)_2[TlAlCl_4]$ can be transformed under vacuum at ambient temperature into the more stable $(C_6H_6)[TlAlCl_4]_2$ [161]. However, definitive structural proof for these two complexes is still not available.

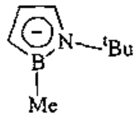
For the intentional synthesis only the trimethylbenzene molecules mesitylene, $C_6H_3\text{-}1,3,5\text{-}Me_3$, or pseudocumol, $C_6H_3\text{-}1,2,4\text{-}Me_3$, as well as [2.2]paracyclophane $(p\text{-}C_6H_4CH_2CH_2)_2$, could be successfully employed as arene ligands for isolation. The complex $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ could be obtained from a solution of $Tl[GaBr_4]$ and mesitylene in hot benzene or toluene [99,164]. Cooling a mesitylene solution of $TlOTeF_5$ afforded crystals of $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2\text{-}TlOTeF_5]_2(C_6H_3\text{-}1,3,5\text{-}Me_3)$. A weak affinity of solid $TlOTeF_5$ for benzene was also demonstrated by titration with benzene vapor and vapor pressure measurements [167,168]. The addition of $B(OTeF_5)_4$ to a mesitylene solution of $TlOTeF_5$ produced $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ (89% yield) [168]. From a room-temperature solution of a mixture of TlCl and $AlCl_3$ or $GaCl_3$ in mesitylene or pseudocumol, the complexes $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ [165], $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$, and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ [166], respectively, could be crystallized almost quantitatively by cooling to 0 °C. When a hot toluene solution of $Tl[GaCl_4]$ and [2.2]paracyclophane was cooled to room temperature crystals of the 1:1 complex $[(p\text{-}C_6H_4CH_2CH_2)_2Tl][GaCl_4]$ separated after a few days. The initial yield of 24% could be increased upon evaporation of the mother liquor [169].

In addition, thallium–arene interactions where the arene ring is part of the organic ligand bonded to thallium can be observed, in these cases, the thallium–arene interaction was not specifically sought for: $[Tl(TolNNNNTol)]_2$ and $[Tl(PhNNNPh)]_2$ (Tol = tolyl) were prepared from the reaction of $TlNO_3$ with 1,5-ditolylpentaazadiene in aqueous ammonia and 1,3-diphenyltriazene in the presence of NaOH, respectively [172]. The tetramer $[2,6\text{-}{}^iPr_2C_6H_3(Me_3Si)NTl]_4$ was obtained from the lithium salt of the 2,6-diisopropylphenyl-*N*-trimethylsilylamine ligand and TlCl in hexane [173]. The syntheses of the aryl-substituted cyclopentadienyl compounds $C_5(CH_2Ph)_5Tl$ [122], $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ [6], where Tl–arene interactions have been discussed, were given above in Section 2.2.1 [see Table 1(a)].

2.4. *Thallium(I) compounds with ligands related to cyclopentadienyl*

Ligands falling under this category are for example the pyrrolyl (azacyclopentadienyl) ligand (**1**), the 1,2-azaborolyl ligand (**2**), the (cyclopentadienyl) cobalt (1,3,4,5-tetramethyl-2,3-dihydro-1,3-borolyl) ligand, $(C_5H_5)Co(C_2B_2C)^-$ (**3**), the borinate ligand $[C_5H_5BR]^-$ (**4**), the *nido*-carborane dianion $[(3)\text{-}1,2\text{-}C_2RR'B_9H_9]^{2-}$ (**5**), the d^6-tricarbonyl(cyclopentadienyl)metallate ion $[(C_5H_5)M(CO)_3]^-$ (M = Cr, Mo, W) (**6**), and the hydro-tris(pyrazolyl)borate ligands, $HB(pz)^{3-}$ (**7**). Since these ligands are viewed as very similar to the cyclopentadienyl system, being isoelectronic or even isolobal [175], their thallium complexes are also discussed in the review.

1



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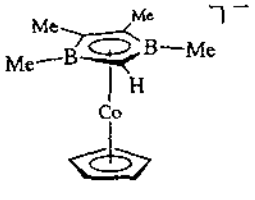

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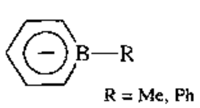
Pyrrolylthallium. The compound C_4H_4NTl is reported to be formed from sodium pyrrolide and thallium sulfate in water. It was formulated as π-bonded [123] which appears questionable based on the knowledge about the π-bonding capabilities of the unsubstituted pyrrolide ligand [329].

1,2-Azaborolylthallium. In the formation of $C_3H_3B(Me)N({}^tBu)Tl$ from the lithium salt of the 1-*tert*-butyl-2-methyl-1,2-azaborolyl ligand and TlCl in THF, it was noted that the reaction is light induced. Photochemical excitation of TlCl through normal



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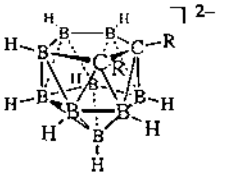

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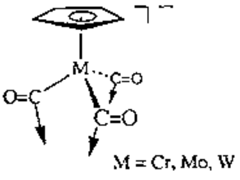

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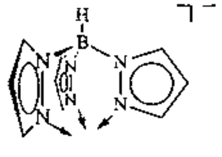

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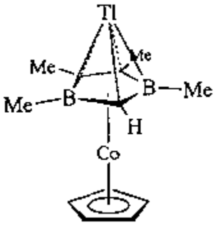
daylight appeared to initiate the reaction since exclusion of light did not give the thallium salt. Furthermore, the formation of $C_3H_3B(Me)N(^tBu)Tl$ is apparently an equilibrium reaction since a subsequent reaction with Ph_2PCl is different for the thallium and lithium salt, and the product *via* the thallium route is only obtained when light is continuously applied to the reaction mixture. Owing to its sensitivity, the thallium compound was not isolated but used for further reactions [22].

$(C_5H_5)Co(C_2B_2C)Tl$. ($C_2B_2C = \eta^5$-1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl) In an acid–base type reaction, C_5H_5Tl is reacted with the less volatile neutral $(C_5H_5)Co(C_2B_2C)H$ in boiling THF to give C_5H_6 and the product [Eq. (14)]. This procedure of a cyclopentadienyl displacement reaction appears so far to have only been employed once in the synthesis of this (η^5-cyclopentadienyl)cobalt(η^5-1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl)thallium complex (**8**) [143].

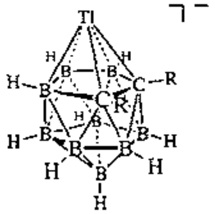
$$(C_5H_5)Co(C_2B_2C)H + C_5H_5Tl \rightarrow (C_5H_5)Co(C_2B_2C)Tl + C_5H_6\uparrow. \qquad (14)$$



8

Thalliumborinates. The 1-methyl and 1-phenyl borinate $[C_5H_5BR]Tl$ (R = Me, Ph) have been prepared from the sodium borinates and TlCl in acetonitrile in 76 and 78% yield, respectively. Their properties show them to be very similar to cyclopentadienylthallium, C_5H_5Tl [176].

Thallacarboranes. Addition of an aqueous solution of thallium(I) acetate to an aqueous alkaline solution of the *nido*-carborane anion $[(3)\text{-}1,2\text{-}C_2H_2B_9H_{10}]^-$ or its C-alkyl derivatives $[(3)\text{-}1,2\text{-}C_2RR'B_9H_{10}]^-$ leads to the precipiation of the new complexes $Tl_2\text{-}1,2\text{-}C_2RR'B_9H_9$ with $R=R'=H$; $R=H$, $R'=Me$; $R=R'=Me$. One of the thallium(I) atoms is a free cation while the other is part of the icosahedral closo-thallacarborane anion (or thallium dicarbollide) $[3,1,2\text{-}TlC_2RR'B_9H_9]^-$ (**9**) [177,178]. Both thallium cations can be readily replaced so that this thallium compound is a useful intermediate for the synthesis of other metallocarboranes containing the dicarbollide anion $[(3)\text{-}1,2\text{-}C_2RR'B_9H_9]^{2-}$ [178]. Reaction of $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ with $[PPN]^+Cl^-$ in MeCN replaces only the free thallium cation and gives $[PPN][3,1,2\text{-}TlC_2B_9H_{11}]$ [203] [PPN = bis(triphenylphosphoranylidene)ammonium].



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Thallium-[tricarbonyl(diphenylfulvene)chromate]. An apparently ionic thallium complex of the formula $Tl[(C_5H_4CHPh_2)Cr(CO)_3]$ has been prepared by first a reduction of diphenylfulvenechromium tricarbonyl with sodium borohydride and then addition of aqueous thallium(I) nitrate upon which the compound precipitated. In the absence of any X-ray structural studies it is not clear whether or not the above thallium complex shows an interaction to the fulvene part of the anion or to the carbonyl groups. Fulvene complexes of metals may readily be reduced to cyclopentadienyl complexes so that in the anion we may have the aromatic ligand bonded to the metal through the five-membered ring $[(\eta^5\text{-}C_5H_4CHPh_2)Cr(CO)_3]^-$ [179]. It is further known that a $d^6\text{-}[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ anion (M = Cr, Mo, W) can be isolobal to the $C_5H_5^-$ anion if it binds trihapto to another metal fragment through the carbonyl carbon atoms as indicated in **6** [180].

Hydrotris(pyrazolyl)borate ligands. The isoelectronic hydrotris(pyrazolyl)borate ligand **7** [general abbreviation $HB(pz)_3$ or simply Tp, cf.[5]] is often compared with the (pentamethyl-) cyclopentadienyl system in the literature ([181–186], see also [16]). The electronic structure of the hydrotris(pyrazolyl)borate ligand has been studied by photoelectron spectroscopy using the sodium and thallium derivatives [186a]. It is also a uninegative, six-electron donor ligand – a frontier orbital diagram in Fig. 1 shows a similar energy and topology of the filled π-levels of the C_5 ring with the σ-donor orbitals of the borate – but both ligands should not be called isolobal [187] as the borate has no π-acceptor orbitals available [182].

The pyrazolyl rings in **7** can be substituted in the 3, 4, and 5 position with alkyl or aryl groups so that again in analogy to substituted cyclopentadienyl rings, a large

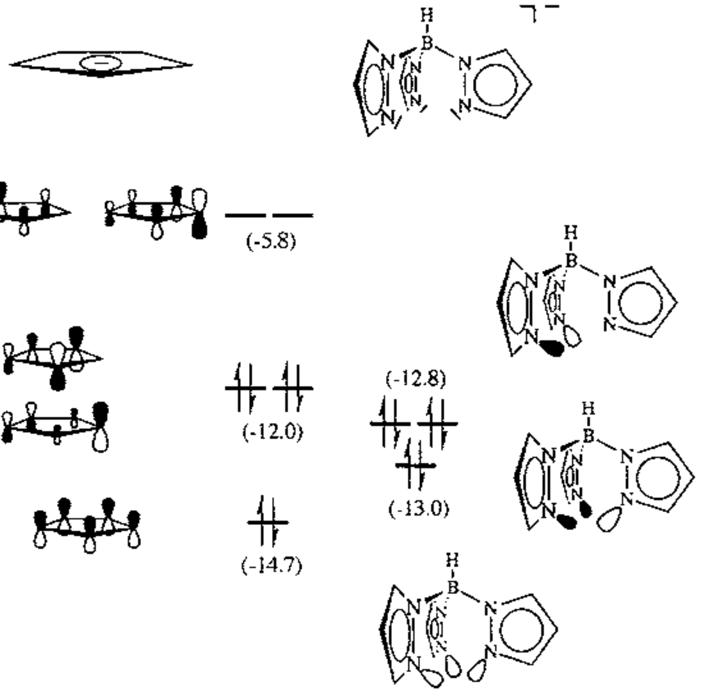


Fig. 1. Comparative frontier orbital diagram of the $C_5H_5^-$ ring and the $HB(pz)_3^-$ anion (pz = pyrazolyl). Note the similar energy and topology (symmetry) of the filled levels and the lack of low-lying empty acceptor orbitals for the tris(pyrazolyl)borate. (Energies, in eV, are based on an extended-Hückel MO calculation.)

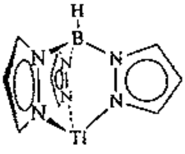
variety of sterically demanding tris(pyrazolyl)borate ligands is available (also called "second-generation Trofimenko ligands") [16,182]. These bulky pyrazolylborate ligands are especially popular in bio-inorganic chemistry as the metal complexes derived therefrom can be models for metallo-enzymes and -proteins. For a more detailed coverage of poly(pyrazolyl)borate–metal chemistry and the reasons behind it, we refer to the excellent review articles available [16,182,188].

Related to the pyrazolyl-borate ligands, but of neutral charge and not covered here, are the pyrazolyl-methane ligands, $H_nC(pz)_{4-n}$ ($n=0$, 1, 2). For a recent example of a cationic tris(pyrazolyl)methane–thallium(I) complex, see Ref. [188a].

By heating solid KBH_4 with the appropriate pyrazole, the hydrotris(pyrazolyl) borate ligands are normally obtained in a melt reaction as the potassium salts, isolated and used as such for the metathesis reaction with the transition-metal compounds [189]. In the case of the sterically hindered tris(pyrazolyl)borate ligands, isolation of pure samples of the potassium (or sodium) salts is often tedious and problematic and conversion to crystalline thallium complexes by treatment with aqueous $TlNO_3$ or methanolic TlOAc in a metathesis reaction (method II above) is then performed in order to obtain the ligands in pure form [Eq. (15)] [15–17]. From this aqueous reaction mixture, the thallium complex (**10**) is extracted with an organic solvent, e.g. CH_2Cl_2, the extracts chromatographed, the solvent evaporated, the remaining solid washed and perhaps recrystallized [15]. The metathesis reaction can also be carried out in the organic solvent, e.g. $CHCl_3$, already [190]:

$$TpK + TlX \rightarrow TpTl + KX. \tag{15}$$

X = NO_3, OAc, O_2CH (formiate).



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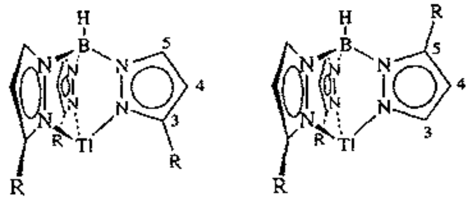
Unlike the Cp–Tl analogs, the thallium(I) salts of the tris(pyrazolyl)borate ligands were not studied per se, except perhaps for a recent NMR study [191], but used for isolation and characterization of ligands, and because of their good solubility in hydrocarbon solvents were employed in metathesis or salt-elimination reactions with metal halides [182]. This applicational aspect is much more pronounced in TpTl than in CpTl chemistry.

Positional isomerism in tris(pyrazolyl)borates. Tp ligands derived from monosubstituted pyrazoles are usually the symmetric tris-3Rpz/3Rpz/3Rpz derivatives (in short 3/3/3) [191]. The tris(mesitylpyrazolyl)borate represents a notable exception as the 3/3/5 isomer, $HB(3\text{-mesityl-pz})_2(5\text{-mesityl-pz})$, was isolated along with the 3/3/3 isomer as the thallium complex (**11**). Through repeated crystallizations, both isomers could be separated from each other. The better soluble, lower melting, and less-symmetrical 3/3/5–thallium complex can thermally be completely isomerized to the (apparently thermodynamically more stable) 3/3/3-complex by heating to 236 °C for 1 h [192].



R = mesityl, $\text{-C}_6H_2\text{-2,4,6-Me}_3$

11

The reverse isomerization to a 3/3/5-isomer starting with a 3/3/3-form can be observed with the $HB(3\text{-}^iPr\text{-4-Br-pz})_3$-ligand upon reflux of the thallium salt with MCl_2 in toluene (M = Fe, Co, Ni) [193] and with the $HB(3\text{-}^tBuCH_2\text{-pz})_3$-ligand ($Tp^{Np}$) upon heating the homoleptic metal complexes Tp^{Np}_2M (M = Fe, Co, Ni) [40]. Subsequently, the octahedral complexes $\{HB(3\text{-}^iPr\text{-4-Br-pz})_2(5\text{-}^iPr\text{-4-Br})\}_2M$ or $\{HB(3\text{-}^tBuCH_2\text{-pz})_2(5\text{-}^tBuCH_2)\}_2M$ were isolated from this reaction. Rearrangement of the coordination mode by one of the pyrazolyl groups relieves steric crowding in the octahedral complexes or may even be a prerequisite for their formation [193].

2.5. Thallium(II) compounds

In some reactions organothallium(II) compounds were suggested as transient intermediates. The reaction of Na metal with Ph_2TlBr in liquid ammonia, which gives Ph_3Tl and thallium metal, was proposed to proceed *via* $Ph_2Tl(II)$ [85]. From polarographic studies of diphenylthallium cations in aqueous solution, the first reduction was suggested to yield a strongly adsorbed $Ph_2Tl(II)$ which then undergoes transmetallation with the dropping mercury electrode to give Ph_2Hg [93]. R_2Tl may also occur in the pyrolysis of Me_3Tl [see above Eq. (2)] [91,92], in reactions where R_3Tl is formed from initially assumed RTl [85,96] or in the electrochemical reduction of R_2Tl-cations in dimethylformamide (DMF) [194,195]. These latter dialkylthallium(III) cations form in polar solvents from R_2TlX complexes [here X = Cl, Br, OAc, NO_3; R = Me, Et, ^{n}Pr, ^{n}Bu (= *normal*-propyl, *normal*-butyl, respectively), n-amyl, Ph] owing to the stability of the R_2Tl^+ species. Their electrochemical reduction was suggested to be initiated by a one-electron reduction to give R_2Tl as a primary product, which is stabilized in DMF. Depending on the reaction conditions, R_2Tl either disproportionates to R_3Tl and Tl^0 or is electrochemically reduced to thallium metal [194–196].

At various places, a personal communication or a conference abstract by C.A. Wilkie and J.P. Oliver is cited which states that reduction of Me_3Tl with potassium in 1,2-dimethoxyethane gave a thallium(II) salt of the composition $K_2[Me_3Tl–TlMe_3]$, with a Tl–Tl bond [197]. This result never seems to have been published, however (see also [108]) and is viewed as doubtful [96].

Successful schemes for the syntheses of isolable *molecular* thallium(II) compounds were only found recently: the reaction of thallium(I)-bis(trimethylsilyl)amide, $TlN(SiMe_3)_2$, with rubidium tris(trimethylsilyl)silyl (hypersilylrubidium) in a toluene/pentane mixture gave tetrakis(hypersilyl)dithallium(*Tl–Tl*) together with thallium metal between −30 and −60 °C [Eq. (16)]. The use of the toluene-soluble thallium amide appears to be crucial since the reaction between TlCl or TlI and alkali-metal derivatives of tris(trimethylsilyl)silane gave only thallium metal, alkali halide and $(Me_3Si)_3Si–Si(SiMe_3)_3$ [108]:

$$4TlN(SiMe_3)_2 + 4(Me_3Si)_3SiRb \rightarrow [(Me_3Si)_3Si]_2Tl–Tl[(Si(SiMe_3)_3]_2 + 4RbN(SiMe_3)_2 + 2Tl. \qquad (16)$$

The reaction of TlBr with supersilylsodium (^{t}Bu$_3$SiNa) in THF at −78 °C gives tetra(supersilyl)dithallium(*Tl–Tl*) together with thallium metal [Eq. (17)] [109]:

$$4TlBr + 4{}^tBu_3SiNa \rightarrow ({}^tBu_3Si)_2Tl–Tl(Si{}^tBu_3)_2 + 4NaBr + 2Tl. \qquad (17)$$

Thallium(II) radicals of the type $({}^tBu_3Si)_2Tl\cdot$ were suggested to be present in benzene solution at room temperature to explain the band-rich EPR signal and the unusual dark-green color of the above tetrasupersilyldithallium(*Tl–Tl*) compound [109].

3. Structures

3.1. Cyclopentadienylthallium(I) compounds

3.1.1. Neutral cyclopentadienylthallium compounds

With a general interest in the structure and bonding of the then-novel cyclopentadienylmetal-π complexes after the discovery of ferrocene, cyclopentadienylthallium, C_5H_5Tl, was also studied [115,198,199]. The structure of C_5H_5Tl was of special interest because of the low solubility of the compound and its air and water stability. A microwave study of gaseous C_5H_5Tl showed the compound to be monomeric with the thallium bonded in a pentahapto fashion to the cyclopentadienyl ring at a thallium-ring centroid distance of 2.41 Å [198]. The solid-state X-ray structural study revealed the formation of a polymeric chain with the thallium equidistant in between two cyclopentadienyl rings at a metal–ring distance of 3.19 Å (the solid-state structure will be described in more detail below) [199]. Early on, the large difference between the metal–ring distance in the gas phase and the solid state was connected to the change of structure: the monomeric half-sandwich in the gas phase and the polymer formed in the solid state [199]. An electron diffraction study of gaseous C_5Me_5Tl (monomeric, Tl–ring centroid distance 2.37 Å) [200] compared with the solid-state structure of the compound (polymeric, Tl–ring centroid distance 2.71 Å) [135] showed the same phenomenon. The thermal expansion of solid cyclopentadienylthallium was determined in the range of 78 to 295 K using X-ray powder diffractometry and found to be very anisotropic [201].

The cyclopentadienylthallium(I) solid-state structures known, so far, can be grouped in two major categories [5]: (1) most common are structures consisting of *alternating Cp and Tl units* in a polymeric zig-zag chain with about *equidistant contacts* between neighboring building blocks (type I). The thallium–carbon distances found in these type-I structures are considerably larger than the covalent Tl–C bond lengths so they are assigned a *large ionic contribution* (see below). In one case, a hexameric arrangement of the CpTl building blocks has been found. (2) For a long time rarely observed or only in the gas phase were molecular structures with essentially isolated Cp–Tl units, showing short, more-covalent thallium–carbon distances (type II). This structural type was recently receiving increased attention because of particular arrangements in the solid state where the thallium atoms are oriented towards each other. While the resulting Tl–Tl contacts are too long to be considered a metal–metal "bond," the presence of an attractive interaction between the $d^{10}s^2$ configurated thallium centers may have been possible and was a matter of discussion (see Section 3.5). Such Tl–Tl contacts can also occur in the type-I structures. Scheme 1 illustrates this structural classification and Table 2 lists the known cyclopentadienylthallium(I) structures according to their type.

The coordination of the cyclopentadienyl ligand to the thallium metal is almost

Table 2
Structurally characterized cyclopentadienylthallium(I) compounds[a] (ordering within each section with increasing molar mass of Cp-ligand). The table is divided into: (a) neutral cyclopentadienylthallium compounds; and (b) anionic cyclopentadienylthallium compounds. Neutral cyclopentadienylthallium compounds listed according to structure type **I** or **II**, cf. Scheme 1

Type	Formula (CpTl)	Tl–Cp[b] (Å)	Cp–Tl–Cp (°)	Remarks	Reference
(a) Neutral cyclopentadienylthallium compounds					
I	C_5H_5Tl (solid state)	3.19	137	Tl···Tl[c] = 3.99 Å	[199,201]
	C_5HMe_4Tl	2.68, 2.71	133.8	Tl···Tl[c] = 6.54 Å	[130]
	C_5Me_5Tl (solid state)	2.71	Tl···Tl···Tl: 145 average	Tl···Tl[c] = 6.41 Å (Three different Tl atoms)	[135]
	$C_5H_4(SiMe_3)Tl$	2.71, 2.84	149	Tl···Tl[c] = 4.59 Å [141]	[7]
	$C_5H_4\{C(CN){-}C(CN)_2\}Tl$	3.01, 3.07	113.6	Tl···Tl[c] = 4.60 Å	[140]
	$C_5H_3\{\text{-}1,3\text{-}(SiMe_3)_2\}Tl$	2.74, 2.78	127, 133		[7]
	$C_5H_3(\text{-}1,3\text{-}Ph_2)Tl(THF)$	2.83, 2.87	127.6, 118.7	Tl···Tl[c] = 4.51 Å	[141]
	$C_5H_4(PPh_2)Tl$	2.80, 2.88	122		[144]
	$C_5Me_4\{Si(Me_2)Ph\}Tl$	2.63, 2.86	142.3	Tl···Tl[c] = 7.52 Å [130]	[147]
	$C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$	2.74	147	Tl···Tl[c] = 8.73 Å [130]	[147]
II	C_5H_5Tl (gas phase, microwave spectroscopy)	2.41 (Tl C = 2.70)			[198]
	C_5Me_5Tl (gas-phase electron diffraction)	2.37 (Tl–C = 2.66)			[200]
	$C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ (2 modifications)				
	Modification 1: zig-zag chain structure	2.56[d], 3.06[d]	-		[6]
	modification 2: two-dimensional coordinate polymer	2.50[d]	-		[6]
	$C_5Me_4(PPh_2)Tl$	2.51		Tl···Tl[c] = 5.77 Å Tl···**P**' = 3.62 Å	[13]
	$Tl(\text{-}1,3\text{-}{}^tBu_2)H_2C_5\ C_5H_2(\text{-}1',3'\text{-}{}^tBu_2)Tl$	2.40, 2.42		Tl···Tl[c] = 3.76, 4.00 Å Zig-zag chain-type structure	[5]
	$C_5(CH_2Ph)_5Tl$ (2 modifications)				

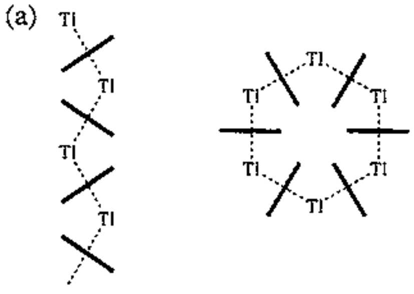
Type	Formula (CpTl)	Tl–Cp[b] (Å)	Cp–Tl–Cp (°)	Remarks	Reference
	Modification 1: needles, linear chain	2.49, 4.88	Tl–Cp···Tl′ 175.7		[213]
	Modification 2: parallelepipeds, dimers	2.49	Cp–Tl···Tl 131.8	Tl···Tl[b] = 3.63 Å	[8]
	$C_5(CO_2Me)_5Tl$	Tl–O: 2.68–3.24, average 2.96		No Tl–C contacts	[160]
(b) Cyclopentadienylthallium anions					
Special	$[C_5H_5Mg(pmdeta)]^+[(C_5H_5)_2Tl]^-$	2.72 (average)	156.7 (average)	separated ion pair	[157]
	$[Li(pmdeta)(\mu\text{-}C_5H_5)Tl(C_5H_5)]$	2.61 (average, terminal C_5H_5), 2.85 (average, bridging C_5H_5)	153.3 (average)	Contact ion pair	[157]
	$[Li([12]\text{-crown-4})_2]^+[(C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(C_5H_5)]^-(THF)$	2.63 (outer rings), 2.83 (inner ring)	134.2		[159]
	$Au_2[(P\text{-}Ph_2PC_5H_4)_2Tl]_2(C_6H_6)_2$ $\{=[TlAu(C_5H_4PPh_2)_2]_2\}$	2.71, 2.75	135.3		[156]

[a] Structural characterization by X-ray crystallography, unless stated otherwise.

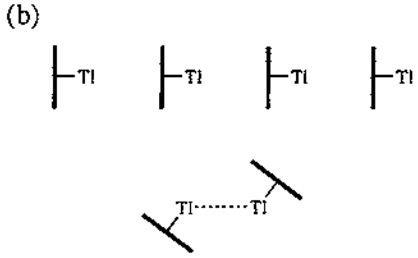
[b] Cp = cyclopentadienyl centroid if not indicated otherwise; average = average value from different molecules in the asymmetric unit.

[c] Shortest thallium–thallium contacts (if provided), excluding contacts bridged by Cp rings.

[d] Tl–Cp plane distance.



Type I



Type II

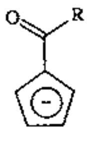
— = Cp

Scheme 1. Schematic illustration of cyclopentadienylthallium structure types. (a) Type I: alternating Cp and Tl units with long, equidistant contacts either as a zig-zag chain or a hexameric oligomer; (b) type II: molecular isolated CpTl units with short Cp···Tl contacts either as a chain arrangement or as a "dimeric" entity (cf. also Refs [5,101]).

always ideally pentahapto [5,8,157], sometimes slightly distorted [6,13], but no significant ring slippages to η^3 or so have been reported, hence the prefix η^5 was omitted in the formula notation. We note, however, that C_5H_5Tl is in the "organic literature" sometimes erroneously depicted as σ- or η^1-bonded to the cyclopentadienyl moiety which then shows two localized double bonds [27,44,46,56–60,70]. A good review on π-bonding to main-group elements is given in [202].

In the case of functionally substituted cyclopentadienyl ligands, where the substituent contains a π system in conjugation to the five-membered ring, two conformations (**12** and **13**) may be adopted. Both forms are distinguished from the appearance of the ^1H or ^{13}C NMR spectra and the results for the complexes $C_5H_4(CHO)Tl$, $C_5H_4\{C(O)Me\}Tl$ and $C_5H_4(CO_2Me)Tl$ suggest that the soft Lewis-acid character of thallium(I) stabilizes form **12**. Only in the case of the strongly withdrawing tricyanovinyl group in the complex $C_5H_4\{C(CN){=}C(CN)_2\}Tl$ [19] or the nitro group in $C_5H_4(NO_2)Tl$ (at ambient temperature) [128] was a preference for form **13** apparent. Similarly, for the thallium salts of the

1,5-diacyl-1,3-cyclopentadienyls, the structures **14** and **15** are to be discussed. NMR spectra suggest the form **14** [for more details, see also below in Section 4.3.1 (NMR spectroscopy)] [54].



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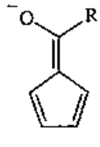

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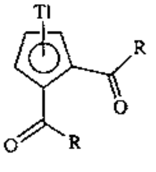

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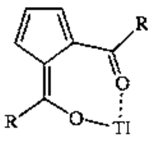


15

For $C_5(CO_2Me)_5Tl$ [160] an X-ray study shows that the coordination environment of thallium is comprised of five oxygen atoms, two from the same ligand and the other three from different ligands. For each ligand all five C=O atoms are involved in coordination to four different thallium atoms. The pentakis(methoxycarbonyl)-cyclopentadienide ligand *can* bind η^5 to certain metals, e.g. Mn, Ru, Os, Rh, and Ir, through the C_5 skeleton. In many other metal complexes with this ligand, the metal is, however, chelated by the carboxylate groups with formation of a metal–oxygen ion pair; such is the case here for thallium [174].

The compounds which are weakly associated in the solid state can be considered monomeric in solution as was shown for $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ (modification 1) [6] and $C_5H_2\{\text{-}1,2,4\text{-}(SiMe_3)_3\}Tl$ [148] by a cryoscopic molar mass determination. Also in the gas phase, the cyclopentadienylthallium complexes are most probably only monomeric as was demonstrated by microwave spectroscopy for C_5H_5Tl [198] and by gas-phase electron diffraction for C_5Me_5Tl [200]. Furthermore, the molecular ion is the peak of highest mass in the mass spectrum of cyclopentadienylthallium compounds [6,7,19,65,122,266]. (Under less energetic conditions, such as chemical ionization and fast atom bombardment mass spectrometry, the zig-zag chain structure may not be entirely disrupted, however, as indicated by the formation of $[CpTl_2]^+$ and $[Cp_2Tl]^-$ [128].)

The monomeric structures of cyclopentadienylthallium complexes can be interpreted on the basis of Wade–Rudolph–Mingos rules [204] as being of the *nido*-type [148]. Similarly, the $Co(\mu\text{-}C_2B_2C)Tl$ moiety of the complex $(C_5H_5)Co(\mu\text{-}C_2B_2C)Tl$ can be described as a seven-atom *closo*-cluster [143].

It can generally be stated that bulky ligands increase the monomeric character of the compound [12,148,205]. With the decrease in the degree of aggregation, a decrease in thallium–carbon (Cp) bond lengths can be seen at the same time by an inspection of Table 2. The shortening of the Tl–C/Cp distance is normally viewed concomittant with an increase in covalent character and a decrease in the ionic character of the bond [7,8,135,206]. Thus, it can be concluded that a bulkier cyclopentadienyl ligand leads to a more covalent thallium–ring interaction [148]. The effect of a decreasing metal–carbon bond distance was also seen upon methylation of the cyclopentadienyl rings in the thallium and related indium complexes: compare the solid-state as well as the gas-phase structures of C_5H_5Tl [198,199] and C_5Me_5Tl [135,200]; between the former, the Tl–ring centroid distance is decreased by about 0.4 Å, between the latter by 0.04 Å upon methylation. For the gaseous indium compounds, a shortening by approximately 0.03 Å is seen when going from C_5H_5In (In–C = 2.62 Å) [207] to C_5Me_5In (In–C = 2.59 Å) [208].

Specific structures from Table 2 will be detailed in the following. *C_5H_5Tl* and other polymeric chain structures of type I. Fig. 2 illustrates the zig-zag arrangement found in these chain structures built by alternating thallium and cyclopentadienyl moieties, which are symmetrically positioned between each other. The cyclopentadienyl ring bridges between two thallium centers at equal Tl–Cp distances and with the ring plane perpendicular to the Tl–Tl axis. While the Tl–Cp(centroid)–Tl angle is almost always close to linear, the bridging thallium centers possess a bending angle. The latter leads to the kinked or puckered nature of these chains and is often thought to reflect the stereochemical significance of the "lone-pair" of electrons on each thallium(I) atom. The angle at thallium varies somewhat (see Table 2), presumably reflecting the different steric situations at the ligand. A Tl–Cp(centroid)–Tl angle which significantly deviates from 180° has only been observed in the structure of $C_5H_4\{C(CN)=C(CN)_2\}Tl$ with an angle of 158° [140,141].

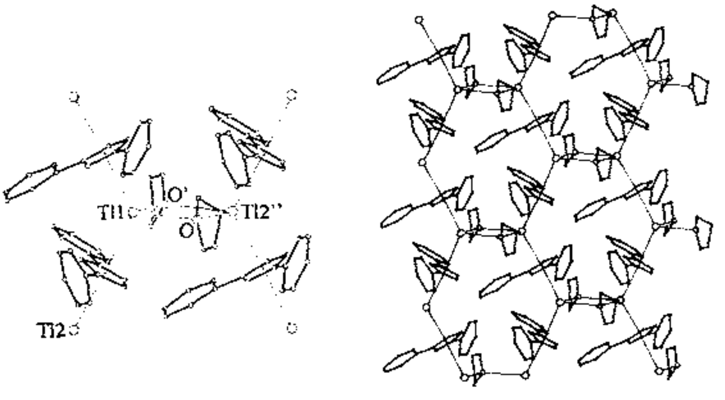
Based on the Tl–C distances the bonding in these structures may be regarded as predominantly ionic [64]. The thallium–carbon distances of, for example, 2.96 Å (average, C_5Me_5Tl) [135], 3.06 Å ($C_5H_4\{C(CN)=C(CN)_2\}Tl$) [140] or 3.09 Å [average, $C_5H_3(\text{-}1,3\text{-}Ph_2)Tl(THF)$] [141] encountered in these structures are close to the sum of the van der Waals radius of carbon (1.7 Å) [209] and the ionic radius of Tl^+ (1.4–1.5 Å) [210]. The covalent radius of a thallium atom is given as 1.55 Å [211,212].

An interesting variation of the chain structure is provided in $C_5H_3(\text{-}1,3\text{-}Ph_2)Tl(THF)$ where two THF molecules bridge between two thallium centers of neighboring zig-zag chains, depicted in Fig. 3(a), to give a honeycomb type layer as shown in Fig. 3(b) [141].

In $C_5H_4(PPh_2)Tl$, the neighboring infinite zig-zag chains are connected by interactions between phosphorus and thallium atoms (Tl–P = 3.58 Å) to form a two-dimensional network [144].

The compounds $C_5Me_4(SiMe_2Ph)Tl$ and $C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ show polymeric chain structures with probably predominantly ionic Tl–C contacts in the range 2.8–3.2 Å, yet in solution, coupling constants to the methyl hydrogen atoms and to

Fig. 2. Schematic drawing of a polymeric cyclopentadienylthallium chain (type I).



(a) (b)

Fig. 3. (a) Coordination sphere around thallium with the two THF molecules bridging two strands; (b) view of an honeycomb-type layer formed with respect to the thallium atoms in the solid-state structure of C_5H_3(-1,3-Ph_2)Tl(THF) (Reprinted from Ref. [141] with permission of the author).

all observed carbon atoms are detected, which would imply the existence of monomeric species therein [see Section 4.3.1 (NMR spectroscopy)] [147]. Fig. 4 illustrates a section of the kinked chain of the benzyldimethylsilyl compound. While there is no thallium–phenyl π-contact in the solid state, such may well be the case in solution with the break-up of the chains. An intramolecular thallium–phenyl interaction is supported by the large and very similar thallium–phenyl carbon coupling constants which suggest a through-space interaction [147] [see also Section 4.3.1 and Table 8(a)].

Still equidistant Cp–Tl–Cp contacts yet no longer a polymeric chain structure is found in C_5H_3\{-1,3-$(SiMe_3)_2$\}Tl [7]. The complex forms a "doughnut"-shaped hex-

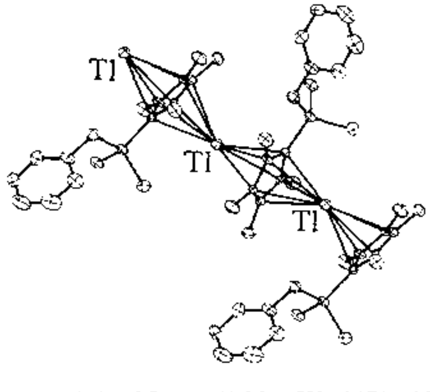


Fig. 4. Section of the bent polymeric chain of C_5Me_4\{Si(Me_2)CH_2Ph\}Tl, with equidistant Tl–ring contacts (reprinted from [147] with permission of the author).

americ oligomer with the six metal atoms arranged in a regular hexagon and bridged by the cyclopentadienyl ligands (Fig. 5). Together with the infinite chain structure of the mono-substituted compound $C_5H_4(SiMe_3)Tl$, the hexameric structure nicely demonstrates the principle that the degree of polymerization of cyclopentadienylthallium compounds falls with increasing substitution in the C_5-ring. Such an oligomeric motif is still the only one of its kind, though, for a compound with a predominantly ionic Cp–Tl interaction as based on bond length.

Monomeric type-II structures. The compound $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ [6] was found to crystallize in two allotropic forms depending on the method of preparation. In both forms, the structure is built up from molecular ligand–thallium entities with a rather covalent cyclopentadienyl–metal interaction as based on the distances. In modification 1, these building blocks are arranged in a slightly kinked chain via a second, albeit considerably longer and strongly asymmetric, Cp···Tl interaction [Fig. 6(a)]. The thallium coordination sphere is completed by an *intra*molecular η^3–π–arene contact to the six-membered ring of the fluorenyl system. In modification 2, it is not the Cp ring which is bridging between thallium metals, but the arene moiety of the fluorenyl system [Fig. 6(b)]. Two of such *inter*molecular π–arene contacts then give rise to the formation of a two-dimensional layer structure.

Two modifications were also isolated for $C_5(CH_2Ph)_5Tl$ [8,213], depending on the crystallization conditions. Upon fast crystallization from a more concentrated hexane solution, needles are obtained, while slow crystallization from the same solvent yields parallelepipeds. In the latter the monomeric CpTl moieties are arranged in quasi-dimeric units with the two symmetry-related thallium atoms facing each other at a contact of about 3.6 Å [Fig. 7(a)]. This distance lead to theoretical

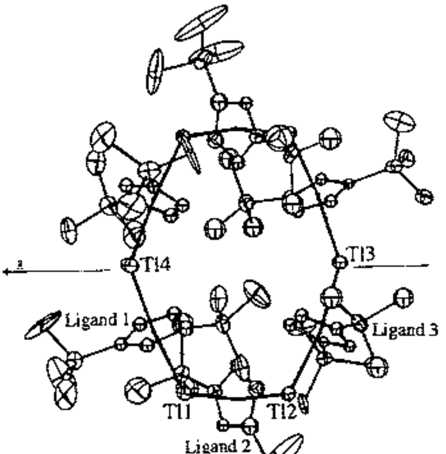


Fig. 5. X-ray structure of the oligomeric hexamer of $C_5H_3\{\text{-}1,3\text{-}(SiMe_3)_2\}Tl$ (reprinted from Ref. [7] with kind permission from Elsevier Science S.A., Switzerland).

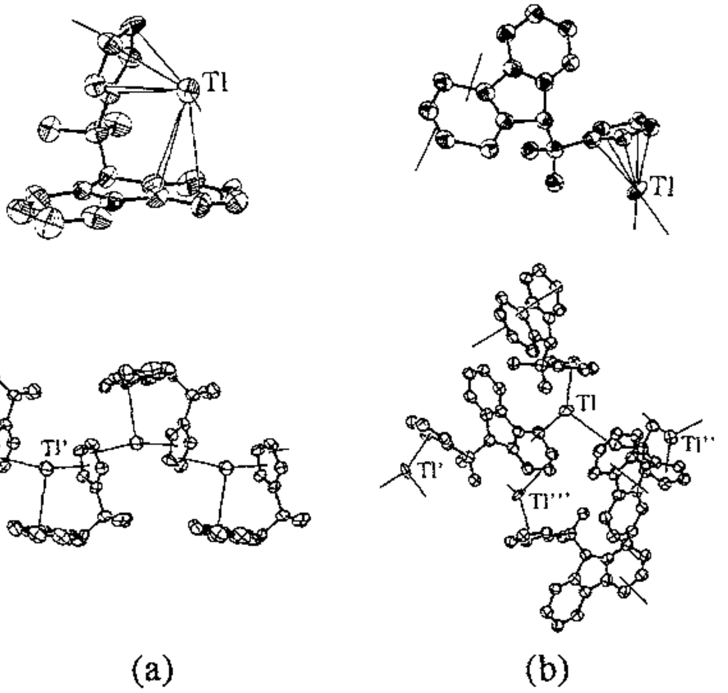


Fig. 6. "Molecular" repeat units (upper row) and sections of the polymeric chain and layer structure (lower row) of $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$: (a) modification 1; (b) modification 2; the directions of further coordination are indicated (reprinted from Ref. [6] with permission of the author).

investigations on the possibility of Tl···Tl interactions (see Section 3.5). The needle modification consists of an almost linear chain of monomeric molecules [Fig. 7(b)]. Both modifications feature the same short, covalent thallium–cyclopentadienyl interactions (Table 2), and in both cases, the thallium atoms are shielded by the benzyl groups, whereby giving a few Tl–phenyl carbon contacts between 3.3–3.5 Å (Table 3).

3.1.2. Cyclopentadienylthallium(I) anions

The special anionic cyclopentadienyl–thallate structures are included in a separate section in Table 2(b) for comparison and complete coverage of the cyclopentadienyl complexes, yet they are electronically different (14-electron moiety) [158] and are discussed in more detail separately in this section.

In 1991, Anderson and Rath reported the X-ray structure of a tetrametallic complex which they described by the formula $[TlAu(C_5H_4PPh_2)_2]_2$. The structure (as its benzene solvate) (Fig. 8) revealed that each gold is coordinated by two phosphino groups (P–Au–P = 176°) and each thallium is symmetrically η^5-bound to two cyclopentadienyl ligands to give a molecular unit [156]. Based on the metal–ligand arrangement, we would suggest that the complex may be better described as

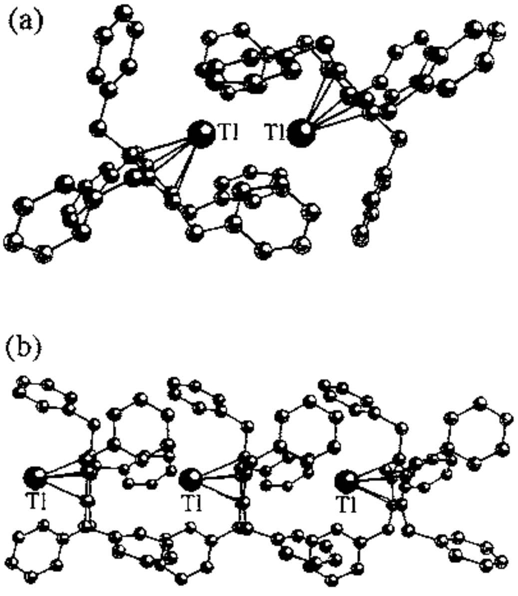


Fig. 7. (a) Structural drawing of the "dimeric" form of $C_5(CH_2Ph)_5Tl$ [8]; (b) of a section of the chain arrangement of the molecules in the "needle" modification of $C_5(CH_2Ph)_5Tl$ [213].

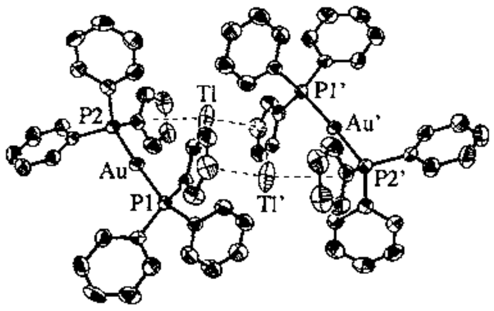


Fig. 8. Drawing of $Au_2[(P\text{-}Ph_2PC_5H_4)_2Tl]_2$ (reprinted from [156] with kind permission from Elsevier Science S.A., Switzerland).

being built up from gold cations and thallium anions according to the formula $Au_2^+[(P\text{-}Ph_2PC_5H_4)_2Tl]_2^-$.

Recently, such bis(cyclopentadienyl)thallate anions with the parent dienyl $C_5H_5^-$ have been structurally elucidated: the formal addition of the cyclopentadienyl anion ($C_5H_5^-$) onto C_5H_5Tl leads to the formation of the 14e anion $(C_5H_5)_2Tl^-$ which could be isolated as a separated ion together with $[C_5H_5Mg(pmdeta)]^+$ or as a contact ion pair in $[Li(pmdeta)(\mu\text{-}C_5H_5)Tl(C_5H_5)]$ (pmdeta = pentamethylethylenetriamine, Eqs. (11) and (12)) [Fig. 9(a and b)] [157,158]. Based on the electron counting, the anion $(C_5H_5)_2Tl^-$ is isoelectronic to the neutral species $(C_5H_5)_2E$ with

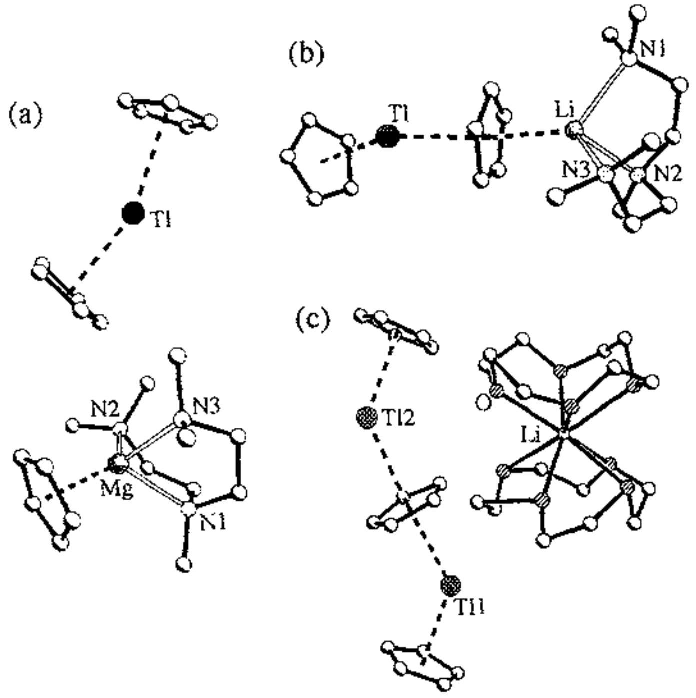


Fig. 9. Structures of the thallate anion containing compounds: (a) $[C_5H_5Mg(pmdeta)]^+[Tl(C_5H_5)_2]^-$; (b) $[Li(pmdeta)(\mu\text{-}C_5H_5)Tl(C_5H_5)]$; and (c) $[Li([12]\text{-crown-4})_2]^-[(C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(C_5H_5)]^-(THF)$ in the crystal (reprinted from Refs [157,159] with permission of the authors).

E being a group-14 element (Si, Ge, Sn, Pb). The structure of $(C_5H_5)_2Tl^-$ has also been studied theoretically (see Section 3.6) [157,158].

Furthermore, the anion $(C_5H_5)_2Tl^-$ can be viewed as a fragment of the polymeric $[C_5H_5Tl]_\infty$ chain. This view was supported by the isolation of the next homologue, namely $[C_5H_5Tl(\mu\text{-}C_5H_5)TlC_5H_5]^-$ as a separated ion together with $[Li([12]\text{-crown-4})_2]$ [Fig. 9(c)] [158,159]. The extended thallium anion was pointed out to be the first homonuclear main-group metal tripeldecker-sandwich complex. This anion contains two Tl(I) centers which are quite symmetrically bridged by a cyclopentadienyl ring. The terminal ligands are a little more closely bonded to the thallium atoms than the bridging ring. The transoid kinked metal–ligand arrangement in the $[C_5H_5Tl(\mu\text{-}C_5H_5)TlC_5H_5]^-$ anion is as found in the polymeric $[C_5H_5Tl]_\infty$ chain, with the angles at thallium being very similar in both cases (134.2° and 137°, respectively) [159].

The absence of coupling in the NMR spectra of the bis(cyclopentadienyl)thallate anions (see Section 4.3.1) most likely indicates that the "thallium(I) anion" description is limited to the solid-state. The thallate(I) anions do not appear to be maintained in solution as a structural entity. Even in the solid-state, the bonding within these anions appears to be predominantly ionic, judging by the Tl–Cp distance criterion (see above Section 3.1.1).

3.2. *Compounds with thallium(I)–arene interactions*

A listing of the relevant structural data of thallium(I) compounds where metal–arene interactions have been observed is provided in Table 3. So far, we are only aware of seven thallium(I)–arene complexes where the arene is a free molecule and not part of ligand system which could be completely structurally characterized: one mono(arene)thallium complex $Tl^+(C_6H_5Me)_{2/3}$[*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$ [162], the mixed mono- and bis(arene)thallium(I) complex $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ [99,164], and five bis(arene)thallium complexes $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ [165], $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ [166], $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ [167,168] and $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ [168]. Except for the fortuitously formed toluene-solvated thallium carborane salt, only the trimethylbenzene molecules mesitylene, C_6H_3-1,3,5-Me_3, or pseudocumol, C_6H_3-1,2,4-Me_3, could be successfully employed intentionally as an arene ligand for the structural elucidation. In solution, however, more arene complexes are certain to be present, as thallium(I) salts like $Tl[AlCl_4]$, $Tl[AlBr_4]$, $Tl[GaCl_4]$ and $Tl[GaBr_4]$ are soluble in hot benzene, mesitylene or hexamethylbenzene. These solution–arene complexes are reported to be very unstable and difficult to access preparatively [99]. The first two thallium–arene complexes reported, namely the benzene adducts $(C_6H_6)[TlAlCl_4]_2$ and $(C_6H_6)_2[TlAlCl_4]$, were never structurally studied [161].

The unit cell of $Tl^+(C_6H_5Me)_{2/3}$[*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2]$ consists of three crystallographically unique aluminacarborane anions, as well as three Tl^+ cations and two toluene solvate molecules. Each toluene molecule lies close to a thallium ion, with the third thallium ion lying in a special position closer to one of the anions. The coordination sphere of the two toluene-solvated thallium ions is then completed by carborane cage contacts [162,163].

An X-ray structural investigation showed the complex $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ to consist of centrosymmetric tetrameric aggregates which contain two mono- and two bis(arene)thallium symmetry-related pairs [99,164]. The coordination sphere of the two different Tl(I) cations and their complicated network with the $[GaBr_4]^-$ anions is shown in Fig. 10. The dihedral plane angle of the mesitylene ligands is 60.5°. A comparison with the arene-complexes of gallium(I) and indium(I) is given in Ref. [99].

Fig. 11 provides a view of the dimeric thallium(I) complex $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ [167,168]. The crystal lattice contains an additional mesitylene molecule. The coordination sphere around the metal is pseudotetrahedral, consisting of two oxygen atoms from two bridging teflate groups and two π-bonded mesitylene molecules. The four Tl–O bond distances range from 2.69 to 2.72 Å. The thallium–arene interaction is described as hexahapto, but it is also stated that the Tl–C bond distances for some of the four different mesitylene ligands vary over a range of values (see Table 3). This variation is suggested to be the consequence of

Table 3
Thallium(I) compounds with structurally authenticated metal–arene interactions

Formula, remarks	Tl–C(arene)[a] (Å)	Reference
$[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$,		[99,164]
two different Tl centers: mono-arene ions	3.28 (average), Tl–C_6(centroid) 2.94	
bis-arene ions	3.32, 3.34 (average), Tl–C_6(centroid) 3.00, 3.02	
$\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$, four symmetrically different arene rings	3.25, 3.29, 3.32, 3.33 (average for each of the four different Tl–mesitylene interactions). Smallest range 3.21–3.34; largest range 3.22–3.46; Tl–C_6(centroid) 2.94, 2.98, 3.01, 3.03	[165]
$\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$	3.27, 3.35 (average for each of the two different Tl–pseudocumol interactions). Ranges: 3.23–3.29; 3.31–3.42, Tl–C_6(centroid) 2.965, 3.06	[166]
$\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$	3.27, 3.37 (average for each of the two different Tl–pseudocumol interactions). Ranges: 3.26–3.30; 3.30–3.41; Tl–C_6(centroid) 2.97, 3.07	[166]
$[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$, four symmetrically different arene rings	3.29, 3.33, 3.38, 3.39 (average for each of the four different Tl–mesitylene interactions). Smallest range 3.35–3.43; largest range 3.13–3.52; Tl–C_6(centroid) 2.99, 3.03, 3.08, 3.10 (from [165])	[167,168]
$Tl^+(C_6H_5Me)_{2/3}[\textit{commo}\text{-}3,3'\text{-}Al(3,1,2\text{-}AlC_2B_9H_{11})_2]^-$	3.18, 3.19, 3.19, 3.21, 3.21, 3.22 (average 3.21)	[162,163]
$[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$	3.17, 3.18 (average for each of the two different Tl–mesitylene interactions). Ranges: 3.12–3.22; 3.14–3.21; Tl–C_6(centroid) 2.85, 2.85 (taken from [165])	[168]
$[(p\text{-}C_6H_4CH_2CH_2)_2Tl][GaCl_4]$	3.26 (average). Range: 3.16–3.44; Tl–C_6 (centroid) 2.95	[169]
$[Tl(TolNNNNNTol)]_2$	3.62 (average). Range: 3.59–3.65; Tl–C_6 (centroid) 3.33	[172]
$[Tl(PhNNNPh)]_2$	3.54 (average). Range: 3.47–3.60; Tl–C_6 (centroid) 3.27	[172]
$[2,6\text{-}{}^iPr_2C_6H_3(Me_3Si)NTl]_4$	Tl–C_6(centroid) average 3.11	[173]
$C_{13}H_9C(Me_2)C_5H_4Tl$ (2 modifications)		
Modification 1: zig-zag chain structure	3.37, 3.50, 3.49, 3.73, 3.80, 3.90	[6]
Modification 2: two-dimensional coordinate polymer	Ring 1: 3.36, 3.46, 3.57, 3.67, 3.75, 3.88. Ring 2: 3.41, 3.45	
$(PhCH_2)_5C_5Tl$ (2 modifications)		
Modification 1: needles, linear chain	3.38, 3.43, 3.67, 3.68 (*intra*molecular); 3.65, 3.70, 3.73, 3.75 (*inter*molecular)	[213]
Modification 2: parallelepipeds, dimers	3.41, 3.49 (*inter*molecular)	[8]

[a] Values are ordered with increasing distance and do not follow the sequence of the ring atoms.

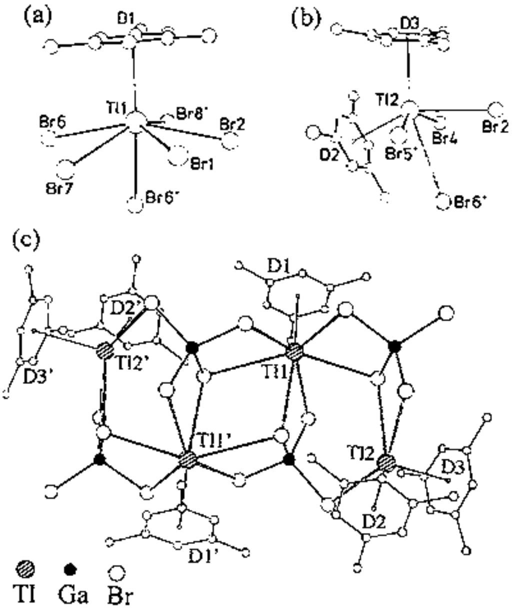


Fig. 10. Coordination sphere of the (a) mono- and (b) bis(arene)-thallium(I) centers and (c) the tetrameric network with the $[GaBr_4]^-$ anions in the solid-state structure of $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ (reprinted from Refs [99,164] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

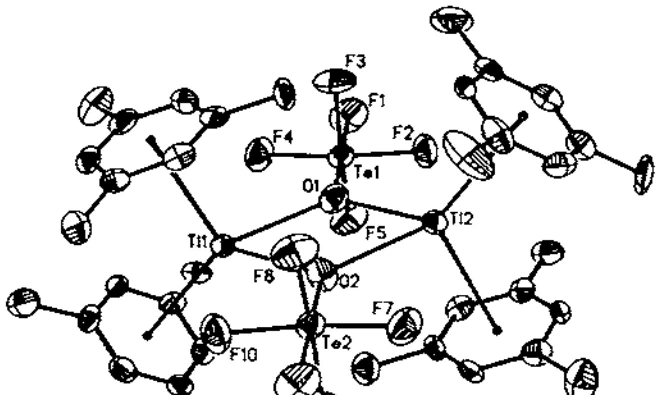


Fig. 11. Drawing of the $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ unit (reprinted from Refs [167,168] with permission, © 1987 American Chemical Society).

nonbonded interactions. The angles formed by the arene centroid–thallium vectors are 118 and 121°, with the dihedral mesitylene plane angles being 51.5 and 49° [167,168].

The structure of $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ consists of a chain of $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl]^+$ cations which are connected by very weak Tl···F interactions (>3.17 Å) with two different "noncoordinating" $[B(OTeF_5)_4]^-$ anions. A drawing of the cation, including the fluorine connectivity, is provided in Fig. 12. The arene centroid–thallium vectors form an angle of 129°, the dihedral angle spanned by the mesitylene ring planes is 55.8° [168].

The structure of the binuclear thallium–arene complex $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ is shown in Fig. 13. Two $AlCl_4$ units bridge between two Tl(I) centers, with Tl–Cl contacts >3.29 Å, in a primarily ionic bonding inter-

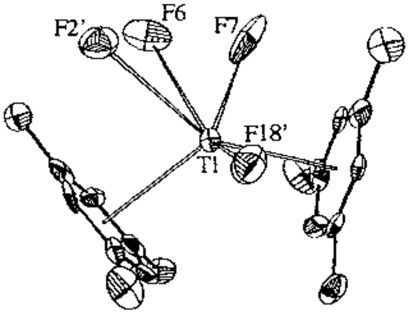


Fig. 12. Drawing of the coordination sphere of the $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl]^+$ cation in $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ (reprinted from Ref. [168] with permission, © 1987 American Chemical Society).

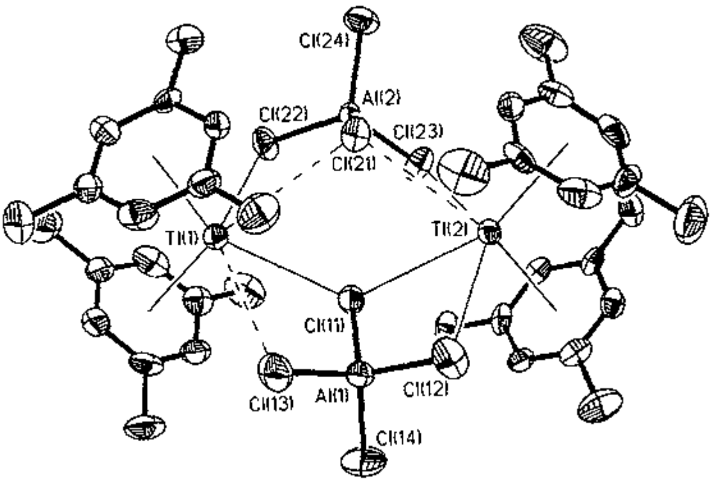


Fig. 13. Structure of the dimeric complex $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$, different ranges for the Tl–Cl contacts are indicated by different line types (solid <3.50 Å, dashed 3.50–3.70 Å). Very similar solid-state structures are obtained for the closely related pseudocumol complexes $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl]\text{-}[GaCl_4]\}_2$ (reprinted from Refs. [165,166] with permission of the author).

action. The four symmetry-independent mesitylene rings complete the coordination sphere of each thallium, in a pairwise almost ideal hexahapto arrangement, to give two lipophilic half-shells around the inorganic core, with angles between the arene ring planes of 50.8 and 54.4°, respectively [165].

A comparison between the related $AlCl_4^-$ and the $OTeF_5$-bridged mesitylene–thallium dimers shows somewhat shorter Tl–C(arene) contacts in the former. Further bond length comparisons of the (genuine) arene-complexes available indicate that the thallium–arene contacts are shorter the smaller the interaction with the anion $\{B(OTeF_5)_4^- < AlCl_4^- < GaCl_4, GaBr_4^-\}$. In turn it can be said that the stronger the Lewis-acid which gives rise to the anion $\{B(OTeF_5)_3 > AlCl_3 > GaCl_3, GaBr_3\}$, the weaker the thallium–anion interaction. A stronger Tl–mesitylene interaction correlates further with a more ideal η^6-coordination, which can be quantized by the ring-slippage (distance between the ring normal to the thallium atom and the ring centroid) or the tilt angle (angle between thallium-ring normal and ring centroid lines) [165].

The two 1,2,4-trimethylbenzene complexes $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ crystallize isotypically and form dimeric units with a center of inversion (unlike the mesitylene coordinated $Tl[AlCl_4]$ complex) [166]. Again, the Tl–Cl contacts are longer than in TlCl (3.326 Å) [214] so a primarily ionic bonding interaction has to be assumed. The arene molecules show almost no distortion from the hexahapto coordination. The angles between the arene ring planes are 61.1 and 62.8°, respectively [166].

The [2.2]paracyclophane complex with $Tl[GaCl_4]$, $[(p\text{-}C_6H_4CH_2CH_2)_2Tl][GaCl_4]$, crystallizes isotypically with the analogous $In[InBr_4]$ and $Ga[GaBr_4]$ complexes. Three-dimensional coordination polymers are formed which exhibit strands of paracyclophane stacks connected by the univalent group-13 ions along the crystallographic *b*-axis. A section of such a bent -M^I-paracyclophane-M^I-paracyclophane strand is shown in Fig. 14. Along the other directions these strands are linked through the $M^{III}X_4$ anions, bridging between the M^I centers [169].

In the paracyclophane-M^I stacks, the metals are in a good approximation twofold η^6-coordinated to the outsides of the adjacent arene rings. The angle between these arene ring planes is 64.6° for $M = Tl$ and the arene–centroid–Tl–arene–centroid angle is 119.0°. The larger range of Tl–C values observed can be ascribed to the deformation of the planarity of the arene rings by the paracyclophane ring stress [169]. It has been noted that in the structures of the arene complexes $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ and $[TlOTeF_5(C_6H_3\text{-}1,3,5\text{-}Me_3)_2]_2$ no stereochemical activity of the $6s^2$ electron pair on Tl(I) is seen in the metal coordination spheres [167].

In addition, thallium–arene interactions where the arene ring is part of the organic ligand bonded to thallium can be observed; in these cases, the thallium–arene interaction was not specifically sought for: In $[Tl(TolNNNNNTol)]_2$ and $[Tl(PhNNNPh)]_2$, the dimeric molecular complexes, are connected in the solid through *inter*-molecular Tl–arene interactions with the tolyl or phenyl rings of the pentaazadienido or triazenido ligand, respectively, of a neighboring molecule [172].

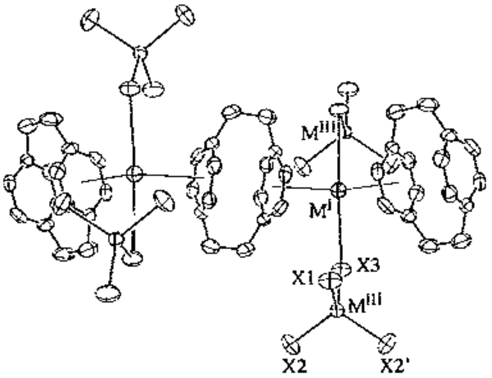


Fig. 14. Section of the bent isostructural M^I-[2.2]paracyclophane-M^I chains (M = Ga, In, Tl), including the $M^{III}X_4^-$ ions which are coordinated to the Tl^I/In^I centers, from the crystal structure of $[(p\text{-}C_6H_4CH_2CH_2)_2M^I][M^{III}X_4]$ ($M^{III}X_4 = GaCl_4$ for Tl^I, $InBr_4$ for In^I, $GaBr_4$ for Ga^I) (reprinted from Ref. [169] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

The tetrametic aggregate $[2,6\text{-}^iPr_2C_6H_3(Me_3Si)NTl]_4$ contains four "inter"-molecular thallium–arene interactions [173].

The structures of the two modifications of $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ [6] were pictured in Fig. 6 and have already been described in Section 3.1.1. The short and hence predominantly covalent Tl–Cp contacts found in both forms are most probably traced to the metal–arene interactions which elevates the necessity for the thallium metal to enter in a strong (ionic) interaction with a second cyclopentadienyl ring to fill the coordination sphere. The observation of Tl–fluorenyl fragments beside the Cp–Tl fragments in the mass spectrum was viewed as an indicator of a certain strength of the metal–arene interaction in the gas phase [6].

In the compound $C_5(CH_2Ph)_5Tl$, short *meta*-phenyl carbon contacts were observed in the solid-state structure to the opposite thallium atom in the "dimeric" form [8] as well as to *ortho*-phenyl carbons of the directly bonded ligand in the linear chain-type, monomeric second modification [213]. The interpretation in the sense of a π-contact of the thallium center was supported by the observation of larger $^{203,205}Tl$–^{13}C coupling constants in the solution NMR spectrum with either the *ortho*- or *meta*-phenyl carbon atoms [122]. Similarly, the coupling constants to the *ortho*- or *meta*-phenyl carbon atoms in $C_5Me_4(SiMe_2Ph)Tl$ are quite large and in $C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ all phenyl carbons have a similar coupling constant of about 20 Hz although Tl-phenyl contacts are absent here in the solid state with its polymeric chain structure (cf. Fig. 4) [147]. The monomeric forms present in solution could, however, give rise to an intermolecular thallium–phenyl contact. For the observation of similar coupling constants to a phenyl group, the hypothesis has been put forward that a conformation might exist in solution where all phenyl carbon atoms have about the same distance from the thallium atom [147]. Such would be the case in a hexahapto thallium–phenyl π-contact.

3.3. Thallium(I) compounds with ligands related to cyclopentadienyl

The structural parameters to the compounds mentioned and discussed here are summarized in Table 4.

$(C_5H_5)Co(\mu\text{-}C_2B_2C)Tl$ [143] (C_2B_2C = 1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl) The cobalt-containing ligand can be considered isolobal to the cyclopentadienyl anion, the structure of this truly molecular compound is provided in Fig. 15. The distances from the thallium to atoms of neighboring molecules are larger than 3.60 Å. On the basis of Wade–Rudolph–Mingos rules [204], the $Co(\mu\text{-}C_2B_2C)Tl$ moiety of the complex $(C_5H_5)Co(\mu\text{-}C_2B_2C)Tl$ can be described as a seven-atom *closo*-cluster [143].

Thallacarboranes. The thallium moiety in the 1,2-dicarba-3-thalla-dodecaborate anion in $[PPh_3Me]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-(THF)_{0.5}$ is rather symmetrically located over the open face of the C_2B_9 cage [Fig. 16(a)], especially in comparison with other metallacarbaboranes. Yet even the shortest thallium–cage distance (2.66 Å) exceeds

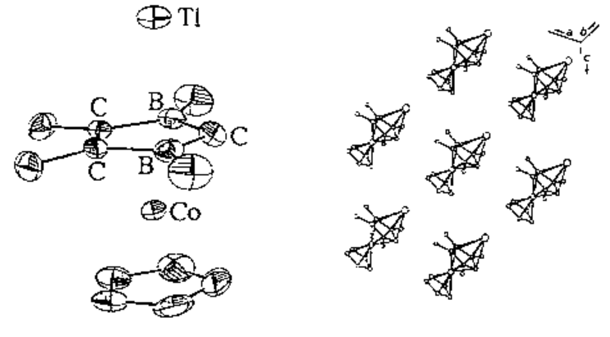


Fig. 15. (a) Molecular structure of $(C_5H_5)Co(\mu\text{-}C_2B_2C)Tl$; (b) packing diagram in the crystal (reprinted from Ref. [143] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

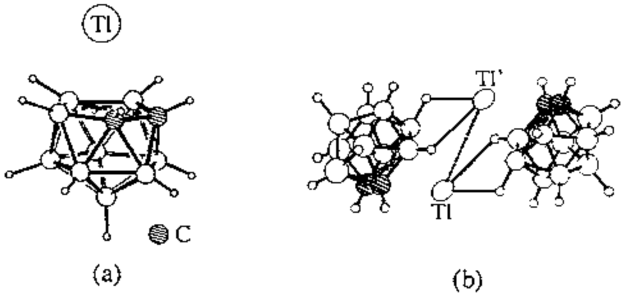


Fig. 16. Structure of the (a) monomeric and (b) dimeric undeca-1,2-dicarba-3-thalla-*closo*-dodecaborate anion in $[PPh_3Me]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-(THF)_{0.5}$ and $[PPN]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$, respectively [203,215] (reprinted from Ref. [216] with permission from Acta Crystallographica).

the sum of the covalent radii, and an ion-pair formulation such as $[Tl^+(C_2B_9H_{11})^{2-}]^-$ is suggested for the anion [215,216]. The structure of the analogous PPN-salt revealed discrete "dimeric" anions with a center of symmetry between the two thallium atoms and an intermetal separation of 4.24 Å. The thallium distances to the dicarbollide anion cage were unchanged. The dicarbollide ligand is bonded in a pentahapto fashion with *one* of the thallium centers and at the same time "bridging" between the *two* thallium ions. Metal–hydrogen–boron interactions to the *other* Tl atom stabilize this bridged array [Fig. 16(b)] [203].

Despite the long Tl–cage distances and the suggested ionic formulation for the thallium–dicarbollide anion, the observation of ^{11}B–^{205}Tl coupling in MeCN solution of the PPN-salt supports the existence of a strong intramolecular interaction between the thallium ion and the dicarbollide ligand in solution (for further information, see Section 4.3.3, below) [203].

In the related compound $Tl^+[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$ [177] which contains a thalla anion with the nonahydro-7,8-dimethyl-7,8-dicarba-nido-undecaborate(2−) ligand, the structure contains two different thallium atoms. One thallium atom is weakly complexed above the open B_3C_2 face of the nido-dicarbollide cluster in a η^3–B_3 π fashion (Fig. 17), albeit with long Tl–B (average 2.82 Å) and even longer Tl–C contacts (>3.1 Å), so that the thalla-dicarbollide subunit $[TlC_2Me_2B_9H_9]^-$ can be also regarded as a contact ion pair $[Tl^+(C_2Me_2B_9H_9)^{2-}]^-$. The thallacarborane anion $[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$ shows much longer Tl–C than Tl–B distances, probably for steric reasons. The other thallium is a cation without any special contact (Tl–B>3.05 Å) to the dicarbollide anion. Most Tl–Tl contacts are above 4.11 Å, only one contact between two symmetry related Tl^+ cations is relatively short with 3.67 Å [177].

Hydrotris(pyrazolyl)borate ligands. Fig. 18 collects examples of the single-crystal X-ray structures, which are available for the thallium(I) complexes of the various substituted tris(pyrazolyl)borate ligands. All structures are clearly built up from molecular units with a pyramidal geometry for the thallium atom with respect to the three nitrogen atoms of the pyrazolylborate ligand. The structures are of local C_3 symmetry if one disregards the rotameric dispositions of the pyrazolyl substituents.

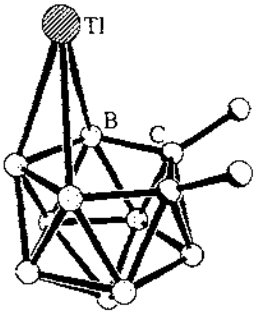
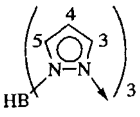
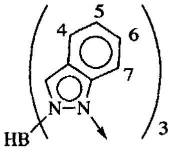


Fig. 17. Structure of the thalla-dicarbollide, $[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$-unit (reprinted from Ref. [177] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

Table 4
Structurally characterized thallium(I) compounds with ligands related to cyclopentadienyl[a] (ordering within each section with increasing molar mass of ligand *L*)

Formula	Tl–ligand (Å)	Remarks	Reference
$(C_5H_5)Co(\mu\text{-}C_2B_2C^b)Tl$	2.47 (Tl–C_2B_2C plane)	Intermolecular contacts to Tl > 3.60 Å	[143]
$[Ph_3MeP]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-(THF)_{0.5}$ (1,2-dicarba-3-thalla-dodecaborate)	Tl–B = 2.66, 2.74, 2.74 Tl–C = 2.92, 2.92	Tl–Tl > 7.97 Å [203]	[215,216]
$[PPN]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$	Tl–B = 2.66, 2.74, 2.74 Tl–C = 2.92, 2.92	Tl–Tl = 4.24	[203]
$Tl^+[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$	Tl–B: average 2.82 Tl–C > 3.1 Å	Tl^+–$Tl^{+\prime}$ = 3.67 Å	[177]
$[PPN]^+[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$		Tl–Tl = 4.09	Footnote 6 in Ref. [203]

Hydro-tris(pyrazolyl)- and -(indazolyl)borate ligands: (pz = pyrazolyl)
(For structural drawings, see also Fig. 18)

Formula	Tl–N (Å)	N–Tl–N (°)	Remarks	Reference
 $HB(pz)_3$  $HB(indazolyl)_3$				
$HB(pz)_3Tl$	2.57, 2.67, 2.73 2.55, 2.59, 2.65	69.6, 72.9, 73.1 71.6, 73.5, 73.6	Two independent molecules in the unit cell, Tl1···Tl1′ = 4.80 Å, Tl2···Tl2′ = 5.12 Å	[216a]
$HB(3\text{-}^tBu\text{-}pz)_3Tl$ $[C_s]^c$	2.58, 2.59	79.3, 75.2	Tl···Tl > 7.22 Å	[183]
$HB(3\text{-}^tBu\text{-}5\text{-}Me\text{-}pz)_3Tl$ $[C_3]^c$	2.50	77.9		[217]

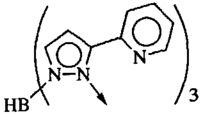
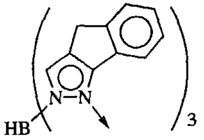
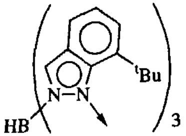
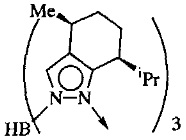
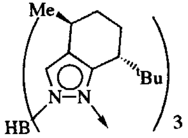
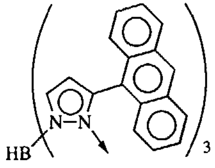
Formula	Tl–N (Å)	N–Tl–N (°)	Remarks	Reference
HB{3-(2-pyridyl)-pz}$_3$Tl 	2.64, 2.67, 2.70	70.2, 71.7, 72.1	Tl–N$_{\mathrm{pyridyl}}$: 3.09, 3.18, 3.26	[218]
HB(1,4-dihydroindeno[1,2-c]-pz)$_3$Tl 	2.52, 2.53, 2.55	72.3, 76.5, 79.4	Tl···Tl > 5.11[d]	[39]
HB{3-(4-MeC$_6$H$_4$)-pz}$_3$Tl [C$_3$][c]	2.59, 2.57	78.2, 75.2	Two independent molecules in the unit cellTl*A*···Tl*B* = 3.86 Å	[219]
HB(7-^{t}Bu-indazolyl)$_3$Tl 	2.65, 2.66	78.2, 78.6		[343]
HB{7(*R*)-^{i}Pr-4(*R*)-Me-4,5,6,7-tetrahydro-2-indazolyl}$_3$Tl 	2.53, 2.55, 2.57	72.7, 79.0, 75.2		[220]

Table 4 (*continued*)

Formula	Tl–N (Å)	N–Tl–N(°)	Remarks	Reference
HB(3,5-^{t}Bu$_2$-pz)$_3$Tl	2.54, 2.58, 2.59	74.9, 79.6, 79.7		[220a]
HB{7(S)-^{t}Bu-4(R)-Me-4,5,6,7-tetrahydro-2-indazolyl}$_3$Tl  	2.56, 2.52, 2.59	79.1, 77.5, 74.2		[220]
HB{3,5-(CF$_3$)$_2$-pz}$_3$Tl $[C_s]$[c]	2.67, 2.72	67.9, 68.7		[190]
HB{3-(9-anthryl)-pz}$_3$Tl  	2.63, 2.69, 2.70	65.3, 65.6, 66.6	Cocrystallization with HB{3-(9-anthryl)-pz}$_3$CoNCS as HB{3-(9-anthryl)-pz}$_3$(CoNCS)$_{0.94}$Tl$_{0.06}$	[221]
HB{3,5-(^{t}BuC$_6$H$_4$)$_2$-pz}$_3$Tl	2.57, 2.58, 2.66	75.2, 77.7, 78.3		[222]

[a] Structural characterization by single-crystal X-ray crystallography.

[b] $C_2B_2C = 1,3,4,5$-tetramethyl-2,3-dihydro-1,3-diborolyl.

[c] Molecular site symmetry in the crystal.

[d] Calculated by SHELX from the data deposited at the Cambridge Crystallographic Database.

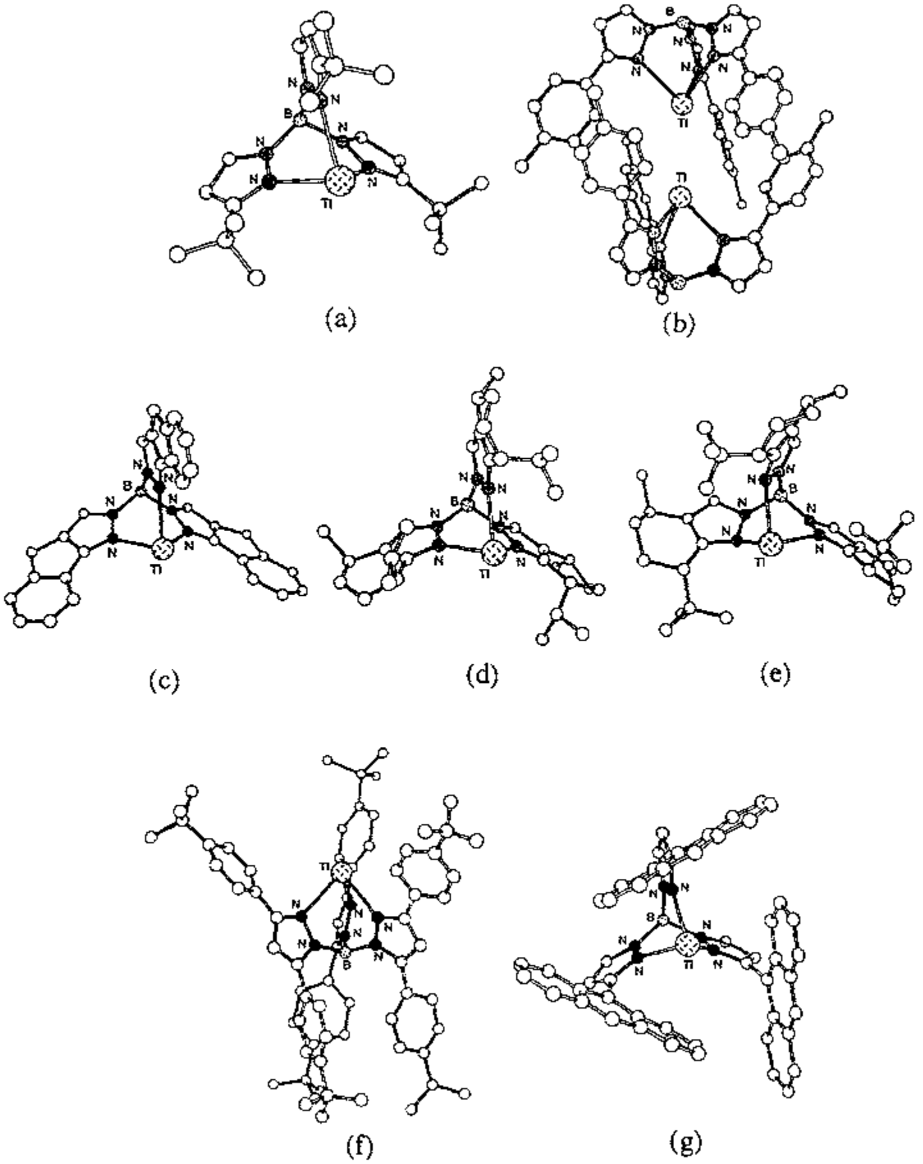


Fig. 18. X-ray crystal structures of hydrotris(pyrazolyl)- and -(indazolyl)borate (Tp) thallium complexes: (a) HB(3-^{t}Bu-pz)$_3$Tl [183]; (b) HB{3-(4-MeC$_6$H$_4$)-pz}$_3$Tl [219]; (c) HB(1,4-dihydroindeno[1,2-c]-pz)$_3$Tl [39]; (d) HB{7(R)-^{i}Pr-4(R)-Me-4,5,6,7-tetrahydro-2-indazolyl}$_3$Tl [220]; (e) HB{7(S)-^{t}Bu-4(R)-Me-4,5,6,7-tetrahydro-2-indazolyl}$_3$Tl [220]; (f) HB{3,5-(^{t}BuC$_6$H$_4$)$_2$-pz}$_3$Tl [222]; (g) HB{3-(9-anthryl)-pz}$_3$Tl [221] (drawings taken from Ref. [16]; © 1995 John Wiley and Sons, reprinted with permission); and (h) packing diagram for HB(pz)$_3$Tl [216a]. The dashed lines between the thallium centers are not meant to imply an interaction but are intended as a visual aid for the chain arrangement.

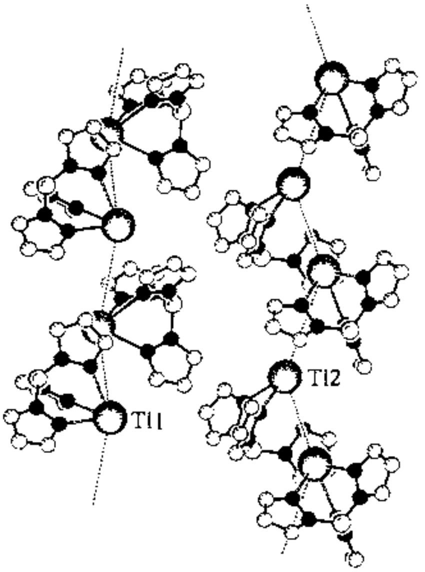


Fig. 18. (continued).

Actual molecular and crystallographic three-fold symmetry is observed only in HB(3-^{t}Bu-5-Me-pz)$_3$Tl (cubic, spacegroup I-43d) [217]. The range of Tl–N distances observed is relatively narrow with 2.50–2.73 Å. The average Tl–N distance exceeds the sum (2.25–2.29 Å) of the covalent radii (Tl 1.55 Å [212], N 0.70–0.74 Å [223]). The bonding between thallium and nitrogen is therefore considered intermediate between a normal covalent and a dative covalent interaction [224] and might imply some ionic character [183]. The obervation of Tl–H and Tl–C coupling in benzene or $CDCl_3$ for many tris(pyrazolyl)borate thallium complexes [cf. Table 8(b), Section 4.3.3] is evidence that the metal–ligand interaction is retained in solution and that it is mainly of covalent character [183,191]. With one exception, these thallium complexes are discrete monomers and neither of them shows any close thallium–thallium contacts. Only HB{3-(4-MeC_6H_4)-pz}$_3$Tl (Tp^{tol}Tl) crystallizes as two independent molecules in the unit cell and the tolyl substituents on the pyrazolyl rings are interwoven such that a Tl–Tl contact of 3.86 Å arises [219]. The TpTl structures are mostly discussed under the aspect of the arrangement of the substituents on the pyrazolyl rings [16]. In HB{3-(2-pyridyl)-pz}$_3$Tl, additional interactions between thallium and the pyridyl nitrogen atoms are noted, which were judged significant on the basis of the pyridyl orientation (towards thallium) and because of a Tl–N$_{pyrazolyl}$ bond lengthening compared with other TpTl structures [218]. The structure of the parent compound, HB(pz)$_3$Tl, reveals kinked chain-type arrangements of the metal-ligand moieties with two different chain types present in the unit cell for the two crystallographically different Tl centers [Fig. 18(h)]. Resulting Tl–Tl′ contacts of 4.80 and 5.12 Å are, however, too long for any metal–metal interaction and the packing is most likely dictated by electrostatic interactions between the thallium and pyrazolyl π manifolds from neighboring molecules [216a].

3.4. *Thallium(II) compounds*

Tetrahypersilyldithallium(*Tl–Tl*), $\{(Me_3Si)_3Si\}_2Tl–Tl\{Si(SiMe_3)_3\}_2$ crystallizes in dark-red square plates [108]: The two thallium atoms are trigonally planar coordinated by two silicon and the respective other thallium atom. The dihedral angle between the two planes defined by the two thallium atoms and either set of silicon atoms on one metal center is 78.1°. The Tl(II)–Tl(II) contact is 2.914 Å at −100 °C and 2.935 Å at +22 °C, thereby being lower than twice the covalent radius of thallium (3.10 Å) [211,212]. The molecule has C_2 symmetry, the structure is shown in Fig. 19. No decomposition during data collection has been reported [108].

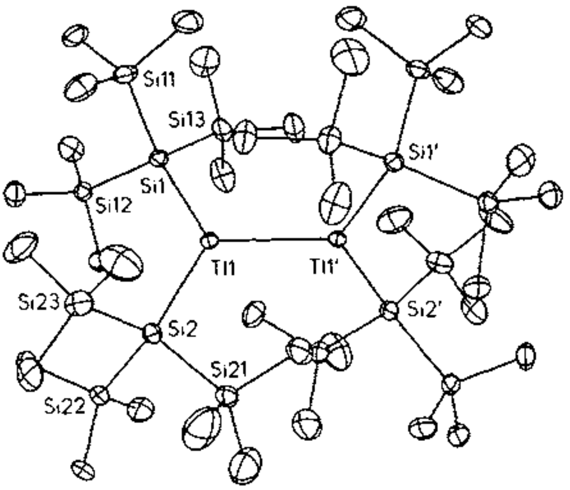


Fig. 19. Structure of $\{(Me_3Si)_3Si\}Tl–Tl\{Si(SiMe_3)_3\}_2$ in the crystal. Tl–Tl = 2.914 Å, Tl–Si = 2.67 Å, Si–Si = 2.36 Å, Si–Tl–Si = 125°, Tl–Si–Si = 107–119°, Tl–Tl–Si = 116–118° (reprinted from Ref. [108] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

Tetrasupersilyldithallium(*Tl–Tl*), $(^tBu_3Si)_2Tl–Tl(Si^tBu_3)_2$: The compound decomposed during data collection on the diffractometer, and only the Tl and Si positions could be determined accurately. The structure of the isomorphous indium analog, tetrasupersilyldiindium(*In–In*) is, however, fully available [109]. In both structures each metal atom is trigonally planar coordinated by two Si and another metal atom, with orthogonal $MMSi_2$ planes (M = In, Tl) (Fig. 20). In the dithallium compound, the Tl(II)–Tl(II) contact is 2.97 Å. In comparison with the other thallium(II) dimer $[\{(Me_3Si)_3Si\}_2Tl]_2$ (see above), the Tl–Tl contact in the supersilyl complex is somewhat elongated, which is ascribed to the higher steric ligand demand of the supersilyl system [109].

The molecular properties of organothallium(I–III) compounds, including the Me_2Tl molecule, have been calculated with spin-orbit-averaged pseudopotential

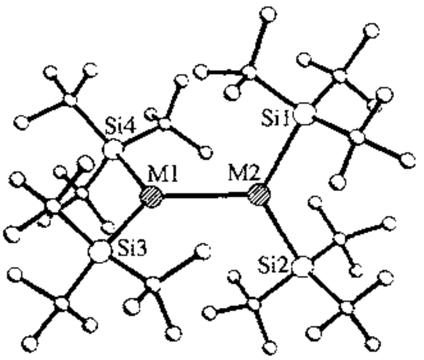


Fig. 20. Structure of $({}^tBu_3Si)_2M$–$M(Si{}^tBu_3)_2$ (M = In, Tl) in the crystal. Tl–Tl = 2.97, Tl–Si = 2.80 Å, Si–Tl–Si = 130°, Tl–Tl–Si = 115° (reprinted from Ref. [109] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

calculations. A bent arrangement (C–Tl–C = 121°) with a thallium–carbon bond length of 2.180 Å is predicted [96].

3.5. *Tl–Tl contacts and the possibility of nonclassical Tl–Tl interactions*

Metal–metal σ- and π-bonding in organometallic complexes of group 13 elements is an intriguing area which has recently attracted considerable attention concerning complexes of aluminum, gallium and indium in their (formal) +I and +II oxidation states [102,225–227]. In complexes where the metal possesses a closed subshell, such as a d^{10} or a $d^{10}s^2$ configuration, one would not immediately expect additional metal–metal bonds. Hence, short contacts between metal centers with such an electronic configuration observed in the solid-state structures of the complexes came somewhat as a surprise and have been the subject of various studies [228].[8]

Already in the first solid-state structure of an organothallium(I) compound, namely that of cyclopentadienylthallium, C_5H_5Tl, it was noticed that the packing of the Cp–Tl chains allows for a minimal *inter*-chain distance between the thallium atoms of 3.99 Å. These equidistant, unbridged metal atoms are also arranged in zig-zag fashion, the angle Tl···Tl···Tl being about 100°. It was suggested that "the metal–metal distance is such as to allow the possibility of interaction between them" [199]. Dimeric and polymeric structures containing Tl atoms in which metal–metal contacts below 4.0 Å occur have now been observed in a sizable number of organo- [229], organic (no Tl–C bonds), and inorganic thallium(I) structures [230] and the potential of thallium–thallium interactions cannot be overlooked. Similarly, metal–metal interactions have been noted in related cyclopentadienylindium(I) complexes, such as $(C_5\,Me_5In)_6$ [231] and $\{C_5(CH_2Ph)_5In\}_2$ [232].

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[8] English title of this reference: Unconventional Interactions in the Chemistry of Metallic Elements, DFG-research report to the special research program "New Phenomena in the Chemistry of Metallic Elements with closed inner Electron Configurations".

Experimental contributions to the problem of Tl(I)–Tl(I) interactions in organometallic compounds were provided specifically with the solid-state structures of $C_5(CH_2Ph)_5Tl$ [8] and $Tl\{-1,3\text{-}{}^tBu_2\}H_2C_5–C_5H_2\{-1',3'\text{-}{}^tBu_2\}Tl$ [5]. The distances of the shorter Tl–Tl contacts observed in these structures are included in Table 2. These compounds show Tl···Tl contacts around 3.6 Å or only about 0.2 Å longer than in thallium metal (shortest Tl–Tl distance in hexagonal closed packed lattice, 3.438 Å; in body-centered cubic lattice, 3.362 Å) [233]. In the absence of bridging, such a Tl···Tl contact is suggestive of some metal–metal interaction. Some bridged complexes with similar length Tl···Tl contacts are also known (see below); however, the apparent consensus is to interpret the latter as resulting from the bridging coordination (*vide infra*). Although, there was some discussion about the possibility of $Tl^I \cdots Tl^I$ interactions for the tetrameric Tl-bridged thallium(I) alkoxides, which were deduced from their Raman and IR spectra [234,235].

The possibility of (weak) metal–metal interactions has been noted repeatedly in organothallium(I) and -indium(I) chemistry, and a theoretical understanding was eventually attempted at the end of the last decade [11,229,236]. [Theoretical studies carried out on the organothallium(I) compound, e.g. C_5H_5Tl, and not considering Tl···Tl interaction will be discussed in more detail in Section 3.6 about theoretical calculations.] Because of the size of the cyclopentadienyl ligand, basic calculations for an understanding of the metal–metal interactions were also carried out with hydrogen bonded to thallium.

The structure of the pentabenzylcyclopentadienylthallium dimer, $\{C_5(CH_2Ph)_5Tl\}_2$ [8], provided the impetus for a theoretical analysis of a model C_5H_5Tl dimer by the extended-Hückel method. A significant role was attributed to the L–Tl–Tl angle (L = ligand) and a calculation of the Tl–Tl overlap population (as a measure of bond order) upon *trans*-bending gave a maximum around L–Tl–Tl = 120° for the $C_5H_5–Tl \cdots Tl–C_5H_5$ model [11,236] (the ligand–Tl–Tl angle in $\{C_5(CH_2Ph)_5Tl\}_2$ was 131.8° [8]). For an understanding of how there can be a bond between two filled s^2 subshells, the orbital interaction with the help of a Walsh diagram was studied in the most simple model, namely HTlTlH. It was also shown that the essentials of the Tl···Tl interaction are retained as the C_5H_5 ligand is simplified to H. The development of a Tl···Tl interaction upon *trans*-bending was explained as a consequence of efficient mixing of formally vacant np orbitals, which is hybridization, which changes the initial repulsion of closed subshells into an attraction by inclusion of unfilled orbitals. Fig. 21 illustrates the important component of this mixing: the interaction of the $2b_u$ HOMO (highest occupied molecular orbit) with the empty $3b_u$ orbital, which pushes both levels apart and changes the character of the HOMO from strongly antibonding to slightly bonding. Hence, the main Tl–Tl bonding orbital, $2a_g$, can govern the attractive interaction around 120° between the thallium centers. Only upon further bending towards a bridging geometry of the ligands does the $2a_g$ orbital lose its bonding character as a consequence of mixing with other levels, and both $2b_u$ and $2a_g$ can then be considered as nonbonding lone-pair combinations [11,236].

In Fig. 22, these changes in the $2a_g$ and $2b_u$ levels are visualized with the help of contour diagrams. The energy minimum upon angle variation in HTl–TlH is

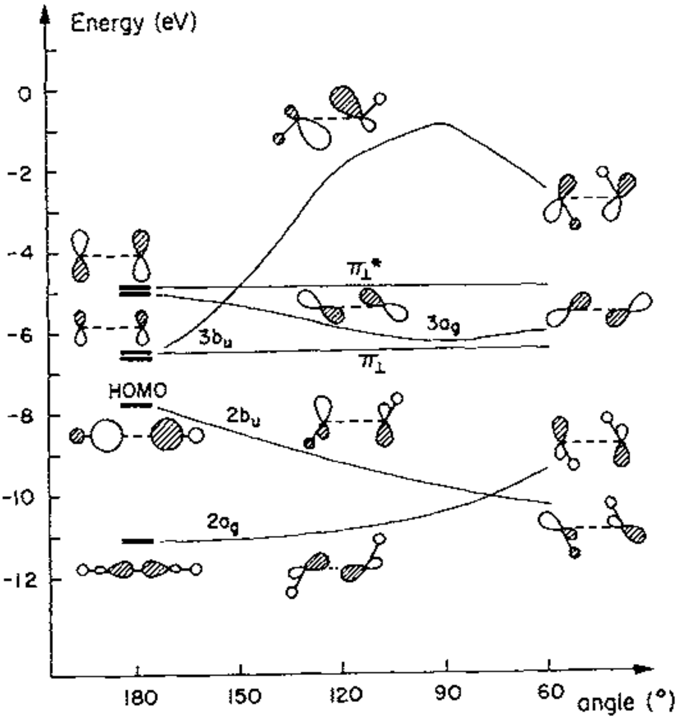


Fig. 21. Partial Walsh diagram for the *trans*-bending in H Tl···Tl-H as a model for $C_5H_5Tl\cdots TlC_5H_5$. The calculations are based on the extended-Hückel method. Symmetry labels are for point group C_{2h}; orbital drawings are schematic [236].

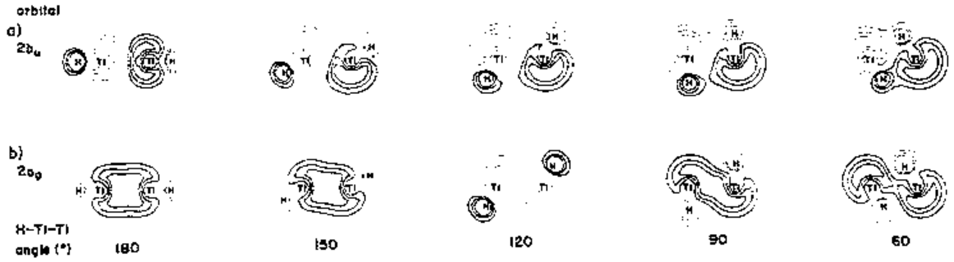


Fig. 22. Contour diagrams for the two highest filled orbitals, $2b_u$ and $2a_g$ in HTl-TlH following the H Tl Tl angle variation. Contour lines of Ψ are ± 0.02, 0.035 and 0.05 [11].

observed around 105° (Tl–Tl = 3.70 Å), thus the *trans*-bent ligand geometry minimizes the total energy and maximizes the Tl–Tl overlap population. The full range of Tl^I–Tl^I and In^I–In^I interactions in molecular and extended (solid-state) structures was analyzed in Ref. [11].

An independent extended-Hückel study by Budzelaar and Boersma on the metal–metal interactions in indium(I) and thallium(I) cyclopentadienyls, C_5H_5In and

C_5H_5Tl, supported the formulation of a weak bonding mode, which they described as a donor–acceptor type interaction, "similar to the Sn–Sn bond in dimeric stannylenes" ($R_2Sn–SnR_2$ [255]). The "bent-bond" approach in such donor acceptor interaction (see Fig. 23) allows for a closer approach of the metal atoms, whereas more symmetrical geometries would result in strong repulsions between the metal lone pairs [229]. Both studies cautioned, however, that in order for a weak Tl···Tl interaction to occur, the ligand–ligand (van der Waals) interactions or crystal packing effects most likely have to provide for the general structural arrangement by orienting the metal centers towards each other, i.e. are decisive in determining the degree of actual metal approach [5,11,229].

In a response to the extended-Hückel MO study in Ref. [236] and [11], the possibility and nature of Tl–Tl bonding in $(CpTl)_2$ was studied with the model compound Tl_2H_2 using correlated nonrelativistic and relativistic self-consistent field (SCF) calculation at different levels of approximation. The best results were obtained at the configuration interaction (CI) level with single and double substitution (CISD), including size consistent quadratic configuration interaction {QCISD(T)} [237]. The potential curve for Tl_2H_2 at various H–Tl–Tl angles and at Tl–Tl = 3.632 Å (the observed distance in $\{C_5(CH_2Ph)_5Tl\}_2$ [8]) gives a repulsive Tl(I)–Tl(I) interaction for the linear molecule (to the extent of 46 kJ mol^{-1}) and a local minimum at a H–Tl–Tl angle of 115.1° (*trans*-bent structure, about 14 kJ mol^{-1} below the dissociation limit). The optimized Tl–Tl contact at 115.1° was then 3.28 Å for Tl_2H_2. The reason for the *trans*-bending was seen in the large repulsive forces for the linear R–Tl–Tl–R arrangement (R = H, Cp) and the Tl–Tl interaction was viewed as "very small" at most. It was not clear if *trans*-bent Tl_2H_2 did have a Tl–Tl "bond" at the level of calculation used. A second deeper minimum was calculated to be the di-hydrogen bridged structure, Tl(μ-H)$_2$Tl [237].

The singlet potential energy surface for Tl_2H_2 (and the other group-13 E_2H_2 systems) has been explored further through ab initio SCF + CI calculations in order to gain insight in the bonding character of the various isomers [HTl = TlH linear or *trans* bent, Tl–TlH$_2$, and Tl(μ-H)$_2$Tl] and to provide structural and energetic data.

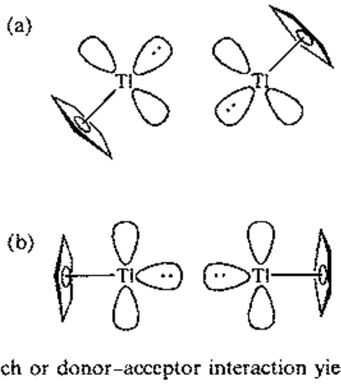


Fig. 23. The "bent-bond" approach or donor–acceptor interaction yielding the observed unsymmetrical geometries in the dimeric thallium(I) and indium(I) cyclopentadienyls (a), and versus the repulsive interaction between the metal lone-pairs in the more symmetric geometry (b) [229].

Effective core potentials including relativistic effects were used for thallium. Tl_2H_2 was thereby viewed as a simple model for Tl_2R_2 (R = alkyl, aryl or cyclopentadienyl) and Tl_2X_2 (X = halogen). The D_{2h} di-H-bridged structure was found as the global minimum. Still, the *trans*-bent structure was of lower energy than the linear H–Tl=Tl–H form. The occurrence of *trans*-bent isomers was explained by a simple rule derived from an MO model treating σ–π mixing: a *trans*-bent distortion was stated to occur when the singlet–triplet energy separation of the EH fragment is larger than half the bond energy of the linear $^1\Delta_g$ state [238].

With respect to the minimum energy two-fold ligand-bridged structure calculated as a minimum for the Tl_2H_2 model compound [237,238], it can be noted that such structures have not yet been observed in organothallium compounds, but that ligand-bridged Tl species are known in many inorganic compounds. Inorganic thallium(I) compounds with two or more ligands bridging between the metals are numerous; selected examples are Tl_2F_2 [239], $[(Ph_3P)_2N][Tl_2Fe_6(CO)_{24}]$, $[Et_4N]_2[Tl_2Fe_4(CO)_{16}]$, $[Et_4N]_4[Tl_4Fe_8(CO)_{30}]$, $[Et_4N]_6[Tl_6Fe_{10}(CO)_{36}]$ (in each case two $Fe(CO)_4$-bridges to give Tl_2Fe_2 parallelograms, additional Tl-triangles with μ_3-$Fe(CO)_3$ bridges for the last compound) [240–242], $(MeSi)_2(N^tBu)_4Tl_2$ (two N ^{t}Bu-bridges) [243], $[Tl(\mu_3\text{-}OSiPh_3)]_4$ [244], $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ (two $OTeF_5$-bridges) [167], $[Tl(PhNNNPh)]_2$ [172], $[TlSSi(O^tBu)_3]_2$ [245], $(2,2,2\text{-crypt-}K^-)_2Tl_2Te_2^{2-}$ [246], tetrameric thallium(I) alkoxides $[Tl(OR)]_4$ (R = alkyl) [234,235,247], dimeric thallium(I) dialkyldithiocarbamates, TlS_2CNR_2 [248,249], thallium chalcogenides of the TlSe-type $TlEX_2$ (E = Ga, In; X = Se, Te) [250], and (benzotriazolato)thallium(I) [251] Despite the often short Tl···Tl contacts in these bridged structures around 3.6 Å, a bonding interaction can be ruled out and the close approach should be explained by chelate effects (geometric constraints of the bridge) and/or an electron withdrawing effect which leads to a smaller atomic radius for thallium [243].

A Tl(I)–Tl(I) interaction which can safely be called a "bond" has hitherto only been observed in an inorganic complex of the composition $(MeSi)_2(N^tBu)_6Tl_6$ which exhibits a structure of two edge-sharing cages (Fig. 24). The Tl–Tl contact along the common edge is unusually short with 3.152 or 3.18 Å (two independent molecules in the unit cell) [252]. Based on the covalent radius for thallium of 1.55 Å [211,212], a Tl^I–Tl^I bond can be expected to be around 3.1 Å long.

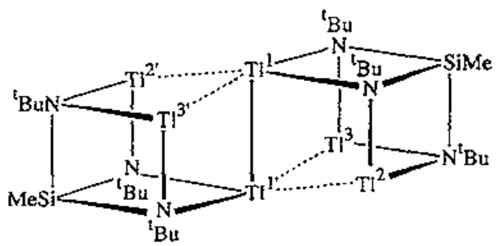


Fig. 24. Schematic drawing of the edge-sharing cage structure of $(MeSi)_2(N^tBu)_6Tl_6$ [252].

Concluding this section, we note that while Tl(I)–Tl(I) interactions are still a matter of discussion, Tl(II)–Tl(II) bonds are a possibility, especially in the solid state. Tl(II) has a $d^{10}s^{1}$ configuration and the probable ability of thallium(II) to form metal–metal bonds on this electronic bases had already discussed by Nyholm in 1961 [253]. The structure of $Tl_{0.8}Sn_{0.6}Mo_{7}O_{11}$ contains a remarkably short Tl–Tl distance of 2.84 Å, which qualitatively was assessed as a single Tl–Tl bond between Tl^{2-} units [254]. In the molecular complexes $\{(Me_3Si)_3Si\}_2Tl–Tl\{Si(SiMe_3)_3\}_2$ and $(^tBu_3Si)_2Tl–Tl(Si^tBu)_2$, the Tl(II)–Tl(II) contacts are 2.91 and 2.97 Å, respectively [108,109].

3.6. Theoretical structural studies on cyclopentadienylthallium(I) compounds

Table 5 gives a list of the thallium(I) compounds whose structures have been assessed together with some of the calculated structural parameters. For a listing and a discussion of the calculated *properties*, see Section 4.4, Table 9.

The structure of monomeric C_5H_5Tl (and C_5H_5In) has been optimized with an SCF pseudopotential method by Canadell, Eisenstein and Rubio and the results were found in good agreement with the experimental information. The influence of d orbitals on Tl has been found to be negligible [206]. The polymeric chain structure was analyzed using cyclopentadienylindium as an example by means of the extended-Hückel tight binding method. The results can, however, also be applied to the thallium analog. The zig-zag structure of the polymer is suggested to be due to a

Table 5
Cyclopentadienylthallium(I) compounds structurally studied by theoretical methods

Formula, remarks	Method, level basis sets[a]	Calculated distances, angles[b] (Å) (°)	Reference
C_5H_5Tl, monomer	SCF, RCP-DZ	Tl–C = 2.832	[206]
	Ab initio MO, HF, MP2, −3, −4 ECP-DZ	Tl–C = 2.815[c] Tl–Cp = 2.542	[157]
C_5H_5Tl, dimer ($C_5H_5Tl\cdots TlC_5H_5$)	Extended-Hückel	No geometry optimization	[11]
Thallium(I) anions $[Tl(C_5H_5)_2]^-$	Ab initio MO, HF, MP2, −3, −4 ECP-DZ	Tl–C = 3.008–3.271, bent Tl–Cp = 2.903 Cp–Tl–Cp = 143.9 Tl–C = 3.158, linear Tl–Cp = 2.918	[157]

[a] MO = molecular orbital, HF = Hartree–Fock, MP = Møller–Plesset, ECP/RCP = effective/relativistic core potential, DZ = double zeta.

[b] Cp = cyclopentadienyl centroid; average = average value.

[c] We note most likely a number exchange error in Ref. [157]. An unreasonable value of Tl–C = 2.185 was given there.

minimization of the repulsive factors [206]. The authors did not discuss the interchain interactions in these compounds.

In $[Tl(C_5H_5)_2]^-$ the (experimentally observed) bent structure was calculated to be only slightly more stable (by 0.82 kcal mol^{-1}) than the linear one, suggesting a very soft potential well and arguing against an electronic reasoning for the bending due to orbital mixing. In addition, in the bent structure, one of the rings was calculated to be closer to the metal (Cp–Tl = 2.846 and 2.903 Å), whereas in the linear conformer both rings were calculated equidistant (Cp–Tl = 2.918) [157].

4. Properties

4.1. The nature of the thallium–carbon bond, vibrational spectroscopic studies

For some time the nature of the bonding in cyclopentadienylthallium, C_5H_5Tl (and other main-group metal cyclopentadienyls) has been the matter of discussion. An ionic thallium–ring interaction was suggested based on the absence of metal–Cp absorptions in the solid-state IR spectrum [256,257], based on the absence of Tl–H spin–spin coupling in the proton NMR spectra in solution [9], and based on X-ray structural investigations, which showed a polymer chain structure with long and equidistant thallium–ring distances [199,201]. On the other hand, covalency of the bond in C_5H_5Tl has been claimed from a microwave spectroscopy study of the gaseous compound, which gave a Tl–C distance of 2.70 Å [198]. This is longer than the sum of the covalent radii for thallium (1.55 Å) and carbon (0.77 Å) [211,212], but about 0.4 Å shorter than the sum of the ionic radius for Tl^+ (1.4–1.5 Å [210]) and the van der Waals radius for C (1.7 Å [209]). In addition, an electron diffraction study on the related gaseous C_5H_5In [207] showed that the metal–carbon bond (2.62 Å) is 0.4 Å shorter than the sum of the ionic radius for In^+ (1.3 Å [210]) and van der Waals radius for C. Furthermore, polarography of C_5H_5Tl in DMF together with the low conductivity of the compound (5×10^{-4} cm^2 Ω^{-1} mol^{-1}) [140] in this solvent suggested that the bond is not "purely ionic". The electrical conductivity of a solution of cyclopentadienylthallium in DMF was 20 times less than an equimolar solution of thallium(I) perchlorate and only 2.5 times that of the solvent [127,258]. The binding energy of the thallium-ring bond was estimated from polarographic studies of C_5H_5Tl ($E_{1/2}$ values of the cathodic waves) to be 11.3 kcal mol^{-1}, which is less than for iron in ferrocene [258].

From a comparison of the ^{19}F NMR chemical shifts of *m*- and *p*-fluorophenylcyclopentadienylthallium and estimated values derived therefrom, with the respective values for alkali cyclopentadienides and for metallocenes, the thallium-cyclopentadienyl bond "ionicity" has been estimated to be at least 40 to 50% [138,139]. A stereochemical approach to the problem of bonding in C_5H_5Tl was proposed which consisted of a ^{13}C NMR study of the diastereotopy of cyclopentadienyl carbon atoms in $C_5H_4\{C^*H(Me)Ph\}Tl$, the potassium and mixed-sandwich ferrocene derivative of this chiral ligand. Results obtained, namely the same resonance signal for the diastereotopic C2/5 and C3/4 ring carbon atoms in the thallium and potassium compound, indicated the absence of a stable (covalent) metal–ring bond in cyclopentadienylthallium (in C_6H_6, CH_2Cl_2 and THF) and the existence in the form of tight ion pairs was suggested [138]. A similar conclusion for an appreciable presence of tight ion pair species (versus solvent separated ionic species) in solution even in highly polar solvents like DMSO (dimethylsulfoxide), was reached from an analysis of the differences in conformational preference found for the lithium, sodium, potassium and thallium(I) cyclopentadienides with functional substituents (cf. **12** and **13** above, Section 3.1.1, or **16** and **17** below, Section 4.3.1) [19,128]. On the other hand, a comparative ^{13}C NMR investigation for the methylcyclopentadienyl derivatives of Ge, Sn, Pb, Li, K and Tl was found consistent "with some degree of covalent character" for the latter [259].

Now, it appears clear that the thallium–ring bond ionicity varies with the aggregate state (solid, vapor) and with the degree of polymerization. In the solid state, the polymeric chain structures (type I, see Section 3.1.1) show thallium–carbon distances which are considerably larger than the covalent Tl–C bond lengths, so that they are concomittant with a large ionic contribution. In the gas phase or with appropriate bulky ligands also in the solid state, molecular structures with essentially isolated Cp–Tl units showing short, covalent thallium–carbon distances (type II, see Section 3.1.1), are observed. The shortening of the Tl–C/Cp distance is normally viewed accompanied by an increase in covalent character and a decrease in the ionic character of the bond [7,8,135,206]. An increase in bond ionicity was suggested in the series $C_5H_5Tl < (C_5H_5BMe)Tl < (C_5H_5BPh)Tl$, based on the mass-spectrometric observation of an increasingly more elementary metal–ligand fragmentation [176]. The orbital description of Cp–Tl bonding is included in Section 4.4 below (photoelectron spectroscopy).

Concerning the thallium–arene bonding interaction, reference can only be made to a study on the electronic structures of the benzene–gallium(I) model complexes $[(C_6H_6)Ga]^+$ and $[(C_6H_6)_2Ga]^+$, which have been calculated by using the discrete variation Xα molecular orbital method. The results show a weak dative bond formed between the C_6H_6 molecule and the Ga^I atom, with the electronic charge being transferred from the π orbitals of the benzene molecule to the three p orbitals of the Ga^I atom [260].

A vibrational (IR and Raman) spectral study on the structure of C_5H_5Tl and C_5H_5In at temperatures of 12–300 K for the pure solids, in solid argon matrices and for C_5H_5In also in the gas phase has been carried out [10]. The analysis of the spectra of the pure solids were interpreted in line with D_{5h} symmetry of the C_5H_5-ring, which is consistent with the predominantly ionic character of the metal–ligand bond in the crystalline complexes [10,256]. A study of the IR spectra of the argon matrices and the gas (C_{5v} symmetry), on the other hand, showed that the monomeric complexes had a predominantly covalent metal–ring bond. The values of the out-of-plane ρ(CH) frequencies were taken as an indicator for the increase in polarity of the M–Cp bond upon transition from the isolated molecule to the polymeric structure [10]. The metal–ring vibrations for molecular C_5H_5Tl (gas phase) were estimated at 160 ± 20 cm^{-1} [ν_s(Tl–Cp), A_1, thallium–ring stretch] and at 290 ± 40 cm^{-1} [ν_{as}(Tl–Cp), E_1, thallium–ring tilt] from the microwave spectrum of cyclopentadienyl thallium in excited vibrational states [261].

A normal-coordinate analysis of molecular C_5H_5Tl was carried out using a general valence force field and good agreement was seen between observed and calculated wavenumbers. The Tl–Cp vibrations were found to be almost completely uncoupled with other vibrations [262]. For a comparison of the C_5H_5-ring fundamental frequencies of C_5H_5Tl with alkali metal cyclopentadienides, see [257,263]; for a comparison with main-group and transition-metal metallocenes and half-sandwich complexes, see [256]; for a comparison with cyclopentadienylmercury compounds, see [119].

The frequency for the Tl(II)–Tl(II) stretch is assigned to 78 cm^{-1} from a Raman spectroscopic investigation on a concentrated n-pentane solution of $\{(Me_3Si)_3Si\}_2Tl–Tl\{Si(SiMe_3)_3\}_2$. The IR spectrum in nujol showed a corresponding medium-to-strong band at 82 cm^{-1} [108].

Theoretical calculations show an increase in stability of the Tl–C bond from MeTl to Me_3Tl; spin-orbit coupling reduces the Tl–C bond stability in MeTl. For a calculated series of methylthallium(I–III) compounds, relativistic bond length contractions were found to be small. An SCF–Xα-SW calculations found little Tl–5d contribution to Tl–C σ bonds [96]. Vibrational frequencies for the yet undetected molecule MeTl have been predicted. The frequencies suggest a weak Tl–C σ bond [264].

4.2. *Stabilities and solubilities*

4.2.1. *Alkyl- and arylthallium(I) compounds*

As noted in Section 2.1 alkyl- and arylthallium(I) compounds are generally very unstable. An appropriate bulky ligand which would provide for a kinetic stabilization has not yet been found (see, however, Section 5.2.1). For alkyl = methyl and aryl = phenyl, the organothallium(I) complexes have sometimes been proposed as transitory species in the synthesis or decomposition of the respective organothallium(III) compound [43,62,65,85–88,90,91,93].

The instability of TlR, the deposition of thallium metal therefrom, has been used as a driving force in the reactions of magnesium, zinc and cadmium dialkyls (MR_2) with HB(3,5-R′,R″-pz)$_3$Tl to give {HB(3,5-R′,R″-pz)$_3$}MR. Similarly, trimethylaluminum and HB(3-^{t}Bu-pz)$_3$Tl gave HB(3-^{t}Bu-pz)$_3$AlMe$_2$ (see below Section 5.2, Eq. (27)).

4.2.2. *Cyclopentadienylthallium(I) compounds*

Table 6 compares the thermal, air and moisture stabilities as well as the solubilities of the organometallic thallium(I) complexes and also provides for a general overview with respect to available analytical data. Among the group-13 organoelement(I) compounds, the cyclopentadienyl derivatives of thallium are generally the most stable, in comparison they have the best resistance towards light and oxygen. Organoaluminum(I) and -gallium(I) has only recently been explored in more detail

[102] and still relatively few cyclopentadienylindium complexes are known, with C_5H_5In exhibiting great sensitivity towards light and oxygen [270]. C_5H_5Tl, on the other hand, is quite stable towards water as it is prepared from this medium and darkens only slowly on standing in air or light [115].

The considerable difference in air and thermal stability among the cyclopentadienylthallium(I) compounds was often addressed as a matter of interest [9,18,122]. Just as an example: C_5H_5Tl was found to be more stable than $C_5H_4{}^tBuTl$ or $C_5H_4(SiMe_3)Tl$ (which were of similar stability), while C_5H_4MeTl was highly air- and water-sensitive. As an explanation, the difference in lattice energies [265] and inductive or mesomeric effects of the ring substituents [18] have been offered. An extremely stable crystal lattice concomittant with the its ionic formation was proposed for C_5H_5Tl [265].

The standard heat of formation of solid C_5H_5Tl was calculated to be 23.85 ± 0.06 kcal mol^{-1} from measurements of the heat of reaction of aqueous TlOH with gaseous C_5H_6 at 25 °C. The standard free energy of formation of solid C_5H_5Tl was calculated to be 42.3 ± 0.5 kcal mol^{-1} from measurement of the ion activity (approximated by the pH value) for the aforementioned reaction at equilibrium at 25 °C. The standard entropy of solid C_5H_5Tl was then calculated as 38.3 ± 3 cal (K mol)$^{-1}$. From a comparison of the thermochemical data and the hydrolysis behavior of C_5H_5Tl, $(C_5H_5)_2Fe$ and $(C_5H_5)_2Mg$, the stability of C_5H_5Tl was shown to depend mainly on the free energy of formation of the metal hydroxide. As a consequence, the hydrolysis reaction would reveal little on the ionic or covalent character or the strength of the metal–cyclopentadienyl bond. The possibility for the preparation of C_5H_5Tl in water is due to the low affinity of Tl for oxygen and the solubility of TlOH in water [271]. The solubility of cyclopentadienylthallium in organic solvents usually increases with the introduction of substituents on the cyclopentadienyl ring [9].

The mass spectrum often shows the molecular ion with a reasonable intensity [5–7,9,122,135,148], the base peak being either the thallium ion [5,7,18,122,135,141,148,266] or a ligand fragment [6,122,136,143,152]. Because of the presence of the molecular ion and the specific isotopic pattern for thallium (natural abundances: ^{203}Tl 29.5, ^{205}Tl 70.5%), mass spectrometry represents a favorable method of identification [20,122]. The mass spectrum of C_5H_5Tl has been examined in detail, with the peak of highest mass being the molecular ion; the base peak is $[Tl]^+$. This was taken to indicate that polymeric species are absent in the gas phase [266]. Under less energetic conditions, such as chemical ionization and positive and negative fast atom bombardment mass spectrometry, the zig-zag chain structure may not be entirely disrupted, however, as indicated by the formation of $[CpTl_2]^+$ and $[Cp_2Tl]^-$ in the case of the compounds C_5H_5Tl, $C_5H_4(COCO_2Et)Tl$ and $C_5H_4(NO_2)Tl$ [128].

Many cyclopentadienylthallium complexes are reported to sublime without or with only slight decomposition [7,9,18–20,122,148]. Major decomposition during sublimation was described for C_5H_4BrTl and C_5H_4ITl [20], and hydropentalenylthallium [9].

Table 6. Properties of Cyclopentadienylthallium(I) Compounds ordering within each section with increasing molar mass of the Cp ligand)

The table is divided in a) mononuclear complexes, b) dinuclear complexes, and c) cyclopentadienylthallium(I) anions

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
a) mononuclear complexes $50 < Cp < 100$ g mol^{-1}					
C_5H_5Tl (colorless, pale yellow)	infusible subl. 100-110 (10 Torr)	air-stable	medium in warm CH_3OH, acetone, pyridine, insol. in H_2O	weakly thermochromic	[111,112]
	dec >150				[111]
	subl 100-120 (10 Torr)				
	ca. 230 dec.	air-stable	insol. in H_2O		[115,265]
	blackening without melting below 270 in evacuated capillary				[115]
	blackening at 60°C in air				[114]
	subl. 80 (5 10^{-3} Torr)				
	subl. 145 (5 10^{-3} Torr)			molar conductivity $5.1 \cdot 10^{-4}$ cm^2 Ω^{-1} mol^{-1}	[140]
(light yellow)	subl. 90-100 (10^{-3} Torr)	slow dec. (solid turns brown) in air and light but the pure product may still sublimed from this material			[117]
				anal. by MS (CI, EI)	[128,266]
			NMR in THF or DMSO	anal. by ^{1}H NMR	[9,127]
				solid-state Tl NMR	[267]
				anal. by X-ray	[199,201]
				anal. by microwave spectrosc.	[198,261]
				vibrational spectrosc.	[10,256,262]
				diamagnetic	[268]
				compound can be determined in the organic phase by gas chromatography	[269]

Table 6 (continued)

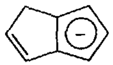
Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
C_5H_4MeTl (*pale yellow needles*)	88-89 (with slight dec.)	vigorously oxidized			[115,124]
	subl. 75 in vacuum		insol. in H_2O		[265]
	109-110, subl. 50 (high vacuum, Hg diff. pump)		NMR in DMSO	anal. by ^1H NMR	[9]
				^{13}C NMR	[259]
$C_5H_4(CN)Tl$ (*white needles*)	150-152		recryst. from MeCN	anal. by ^1H NMR, IR, MS	[125,126]
$C_5H_4(CH{=}CH_2)Tl$ (*yellow-orange*)		not air-stable	insol. in THF, Et_2O, pentane	anal. by ^1H NMR	[118]
$C_5H_4(CHO)Tl$ (*off-white microcrystals*)	150-152		recryst. from MeCN, NMR in DMSO	anal. by ^1H, ^{13}C NMR	[19]
(*tan powder*)	163-170 (vacuum) 144 in air, dec.	air-stable	recryst. from PhCN	anal. by ^1H, ^{13}C NMR, IR	[37]
C_5H_4EtTl (*light yellow needles*)	50-52 subl. 63-73 (0.08 Torr)		readily sol. in THF		[127]
C_5H_4ClTl (*cream solid*)	140-142 subl. 95 (10^{-2} Torr)	slightly air-sensitive	slightly sol. only in THF and DMSO	anal. by ^1H NMR, IR, MS	[19,20]
$100 < Cp < 150$ g mol^{-1}					
C_8H_7Tl (*bright yellow solid*) (hydropentalenyl)	87-89 dec. (vacuum) subl. 80 ($5\cdot10^{-6}$ Torr) with dec.	air-stable, dec. only after prolonged exposure	insol. in water, hexane, C_6H_6, THF, Et_2O	anal. by IR, MS	[18]
	86-90		NMR in DMSO or pyridine	anal. by ^{1} H NMR	[9]
$C_5H_3\{$-1,2/1,3-Me(CHO)$\}Tl$ (mixture of isomers) (*beige solid*)			recryst. from MeCN	anal. by ^1H NMR, MS	[125]
$C_5H_4\{C(O)Me\}Tl$ (*gray plates*)	145		recryst. from MeCN	anal. by ^1H, ^{13}C NMR	[19]
(*tan powder*)	222-223 (vacuum) 118 in air, dec.	air-stable		anal. by ^1H, ^{13}C NMR, IR	[37]
$C_5H_4(NO_2)Tl$ (*orange solid*)	152-155 dec. subl. 100 (10^{-3} Torr)			anal. by IR, MS (CI)	[128]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5H_4(SMe)Tl$ (white powder)	74 dec.	not air-stable	NMR in DMSO	anal. by ^1H, ^{13}C NMR, IR	[53]
C_9H_7Tl (pale yellow solid) (indenyl)	250 dec.	air-stable	more sol. in polar organic solvents than C_5H_5Tl	anal. by IR	[129]
$C_5H_3\{\text{-}1,2\text{-}(CHO)_2\}Tl$ (yellow powder)	145 dec.		NMR in DMSO	anal. by ^1H, ^{13}C NMR, IR	[54]
$C_5H_4{}^tBuTl$ (cream-colored scales)	169.8-170.5 subl. 70 (0.08 Torr)		readily sol. in hexane and C_6H_6, moderately sol. in THF	anal. by ^1H NMR	[127]
	151 subl. 50 (high vacuum, Hg diff. pump)		NMR in DMSO	anal. by ^1H NMR	[9]
C_5HMe_4Tl (yellow needles)	subl. 140 (10^{-3} Torr)	not air-stable	good sol. in Et_2O, THF, C_6H_6, toluene, pentane	anal. by ^1H, ^{13}C NMR, MS, X-ray	[130]
$C_5H_4(PMe_2)Tl$ (gray-white)	subl. 80 (10^{-3} Torr) extensive dec.	not air-stable	sol. in THF, C_6H_6, CH_2Cl_2	anal. by ^1H, ^{31}P NMR, MS	[131]
$C_5H_3(C_5H_8)Tl$ (pale yellow solid) (isodicyclopentadienyl) 	subl. 80 (5 10^{-6} Torr)	very air-sensitive			[18]
	163-164, subl. 50-60 (high vacuum, Hg diff. pump)			anal. by ^1H NMR, IR, MS	[9]
$C_5H_4(CF_3)Tl$	rapid dec. at room temp.		very insol.	no characterization	[14]
$C_5H_4(CO_2Me)Tl$ (white needles)	140-142 w. dec.		recryst. from MeCN	anal. by ^1H NMR, IR	[133]
(white powder)	136-139	air-stable		anal. by ^1H	[134]
	136-140	air-stable			[132]
(tan solid)	179-192 (vacuum)	air-stable		anal. by ^1H, ^{13}C NMR, IR	[37]
	144 in air			anal. by ^1H, ^{13}C NMR	[19]
C_5Me_5Tl (bright yellow to yellow-orange)	subl. 70 (10^{-5} Torr)		sol. in THF, pentane	anal. by ^1H NMR	[21]
	subl. 140-150 (10^{-2} Torr)	not air-stable pyrophoric as a powder	sol. in pentane and other hydrocarbons	anal. by ^1H,^{13}C NMR, MS, X-ray light-sensitive	[135]
				gas phase electron diffraction	[200]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5H_4\{C(O)NMe_2\}Tl$ (white)	134-136		recryst. from MeCN	anal. by ^1H NMR, MS	[125]
$C_5H_4(CH_2CH_2NMe_2)Tl$ (colorless)		not air-stable	very good sol. in organic solvents	anal. by ^1H, ^{13}C NMR, MS	[136]
$C_5H_4(CO_2Et)Tl$ (white needles)	80-82			anal. by IR	[126]
(tan powder)	152-160 (vacuum) 143 in air	air-stable		anal. by ^1H, ^{13}C NMR, IR	[37]
$C_5H_4\{C(O)CH_2OMe\}Tl$ (cream white solid)				anal. by ^1H NMR	[120]
$C_5H_4(CH_2CO_2Me)Tl$ (light yellow solid)				not obtained pure, but in mixture with either $C_5H_4(CH_2CO_2Et)Tl$ or C_5H_5Tl, anal. by ^1H NMR	[120]
$C_5H_4(SiMe_3)Tl$	115-116 subl. 30 (10^{-1} Torr)		sparingly sol. in cold C_6H_6, good sol. in hot C_6H_6, toluene	anal. by ^1H, ^{13}C NMR, MS, X-ray	[7]
			NMR in DMSO and C_6H_6	anal. by ^1H NMR, IR	[9]
C_5H_4PhTl (yellow solid)		only briefly air-stable		anal. by ^1H NMR, darkens on exposure to light	[24]
	subl. 60 (10^{-3} Torr)			anal. by ^1H, ^{13}C NMR, IR	[19]
C_5H_4BrTl (cream solid)	130 dec. (N_2) subl. 85 (10^{-2} Torr)	not air-stable	slightly sol. only in THF and DMSO	anal. by ^1H NMR, IR, MS	[20]
$C_5H_3\{-1,2\text{-}C(O)Me\}_2Tl$ (off-white platelets)	155 dec.		NMR in DMSO	anal. by ^1H NMR, IR	[54]
$150 < Cp < 200$ g mol^{-1}					
$C_5H_4(CO_2{}^iPr)Tl$ (off-white needles)	101-102				[126]
$C_5H_4(CH_2CO_2Et)Tl$				not obtained pure, but in mixture with $C_5H_4(CH_2CO_2Me)Tl$, anal. by ^1H NMR	[120]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5H_4(CH_2CH_2CO_2Me)Tl$				not obtained pure, but in mixture with $C_5H_4(CH_2CH_2CO_2Et)Tl$ or C_5H_5Tl, anal. by ^1H NMR	[120]
$C_5H_4(CH_2CH_2O_2CMe)Tl$ (yellow brown solid)				anal. by ^1H NMR	[120]
C_5F_5Tl	dec. at -30		no further details provided		[137]
$C_5H_4(CH_2Ph)Tl$ (shiny, grey-white)		rel. air-stable		anal. by ^1H NMR, darkens on exposure to light	[24]
$C_5H_4(C_6H_4\text{-}3\text{-}F)Tl$ (cream-colored, almost white)	123-125 dec	air-stable	sol. in THF; moderately sol. in MeOH, acetone, pyridine; poorly sol. in CCl_4	darkens slowly on storage	[138]
$C_5H_4(C_6H_4\text{-}4\text{-}F)Tl$ (light-yellow needles)	157-160 dec.	air-stable	recryst. from DMSO, less sol. than 3-isomer	darkens slowly on storage	[138]
$C_5H_4\{C(O)CO_2Et\}Tl$ (yellow solid)	70-72 subl. 100 (10^{-3} Torr)			anal. by IR, MS (±FAB)	[128]
$C_5H_4(CH_2CH_2CO_2Et)Tl$				not obtained pure, but in mixture with $C_5H_4(CH_2CH_2CO_2Me)Tl$, anal. by ^1H NMR	[120]
$C_5H_4\{C(CN)=C(CN)_2\}Tl$ (dark red)	175 dec.		sol. in MeCN, DMF	molar conductivity $6.5\ 10^{-2}$ cm^2 Ω^{-1} mol^{-1}, anal. by IR, ^1H NMR, UV/Vis, X-ray	[32,140]
$C_5H_4\{C^*H(Me)Ph\}Tl$ (brown)		not air-stable, rapid dec.		anal. by ^1H, ^{13}C NMR ident. by ^1H, ^{13}C NMR and by conversion into ferrocene derivative	[19] [138]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5H_4(SPh)Tl$ (white powder)	121 dec.		NMR in DMSO	anal. by ^1H, ^{13}C NMR, IR	[53]
$C_5H_3(-1,3-{}^tBu_2)Tl$ (lustrous cream plates)	subl. 80 (0.08 Torr)		readily sol. in THF		[127]
$C_5H_2[-1,5-\{C(O)Me\}_2-3-NO_2]Tl$ (yellow crystals)	165 dec.		NMR in DMSO	anal. by ^1H NMR, IR	[54]
$C_5H_4(SC_6H_4-4-Me)Tl$ (white powder)	128 dec.		NMR in DMSO	anal by ^1H NMR, IR	[53]
$[C_5H_4\{S(Me)Ph\}Tl]^+BF_4^-$ (colorless to light pink needles)	140.5		NMR in MeCN	anal. by ^1H, ^{13}C NMR, IR	[53]
C_5H_4ITl (light yellow powder)	98 dec. (N_2) subl. 62 (10^{-2} Torr)	not air-stable	slightly sol. only in THF and DMSO	anal. by ^1H NMR, IR, MS	[20]
$C_5Me_4(CH_2CH_2NMe_2)Tl$ (yellow needles)		not air-stable	very good sol. in organic solvents	anal. by ^1H, ^{13}C NMR, MS	[136]
$\underline{200 < Cp < 300}$ g mol^{-1}					
$[C_5H_4\{S(Me)C_6H_4-4-Me\}Tl]^+BF_4^-$ (colorless to light pink crystals)	138		NMR in MeCN	anal. by ^1H, ^{13}C NMR, IR	[53]
$C_5H_3\{-1,3-(SiMe_3)_2\}Tl$	>120 dec. subl. 30 (10^{-1} Torr)		sparingly sol. in cold C_6H_6, good sol. in hot C_6H_6, toluene	anal. by ^1H, ^{13}C NMR, MS, X-ray	[7]
$C_5H_3(-1,3-Ph_2)Tl$ (bright-yellow)	245 dec.	air-stable	slightly sol. in THF and DMSO	anal. by ^1H, ^{13}C NMR, MS, X-ray	[141]
$C_5H_4\{C({}^iPr)=N-C_6H_4-4-Me\}Tl$ (yellow microcrystals)	192-193 dec. subl. 80		low solubility	anal. by IR, MS	[142]
C_5Cl_5Tl (white)	dec. at -15, spontaneous ignition	not air-stable	sol. in Et_2O, MeOH and chlorinated solvents	anal. by IR	[150,151]
$C_5Cl_5Tl(toluene)_2$	dec above -15, slightly more stable than the unsolvated form			anal. by IR, ^{35}Cl nuclear quadrupole resonance	[150]

Table 6 (continued)

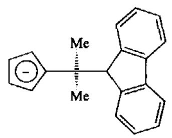
Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5H_4(PPh_2)Tl$ (yellowish)		air-and moisture sensitive		anal. by ^1H, ^{31}P NMR, IR, X-ray	[144]
(white)	subl. 120 (10^{-3} Torr) with dec	moderately air-stable		anal. by ^1H NMR	[145]
(crystalline)				anal. by ^1H, ^{31}P NMR	[146]
$C_5Me_4\{Si(Me_2)Ph\}Tl$ (light yellow)	90	not air-stable	sol. in C_6H_6, hexane, THF	anal. by ^1H, ^{13}C NMR, MS, X-ray	[147]
$C_5H_4\{SC_6H_3\text{-}2,4\text{-}(NO_2)_2\}Tl$ (dark-brown, microcrystalline)	>250		NMR in DMSO	anal. by ^1H, ^{13}C NMR, IR	[53]
$C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ (light yellow)	145 dec.	not air-stable	sol. in C_6H_6, hexane, THF	anal. by ^1H, ^{13}C NMR, MS, X-ray	[147]
$C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ (2 modifications)					
modif. 1: zig-zag chain structure	123 dec.		very good sol. in C_6H_6 and other aromatics, little in CH_2Cl_2, not in hexane	anal. by MS, cryoscopy, X-ray	[6]
modif. 2: 2-D coord. polymer 	97 (2nd heating 105-107)		very good sol. in aromatics, not in hexane	anal. by X-ray both modif. agree in ^1H, ^{13}C NMR	[6]
$C_5H_4\{C(CF_3)_2CH(CN)_2\}Tl$ (pale orange)		extremely air-sensitive		no anal. given	[32]
$C_5H_2\{1,2,4\text{-}(SiMe_3)_3\}Tl$ (colorless microcrystalline solid)	subl. 100-120 (10^{-2} Torr)	air-stable	fairly sol. in aromatic solvents	anal. by ^1H, ^{13}C NMR, MS	[148]
$C_5H_4(AsPh_2)Tl$ (light yellow)		not air-stable, rapid dec.	sol. in THF	anal. by ^1H, ^{13}C NMR	[154]
$300 < Cp < 400$ g mol^{-1}					
$C_5H_3[\text{-}1,2\text{-}\{C(O)C_6H_4\text{-}4\text{-}Me\}_2]Tl$ (yellow crystals)	205 dec.		NMR in DMSO	anal. by ^1H NMR, IR	[54]
$C_5Me_4(PPh_2)Tl$ (yellow crystals)	90 dec. (argon)	air-stable	sol. in toluene, C_6H_6, THF, Et_2O	anal. by ^1H,^{13}C,^{31}P NMR,MS,X-ray	[13]

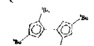
Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5(CO_2Me)_5Tl$ (white)	197-198	air-stable	sol. in water, alcohols	anal. by ^1H NMR,IR,UV/Vis,X-ray conductivity measured	[160]
C_5HPh_4Tl (orange-yellow microcrystalline powder)	260-262 dec. subl. 220 (10^{-5} Torr)	not air-stable, visible dec. after 10 min	no solvent found for dissolution	anal. by IR, MS	[122]
400 < Cp < 500 g mol^{-1}					
$Cr(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$ (greenish-yellow crystals)	178-180 dec.		insol. in hexane, sol. in C_6H_6, toluene Et_2O, THF, $CHCl_3$, CH_2Cl_2 with slow dec. in $CHCl_3$ and CH_2Cl_2 NMR in C_6D_6	anal. by ^1H, ^{31}P NMR, IR	[149]
C_5Ph_5Tl (yellow microcrystalline powder	>330 (undetermined) subl. 250 (10^{-5} Torr)	air-stable	no solvent found for dissolution	anal. by IR, MS	[122]
$Mo(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$ (white crystalline solid)	130 dec.		insol. in sat. hydrocarbons; sol. in C_6H_6, toluene, Et_2O, THF; sol. with slow dec. in $CHCl_3$ and CH_2Cl_2	anal. by ^1H, ^{31}P NMR, IR	[149]
500 < Cp < 1100 g mol^{-1}					
$C_5Ph_4(C_6H_4\text{-}4\text{-}^tBu)Tl$ (yellow powder)	>330 (undetermined) subl. 250 (10^{-5} Torr)	moderately air-stable, visible dec. after a week	no solvent found for dissolution	anal. by IR, MS	[122]
$C_5(CH_2Ph)_5Tl$ (2 modifications)					
modif. 1: yellow needles, linear chain-type structure	133-136	air-stable	good sol. in C_6H_6, toluene, THF; slightly sol. in hexane	anal. by IR, X-ray	[122,213]
modif. 2: yellow parallelepipeds, dimers	137-140	air-stable	good sol. in C_6H_6, toluene, THF; slightly sol. in hexane	anal. by IR, X-ray both modif. agree in ^1H,^{13}C NMR,MS	[8,122]
$C_5(C_6H_4\text{-}4\text{-}Et)_5Tl$ (yellow)	209 dec.	only briefly air-stable	low solubility, NMR in DMSO	anal. by ^1H, ^{13}C NMR, MS in solution light-sensitive	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O)Me\}_5Tl$ (yellow)	300 dec.	air-stable in the solid, not in solution	good sol. in polar solvents, THF, DMSO, pyridine; insol. in hexane	anal. by ^1H, ^{13}C NMR	[153]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$C_5(C_6H_4\text{-}4\text{-}^nBu)_5Tl$ (yellow)	189 dec.	only briefly air-stable	low solubility, NMR in THF	anal. by ^1H, ^{13}C NMR, MS in solution light-sensitive	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O)^nPr\}_5Tl$ (yellow)	250	air-stable in the solid, not in solution	good sol. in polar solvents, THF DMSO, pyridine; insol. in hexane	anal. by ^1H, ^{13}C NMR, MS	[153]
$C_5(C_6H_4\text{-}4\text{-}CO_2Et)_5Tl$ (yellow)	235	air-stable in the solid; not in solution	good sol. in polar solvents, THF DMSO, pyridine; insol. in hexane	anal. by ^1H, ^{13}C NMR, MS	[153]
$C_5(C_6H_4\text{-}4\text{-}nC_6H_{13})_5Tl$ (yellow)	172 dec.	only briefly air-stable	low solubility, NMR in THF	anal. by ^1H, ^{13}C NMR, MS in solution light-sensitive	[152]
$C_5\{C_6H_4\text{-}4\text{-}C(O)nC_5H_{11}\}_5Tl$ (yellow)	230	air-stable in the solid, not in solution	good in polar solvents, THF DMSO, pyridine, Et_2O, C_6H_6, toluene; insol. in hexane	anal. by ^1H, ^{13}C NMR, MS	[153]
$C_5(C_6H_4\text{-}4\text{-}nC_8H_{17})_5Tl$ (yellow)	171 dec.	only briefly air-stable	low solubility, NMR in THF	anal. by ^1H, ^{13}C NMR, MS in solution light-sensitive	[152]
$C_5(C_6H_4\text{-}4\text{-}CO_2\text{-}nC_5H_{11})_5Tl$ (yellow)	180	air-stable in the solid, not in solution	good in polar solvents, THF DMSO, pyridine; insol. in hexane	anal. by ^1H, ^{13}C NMR, MS	[153]
$C_5(C_6H_4\text{-}4\text{-}C(O)nC_7H_{15})_5Tl$ (yellow)	160	air-stable in the solid, not in solution	good in polar solvents THF DMSO, pyridine, Et_2O, C_6H_6, toluene; insol. in hexane	anal. by ^1H, ^{13}C NMR, MS	[153]
b) dinuclear complexes					
Tl $C_5H_4\text{-}C_5H_4$ Tl (chocolate brown) (fulvalene-dithallium)	therm. stable at room temp.	not air-stable	low solubility in organic solvents	storable at -20 °C for long periods without dec.	[27,29]
Tl $C_5H_4\text{-}CH_2\text{-}C_5H_4Tl$		longer exposure to air darkens compd.	not sol., reported insoluble in DMSO		[30]
$PhP(C_5H_4Tl)_2$					[155a]

Table 6 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	Air-, water stability	Solubility	Further remarks	Ref.
$Tl(-1,3\text{-}^{t}Bu_2)H_2C_5\text{-}C_5H_2(-1',3'\text{-}^{t}Bu_2)Tl$ (colorless to yellow-orange rhombuses) 	102	not air-stable	sol. in C_6H_6, toluene, pentane	anal. by ^1H, ^{13}C NMR, MS, X-ray *solutions photolabile*	[5]
trans-$Cr(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$ (greenish-yellow solid)	180 dec.		insoluble	anal. by IR	[149]
cis-$Mo(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$ (greenish-yellow solid)	130 dec.		insoluble	anal. by IR	[149]
cis-$PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$ (yellow)			sol. in DMSO	anal. by ^1H, ^{13}C ^{31}P NMR	[155]
c) cyclopentadienylthallium(I) anions					
$[Li(pmdeta)(\mu\text{-}C_5H_5)Tl(C_5H_5)]$ (colorless)	< 0	not air-stable	sol. in THF	anal. by X-ray	[157]
$[C_5H_5Mg(pmdeta)]^+[Tl(C_5H_5)_2]^-$ (light pink crystals)	120 dec.	not air-stable	sol. in THF	anal. by ^1H, ^{13}C NMR, X-ray	[157]
$[Li([12]\text{-crown-}4)_2]^+[(C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(C_5H_5)]^-$ (pink blocks)	gradual dec. up to 180		sol. in THF	anal. by IR, X-ray	[159]
$Au_2[(P\text{-}Ph_2PC_5H_4)_2Tl]_2$			sol. in CH_2Cl_2, $CHCl_3$; somewhat sol. in aromatic hydrocarbons	anal. by ^1H, ^{13}C, ^{31}P NMR, X-ray	[156]

For the ionic thallium dicarbollide or carborane thallate complexes see Table 7.

4.2.3. *Compounds with thallium(I)–arene interactions*

The thallium(I)–arene complexes where the arene is a free molecule and not part of ligand system, namely $(C_6H_6)[TlAlCl_4]_2$ and $(C_6H_6)_2[TlAlCl_4]$ [161], $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_6Tl_4(GaBr_4)_4]$ (colorless) [99,164], $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ (colorless) [165], $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ (both colorless) [166], and $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ (colorless) [167,168] are reported to be subject to hydrolysis, to be air-sensitive and vacuum labile. The reported difficulty to obtain more arene complexes from solutions of thallium(I) salts like $Tl[AlCl_4]$, $Tl[AlBr_4]$, $Tl[GaCl_4]$ and $Tl[GaBr_4]$ in benzene, mesitylene or hexamethylbenzene is evidence of this lability [99]. In $C_5Cl_5Tl(C_6H_5Me)_2$, the instability (handable at −15 °C for 30 min, decomposition within minutes at +25 °C), albeit noted less than for the solvate-free compound, stems from the pentachlorocyclopentadienide anion [150]. In contrast, the mesitylene ligands in $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ are noted to be difficult to remove: after 6 weeks of vacuum-drying at 10^{-5} torr at room temperature, not all of the mesitylene had been removed [168]. In addition, the [2.2]paracyclophane complex of $Tl[GaCl_4]$ $[(p\text{-}C_6H_4CH_2CH_2)_2Tl][GaCl_4]$ (colorless) is noted to be only slightly air- and moisture-sensitive, a short handling in air was possible and the compound melted at 251 °C without decomposition. Thus, this and the analogous [2.2]paracyclophane complexes of $In[InBr_4]$ and $Ga[GaBr_4]$ are among the most stable main-group metal–arene complexes [169]. No statement has been made on the solvent lability of $Tl^+(C_6H_5Me)_{2/3}[\textit{commo}\text{-}3,3'\text{-}Al(3,1,2\text{-}AlC_2B_9H_{11})_2]$ (white solid, colorless crystals) [162,163]. A DTA investigation coupled with X-ray powder diffractometry showed that the complexes $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$, $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ give off, simultaneously, all arene molecules at 61, 58.8, and 50.8 °C, respectively, to give phase-pure $Tl[AlCl_4]$ or $Tl[GaCl_4]$ [165,166]. In the case of the mesitylene complex, this loss was reported to be reversible since below 61 °C, the arene is absorbed again with reformation of the complex [165]. The temperature determined for the arene loss is a measure of the thermal stability of the thallium–arene solvates.

The solubility of the complex $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ in other aromatic solvents such as benzene was reported to be low [165]. For the tetramer $[2,6\text{-}{}^iPr_2C_6H_3(Me_3Si)NTl]_4$ only the monomeric unit is observed under mass spectrometric conditions [173]. Selected IR and Raman spectral data for the complexes $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ and $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ [168], as well as $[(p\text{-}C_6H_4CH_2CH_2)_2Tl][GaCl_4]$ [169] have been reported. In $C_5Cl_5Tl(C_6H_5Me)_2$, the comparison of the IR spectrum with that of the solvate-free compound indicated a weakening of the second C_5-ring stretching absorption for the former, and it was suggested that this may reflect a decrease in interaction of the Tl^+ cation with the anion due to the formation of a bis(toluene)thallium(I) cation [150,151].

4.2.4. *Thallium(I) compounds with ligands related to cyclopentadienyl*

Table 7 compiles the properties of these thallium(I) compounds. The thallium 1-methyl- and 1-phenylborinate complexes are found to be remarkably similar to cyclopentadienylthallium in their properties: all three can be sublimed, show a low solubility in many organic solvents, are air- and water-stable in the solid, withstand an aqueous potassium hydroxide solution but are decomposed by acids. The mass spectra of the borinates give the molecular ion as the highest mass peak, with Tl^+ being the base peak [176].

The icosahedral anions $[3,1,2\text{-}TlC_2RR'B_9H_9]^-$ (R = R′ = H; R = H, R′ = Me, R = R′ = Me) in the form of their Tl^+ salts are stable in air and water and may apparently stored indefinitely without special precautions [178]. The $[PPh_3Me]^+$-salt is, however, reported as air-sensitive [215].

The thallium(I) salts of the hydrotris(pyrazolyl)borate ligands are generally air- and moisture-stable substances. (Even the related indium(I) complexes can be air-stable [274].) Their stability towards hydrolysis is increased with respect to the potassium salts. They show a good solubility even in hydrocarbon solvents. In their mass spectra the molecular ion can be observed.

4.2.5. Thallium(II) compounds

The dark-red compound $\{(Me_3Si)_3Si\}_2Tl\text{–}Tl\{Si(SiMe_3)_3\}_2$ melts at 130 °C. While the solid material shows no visible decomposition on handling and is even air-stable for some time, the solutions (under anaerobic conditions) show rapid degradation, which starts after a few minutes at +20 °C and after a few hours at −60 °C and manifests itself in a lightening of the color, formation of $(Me_3Si)_3Si\text{–}Si(SiMe_3)_3$ and precipitation of thallium metal. The decomposition does not appear to involve long-lived radicals, since an n-pentane solution even after short-wave UV irradiation does not give an ESR signal. The tetra(hypersilyl)dithallium compound is well soluble in aliphatic and aromatic hydrocarbon solvents, but only slightly so in polar solvents like diethyl ether or acetonitrile [108].

The black–green compound $(^tBu_3Si)_2Tl\text{–}Tl(Si^tBu_3)_2$ decomposes at 52 °C in the solid. Rapid decomposition is observed in d_8-toluene already at 40 °C with the formation of (*inter alia*) $^tBu_3SiD$, $(^tBu_3Si)_2$, and elemental thallium. The solubility of tetrasupersilyldithallum(*Tl–Tl*) is very good in nonpolar solvents like benzene and alkanes, but only moderate in polar solvents such as THF and acetone. In C_6D_6, the compound exhibits a band-rich EPR signal at room temperature and it is suggested that this is due to the intermediate formation of $(^tBu_3Si)_2Tl^{\cdot}$ radicals, which would also explain the unusual black–green color. Comparable indium and thallium dimers with bulky alkyl, aryl or silyl ligands are orange to dark-red in color [109].

The molecular properties of organothallium(I–III) compounds, including the Me_2Tl molecule have been calculated with spin-orbit averaged pseudopotential calculations. A Tl–Me dissociation energy of 55 kJ mol^{-1} was obtained. From the dissociation energy, Me_2Tl is stable with respect to dissociation in Tl and Me, but further calculations show it to be unstable with respect to the exothermic disproportionation into either Me_3Tl and MeTl or $2Me_3Tl$ and Tl. Me_2Tl would also be unstable with respect to the formation of Tl and C_2H_6 [96].

Table 7. Properties of Thallium(I) Compounds With Ligands Related to Cyclopentadienyl (ordering within each section with increasing molar mass of the ligand)

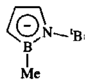
Formula (color, appearance)	m.p., thermal stability [°C]	air-, water stability	solubility	further remarks	Ref.
$C_3H_3B(Me)N(^tBu)Tl$ 	dec < -50	extremely air-sensitive		not isolated	[22]
$(C_5H_5)Co(\mu\text{-}C_2B_2C)Tl$ (orange-brown) C_2B_2C = 1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl	145 subl. 80-90 (10^{-2} Torr)	not air-stable	sol. in hydrocarbons	anal. by ^1H, ^{11}B NMR, X-ray	[143]
$(C_5H_5BMe)Tl$ (light yellow)	149-150 subl. 60 (10^{-3} Torr)	air-stable in the solid, slow decolorization; water and base stable; solution air-sensitive	good sol. in pyridine, DMSO; slightly sol. in MeCN	anal. by ^1H, ^{13}C, ^{11}B NMR, MS, UV	[176]
$(C_5H_5BPh)Tl$ (light yellow)	193-194 subl. 80-100 (10^{-3} Torr) with dec.	solid air-and water (base) stable, solution air-sensitive	good sol. in pyridine, DMSO; slightly sol. in MeCN	anal. by ^1H, ^{13}C, ^{11}B NMR, MS UV	[176]
$Tl^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$ (pale yellow)		air-stable			[178]
$[Ph_3MeP]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-(THF)_{0.5}$		not air-stable		anal. by X-ray	[215]
$[PPN]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$			very sol. in coord. solvents, like THF, MeCN	anal. by ^{11}B NMR, X-ray	[203]
$Tl^+[3,1,2\text{-}TlC_2MeB_9H_{10}]^-$ (yellow)		air-stable			[178]
$Tl^+[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$ (yellow needles)	> 200 dec.	solid air-stable, THF sol. extremely moisture sensitive	insol. in most solvents, low sol. in THF	anal. by ^1H, ^{11}B NMR, X-ray	[177,178]
$[(C_5H_4CHPh_2)Cr(CO)_3]Tl$ (orange)		not air-stable, solutions extremely air-sensitive	sol. in C_6H_6, acetone, ethyl acetate	anal. by ^1H NMR, IR	[179]

Table 7 (continued)

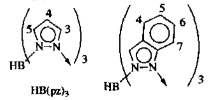
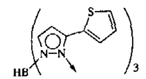
Formula (color, appearance)	m.p., thermal stability [°C]	solubility	further remarks	Ref.
Hydro-tris(pyrazolyl)- and -(indazolyl)borate ligands (pz = pyrazolyl)				
(The hydro-tris(pyrazolyl)borate thallium complexes can generally be regarded as air- and water stable.)				
LTl 				
(For additional schematic drawings of the ligands, see Table 4; for structural drawings, see Figure 18)				
$HB(pz)_3Tl$	156 sublimes	recryst. from toluene	anal. by ^1H NMR, IR, MS, photoelectron spectroscopy study anal. by ^{13}C NMR, X-ray	[186a] [216a]
$HB(3\text{-}^tBu\text{-}pz)_3Tl$ (white solid)	191 (DSC)	sol. in C_6H_6 and toluene	anal. by ^1H,^{13}C NMR, IR, X-ray, parent peak in MS	[15,183,191]
$HB(3\text{-}^tBuCH_2)_3Tl$ (white solid) ($^tBuCH_2$ = neopentyl)	117-118	very sol. in aliphatic hydrocarbons, recryst. from MeOH	anal. by ^1H, ^{13}C NMR, IR	[40]
$HB(3\text{-}^tBuCH_2)_2(5\text{-}^tBuCH_2)Tl$			anal. by ^1H NMR, IR	[40]
$HB(3\text{-}^tBu\text{-}5\text{-}Me\text{-}pz)_3Tl$	184	sol. in CH_2Cl_2, recryst. from toluene/ heptane	anal. by ^1H, ^{13}C NMR, IR	[17,191]
$HB(3\text{-}Ph\text{-}pz)_3Tl$ (white solid)	185-187		anal. by ^1H, ^{13}C NMR, IR	[15,191]
$HB\{3\text{-}(2\text{-}pyridyl)\text{-}pz\}_3Tl$ (white solid)	283-285	sol. in $CHCl_3$	anal. by ^1H, ^{13}C NMR, MS, IR, X-ray	[191,218]
$HB(3\text{-}cyclohexyl\text{-}pz)_3Tl$	142-143	sol. in CH_2Cl_2	anal. by ^1H, ^{13}C NMR	[272]
$HB\{3\text{-}(2\text{-}thienyl)\text{-}pz\}_3Tl$ 			anal. by ^1H, ^{13}C NMR	[191]
$HB(1,4\text{-}dihydroindeno[1,2\text{-}c]\text{-}pz)_3Tl$	243-244	sol. in CH_2Cl_2, recryst. from xylene	anal. by ^1H, ^{13}C NMR, IR	[39]
$HB\{3\text{-}(4\text{-}MeC_6H_4)\text{-}pz\}_3Tl$ (colorless prisms)	246-247	sol. in CH_2Cl_2	anal. by ^1H, ^{13}C NMR, IR	[17,191,219]

Table 7 (continued)

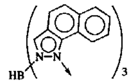
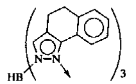
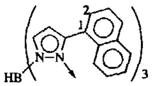
Formula (color, appearance)	m.p., thermal stability [°C]	solubility	further remarks	Ref.
$HB(3\text{-}Ph\text{-}5\text{-}Me\text{-}pz)_3Tl$ (white crystals)	242-243	recryst. from toluene	anal. by ^1H, ^{13}C NMR, IR	[39]
HB(2*H*-benz[g]indazol-2-yl)$_3$Tl 	286-289		anal. by NMR, IR	[273]
HB(2*H*-benz[g]-4,5-dihydroindazol-2-yl)$_3$Tl 	302 dec		anal. by ^1H, ^{13}C NMR, IR	[39]
$HB\{3\text{-}(4\text{-}MeOC_6H_4)\text{-}pz\}_3Tl$	248-250		anal. by ^1H, ^{13}C NMR, IR	[17,191]
$HB(3\text{-}{}^tBu\text{-}5\text{-}{}^iPr\text{-}pz)_3Tl$	119-121	sol. in $CHCl_3$	anal. by ^1H, ^{13}C NMR, IR	[191]
$HB(7\text{-}{}^tBu\text{-}indazolyl)_3Tl$	265-266		anal. by ^1H, ^{13}C NMR, IR, X-ray	[343]
$HB\{3\text{-}(4\text{-}ClC_6H_4)\text{-}pz\}_3Tl$			anal. by ^1H, ^{13}C NMR	[191]
HB{7(*R*)-^{i}Pr-4(*R*)-Me-4,5,6,7-tetrahydro-2-indazolyl}$_3$Tl	178-179	sol. in CH_2Cl_2, recryst. from toluene/ MeOH	anal. by ^1H, ^{13}C NMR, IR, X-ray $[\alpha]_D^{24} = +210\pm2°$	[220]
$HB(3,5\text{-}{}^tBu_2\text{-}pz)_3Tl$		sol. in THF	anal. by ^1H, ^{13}C NMR, IR, X-ray	[220a]
HB(3-Me-2*H*-benz[g]-4,5-dihydroindazol-2-yl)$_3$Tl (white solid)	290 (darkening from 240 °C)		anal. by ^1H, ^{13}C NMR, IR	[39]
$HB(3\text{-}mesityl\text{-}pz)_3Tl$ (white solid) (mesityl = $C_6H_2\text{-}2,4,6\text{-}Me_3$)	303-305	sol. in CH_2Cl_2, low sol. in MeOH, recryst. from toluene	anal. by ^1H, ^{13}C NMR, IR	[192]
$HB(3\text{-}mesityl\text{-}pz)_2(5\text{-}mesityl\text{-}pz)Tl$	222-223	sol. in CH_2Cl_2, low sol. in MeOH, recryst. from octane	anal. by ^1H, ^{13}C NMR, IR	[192]

Table 7 (continued)

Formula (color, appearance)	m.p., thermal stability [°C]	solubility	further remarks	Ref.
HB(3-^{i}Pr-4-Br-pz)$_3$Tl (white solid)	187-189	sol. in CH_2Cl_2, recryst. from toluene/ heptane	anal. by IR	193
HB{7(*S*)-^{t}Bu-4(*R*)-Me-4,5,6,7-tetra-hydro-2-indazolyl}$_3$Tl	193-195	sol. in CH_2Cl_2, C_6H_6, recryst. from toluene/ MeOH	anal. by ^{1}H, ^{13}C NMR, IR, X-ray $[\alpha]_D^{24}$ = -593±9°	220
HB(3-(1-naphthyl)-pz)$_3$Tl	216-218	sol. in $CHCl_3$	anal. by ^{1}H, ^{13}C NMR	191
				
HB(3-(2-naphthyl)-pz)$_3$Tl	142-146	sol. in $CHCl_3$	anal. by ^{1}H, ^{13}C NMR	191
HB{3,5-$(CF_3)_2$-pz}$_3$Tl (white crystals)		sol. $CHCl_3$, MeCN	anal. by ^{1}H, ^{13}C, ^{19}F NMR, IR	190
HB{3-(9-anthryl)-pz}$_3$Tl (white solid)	299-303	sol. in CH_2Cl_2, recryst. from toluene	anal. by ^{1}H NMR, ^{13}C NMR, IR (X-ray)	191,221
HB{3,5-(^{t}BuC$_6$H$_4$)$_2$-pz}$_3$Tl			anal. by ^{1}H, ^{13}C NMR, X-ray	222

4.3. NMR spectroscopy

Thallium-containing compounds are especially interesting to study by nuclear magnetic resonance spectroscopy. Both natural thallium isotopes ^{203}Tl and ^{205}Tl (abundance 29.5 and 70.5%, respectively) have spin 1/2 and can thus easily be studied by NMR spectroscopy, even in the solid state. The ^{205}Tl nucleus is the third most receptive spin-1/2 nuclide with a relative receptivity of 0.1355 with respect to the proton with a value of 1 (receptivity is sensitivity times natural abundance) [267,275]. The resonance frequency of thallium in the +1 oxidation state is normally lower than that of thallium in the +3 oxidation state. Including both oxidation states, the chemical shift range in inorganic and organometallic thallium compounds, in solution and in the solid state, encompasses over 7000 ppm for Tl(III) species and over 3400 ppm for Tl(I) species. In general, aqueous solution studies have been performed with Tl(I) – the interest being ion–solvent interactions, ion-pairing, etc. – and organothallium compounds have been used to study Tl(III). Except for the chemical shift for C_5H_5Tl in the solid state (+418 ppm) [267], we are not aware of another report of a chemical shift for a cyclopentadienylthallium(I) compound, only the thallium coupling to hydrogen or carbon of the organic ligand, if present, is given. The thallium–hydrogen or –carbon coupling can be useful to understand the solution behavior of the complex. Just as the chemical shift range for thallium is quite large, so is the range of the magnitude of the spin–spin coupling constants involving the thallium nucleus [267,275].

4.3.1. Cyclopentadienylthallium(I) compounds

The presence or absence of Tl–H and –C coupling in their NMR spectra is often viewed as an indicator for the covalency or ionicity, respectively, of the thallium–cyclopentadienyl interaction (in solution). From the examples available, it appears unambiguous that the observation of Tl–element coupling is indicative of high covalent bonding character in a monomeric (or oligomeric) species [136,183]. The reverse conclusions cannot simply be drawn, however; a covalent thallium–ring bond deduced from the solid-state structure does not necessarily lead to thallium–hydrogen or –carbon coupling in solution. Hence, from the absence of coupling to thallium it does not necessarily follow that the thallium–ring interaction is predominantly ionic. The suppression of Tl–coupling could also be due to fast intermolecular exchange processes. Furthermore, the polymeric ionic structures in the solid-state may show such coupling in solution (see below). We point to the difference in structure between the solid state and the gas phase for, for example, C_5H_5Tl [198,199,201] and C_5Me_5Tl [135,200], to indicate that the solution structure may be different from the often well-known solid-state structure.

Table 8(a) provides a list of the Tl–H and Tl–C coupling constants for the cyclopentadienyl–metal complexes. Generally, a decrease in coupling constants with increasing distance can be observed in a compound. In this respect, the large coupling constant for the *ortho*- or *meta*-phenyl carbons of $C_5(CH_2Ph)_5Tl$ [122] and $C_5Me_4(SiMe_2Ph)Tl$ [147] is noteworthy. It has been suggested that the large value could be explained with a through-space interaction by assuming a relatively close *ortho-* or *meta*-phenyl carbon π-contact in solution [122,147]. In $C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ all phenyl carbons have a similar coupling constant of about 20 Hz, so that a conformation might exist in solution where all phenyl carbon atoms have about the same distance from the thallium atom [147]. Similarly, in the monomeric tris(pyrazolyl)borate system $HB(3\text{-}^tBu\text{-}pz)_3Tl$, the relatively large couplings to the *tert*-butyl methyl carbons and hydrogens were suggested to imply a through-space interaction (see also Section 4.3.3, below) [183].

For $C_5H_4\{C(Me_2)C_{13}H_9\}Tl$ [6], the ^1H NMR spectrum was found to be temperature dependent. An intramolecular dynamic process (yielding a C_2-symmetric molecule) and eventually metal–ligand dissociation (breakdown of Tl–H coupling) was invoked to explain the change in the NMR spectra with increasing temperature [6].

No Tl–H or Tl–C coupling has been observed in $Tl(\text{-}1,3\text{-}^tBu_2)H_2C_5\text{–}C_5H_2(\text{-}1',3'\text{-}^tBu_2)Tl$ (solvent C_6D_6) [5] and $C_5Me_4(PPh_2)Tl$ (solvent d_8-THF) [13], despite the apparent covalent nature of their thallium–ring bonding in the solid state. Tl–C and Tl–H coupling constants were observed for $C_5H_{5-n}(SiMe_3)_nTl$ for $n=3$ only but not for $n=1$ or 2 [7,148]. On the other hand, C_5Me_5Tl, $C_5Me_4(SiMe_2Ph)Tl$ and $C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ show polymeric chain structures with probably predominantly ionic Tl–C contacts in the range 2.8–3.2 Å, yet in solution, coupling constants to the methyl hydrogen atoms and to all observed carbon atoms are observed, which would imply the existence of monomeric species therein [21,135,147]. Again, it is then noteworthy that the related tetramethylcyclopentadienylthallium, C_5HMe_4Tl, does not show any proton or carbon coupling to thallium [130].

In the literature, it was sometimes suggested that the lack of Tl–C/H coupling suggested a largely ionic nature of the cyclopentadienylthallium(I) derivatives in solution [9,65,127,141,152]. As a different explanation, a rapid *inter*molecular exchange of the cyclopentadienyl groups between molecular complexes may be assumed [141,152]. This was shown to be the case for the phenyl groups of the molecular triphenylthallium(III) compound. Here also no thallium splitting of the proton resonances is observed in CH_2Cl_2, but in trimethylamine solution the *ortho-*, *meta-*, and *para*-proton–thallium coupling constants can be determined. This was interpreted as a slowing down of the otherwise rapid intermolecular exchange of phenyl groups in the coordinating solvent [276]. The ^{13}C NMR spectra of the thallium and potassium compound with the chiral ligand $C_5H_4\{C^*H(Me)Ph\}^-$ gave only one signal in C_6H_6, CH_2Cl_2 and THF for the formally diastereotopic pair of carbons 2/5 or 3/4, which can be explained by a rapid intermolecular exchange or by the dissociation into ions or ion pairs. In the mixed ferrocene $[C_5H_4\{C^*H(Me)Ph\}](C_5H_5)Fe$, on the other hand, separate signals are observed for each diasteromer and ferrocene is known to be a stereochemically rigid, covalent bound molecule [138].

In $C_5H_4(SiMe_3)Tl$, a rapid migration of the silyl group around the ring has been observed at low field but not at high field [7,9]. For $C_5H_4(PPh_2)Tl$ "two singlets" (at 24.89 and −21.06 ppm) were reported in the ^{31}P NMR spectrum in Ref. [144] (in THF at room temperature, proton decoupled, probably measured at 108 MHz). The two signals were interpreted as being due either to a phosphorus atom coordinating to thallium or to a phosphorus atom not coordinated to the metal. Unfortunately,

Table 8

Tl–H and Tl–C coupling constants: (a) in cyclopentadienylthallium(I) compounds; and (b) in hydrotris(pyrazolyl)borate thallium(I) complexes (ordering of the compounds within each section with increasing molar mass of the ligand; the coupling constants are listed with decreasing value)

Formula, remarks	Solvent (Hz)	J(Tl–H) (Hz)	J(Tl–C)	Reference
Cyclopentadienylthallium compounds				
C_5H_4MeTl	DMSO	2.0 $^3J(Tl–CH_3)$		[9]
$C_5H_4{}^tBuTl$	DMSO	2.5 $^4J(Tl–CH_3)$		[9]
C_5Me_5Tl	C_6D_6	18 $^3J(Tl–CH_3)$	102.2 $^1J(Tl–C_5)$ 79.4 $^2J(Tl–CH_3)$	[21,135]
$C_5Me_4(CH_2CH_2NMe_2)Tl$	C_6D_6	9.9/3.9 $^3J(Tl–C_5C\mathit{H}_3)$	78 $^2J(Tl–C_5\mathit{C}H_3)$ 37 $^5J(Tl–NCH_3)$ 34.1 $^2J(Tl–C_5\mathit{C}H_2)$ 7.4 $^3J(Tl–CH_2N)$	[136]
$C_5Me_4(SiMe_2Ph)Tl$	C_6D_6	16.8/14.9 $^3J(Tl–C_5CH_3)$ 4 $^4J(Tl–SiCH_3)$	100.3/67.3 $^1J(Tl–\mathit{C}_5Me)$ 73.8/68.7 $^2J(Tl–C_5\mathit{C}H_3)$ 31.7/31.7 $^{4/5}J(Tl–\mathit{o}/\mathit{m}\text{-}Ph\text{-}C)$ 25.2 $^3J(Tl–SiCH_3)$ 13.1 $^6J(Tl–\mathit{p}\text{-}Ph\text{-}C)$ 1.6 ^3J(Tl–quart. Ph-C)	[147]
$C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$	C_6D_6	15.4/14.9 $^3J(Tl–C_5CH_3)$ 1.6 $^4J(Tl–SiCH_3)$	99.15/54.6 $^1J(Tl–\mathit{C}_5Me)$ 73.9/67.2 $^2J(Tl–C_5\mathit{C}H_3)$ 22.7/20.9 $^{4/5}J(Tl–\mathit{o}/\mathit{m}\text{-}Ph\text{-}C)$ 19.9 ^3J(Tl–quart. Ph-C) 18.3 ^6J(Tl–p-Ph-C) 14.2 $^3J(Tl–SiCH_3)$ 8.1 $^3J(Tl–SiCH_2)$	[147]
$C_5H_4\{C(Me_2)C_{13}H_9\}Tl$	d_8-toluene	198 K: broad signals 298 K: $Tl–C_5\mathit{H}_4$ 28, 21		[6]
	C_6D_6		300 K: part of the Cp- and arene-C broadened	
$C_5H_2\{\text{-}1,2,4\text{-}(SiMe_3)_3\}Tl$	C_6D_6	75.5 $^2J(Tl–C_5H_2)$	20 $^3J(Tl–CH_3)$ 2.8, 3.0 $^4J(Tl–CH_3)$	[148]

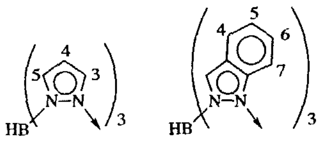
Formula, remarks	Solvent (Hz)	J(Tl–H) (Hz)	J(Tl–C)	Reference
$C_5(CH_2Ph)_5Tl$	C_6D_6/C_4D_8O	10.7/9.6 $^3J(Tl–CH_2)$	88.9/83.4 $^1J(Tl–C_5)$ 43.7/43.2 $^2J(Tl–CH_2)$ 43.5/42.4 $^{4/5}J$(Tl–*o*/*m*-Ph-C) 9.4/8.1 ^3J(Tl–quart. Ph–C) 5.8/5.8 $^{4/5}J$(Tl–*o*/*m*–Ph–C) 3.3/2.7 ^6J(Tl–p–Ph–C)	[122]
Hydrotris(pyrazolyl)- and -(indazolyl)borate thallium complexes (pz = pyrazolyl)  (For additional schematic drawings of the ligands, see Tables 4 and 7; for structural drawings, see Fig. 18)				
HB(3-^{t}Bu-pz)$_3$Tl	C_6D_6	15.9 ^4J(Tl–pz-4-H) 13.2 $^5J(Tl–CH_3)$		[183]
	$CDCl_3$	15.7 ^4J(Tl–pz-4-H) 10.4 $^5J(Tl–CH_3)$		[191]
	$CDCl_3$ (298 K)		170.6 $^4J(Tl–CH_3)$ (175.0) 50.9 ^2J(Tl–pz-3-C) (65.5) 13.5 ^3J(Tl–pz-4-C) (38.6)	[183] [191]
HB(7-Me-indazolyl)$_3$Tl			416 $^4J(Tl–CH_3)$	[343]
HB(3-^{t}BuCH$_2$-pz)$_3$Tl			61.4 $^3J(Tl–CH_2)$ 60.7 ^2J(Tl–pz-3-C) 57.0 ^5J(Tl–^{t}Bu–CH$_3$) 29.3 ^3J(Tl–pz-4-C) 14.5 $^{(3)4}J$(Tl–pz-5-C)	[40] [191]
HB(3-^{t}Bu-5-Me-pz)$_3$Tl		12.6 ^4J(Tl–pz-4-H) [220a] 10.1 ^5J(Tl–3-^{t}Bu) [220a]	197 ^4J(Tl–^{t}Bu–CH$_3$) 59.4 ^2J(Tl–pz-3-C) 35.9 ^3J(Tl–pz-4-C)	[17,277] [191]

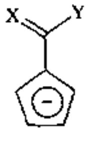
Table 8 (*continued*)

Formula, remarks	Solvent (Hz)	J(Tl–H) (Hz)	J(Tl–C)	Reference
HB(3-cyclohexyl-pz)$_3$Tl			51.4 ^{4}J(Tl–cyclohexyl-C2/6) 47.0 ^{2}J(Tl–pz-3-C) 27.0 ^{3}J(Tl–cyclohexyl-C1)	[191]
HB(3-^{t}Bu-5-^{i}Pr-pz)$_3$Tl	$CDCl_3$		167 ^{4}J(Tl–^{t}Bu-CH_3)	[191]
HB{3-(4-ClC_6H_4)-pz}$_3$Tl	$CDCl_3$ (290 K)		124.7 ^{4}J(Tl–C_6H_4-C2/6) 48.8 ^{2}J(Tl–pz-3-C) 24.4 ^{3}J(Tl–pz-4-C)	[191]
HB{7(*R*)-^{i}Pr-4(*R*)-Me-4,5,6,7-tetra-hydro-2-indazolyl}$_3$Tl	CD_2Cl_2		148.6 ^{4}J(Tl–isopropyl-CH) 119.9 ^{5}J(Tl–isopropyl-CH_3)	[220] [220]
HB(3,5-^{t}Bu$_2$-pz)$_3$Tl	C_6D_6	10.7 ^{4}J(Tl–pz-4-H) 9.4 ^{5}J(Tl–3-^{t}Bu)	163 ^{4}J(Tl–3–^{t}Bu-CH_3) 24 ^{2}J(Tl–pz-3-C) 20 ^{3}J(Tl–pz-4-C)	[220a]
HB(3-Me-2*H*-benz[g]-4,5-dihydro-indazol-2-yl)$_3$Tl			317.3 ^{4}J(Tl–benz-2-C)	[39]
HB(3-mesityl-pz)$_3$Tl (mesityl = C_6H_3-2,4,6-Me_3)			62.0 ^{5}J(Tl–mesityl-CH_3-2/6) 25.2 ^{3}J(Tl–pz-4-C) ~20 ^{2}J(Tl–pz-3-C)	[192] [191]
HB{7(*S*)-^{t}Bu-4(*R*)-Me-4,5,6,7-tetra-hydro-2-indazolyl}$_3$Tl	C_6D_6		80 ^{5}J(Tl–*tert*-butyl-CH_3)	[220]
HB{3-(1-naphthyl)-pz}$_3$Tl	$CDCl_3$	14 ^{6}J(Tl–naphthyl-H8) 7.5 ^{4}J(Tl–pz-4-H)	43.6 ^{2}J(Tl–pz-3-C) 23.6 ^{3}J(Tl–pz-4-C) <10 ${}^{(3)4}$J(Tl–pz-5-C)	[191]
HB{3-(9-anthryl)-pz}$_3$Tl			33.3 ^{2}J(Tl–pz-3-C) 28.4 ^{3}J(Tl–pz-4-C) 11.3 ${}^{(3)4}$J(Tl–pz-5-C)	[191]

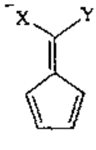
the spectrum was not displayed and the relative intensity of both signals was not stated. Since in Ref. [154] the ^{31}P NMR spectrum (d_8-THF, proton decoupled, 32.9 MHz) was given as a singlet (at −16.2 MHz), we feel that the above interpretation should be reconsidered carefully by, for example, measuring the NMR spectra at different concentrations, which should then lead to varying intensities of the two signals, if the above conclusion is valid. Tl–P coupling can probably ruled out as the origin of the two signals, as no Tl–C coupling but only P–C coupling is reported for the ^{13}C NMR spectrum (relatively small coupling constants) [154]. For the related compound $C_5Me_4(PPh_2)Tl$, the phosphorus NMR spectrum was reported with a single peak at −21.4 ppm [13].

A slight solvent dependency of the T–H and Tl–C coupling constants was observed for $C_5(CH_2Ph)_5Tl$ [122]. A strong solvent dependency of the ^{1}H-NMR chemical shifts was pointed out for C_5H_4RTl (with R = H, Me, ^{t}Bu, SiMe$_3$) and was interpreted as an indication for a predominant ionic bonding interaction [9].

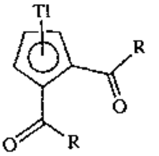
^{1}H and ^{13}C NMR spectroscopy was used in the case of the functionally substituted complexes $C_5H_4(CHO)Tl$, $C_5H_4\{C(O)Me\}Tl$, and $C_5H_4(CO_2Me)Tl$ to show that the negative charge is predominantly localized on the C_5 moiety (form **12**, see Section 3.1.1 above) unlike in $C_5H_4\{C(CN)=C(CN)_2\}Tl$ where the charge is found on the strongly withdrawing tricyanovinyl group (form **13**, see Section 3.1.1 above) [19]. Generally, in the case of functionally substituted cyclopentadienyl ligands where the substituent contains a π system in conjugation to the five-membered ring,



16



17



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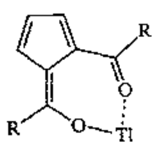


19

two conformations (**16** and **17**) may be adopted. Both forms are distinguished from the appearance of the ^{1}H or ^{13}C NMR spectra and the results for the complexes $C_5H_4(CHO)Tl$, $C_5H_4\{C(O)Me\}Tl$, and $C_5H_4\{CO_2Me\}Tl$ suggest that the soft Lewis-acid character of thallium(I) stabilizes form **16**. An A_2X_2 pattern is observed in ^{1}H NMR and the ^{13}C NMR spectrum shows a single peak for each of the atom pairs C2/5 and C3/4. Only in the case of the strongly withdrawing tricyanovinyl group in the complex $C_5H_4\{C(CN)=C(CN)_2\}Tl$ [19] or the nitro group in $C_5H_4(NO_2)Tl$ [128] was a preference for form **17** apparent. For the former, the chemical and magnetic inequivalence of the ring hydrogens and carbons gives an approximate ABCD situation in ^{1}H NMR and one peak for each of the ring carbon nuclei. In $C_5H_4(NO_2)Tl$, the ring substituent is highly symmetric and at ambient temperature (298 K) in the ^{1}H NMR spectrum, the pattern resembles the AA′XX′ case with two ten-line multiplets. Due to the chemical equivalence within each set of ring nuclei in $C_5H_4(NO_2)Tl$, ^{13}C NMR gives only one signal each for C2/5 and

C3/4 [19,128]. On warming a d_6-DMSO solution of $C_5H_4(NO_2)Tl$ to 369 K, the appearance of each multiplet in ^{1}H NMR is considerably simplified, however, and the carbon signals are split into asymmetric doublets. This is interpreted as evidence that near-equal amounts of conformers **16** and **17** are present in solution at 369 K and that conformer **17** dominates at 298 K [128].

For the two possible structures of the thallium salts of the 1,5-diacyl-1,3-cyclopentadienes, form **18** was suggested, based on the NMR spectra. For R = H, the formyl protons showed a typical value for aldehydes, whereas for the chelate structure **19** a chemical shift below 9 ppm would have to be expected. In addition, a high field shift of the other hydrogen, as well as carbon atoms with respect to the thallium-free ligand, indicate an increase in shielding due to a negative charge in the five-membered ring [54].

Sometimes it was stated that all or part of the carbon signals of the cyclopentadienyl ring could not be clearly observed. For all C_5 signals this was the case in $C_5H_2\{\text{-}1,2,4\text{-}(SiMe_3)_3\}Tl$ [148]. In $C_5H_4(PPh_2)Tl$ and $C_5Me_4(PPh_2)Tl$, the resonance of the C_5-ring carbon bonded to phosphorus [13,154] could not be found; the same was true for $C_5Me_4(SiMe_2Ph)Tl$ and $C_5Me_4\{Si(Me_2)CH_2Ph\}Tl$ for the C_5-ring carbon bonded to silicon [147].

The ^{19}F NMR chemical shifts of (*m*- and *p*-fluorophenyl)cyclopentadienylthallium and the estimated constants for the induction and resonance components of the total electron effect of benzene substituents (σ_I and σ_R^0), derived therefrom, were compared with respective values for alkali cyclopentadienides and for metallocenes. From this comparison, the thallium–cyclopentadienyl bond "ionicity" has been estimated to be at least 40–50% [138,139].

Neither of the complexes which are discussed as organothallium(I) anions $Au_2[(P\text{-}Ph_2PC_5H_4)_2Tl]_2$ $\{=[TlAu(C_5H_4PPh_2)_2]_2\}$ [156], $[C_5H_5Mg(pmdeta)]^+[(C_5H_5)_2Tl]^-$ [157], $[Li(pmdeta)(\mu\text{-}C_5H_5)Tl(C_5H_5)]$ [157], and $[Li([12]\text{-crown-}4)_2]^+[(C_5H_5)Tl(\mu\text{-}C_5H_5)Tl(C_5H_5)]^-(THF)$ [159] shows any evidence for thallium–hydrogen or -carbon coupling interactions in the NMR spectra. The absence of coupling in the case of the "bis(cyclopentadienyl)thallate anions" most probably indicates that the "thallium(I) anion" description is limited to the solid-state. The thallium(I) anions do not appear to be maintained in solution as a structural entity. Even in the solid-state, the bonding in the thallium(I) anions appears to be predominantly ionic judging by the Tl–Cp distance criterion.

4.3.2. *Compounds with thallium(I)–arene interactions*

^{1}H and ^{13}C NMR spectra of solutions of the complexes $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ [165], $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ [166] in benzene did not show a shift in the mesitylene resonances with respect to free mesitylene. This is indicative of labile complexes giving a rapid exchange of the arene ligands in solution.

The increased line width in the ^{27}Al NMR spectra of the complexes $\{[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][AlCl_4]\}_2$ (in mesitylene) and $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][AlCl_4]\}_2$ (in pseudocumol) (59 and 85 Hz, respectively) with respect to "free" $AlCl_4^-$ (about 4 Hz) indicated a sizable deviation from T_d symmetry and it was suggested that a close contact of the $AlCl_4^-$ ions with the arene solvated

Tl^+ ions was retained under these experimental conditions, even a dimeric aggregate was considered likely [165,166]. The ^{71}Ga resonance signal in $\{[(C_6H_3\text{-}1,2,4\text{-}Me_3)_2Tl][GaCl_4]\}_2$ could not be observed, presumably due to the large line width of several thousand Hertz [166].

The ^{19}F NMR spectra for solutions of the complexes $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2TlOTeF_5]_2$ and $[(C_6H_3\text{-}1,3,5\text{-}Me_3)_2Tl][B(OTeF_5)_4]$ have been reported [168].

4.3.3. Thallium(I) compounds with ligand related to cyclopentadienyl

No coupling to thallium is reported in the ^1H, ^{13}C or ^{11}B NMR spectra of the thallium borinates, $(C_5H_5BMe)Tl$ and $(C_5H_5BPh)Tl$ [176] or the thallium carboranes $[Ph_3MeP]^+[3,1,2\text{-}TlC_2B_9H_{11}]^-(THF)_{0.5}$ [215,216] and $Tl^+[3,1,2\text{-}TlC_2Me_2B_9H_9]^-$ [177]. For the $[PPN]^+$-salts of $[3,1,2\text{-}TlC_2R_2B_9H_9]$ (R = H, Me), ^{11}B–^{205}Tl coupling was observed in the $^{11}B\{^1H$ decoupled$\}$ NMR spectrum in MeCN solution, with coupling constants of 910, 480 and 100 Hz for $[3,1,2\text{-}TlC_2B_9H_{11}]^-$. The coupling supports the existence of a strong intramolecular interaction between the thallium ion and the dicarbollide ligand in solution [203]. The parent dithallium complex $Tl^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$ was also said to exhibit boron–thallium coupling (see footnote 18 in Ref. [203]).

The obervation of Tl–H and Tl–C coupling in solutions of hydrotris(pyrazolyl)borate thallium complexes is taken as evidence for their covalent character [191]. While broad signals are common for TpTl derivatives, actual coupling constants have been observed only for some of the complexes. Table 8(b) lists these coupling constants. Coupling from thallium to carbon was still more often observed than coupling to hydrogen. A broadening of the 9-H proton resonance in HB(2*H*-benz[g]indazol-2-yl)$_3$Tl was associated with proximity to thallium [273]. The coupling constants are found to be extremely dependent on the basicity of the pyrazolyl group and on the solvent. They could be measured in $CDCl_3$ or benzene, albeit not in DMSO [183,191]. Addition of a small (catalytic) amount of a strong acid, CF_3COOH, leads to the disappearance of the coupling. An increase in the rate of breaking of the thallium–nitrogen bonds is assumed [191]. In addition, temperature is important: in the compound $HB\{3\text{-}(4\text{-}ClC_6H_4)\text{-}pz\}_3Tl$, coupling could only be observed at 290 K and no longer at 318 K [191]. It is pointed out that the coupling constants reported should be viewed as lower limits since they correspond to more or less broad signals. The difference in two reports on the coupling constants in $HB(3\text{-}^tBu\text{-}pz)_3Tl$ [183,191] is traced to temperature effects. It is suggested that temperature and solvent influence the rate of Tl–N bond breaking and bond formation and that this fluxionality results in a loss of coupling to thallium. Hence, TpTl compounds for which no couplings has been measured may have larger rates of Tl–N bond breaking [191]. No coupling has, for example, been observed in the NMR spectra of $HB\{3,5\text{-}(CF_3)_2\text{-}pz\}_3Tl$ and the sharp resonances were attributed to a predominantly ionic nature of the Tl–N bonds in this compound [190].

The relatively large coupling constant to the *tert*-butyl-methyl carbons and protons (171 and 13 Hz, respectively) in $HB(3\text{-}^tBu\text{-}pz)_3Tl$ may suggest a proximity of thallium to these atoms [183]. In the tris(3-*tert*-butyl-5-methyl-pyrazolyl)borate, the thallium to *tert*-butyl-methyl carbon coupling constant is even larger (197 Hz), which may be due to a different ligand bite with attendent shortening of the nonbonding Tl···C contacts (no X-ray structure is available for $HB(3\text{-}^tBu\text{-}5\text{-}Me\text{-}pz)_3Tl$, though) [17,277]. Conversely, in $HB(3\text{-}^tBuCH_2\text{-}pz)_3Tl$ the *tert*-butyl-methyl carbon coupling is much smaller (57.0 Hz), commensurate with the greater distance of these methyls from the Tl atom [40]. Large coupling constants, probably indicative of a through-space interaction (cf. the X-ray structures in Fig. 24), were also found in $HB\{7(R)$-isopropyl-4(R)-methyl-4,5,6,7-tetra-hydro-2-indazolyl$\}_3Tl$ to the carbon atoms of the isopropyl groups and to $HB\{7(S)$-*tert*-butyl-4(R)-methyl-4,5,6,7-tetra-hydro-2-indazolyl$\}_3Tl$ to the methyl carbons of the *tert*-butyl group [220]. Apparently, the largest coupling constants were found for the 6′-C peak in HB(3-methyl-2*H*-benz[g]-4,5-dihydroindazol-2-yl$)_3Tl$ with 317 Hz [39] and to the 7-Me carbon in HB(7-Me-indazolyl$)_3Tl$ with 416 Hz [343]. The absence of coupling in the related "super-hindered" $HB(7\text{-}^tBu$-indazolyl$)_3$ derivative was explained by a weak Tl–N bonding due to steric pressure, with the molecule becoming an ion pair in solution [343].

4.3.4. Thallium(II) compounds

The hypersilyl compound $\{(Me_3Si)_3Si\}_2Tl–Tl\{Si(SiMe_3)_3\}_2$ has been investigated by NMR spectroscopy, although a high temperature sensitivity of the solution was noted. Both the carbon-13 and the silicon-29 NMR spectra showed coupling to thallium. The Tl–C coupling constant $\{^3J(Tl–CH_3)\}$ in d_8-toluene is 48.2 Hz, ^2J (Tl–Si) is 22.4 Hz [108].

4.4. Photoelectron spectroscopy and theoretical (electronic) properties calculations

The photoelectron spectrum of C_5H_5Tl has been measured together with the indium derivative and other main group metallocenes, and for C_5H_5Tl, the vertical ionization potentials (in eV) were reported and assigned as follows: 8.12 (ring e_1''-type π bonding), 10.28 (metal "lone pair"), 12.7 and 16.28 (ring σ bonding, C 2p), 19.6 and 22.0 (Tl 5d) [278]. A second photoelectron study of cyclopentadienylthallium and -indium, emphasizing He II radiation, gave as ionization energies for C_5H_5Tl (in eV) 7.96 $\{e_1(\pi)\}$, 10.12 (Tl 6s "lone-pair"), 11.76 and 12.61 $\{a_1\text{-}\pi, \sigma(C–H), \sigma(C–C)\}$, 16.49 $\{a_1(\sigma)+e(\sigma)\}$, 19.46 and 21.57 (Tl 5d). The metal d orbitals, probed by He II radiation, show no fine structure, which suggests that they are highly localized and subject to a weak ligand field [279].

The He I and He II photoelectron spectra of the thallium(I) (and sodium) derivatives of $HB(pz)_3$ have been measured and the ionization potentials (in eV) were assigned as follows: 8.4–9.4 (pyrazole π MOs and Tl 6s), 10.41 and 11.29 (σN and σBH), 13.0 18.0 (σN, inner π and σ MOs), 19.3 and 21.5 (Tl 5d) [186a].

Table 9 gives a list of the thallium(I) compounds where properties have been assessed by theoretical methods. For theoretical structure calculations, see Section 3.6, Table 5. A first qualitative MO treatment of the bonding in C_5H_5Tl was given by Cotton and Reynolds. They estimated a negligible magnitude of the Tl–C overlap integrals and from this an essentially ionic bonding in molecular C_5H_5Tl was deduced [115].

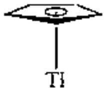
Table 9
Thallium(I) compounds and electronic and physical properties obtained by theoretical calculations

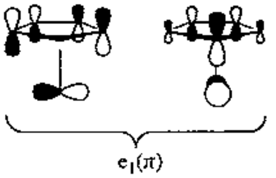
Formula, Remarks	Method, level basis sets[a]	Property	Reference
MeTl (still undetected)	SCF, relativistic pseudo-potentials	Vibrational frequencies, Tl–C stretch 411 cm^{-1}, Tl–C–H bend 706 cm^{-1}	[264]
C_5H_5Tl, monomer	SCF, (NOCOR), effective potentials	Charge distribution, Tl-charge +0.10, metal–ligand overlap population 0.47, orbital energies	[280]
	SCF, RCP-DZ	Gross atomic population, Tl–charge +0.5, metal–ligand overlap, orbital energies	[206]
	Ab initio-MO, HF, MP2,-3,-4 ECP-DZ	Charge distribution, Tl: +0.58	[157]
	Normal coordinate nalysis, general valence force field	Wavenumbers, force constants, potential energy distribution	[262]
C_5H_5Tl, dimer ($C_5H_5Tl \cdots TlC_5H_5$)	Extended-Hückel	Tl–Tl overlap population	[11]
Thallium(I) anions $[Tl(C_5H_5)_2]^-$	Ab initio-MO, HF, MP2,-3,-4 ECP-DZ	Charge distribution, Tl: +0.63, bent; +0.64, linear	[157]

[a] MO = molecular orbital, HF = Hartree–Fock, MP = Møller–Plesset, ECP/RCP = effective/relativistic core potential, DZ = double zeta.

An SCF calculation using effective potentials has been carried for gaseous C_5H_5Tl in its experimental equilibrium conformation. The thallium atom was calculated to be nearly neutral with an electron distribution of $s^{1.75}p^{0.45}d^{0.71}$ from a Mullikan population analysis. An overlap population of 0.47 between thallium and the cyclopentadienyl ring has been obtained. The thallium a_1 lone-pair combination was calculated as the highest occupied molecular orbital (HOMO) followed by the principal Tl–C_5 bonding combination of e_1 symmetry, based on pd^2 of Tl and p of C atoms interacting in π symmetry [280]. It was, however, criticized later that the spectroscopically assigned levels are not in agreement with those computed by this SCF method [281].

From an SCF pseudopotential calculation of monomeric C_5H_5Tl (and C_5H_5In) it was suggested that the bonding has a large covalent component. The highest occupied orbitals were calculated as a pair of degenerate e_1 orbitals which are the bonding combination of the cyclopentadienyl $e_1(\pi)$ orbitals with the $p_{x,y}$ orbitals of thallium (**20**). The next orbital was then the metal "lone-pair" (**21**), which results from the antibonding combination of the ligand $a_1(\pi)$ with s (out-of-phase) and p_z (in phase) of Tl (or In). For both cyclopentadienylthallium and -indium, photoelectron spectra were available for comparison and the single spectra as well as their relative differences were found to be reproduced by the calculations [206].





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21

An SCF-Xα-scattered wave calculation has been performed on molecular C_5H_5In and the results were also extended to C_5H_5Tl, so we include a summary of the results: the transition-state calculations for the various ionizations of C_5H_5In found the computed ionization potentials in very satisfactory agreement with the experimental values. The Xα-SW results indicate that the HOMO of C_5H_5In is doubly degenerate and originates from the interaction of the e_1 C_5H_5 π MO with the indium valence p_x and p_y AOs. The next two MOs are of a_1 symmetry, with the higher energy a_1 corresponding to the In lone pair. According to the charge densities, the major contribution to this a_1 MO comes from the In(5s) atomic orbital. The lone-pair character is, however, not confined to one particular orbital but tends to be distributed among other MOs of the same symmetry. Thus, the next a_1 MO, albeit localized mostly on the C_5H_5 ring, still possesses a distinct lone-pair appearence [281]. For further comparison to the electronic structure of C_5H_5In, see Eef. [282] (CNDO calculation).

In addition, a qualitative MO diagram and description have been given for the bonding in the mono- and bis(arene)gallium(I) complexes as an example also for the other group-13 elements [99]. The electronic structures of the benzene–gallium(I) model complexes $[(C_6H_6)Ga]^+$ and $[(C_6H_6)_2Ga]^+$ have been calculated by using the discrete variation Xα molecular orbital method [260]. The results show a weak dative bond formed between the C_6H_6 molecule and the Ga^I atom, with the electronic charge being transferred from the π orbitals of the benzene molecule to the three p orbitals of the Ga^I atom.

A normal-coordinate analysis and a general valence force field for molecular C_5H_5Tl is presented. Good agreement between observed and calculated wavenumbers has been achieved and the force fields together with the force constants and potential energy distribution are given [262].

5. Applications

5.1. Cyclopentadienylthallium(I) compounds

Cyclopentadienylthallium(I) compounds are often valued as ligand transfer reagents for lab-scale syntheses of metallocenes [25,30,32,33] and other cyclopentadienyl main group element and transition metal compounds. This is because they are generally very mild reagents for the careful Cp transfer and because of their relative ease of preparation and handling, e.g. often stable upon brief exposure to air, allowing for the precise determination of the quantity of the cyclopentadienide ion in the initial reaction mixture [31,38,44]. In the case of complexes prone to reduction or in the case of functionalized cyclopentadienyl ligands [283], the thallium derivatives are often better suited, i.e. "milder" or less reducing, for the Cp-transfer than the sodium or lithium analogs [22,28,29,34,118,120,136,284]. With functionalized cyclopentadienyl ligands, the thallium compounds have the advantage of being generally more stable than the corresponding lithium and sodium derivatives [23,37]. In addition, in the case of cyclopentadienes which are unstable when treated with base, preparation of the thallium salt can be successful. An example for the latter is given with (trifluoromethyl)cyclopentadiene, which, with base, gives 6,6-disubstituted fulvenes [14]. Table 10 provides a list of the thallium compounds used as ligand transfer reagents, their reactants and the products obtained with them (please also see [6]).

Most often, the cyclopentadienylthallium reagent reacts with a halide containing a transition metal complex in a salt-elimination or metathesis reaction [Eq. (18)] with the formation of the cyclopentadienylmetal complex, thallous halide (TlX) and possibly elimination of additional ligands (e.g. CO) as the by-products. The thallium compounds are particularly suitable reagents in metathesis reactions with metal halides owing to the thermodynamic driving force in favor of the formation of insoluble TlX. This method was even patented [25]. Cyclopentadienylthallium reagents are normally stirred or heated at reflux in ethereal or hydrocarbon solution with the substrate for some time under an inert atmosphere. The insoluble thallium halide produced may be filtered from the reaction solution. For an *Inorganic Synthesis* preparation of $(C_5H_5)_2TiCl$ and $(C_5H_5)_2VCl$ using this route, see Ref. [288]:

$$\mathrm{CpTl} + \mathrm{MXL}_y \rightarrow \mathrm{CpML}_z + \mathrm{TlX} + (y - z)\mathrm{L}. \tag{18}$$

There is, however, also the possibility for cyclopentadienylthallium to transfer the cyclopentadienyl moiety in a redox reaction with activated metal and the reduction to thallium metal [Eq. (19)]. This is a particularly elegant route with lanthanide metals, which are activated by mercury (reduction of induction time; the addition of mercury is, however, not essential for the reaction to occur, nor does it affect the outcome) [144,304,305,324]. This reductive transmetallation reaction of thallium(I) cyclopentadienide has also been worked out for *Inorganic Synthesis* [306]:

$$2\mathrm{CpTl}^{+1} + \mathrm{M}^0 \rightarrow \mathrm{Cp}_2\mathrm{M}^{+2} + 2\mathrm{Tl}^0. \tag{19}$$

Alternatively, a ligand transfer together with oxidation to Tl(III) has also been observed. Reaction of C_5H_5Tl with $Mo(CO)_6$ resulted in the formation of the thallium(III) derivative $Tl[Mo(CO)_3(C_5H_5)]_3$ [33].

We note that the thallium compounds containing the very bulky ligands C_5HPh_4, C_5Ph_5 and $C_5(CH_2Ph)_5$, unlike C_5H_5Tl, failed to function as ligand transfer agents towards lanthanide metals like samarium or ytterbium, both according to the salt-elimination reaction and the redox route [Eqs. (18) and (19)] [326].

Cyclopentadienylthallium also reacts with organic halides to give an alkylated cyclopentadiene. The alkylation of C_5H_5Tl found important applications in the prostaglandin work by Corey and others. Compared with the lithium and sodium cyclopentadienide, the thallium derivative minimizes the cyclopentadiene isomers formed. Reaction of C_5H_5Tl with benzyl chloro- or bromomethyl ether affords the

Table 10
Applications of thallium(I) compounds as ligand transfer reagent in inorganic, organometallic or organic synthesis. The table is divided into: (a) cyclopentadienylthallium compounds, including mononuclear and dinuclear complexes; (b) thallium(I) complexes with ligands related to cyclopentadienyl (ordering of the thallium compounds within each section with increasing molar mass of the ligand; reactands arranged by increasing atomic mass of central or Cp-bond forming atom)

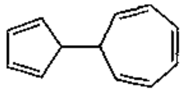
Tl compound	Reactand	Solvent	Product	Ref.
a) Cyclopentadienylthallium compounds				
aa) mononuclear CpTl compounds				
C_5H_5Tl	Cl_2BPh	pentane	$(C_5H_5)_2BPh$	[284a]
	$ClCH_2OMe$	Et_2O	$C_5H_5CH_2OMe$	[44]
	$ClCH_2OCH_2Ph$	Et_2O	$C_5H_5CH_2OCH_2Ph$	[52,57]
	$ClC(^iPr)=N\text{-}C_6H_4Me$	C_6H_6	$C_5H_5C(^iPr)=N\text{-}C_6H_4Me$	[142]
	$BrCH_2OMe$	Et_2O	$C_5H_5CH_2OMe$	[51]
	$BrCH_2OCH_2Ph$	Et_2O	$C_5H_5CH_2OCH_2Ph$	[51]
	$RC(O)I$ ($R = Me$, ^iPr, ^tBu,- $n\text{-}C_7H_{15}$)	CH_2Cl_2	$C_5H_5C(O)R$	[58]
	$[C_3Ph_3]^+ClO_4^-$	MeCN	$C_3Ph_3\text{-}C_5H_5$ 1-(1,2,3-triphenylcyclopropen-1-yl)-cyclopenta-1,3-diene	[56]
	$[C_7H_7]^+BF_4^-$	MeCN	$C_7H_7\text{-}C_5H_5$ 11,12-dihydrosesquifulvalene 	[47]
	7-norbornadienyl chloride	diglyme	7-(5-cyclopentadienyl)norbornadiene (as a not isolated intermediate) → hexahydro-3,4,7-methenocyclopenta-[a]pentalene	[42]
	1-chloro-4-fluoro-1,4-diazoniabicyclo-[2.2 2] octane-bis-tetrafluoroborate (F^+ source)	MeCN	$[C_5H_5F]$ in situ generation, trapping by dienophiles (cf. equation 25)	[59]
			$(C_5H_5)Al_2Cl_5(Et_2O)_2$	[25]
	Me_3SiCl	THF	$C_5H_5SiMe_3$	[38]
	PF_2Cl or PF_2Br	none	$C_5H_5PF_2$	[285]
	$PFCl_2$	none	$(C_5H_5)_2PF$	[285]
	Me_2PCl	Et_2O	$Me_2PC_5H_5$	[131,284]
	$MePCl_2$	Et_2O	$MeP(C_5H_5)_2$	[284]
	Ph_2PCl	Et_2O	$Ph_2PC_5H_5$	[145,284,286]
	$PhPCl_2$	Et_2O	$PhP(C_5H_5)_2$	[155a,284]

Table 10 (*continued*)

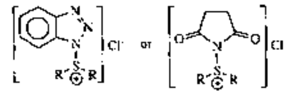
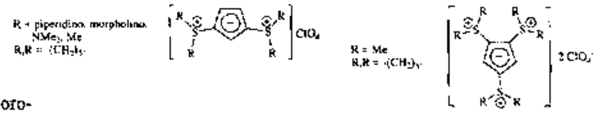
Tl compound	Reactand	Solvent	Product	Ref.
	SCl_2	hexane	$S(C_5H_5)_2$	[41]
	RSCl	CCl_4	C_5H_5SR	[53]
	{R = Me, Ph, $-C_6H_4$-4-Me, $-C_6H_3(-2,4-NO_2)_2$}			
	1. azasulfonium salts	CH_2Cl_2		
				
	2. $LiClO_4$/MeOH		bis- and tris(sulfonio)-cyclopentadienes	[61]
				
	N-chlorosuccinimide	CCl_4	C_5H_5Cl	[40,60,287]
	$ScCl_3$	THF	$(C_5H_5)_2ScCl$	[28]
	$TiCl_4$	C_6H_6	$(C_5H_5)_2TiCl_2$	[31]
	$TiCl_3$	THF	$(C_5H_5)_2TiCl$	[28,288]
	$\{C_5Me_4(CH=CH_2)\}$-$TiCl_3$	toluene	$(C_5H_5)\{C_5Me_4(CH=CH_2)\}TiCl_2$	[118]
	VCl_3	THF	$(C_5H_5)_2VCl$	[28,288]
			$(C_5H_5)_2VCl_2$	[25]
	1. $CrCl_3$ + 2. NO	THF	$(C_5H_5)Cr(NO)_2Cl$	[289]
			$(C_5H_5)_2Cr$	[25]
	$(C_5H_5)Cr(NO)_2Cl$	C_6H_6	$(\pi-C_5H_5)Cr(NO)_2(\sigma-C_5H_5)$	[290]
	trans-$Cr(CO)_4(PPh_2Cl)_2$	toluene	$Cr(CO)_4(PPh_2C_5H_5)_2$ rearrangement of the P-and CO-groups and Diels–Alder reaction of the C_5H_5-moieties gives cis-$Cr(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$	[149]
	$MnCl(CO)_5$	C_6H_6	$(C_5H_5)Mn(CO)_3$	[291]
	$FeCl_2$	THF	$(C_5H_5)_2Fe$	[115,289]
	$FeCl_2$	Et_2NH	$(C_5H_5)_2Fe$	[289]
	$FeCl_2$	C_6H_6	$(C_5H_5)_2Fe$	[31]
	$FeCl_2(H_2O)_4$	Et_2O	$(C_5H_5)_2Fe$	[25]
	$FeCl_3$	THF	$(C_5H_5)_2Fe$	[70,289]
	$FeCl_3(H_2O)_6$	Et_2O	$(C_5H_5)_2Fe$	[114]
	$(CF_3)_2CFFe(CO)_4I$	THF	$(C_5H_5)\{(CF_3)_2CF\}Fe(CO)_2$	[292]
	$C_2F_5Fe(CO)_4I$	THF	$(C_5H_5)(C_2F_5)Fe(CO)_2$	[292]
	1. $[C_5H_4C(CN)=C(CN)_2]Fe(C_5H_5)$ + 2. $C_5H_5Fe(CO)_2I$	THF	$(C_5H_5)Fe\{\mu-C_5H_4[C=C(CN)_2]C_5H_4\}Fe$-$(C_5H_5)$	[32,140]
	1. $[C_5H_4C(CN)=C(CN)_2]Fe(C_5H_5)$ + 2. $MnBr(CO)_5$	THF	$(C_5H_5)Fe\{\mu-C_5H_4[C=C(CN)_2]C_5H_4\}Mn$-$(CO)_3$	[32]
	$CoCl_2$	C_6H_6	$(C_5H_5)_2Co$	[31]
			$[(C_5H_5)_2Co]^+BPh_4^-$	[25]
	1. $CoBr_2$ + 2. Br_2		$(C_5H_5)_2CoBr_3$	[289]
	$NiBr_2$	C_6H_6	$(C_5H_5)_2Ni$	[25,31,289]
	$NiCl_2(PPh_3)_2$	not specif.	$(C_5H_5)NiCl(PPh_3)$	[35]
	$[Ni(NH_3)_6]Cl_2$		$(C_5H_5)_2Ni$	[293]
	$CuISMe_2$	Et_2O/Me_2S	$(C_5H_5)Cu(SMe_2)$	[294]
	CuIL	pentane	$(C_5H_5)CuL$	[36]
	(L = Et_3P, Bu_3P, Ph_3P, $(MeO)_3P$, MeCN)			
	CuCl/CO	pentane	$(C_5H_5)Cu(CO)$	[36]
	$GeBr_2$	THF	$(C_5H_5)_2Ge$	[295]
	N-bromosuccinimide	variable	C_5H_5Br	[46,60]
	Br_2	heptane	$C_5H_5Br_3$	[50]
	KOBr	H_2O/C_6H_6	C_5Br_6	[50]

Table 10 (*continued*)

Tl compound	Reactand	Solvent	Product	Ref.
	$ZrCl_4$	THF	$(C_5H_5)_2ZrCl_2$	[38]
	$ZrCl_4$	THF	$(C_5H_5)ZrCl_3$	[296]
	$Nb(CH^tBu)(THF)_2Cl_3$	Et_2O/THF	$(C_5H_5)Nb(CH^tBu)Cl_2$	[21]
	$Mo(CO)_6$	THF	$Tl[Mo(CO)_3(C_5H_5)]$	[33]
	$[C_5H_5Mo(NO)_2I_2]_2$	THF	$(C_5H_5)_2Mo(NO)I$	[34]
	$[C_5H_5Mo(NO)_2I_2]_2$	THF	$(C_5H_5)_3Mo(NO)$ (4 eq. CpTl)	[297]
	$[Mo(NO)_2Cl_2]_n$	THF	$(C_5H_5)Mo(NO)_2Cl$	[34]
	$[RhCl(cot)]_2$		$(C_5H_5)Rh(cot)$	[27]
	$[RhCl(diene)]_2$	Et_2O or THF	$(C_5H_5)Rh(diene)$	[126,133,298]
	(diene = general, substituted 1,3- or 1,4-dienes)			
	$[RhCl(all)_2]_2$	CH_2Cl_2	$(C_5H_5)Rh(\sigma\text{-all})(\pi\text{-all})$	[299]
	(all = allyl, 1-phenylallyl)			
	$[PdCl_2(PREt_2)]$		$(C_5H_5)PdCl(PREt_2)$	[142,300]
	(R = Ph, Et)			
	$[PdBr_2(PR_3)]_2$	THF	$(C_5H_5)PdBr(PR_3)$	[35,300]
	(R = Ph, Et, ^{i}Pr)			
	$PdBr_2(PEt_3)_2$	$CHCl_3$	$(C_5H_5)PdBr(PEt_3)_2$	[300]
	$[PdI_2(PEt_3)]_2$	THF	$(C_5H_5)PdI(PEt_3)$	[300]
	$[MeOC_{10}H_{12}PdCl]_2$	C_6H_6	$(C_5H_5)Pd(MeOC_{10}H_{12})$	[31]
	$[PdCl(C_8H_{12})acac]_2$		"$(C_5H_5)Pd(C_8H_{12})acac$"	[301]
	(C_8H_{12} = cyclooct-5-en-yl)		(rapid product decomposition)	
	$SnCl_2(OAc)_2$	THF	$(C_5H_5)_2Sn(OAc)_2$	[302]
			$(C_5H_5)SnPh_3$	[25]
			$(C_5H_5)_2SnCl_2$	[25]
	I_2	CS_2 or CH_2Cl_2	C_5H_5I	[303]
	Ce	THF	$(C_5H_5)_3Ce(THF)$	[304]
	Nd	THF	$(C_5H_5)_3Nd(THF)$	[304-306]
	Sm	THF	$(C_5H_5)_3Sm(THF)$	[304-306]
	Gd	THF	$(C_5H_5)_3Gd(THF)$	[304]
	Er	THF	$(C_5H_5)_3Er(THF)$	[304]
	Yb (excess)	DME	$(C_5H_5)_2Yb(DME)$	[304-307]
	Yb (excess)	THF	$(C_5H_5)_2Yb$	[304-305]
	Yb (equimolar)	THF	$(C_5H_5)_3Yb$	[304-305]
	$HfCl_4$	THF	$(C_5H_5)_2HfCl_2$	[38]
	$ReCl(CO)_5$	THF or C_6H_6	$(C_5H_5)Re(CO)_3$	[308]
			$(C_5H_5)_2Os$	[25]
	$IrCl(CO)_3$	hexane	$(C_5H_5)Ir(CO)_2$	[309]
	$[PtCl(COPh)(PBu_3)]_2$	THF	$(C_5H_5)Pt(COPh)(PBu_3)$	[300]
	$PtCl_2(PEt_3)_2$	THF	$(C_5H_5)PtCl(PEt_3)_2$	[300]
	$PtCl_2(CO)PPh_3$	C_6H_6	$(C_5H_5)PtCl(CO)PPh_3$	[300]
	$PtCl_2(Et_2AsC_6H_4AsEt_2)$	THF	$(C_5H_5)PtCl(Et_2AsC_6H_4AsEt_2)$	[300]
	$[PtBr(R')(PR_3)]_2$	THF	$(C_5H_5)Pt(R')(PR_3)$	[35,300]
	(R' = Ph, o-tolyl; R = Pt, Et)			
	$[PtI_2(PEt_3)]_2$	THF	$(C_5H_5)PtI(PPh_3)$	[300]
	$[MeOC_{10}H_{12}PtCl]_2$	C_6H_6	$(C_5H_5)Pt(MeOC_{10}H_{12})$	[31]
	$[PtCl(C_8H_{12})acac]_2$		"$(C_5H_5)Pt(C_8H_{12})acac$"	[301]
	(C_8H_{12} = cyclooct-5-en-yl)		(rapid product decomposition)	
	$HgCl_2$	THF	$(C_5H_5)_2Hg$	[70,278,289]
	$ThCl_4$	THF	$(C_5H_5)ThCl_3(THF)_{2.5}$	[310]
	UCl_4	DME	$(C_5H_5)UCl_3(DME)$	[311]
	UCl_4	DME	$(C_5H_5)_2UCl_2$	[312]
	UCl_4	THF	$(C_5H_5)_3UCl$	[313]
		C_6H_6 or DME		[314,315]
C_5H_4MeTl	UCl_4	DME	$[(C_5H_5)_3U][UCl_6(DME)_2$	[316]
	PF_2Cl or PF_2Br	none	$C_5H_4MePF_2$	[285]
	$PFCl_2$	none	$(C_5H_4Me)_2PF$	[285]
	$TiCl_4$	THF	$(C_5H_4Me)_2TiCl_2$	[317]
			$(C_5H_4Me)Mn(CO)_3$	[25]

Table 10 (*continued*)

Tl compound	Reactand	Solvent	Product	Ref.
	$FeCl_2$	Et_2O	$(C_5H_4Me)_2Fe$	[25]
			$(C_5H_4Me)_2Ni$	[25]
	$[RhCl(diene)]_2$	Et_2O or THF	$(C_5H_4Me)Rh(diene)$	[126]
	(diene = general, substituted 1,3- or 1,4-dienes)			
	$[RhCl(L)_2]_2$	Et_2O or THF	$(C_5H_4Me)Rh(L)_2$	[126]
	(L = CO or ethene)			
	Nd	THF	$(C_5H_4Me)_3Nd$	[300]
	Sm	THF	$(C_5H_4Me)_3Sm$	[300]
	Gd	THF	$(C_5H_4Me)_3Gd$	[300]
	Yb	THF	$(C_5H_4Me)_2Yb(THF)$	[300]
$C_5H_4(CN)Tl$	$[RhCl(diene)]_2$	Et_2O or THF	$\{C_5H_4(CN)\}Rh(diene)$	[126]
	(diene = general, substituted 1,3- or 1,4-dienes)			
	$[RhCl(L)_2]_2$	Et_2O or THF	$\{C_5H_4(CN)\}Rh(L)_2$	[126,318]
	(L = CO or ethene)			
	$IrCl(CO)(PPh_3)_2$	C_6H_6	$\{C_5H_4(CN)\}Ir(CO)PPh_3$	[23]
	$IrCl(CO)_2(C_5H_5N)$	C_6H_6	$\{C_5H_4(CN)\}Ir(CO)_2$	[26]
$C_5H_4(CH{=}CH_2)Tl$	$C_5H_5TiCl_3$	THF	$\{C_5H_4(CH{=}CH_2)\}(C_5H_5)TiCl_2$	[118]
$C_5H_4(CHO)Tl$	$MnBr(CO)_5$	toluene	$\{C_5H_4(CHO)\}Mn(CO)_3$	[37]
	$[RhCl(CO)_2]_2$	C_6H_6	$\{C_5H_4(CHO)\}Rh(CO)_2$	[37]
	$ReBr(CO)_5$	C_6H_6	$\{C_5H_4(CHO)\}Re(CO)_3$	[37]
C_5H_4EtTl	$FeCl_2$	Et_2O	$(C_5H_4Et)_2Fe$	[25]
	$CoBr_2/Br_2/H_2PtCl_6$	THF	$[(C_5H_4Et)_2Co]_2^{2+}[PtCl_6]^{2-}$ via $[(C_5H_4Et)_2Co]^+Br_3^-$	[319]
C_5H_4ClTl	$C_5H_5TiCl_3$	THF	$(C_5H_4Cl)(C_5H_5)TiCl_2$	[20]
	$TiCl_4$	benzene	$(C_5H_4Cl)_2TiCl_2$	[20]
	$MnBr(CO)_5$	THF	$(C_5H_4Cl)Mn(CO)_3$	[20]
	$FeCl_2$	benzene	$(C_5H_4Cl)_2Fe$	[20]
	$Co_2(CO)_8/I_2$	THF	$(C_5H_4Cl)Co(CO)_2$	[20]
	$NiBr_2 \cdot 2\,DME$	THF	$(C_5H_4Cl)_2Ni$	[20]
	$[CuCl(PEt_3)]_4$	pentane	$(C_5H_4Cl)Cu(PEt_3)$	[20]
	$[RhCl(C_2H_4)_2]_2$	hexane	$(C_5H_4Cl)Rh(C_2H_4)_2$	[19]
	$[RhCl(CO)_2]_2$	THF	$(C_5H_4Cl)Rh(CO)_2$	[20]
	$IrCl(CO)_3$	C_6H_6	$(C_5H_4Cl)Ir(CO)_2$	[23]
	$IrCl(CO)_2(C_5H_5N)$	C_6H_6	$(C_5H_4Cl)Ir(CO)_2$	[26]
C_8H_7Tl (hydropentalenyl-Tl)	$FeCl_2$	THF	$(C_8H_7)_2Fe$	[18]
	$[RhCl(cod)]_2$	THF	$(C_8H_7)Rh(cod)$	[18]
	$(CH_3)_3PtI$	THF	$(C_8H_7)Pt(CH_3)_3$	[18]
$C_5H_3\{\text{-}1,2/1,3\text{-}Me(CHO)\}Tl$ (mixture of isomers)	$[RhCl(C_2H_4)_2]_2$	Et_2O	$[C_5H_3\{\text{-}1,2/1,3\text{-}Me(CHO)\}]$- $\text{-}Rh(C_2H_4)_2$	[125]
$C_5H_4\{C(O)Me\}Tl$	$MnBr(CO)_5$	toluene	$[C_5H_4\{C(O)Me\}]Mn(CO)_3$	[37]
	$[RhCl(C_2H_4)_2]_2$	hexane	$[C_5H_4\{C(O)Me\}]Rh(C_2H_4)_2$	[19]
	$[RhCl(CO)_2]_2$	C_6H_6	$[C_5H_4\{C(O)Me\}]Rh(CO)_2$	[37]
	$ReBr(CO)_5$	C_6H_6	$[C_5H_4\{C(O)Me\}]Re(CO)_3$	[37]
	$[IrCl(C_2H_4)_2]_2$	hexane	$[C_5H_4\{C(O)Me\}]Ir(C_2H_4)_2$	[19]
$C_5H_4(SMe)Tl$	MeI	CCl_4	$C_5H_4^{-}\text{–}^{+}SMe_2$	[53]
C_9H_7Tl (indenyl)	$TiCl_3$	THF	$(C_9H_7)TiCl_3$	[320,321]
	$(C_5H_5)TiCl_3$	THF	$(C_9H_7)(C_5H_5)TiCl_3$	[320,321]
	$ZrCl_4$	THF	$(C_9H_7)_2ZrCl_2$	[320,321]
	$ZrCl_4$	THF	$(C_9H_7)ZrCl_3$	[296]

Table 10 (*continued*)

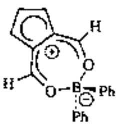
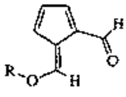
Tl compound	Reactand	Solvent	Product	Ref.
$C_5H_3\{-1,2-(CHO)_2\}Tl$	Ph_2BBr	CH_2Cl_2	3,3-diphenyl-1H-cyclopenta[e]-[1,3,2]dioxaborepin 	[54]
	MeC(O)Cl (acetyl chloride)	Et_2O	(5E)-5-(acetoxymethylene)-1,3-cyclopentadiene-1-carbaldehyde	[54]
	Me_3SiCl	Et_2O	(5Z)-5-[(trimethylsilyloxy)-methylene]-1,3-cyclopentadiene-1-carbaldehyde  R = MeC(O), Me_3Si	[54]
$C_5H_4{}^tBuTl$	$FeCl_2$	Et_2O	$(C_5H_4{}^tBu)_2Fe$	[25]
	$CoBr_2/Br_2$	THF	$[(C_5H_4{}^tBu)_2Co]^+Br_3^-$	[319]
			$(C_5H_4{}^tBu)_2Ni$	[25]
	$ZrCl_4$	C_6H_6	$(C_5H_4{}^tBu)_2ZrCl_2$	[38]
	$[RhCl(diene)]_2$ (diene = general, substituted 1,3- or 1,4-dienes)	Et_2O or THF	$(C_5H_4{}^tBu)Rh(diene)$	[126]
	$[RhCl(L)_2]_2$ (L = CO or ethene)	Et_2O or THF	$(C_5H_4{}^tBu)Rh(L)_2$	[126]
$C_5H_4(PMe_2)Tl$	$[RhCl(CO)_2]_2$	THF	$[\mu-(\eta^5-C_5H_4PMe_2-P)Rh(CO)]_2$	[131]
	$IrCl(CO)_3$	THF	$[\mu-(\eta^5-C_5H_4PMe_2-P)Ir(CO)]_2$	[131]
$C_5H_3(C_5H_8)Tl$ (isodicyclopentadienyl-Tl)	$FeCl_2$	THF	$[C_5H_3(C_5H_8)]_2Fe$	[18]
$C_5H_4(CF_3)Tl$	$C_5H_5TiCl_3$	THF	$\{C_5H_4(CF_3)\}(C_5H_5)TiCl_2$	[14]
	$MnBr(CO)_5$	THF	$\{C_5H_4(CF_3)\}Mn(CO)_3$	[14]
	$FeCl_2$	THF	$\{C_5H_4(CF_3)\}_2Fe$	[14]
	$[RhCl(cod)]_2$	THF	$\{C_5H_4(CF_3)\}Rh(cod)$	[14]
	$[IrCl(cod)]_2$	C_6H_6	$\{C_5H_4(CF_3)\}Ir(cod)$	[14]
$C_5H_4(CO_2Me)Tl$	$C_5H_5TiCl_3$	THF	$\{C_5H_4(CO_2Me)\}(C_5H_5)TiCl_2$	[134]
	$TiCl_4$	C_6H_6	$\{C_5H_4(CO_2Me)\}_2TiCl_2$	[134]
	$MnBr(CO)_5$	C_6H_6	$\{C_5H_4(CO_2Me)\}Mn(CO)_3$	[37]
	$Co_2(CO)_8/I_2$	THF	$\{C_5H_4(CO_2Me)\}Co(CO)_2$	[132]
	$[RhCl(diene)]_2$ (diene = general, substituted 1,3- or 1,4-dienes)	Et_2O or THF	$\{C_5H_4(CO_2Me)\}Rh(diene)$	[126,133]
	$[RhCl(L)_2]_2$ (L = CO or ethene)	Et_2O or THF	$\{C_5H_4(CO_2Me)\}Rh(L)_2$	[126,318]
	$[RhCl(CO)_2]_2$	THF	$\{C_5H_4(CO_2Me)\}Rh(CO)_2$	[37]
	$IrCl(CO)(PPh_3)_2$	C_6H_6	$\{C_5H_4(CO_2Me)\}Ir(CO)PPh_3$	[23]
	$IrCl(CO)_2(C_5H_5N)$	C_6H_6	$\{C_5H_4(CO_2Me)\}Ir(CO)_2$	[26]
C_5Me_5Tl	$Nb(CH{}^tBu)(THF)_2Cl_3$	C_6H_6	$(C_5Me_5)Nb(CH{}^tBu)Cl_2$	[21]
$C_5H_4\{C(O)NMe_2\}Tl$	$[RhCl(C_2H_4)_2]_2$	Et_2O	$[C_5H_4\{C(O)NMe_2\}]Rh(C_2H_4)_2$	[125]
$C_5H_4(CO_2Et)Tl$	$MnBr(CO)_5$	C_6H_6	$\{C_5H_4(CO_2Et)\}Mn(CO)_3$	[37]
	$[RhCl(diene)]_2$ (diene = general, substituted 1,3- or 1,4-dienes)	Et_2O or THF	$\{C_5H_4(CO_2Et)\}Rh(diene)$	[126]
	$[RhCl(L)_2]_2$ (L = CO or ethene)	Et_2O or THF	$\{C_5H_4(CO_2Et)\}Rh(L)_2$	[126]
	$[RhCl(CO)_2]_2$	C_6H_6	$\{C_5H_4(CO_2Et)\}Rh(CO)_2$	[37]
	$ReBr(CO)_5$	C_6H_6	$\{C_5H_4(CO_2Et)\}Re(CO)_3$	[37]

Table 10 (*continued*)

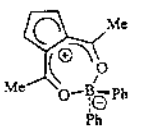
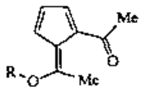
Tl compound	Reactand	Solvent	Product	Ref.
$C_5H_4\{C(O)CH_2OMe\}Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4\{C(O)CH_2OMe\}]Mn(CO)_3$	[120]
$C_5H_4(CH_2CO_2Me)Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4(CH_2CO_2Me)\}Mn(CO)_3$	[24]
C_5H_4PhTl	$(C_5H_5)TiCl_3$	C_6H_6	$(C_5H_4Ph)(C_5H_5)TiCl_2$	[24]
	$MnBr(CO)_5$	C_6H_6	$(C_5H_4Ph)Mn(CO)_3$	[24]
	$[RuCl_2(CO)_3]_2$	C_6H_6	$[(C_5H_4Ph)Ru(CO)_2]_2$	[24]
			$(C_5H_4Ph)RuCl(CO)_2$	[24]
	$[RhCl(CO)_2]_2$	C_6H_6	$(C_5H_4Ph)Rh(CO)_2$	[24]
			$(C_5H_4Ph)_2Rh_2(CO)_3$	[24]
			$[(C_5H_4Ph)Rh(CO)]_3$	[24]
	$[RhCl(C_2H_4)_2]_2$	hexane	$(C_5H_4Ph)Rh(C_2H_4)_2$	[19]
C_5H_4BrTl	$MnBr(CO)_5$	THF	$(C_5H_4Br)Mn(CO)_3$	[20]
	$FeCl_2$	C_6H_6	$(C_5H_4Br)_2Fe$	[20]
	$Co_2(CO)_8/I_2$	THF	$(C_5H_4Br)Co(CO)_2$	[20]
$C_5H_3\{\text{-}1,2\text{-}C(O)Me\}_2Tl$	Ph_2BBr	CH_2Cl_2	1,5-dimethyl-3,3-diphenyl-1H-cyclopenta[c]-[1,3,2]dioxaborepin 	[54]
	MeC(O)Cl (acetyl chloride)	Et_2O	1-[5-(1-acetoxyethylidene)-1,3-cyclopentadien-1-yl]ethanone	[54]
	Me_3SiCl	Et_2O	(5E and 5Z)-1-{5-[1-(trimethylsilyloxy)ethylidene]-1,3-cyclopentadien-1-yl}ethanone  R = MeC(O), Me_3Si	[54]
$C_5H_4(CO_2{}^iPr)Tl$	$[RhCl(diene)]_2$ (diene = general, substituted 1,3- or 1,4-dienes)	Et_2O or THF	$\{C_5H_4(CO_2{}^iPr)\}Rh(diene)$	[126]
	$[RhCl(L)_2]_2$ (L = CO or ethene)	Et_2O or THF	$\{C_5H_4(CO_2{}^iPr)\}Rh(L)_2$	[126]
$C_5H_4(CH_2CO_2Et)Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4(CH_2CO_2Et)\}Mn(CO)_3$	[120]
$C_5H_4(CH_2CH_2CO_2Me)Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4(CH_2CH_2CO_2Me)\}Mn(CO)_3$	[120]
$C_5H_4(CH_2CH_2O_2CMe)Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4(CH_2CH_2O_2CMe)\}Mn(CO)_3$ [120]	[120]
$C_5H_4(CH_2Ph)Tl$	$TiCl_4$	C_6H_6	$\{C_5H_4(CH_2Ph)\}_2TiCl_2$	[24]
	$(C_5H_5)TiCl_3$	C_6H_6	$\{C_5H_4(CH_2Ph)\}(C_5H_5)TiCl_2$	[24]
	$MnBr(CO)_5$	C_6H_6	$\{C_5H_4(CH_2Ph)\}Mn(CO)_3$	[24]
	$FeCl_2$	THF	$\{C_5H_4(CH_2Ph)\}_2Fe$	[24]
	$Co_2(CO)_8/I_2$	THF	$\{C_5H_4(CH_2Ph)\}Co(CO)_2$	[24]
	$ReBr(CO)_5$	C_6H_6	$\{C_5H_4(CH_2Ph)\}Re(CO)_3$	[24]
	$[RuCl_2(CO)_3]_2$	C_6H_6	$[\{C_5H_4(CH_2Ph)\}Ru(CO)_2]_2$	[24]
			$\{C_5H_4(CH_2Ph)\}RuCl(CO)_2$	[24]
	$\{RhCl(CO)_2\}_2$	C_6H_6	$\{C_5H_4(CH_2Ph)\}Rh(CO)_2$	[24]
			$\{C_5H_4(CH_2Ph)\}_2Rh_2(CO)_3$	[24]
			$[\{C_5H_4(CH_2Ph)\}Rh(CO)]_3$	[24]
	$IrCl(CO)(PPh_3)_2$	C_6H_6	$\{C_5H_4(CH_2Ph)\}Ir(CO)PPh_3$	[23]
	$IrCl(CO)_2(C_5H_5N)$	C_6H_6	$\{C_5H_4(CH_2Ph)\}Ir(CO)_2$	[26]
$C_5H_4(C_6H_4\text{-}3\text{-}F)Tl$	$[PdCl(C_3H_5)]_2$	THF	$\{C_5H_4(C_6H_4\text{-}3\text{-}F)\}Pd(C_3H_5)$	[138]
$C_5H_4(C_6H_4\text{-}4\text{-}F)Tl$	$[PdCl(C_3H_5)]_2$	THF	$\{C_5H_4(C_6H_4\text{-}4\text{-}F)\}Pd(C_3H_5)$	[138]

Table 10 (*continued*)

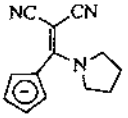
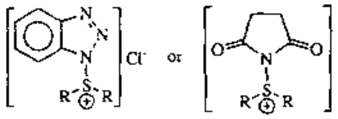
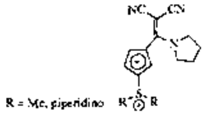
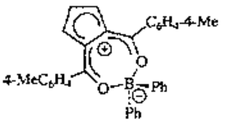
Tl compound	Reactand	Solvent	Product	Ref
$C_{13}H_9Tl$ (fluorenyl-Tl)	$C_5H_5MCl_3$	THF	$(C_{13}H_9)(C_5H_5)MCl_2$ (M=Ti, Zr)	[123]
$C_5H_4(CH_2CH_2CO_2Et)Tl$	$MnBr(CO)_5$	THF	$\{C_5H_4(CH_2CH_2CO_2Et)\}Mn(CO)_3$	[120]
$C_5H_4\{C(CN)=C(CN)_2\}Tl$	$MnBr(CO)_5$	THF	$[C_5H_4\{C(CN)=C(CN)_2\}]Mn(CO)_3$	[32,140]
	$C_5H_5Fe(CO)_2I$	THF	$[C_5H_4\{C(CN)=C(CN)_2\}]Fe(C_5H_5)$	[32,140]
	$CuClPPh_3$	THF	$[C_5H_4\{C(CN)=C(CN)_2\}]CuPPh_3$	[32,140]
$C_5H_4\{C^*H(Me)Ph\}Tl$	$FeCl_2/C_5H_5Tl$		$[C_5H_4\{C^*H(Me)Ph\}]Fe(C_5H_5)$	[138]
$C_5H_3(\text{-}1,3\text{-}^tBu_2)Tl$	$CoBr_2/Br_2$	THF	$[\{C_5H_3(\text{-}1,3\text{-}^tBu_2)\}_2Co]^+Br_3$	[319]
C_5H_4ITl	$Co_2(CO)_8/I_2$	THF	$(C_5H_4I)Co(CO)_2$	[20]
$C_5H_3(\text{-}1,3\text{-}Ph_2)Tl$	$FeCl_2$	THF	$\{C_5H_3(\text{-}1,3\text{-}Ph_2)\}_2Fe$	[141]
$C_5H_4[C\{N(CH_2)_5\}=C(CN)_2]Tl$	1.azasulfonium salts	CH_2Cl_2	mono(sulfonio)cyclopentadienides	[61]
			 R = Me, piperidino	
$C_5H_4\{C(^iPr)=N\text{-}C_6H_4Me\}Tl$	$[PdCl_2(PREt_2)]_2$ (R = Et, Ph)	THF	$[C_5H_4\{C(^iPr)=N\text{-}C_6H_4Me\}]\text{-}$ $PdCl(PREt_2)$	[142]
C_5Cl_5Tl	$HgCl_2$	THF	$(C_5Cl_5)_2Hg$	[151]
	$HgCl_2$	THF	$(C_5Cl_5)HgCl$	[151]
	$PhHgCl$	Et_2O	$(C_5Cl_5)HgPh$	[151]
$C_5H_4(PPh_2)Tl$	$C_5H_5TiCl_3$	THF	$\{C_5H_4(PPh_2)\}(C_5H_5)TiCl_2$	[151]
	$Cr(CO)_6/Me_3NO$	THF	$Cr(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$	[149]
	$C_7H_8Cr(CO)_4$	THF	trans- $Cr(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	[149]
	$CoCl_2$	THF	$\{C_5H_4(PPh_2)\}_2Co$	[146]
	$Co_2(CO)_8$	THF	$[\mu\text{-}\{\eta^5\text{-}C_5H_4PPh_2\text{-}P\}Co(CO)]_2$	[131]
	$ZrCl_4(THF)_2$	toluene	$\{C_5H_4(PPh_2)\}_2ZrCl_2$	[155]
	$Mo(CO)_6/Me_3NO$	THF	$Mo(CO)_5(P\text{-}Ph_2PC_5H_4Tl)$	[149]
	$C_7H_8Mo(CO)_4$	THF	cis-$Mo(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	[149]
	$[RhCl(CO)_2]_2$	THF	$[\mu\text{-}(\eta^5\text{-}C_5H_4PPh_2\text{-}P)Rh(CO)]_2$	[131]
	$IrCl(CO)_3$	THF	$[\mu\text{-}(\eta^5\text{-}C_5H_4PPh_2\text{-}P)Ir(CO)]_2$	[131]
	$PtPh_2(cod)$	THF	cis-$PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$	[155]
	Yb/Hg	THF, DME	$(C_5H_4PPh_2)_2Yb(DME)$	[144,324,325]
$C_5H_4\{C(CF_3)_2CH(CN)_2\}Tl$	$C_5H_5Fe(CO)_2I$	THF	$[C_5H_4\{C(CF_3)_2CH(CN)_2\}]Fe(C_5H_5)$	[32]
$C_5H_3[\text{-}1,2\text{-}\{C(O)C_6H_4\text{-}4\text{-}Me\}_2]Tl$				
	Ph_2BBr	CH_2Cl_2	1,5-bis(4-methylphenyl)-3,3'-diphenyl-1H-cyclopenta[e]-[1,3,2]dioxaborepin	[54]
				
	MeC(O)Cl (acetyl chloride)	Et_2O	{5-[acetoxy(4-methylphenyl)-methylene]-1,3-cyclopentadien-1-yl}(4-methylphenyl)methanone	[54]
	$O_2NC_6H_4C(O)Cl$ (4-nitrobenzoyl-chloride)	Et_2O	(4-methylphenyl){5-[(4-methyl-phenyl)(4-nitrobenzoyloxy)methylene]-1,3-cyclopentadien-1-yl}-methanone	[54]

Table 10 (*continued*)

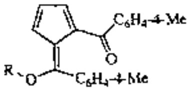
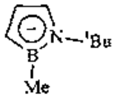
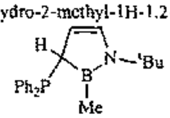
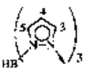
Tl compound	Reactand	Solvent	Product	Ref.
	Me_3SiCl	Et_2O	(4-methylphenyl){5-[(4-methylphenyl)(trimethylsilyloxy)-methylene]-1,3-cyclopentadien-1-yl}methanone  R = MeC(O), O_2N-C_6H_4-C(O) Me_3Si	[54]
$C_5Me_4(PPh_2)Tl$	InCl	Et_2O	$C_5Me_4(PPh_2)In$	[13]
$C_5(CO_2Me)_5Tl$	$C_5H_5RuCl(PPh_3)_2$		$\{C_5(CO_2Me)_5\}Ru(C_5H_5)$	[174]
	$C_5H_5RuCl(CO)_2$		$\{C_5(CO_2Me)_5\}Ru(C_5H_5)$	[174]
	$[RhCl(cod)]_2$		$\{C_5(CO_2Me)_5\}Rh(cod)$	[174]
	$C_5H_5OsCl(PPh_3)_2$		$\{C_5(CO_2Me)_5\}Os(C_5H_5)$	[174]
	$[IrCl(cod)]_2$		$\{C_5(CO_2Me)_5\}Ir(cod)$	[174]
ab) dinuclear CpTl complexes				
Tl C_5H_4-C_5H_4 Tl	$C_5Me_5TiCl_3$	C_6H_6	$(C_5H_4\text{-}C_5H_4)\{Ti(C_5Me_5)Cl_2\}_2$	[29]
(fulvalene-dithallium)	$MnBr(CO)_5$	C_6H_6	$(C_5H_4\text{-}C_5H_4)\{Mn(CO)_3\}_2$	[27,29]
	$Co_2(CO)_8/I_2$	THF	$(C_5H_4\text{-}C_5H_4)\{Co(CO)_2\}_2$	[27]
	$ReBr(CO)_5$	C_6H_6	$(C_5H_4\text{-}C_5H_4)\{Re(CO)_3\}_2$	[27,29]
	$[RhCl(CO)_2]$	THF	$(C_5H_4\text{-}C_5H_4)\{Rh(CO)_2\}_2$	[27,29]
	$[RhCl(C_2H_4)_2]_2$	THF	$(C_5H_4\text{-}C_5H_4)\{Rh(C_2H_4)_2\}_2$	[27,29]
	$[RhCl(cod)]_2$	THF	$(C_5H_4\text{-}C_5H_4)\{Rh(cod)\}_2$	[27,29]
	$[RhCl(cot)]_2$	THF	$(C_5H_4\text{-}C_5H_4)\{Rh(cot)\}_2$	[27,29]
	$C_5H_5Rh(cot)$ + $[RhCl(C_2H_4)_2]_2$	THF	$(C_5H_4\text{-}C_5H_4)\{Rh(\mu\text{-}cot)RhC_5H_5\}_2$	[27]
	$IrCl(CO)_3$	THF	$(C_5H_4\text{-}C_5H_4)\{Ir(CO)_2\}_2$	[27,29]
Tl C_4H_4-CH_2 C_5H_4Tl	$MnBr(CO)_5$	C_6H_6	$CH_2[C_5H_3Mn(CO)_3]_2$	[30]
	$FeBr_2(CO)_4$	THF	$CH_2[C_5H_3FeBr(CO)_2]_2$	[30]
	$[RuCl_2(CO)_3]_2$	C_6H_6	$CH_2[C_5H_3RuCl(CO)_2]_2$	[30]
			$CH_2[C_5H_3Ru(CO)_2]_2$	[30]
	$[RhCl(CO)_2]_2$	hexane	$CH_2[C_5H_3Rh(CO)_2]_2$	[30]
			$CH_2[C_5H_3Rh(CO)]_2\text{-}\mu\text{-}CO$	[30]
	$IrCl(CO)_3$	C_6H_6	$CH_2[C_5H_3Ir(CO)_2]_2$	[30]
$PhP(C_5H_4Tl)_2$	$ZrCl_4(THF)_2$	THF	$PhP(C_5H_4)_2ZrCl_2$	[155]
trans-$Cr(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	CF_3COOH	THF	$Cr(CO)_4(P\text{-}Ph_2PC_5H_5)_2$ rearrangement of the P-and CO-groups and Diels-Alder reaction of the C_5H_5-moieties gives cis-$Cr(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$	[149]
cis-$Mo(CO)_4(P\text{-}Ph_2PC_5H_4Tl)_2$	CF_3COOH	THF	$Mo(CO)_4(P\text{-}Ph_2PC_5H_5)_2$ rearrangement of the P-and CO-groups and Diels-Alder reaction of the C_5H_5-moieties gives cis-$Mo(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$	[149]
cis-$PtPh_2(P\text{-}Ph_2PC_5H_4Tl)_2$	$ZrCl_4(THF)_2$		cis-$PtPh_2(P\text{-}Ph_2PC_5H_4)_2ZrCl_2$	[155]
b) Thallium(I) complexes with ligands related to cyclopentadienyl				
C_4H_4NTl (see also text)	$C_5H_5MCl_3$	THF	$(C_5H_5)(C_4H_4N)MCl_2$ (M=Ti, Zr)	[123]
$C_3H_3B(Me)N(^tBu)Tl$ 	Ph_2PCl	THF	$C_3H_3(PPh_2)B(Me)N(^tBu)$ [1-tert-butyl-3-(diphenylphosphanyl)-2,3-dihydro-2-methyl-1H-1,2-azaborol] 	[22]

Table 10 (*continued*)

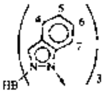
Tl compound	Reactand	Solvent	Product	Ref.
Tl$^+$[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$	AlMe$_2$Cl	toluene	Tl$^+$(C$_6$H$_5$Me)$_{2.3}$[*commo*-3,3'-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]$^-$ 162	[162]
	GaCl$_3$	toluene	Tl$^+$[*commo*-3,3'-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ 162	[162]
	1. PPN$^+$Cl$^-$, 2. M(CO)$_3$(MeCN)$_3$ 3. CuCl M = Mo, W	MeCN	[PPN]$_2$[M$_2$Cu$_2$(μ-CO)$_4$(CO)$_2$-(μ-H)$_2$(C$_2$B$_9$H$_{10}$)$_2$]	[344]
	Yb	THF	Yb(C$_2$B$_9$H$_{11}$)(THF)$_4$	[346]
	[PPh$_3$HgCl$_2$]$_2$	CH$_2$Cl$_2$	(Ph$_3$P)- 3,1,2-HgC$_2$B$_9$H$_{11}$	[215]
[PPN]$^+$[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$	Yb	THF	Yb(C$_2$B$_9$H$_{11}$)(THF)$_4$	[346]
	Ln(C$_2$B$_9$H$_{11}$)(THF)$_4$ Ln = Sm, Yb	THF	[PPN][3,3-(THF)$_2$- *commo*-3,3'-Ln(3,1,2-LnC$_2$B$_9$H$_{11}$)$_2$]	[345,346]
Tl$^+$[3,1,2-TlC$_2$R$_2$B$_9$H$_9$]$^-$ (R = H, Me)	FeCl$_2$ CoCl$_2$	THF THF	"π-(3)-1,2-dicarbollyl derivatives", probably Tl$_2$[*commo*-3,3'-M(3,1,2-MC$_2$R$_2$B$_9$H$_9$)$_2$] with M = Fe, Co	[178]
	PdCl$_2$(PPh$_3$)$_2$ PtCl$_2$(cod)	THF THF	"π-(3)-1,2-dicarbollyl derivatives", probably L$_2$M[C$_2$R$_2$B$_9$H$_9$] with ML$_2$ = Pd(PPh$_3$)$_2$, Pt(cod)	[178]

Hydrotris(pyrazolyl)- and -(indazolyl)borate complexes

{Due to space requirements, the tris(pyrazolyl)- and -(indazolyl)borato ligands are also represented by the abbreviation Tp, with the 3- and 5-alkyl substituents listed respectively as superscripts, according to a nomenclature described by Trofimenko [182]}.



HB(pz)$_3$



HB(indazolyl)$_3$

(For additional schematic drawings of the ligands, see Table 4 and 7; for structural drawings, see Figure 18)

Tl compound	Reactand	Solvent	Product	Ref.
HB(3,5-Me$_2$-pz)$_3$Tl	ZnMe$_2$	THF,decalin	HB(3,5-Me$_2$-pz)$_3$ZnMe	[334]
	CdCl$_2$/KBH$_4$	Et$_2$O	HB(3,5-Me$_2$-pz)$_3$CdBH$_4$	[327]
	CdCl$_2$/LiBHEt$_3$	Et$_2$O	[HB(3,5-Me$_2$-pz)$_3$Cd]$_2$(*Cd-Cd*)	[327]
	CdR$_2$	Et$_2$O	HB(3,5-Me$_2$-pz)$_3$CdMe	[338]
	(CdR$_2$ from CdCl$_2$ + 2 RLi; R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{s}Bu, ^{t}Bu, Ph)			
HB(3-^{i}Pr-pz)$_3$Tl	CuCl$_2$	THF	HB(3-^{i}Pr-pz)$_3$CuCl	[272]
HB(3-^{t}Bu-pz)$_3$Tl = Tp^{tBu}Tl	BeX$_2$	Et$_2$O	HB(3-^{t}Bu-pz)$_3$BeX	[186]
	(X = Cl, Br)			
	MgR$_2$	Et$_2$O	HB(3-^{t}Bu-pz)$_3$MgR	[332,339]
	(R = Me, Et, ^{i}Pr, ^{n}Bu, ^{t}Bu, CH$_2$SiMe$_3$, CH=CH$_2$, Ph)			
	RMgX	Et$_2$O	HB(3-^{t}Bu-pz)$_3$MgX	[332,336]
	(R = Me, Et, ^{i}Pr, ^{t}Bu; X = Cl, Br)			
	MeMgI	Et$_2$O	HB(3-^{t}Bu-pz)$_3$MgMe and HB(3-^{t}Bu-pz)$_3$MgI	[332,336]
	AlMe$_3$	C$_6$H$_6$	HB(3-^{t}Bu-pz)$_3$AlMe$_2$	[335]
	HCl/AlCl$_3$	CHCl$_3$	[HB(3-^{t}Bu-pzH)$_3$Cl]$^+$AlCl$_4^-$	[340]
	trans-[NiBr(C$_6$H$_4$R-4)(PMe$_3$)$_2$]	THF	trans-[Tp^{tBu} Ni(C$_6$H$_4$R-4)(PMe$_3$)$_2$]	[184]
	(R = H, Me, OMe)			
	trans-[NiBr(C(O)C$_6$H$_4$R-4)(PMe$_3$)$_2$]	THF	trans-[Tp^{tBu} Ni{C(O)C$_6$H$_4$R-4}(PMe$_3$)$_2$]	
	(R = H, Me, OMe)			[184]
	CuCl	THF	[HB(3-^{t}Bu-pz)$_3$Cu]$_2$	[341]
	ZnH$_2$	THF	HB(3-^{t}Bu-pz)$_3$ZnH	[334,342]
	ZnR$_2$	THF,pentane	HB(3-^{t}Bu-pz)$_3$ZnR	[333,334]

Table 10 (*continued*)

Tl compound	Reactand	Solvent	Product	Ref
	(R = Me, Et)			
	ZnX_2	THF	$HB(3\text{-}{}^{t}Bu\text{-}pz)_3ZnX$	[334]
	(X = Cl, Br, I, CN, NCS, O_2CMe)			
	$CdCl_2/KBH_4$ or $LiBHEt_3$	Et_2O	$HB(3\text{-}{}^{t}Bu\text{-}pz)_3CdH$	[337]
	CdI_2	THF	$HB(3\text{-}{}^{t}Bu\text{-}pz)_3CdI$	[331]
$HB(3\text{-}{}^{t}BuCH_2\text{-}pz)_3Tl$ (${}^{t}BuCH_2$ = neopentyl) = $Tp^{Np}Tl$	MCl_2/KCl	Et_2O/H_2O	$Tp^{Np}MCl$	[40]
	(M = Co, Ni, Zn)			
	$M(NO_3)_2/KNCO$	Et_2O/H_2O	$Tp^{Np}MNCO$	[40]
	(M = Co, Ni, Cu, Zn)			
	$M(NO_3)_2/KNCS$	Et_2O/H_2O	$Tp^{Np}MNCS$	[40]
	(M = Co, Ni, Zn)			
	$M(NO_3)_2/NaN_3$	Et_2O/H_2O	$Tp^{Np}MN_3$	[40]
	(M = Co, Ni, Zn)			
	$MoCl(\eta^3\text{-}CH_2CRCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{Np}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[40]
	$[Rh(CO)_2Cl]_2$	CH_2Cl_2	$Tp^{Np}Rh(CO)_2$	[40]
$HB(3\text{-}{}^{t}Bu\text{-}5\text{-}Me\text{-}pz)_3Tl$	CuCl	THF/NH_3	$[HB(3\text{-}{}^{t}Bu\text{-}5\text{-}Me\text{-}pz)_3Cu]_2$	[217]
	$CuCl_2$	C_6H_6	$HB(3\text{-}{}^{t}Bu\text{-}5\text{-}Me\text{-}pz)_3CuCl$	[217]
	$CdMe_2$	toluene/Et_2O	$HB(3\text{-}{}^{t}Bu\text{-}5\text{-}Me\text{-}pz)_3CdMe$	[331]
$HB(3\text{-}Ph\text{-}pz)_3Tl$	$MoCl(\eta^3\text{-}CH_2CRCH_2)(MeCN)_2(CO)_2$ (R = H, Me)	$DMAC/CH_2Cl_2$	$HB(3\text{-}Ph\text{-}pz)_3Mo(\eta^3\text{-}CH_2CRCH_2)(CO)_2$	[15]
	$[PdCl(\eta^3\text{-}CH_2CRCH_2)]_2$ (R = Me, Ph)	$DMAC/CH_2Cl_2$	$HB(3\text{-}Ph\text{-}pz)_3Pd(\eta^3\text{-}CH_2CRCH_2)$	[15]
$HB(3\text{-}cyclohexyl\text{-}pz)_3Tl$	MCl_2	CH_2Cl_2	$HB(3\text{-}cyclohexyl\text{-}pz)_3MCl$	[272]
	(M = Co, Ni, Zn)			
	$CuCl_2$	CH_2Cl_2	$HB(3\text{-}cyclohexyl\text{-}pz)_3CuCl$	[272]
	$CuCl_2(H_2O)_2$	THF/CH_2Cl_2	$HB(3\text{-}cyclohexyl\text{-}pz)_3CuCl_2$	[272]
$HB(1,4\text{-}dihydroindeno[1,2\text{-}c]\text{-}pz)_3Tl$ = $Tp^{b}Tl$	$CoCl_2$	THF/CH_2Cl_2	$Tp^{b}{}_2Co$	[39]
	$Tp^{Np}CoCl$	CH_2Cl_2	$Tp^{b}CoTp^{Np}$	[39]
	$Zn(ClO_4)_2/KY$	DMF/CH_2Cl_2	$Tp^{b}MY$	[39]
	(Y = Cl, I, NCO, NCS)			
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{b}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[39]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^{b}Rh(cod)$	[39]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$		$Tp^{b}Pd(\eta^3\text{-}CH_2CMeCH_2)$	[39]
$HB(3\text{-}Ph\text{-}5\text{-}Me\text{-}pz)_3Tl$ = $Tp^{Ph,Me}Tl$	MCl_2 or $M(ClO_4)_2$	THF/CH_2Cl_2	$Tp^{Ph,Me}{}_2M$	[39]
	(M = Fe, Co, Zn)			
	$Tp^{Np}CoCl$	CH_2Cl_2	$Tp^{Ph,Me}CoTp^{Np}$	[39]
	MX_2/KY	DMF/CH_2Cl_2	$Tp^{Ph,Me}MY$	[39]
	(M = Co, Ni, Zn; X = Cl, I, ClO_4; Y = Cl, I, NCS)			
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{Ph,Me}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[39]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^{Ph,Me}Rh(cod)$	[39]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$		$Tp^{Ph,Me}Pd(\eta^3\text{-}CH_2CMeCH_2)$	[39]
$HB(2H\text{-}benz[g]indazol\text{-}2\text{-}yl)_3Tl$ = $Tp^{bn}Tl$	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$		$Tp^{bn}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[273]

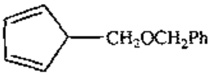
Table 10 (*continued*)

Tl compound	Reactand	Solvent	Product	Ref
HB(2*H*-benz[g]-4,5-dihydroindazol-2-yl)$_3$Tl = Tp^{a}Tl	MCl_2 or $M(ClO_4)_2$ (M = Fe, Co, Zn)	THF/CH_2Cl_2	$Tp^a{}_2M$	[39]
	$Tp^{Np}CoCl$	CH_2Cl_2	Tp^aCoTp^{Np}	[39]
	ZnX_2/KY (X = I, ClO_4; Y = I, NCO, NCS)	DMF/CH_2Cl_2	Tp^aMY	[39]
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^aMo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[39]
	$Mo(CO)_6$	THF	$[Tp^aMo(CO)_3][Et_4N]$	[39]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^aRh(cod)$	[39]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$		$Tp^aPd(\eta^3\text{-}CH_2CMeCH_2)$	[39]
	$W(CO)_6$	THF	$[Tp^aW(CO)_3][Et_4N]$	[39]
HB(7-^{t}Bu-indazolyl)$_3$Tl	Co(NCS)	xylene/Δ	HB(7-^{t}Bu-indazolyl)$_2$(3-^{t}Bu-indazol-1-yl)CoNCS (ligand rearrangement)	[343]
HB(3,5-^{t}Bu$_2$-pz)$_3$Tl	ZnI_2	C_6H_6	HB(3,5-^{t}Bu$_2$-pz)$_3$ZnI	[220a]
	CdI_2	C_6H_6	HB(3,5-^{t}Bu$_2$-pz)$_3$CdI	[220a]
HB(3-Me-2*H*-benz[g]-4,5-dihydroindazol-2-yl)$_3$Tl = Tp^{a,Me}Tl	MCl_2 or $M(ClO_4)_2$ (M = Fe, Co, Zn)	THF/CH_2Cl_2	$Tp^{a,Me}{}_2M$	[39]
	$Tp^{Np}CoCl$	CH_2Cl_2	$Tp^{a,Me}CoTp^{Np}$	[39]
	MX_2/KY (M = Co, Ni, Zn; X = Cl, I, ClO_4; Y = Cl, I, NCO, NCS)	DMF/CH_2Cl_2	$Tp^{a,Me}MY$	[39]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^{a,Me}Rh(cod)$	[39]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$		$Tp^{a,Me}Pd(\eta^3\text{-}CH_2CMeCH_2)$	[39]
HB(3-mesityl-pz)$_3$Tl = Tp^{Ms}Tl (mesityl = C_6H_2-2,4,6-Me_3)	$Co(NCO)_2$	H_2O/CH_2Cl_2*	$Tp^{Ms}CoNCO$	[192]
	$Zn(NO_3)_2/KX$ (X = Cl, I, NCS, NCO)	H_2O/CH_2Cl_2*	$Tp^{Ms}ZnX$	[192]
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{Ms}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[192]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^{Ms}Rh(cod)$	[192]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$	CH_2Cl_2	$Tp^{Ms}Pd(\eta^3\text{-}CH_2CMeCH_2)$	[192]
	$Cd(NO_3)_2/KCl$	H_2O/CH_2Cl_2*	$Tp^{Ms}CdCl$	[192]
HB(3-mesityl-pz)$_2$(5-mesityl-pz)Tl = Tp^{Ms*}Tl	$Zn(NO_3)_2/KX$ (X = Cl, I, NCS, NCO)	H_2O/CH_2Cl_2*	$Tp^{Ms*}ZnX$	[192]
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{Ms*}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[192]
	$[RhCl(cod)]_2$	CH_2Cl_2	$Tp^{Ms*}Rh(cod)$	[192]
	$[PdCl(\eta^3\text{-}CH_2CMeCH_2)]_2$	CH_2Cl_2	$Tp^{Ms*}Pd(\eta^3\text{-}CH_2CMeCH_2)$	[192]
	$Cd(NO_3)_2/KCl$	H_2O/CH_2Cl_2*	$Tp^{Ms*}CdCl$	[192]
HB(3-^{i}Pr-4-Br-pz)$_3$Tl	MCl_2 (M = Fe, Co, Ni)	toluene/reflux	{HB(3-^{i}Pr-4-Br-pz)$_2$(5-^{i}Pr-4-Br)}$_2$M	[193]
HB{3-(9-anthryl)-pz}$_3$Tl = Tp^{Ant}Tl	$Co(NCS)_2$	toluene	HB{3-(9-anthryl)-pz}$_3$CoNCS	[221]
	$MoCl(\eta^3\text{-}CH_2CMeCH_2)(MeCN)_2(CO)_2$	CH_2Cl_2	$Tp^{Ant}Mo(\eta^3\text{-}CH_2CMeCH_2)(CO)_2$	[221]

†Together with a catalytic amount of tetrabutylammonium bromide as phase-transfer agent

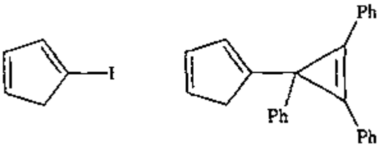
cyclopenta-2,4-diene isomer (**22**) exclusively [Eq. (20)] [44,51,52,55,57]:

$C_5H_5Tl + Cl - CH_2OCH_2Ph \rightarrow TlCl +$



22 (20)

Upon reaction of C_5H_5Tl with acyl iodides or triphenylcyclopropenyl perchlorate only the 1,3-isomers (**23**) are obtained [56,58]:



23

Reaction of C_5H_5Tl with sulfenyl chlorides gives unstable *S*-alkyl or *S*-aryl cyclopentadienes [Eq. (21)], which can be deprotonated again with TlOEt [Eq. (22)]. The thallium salts can then be *S*-alkylated to form dialkylsulfonium cyclopentadienides or alkylarylsulfonium cyclopentadienides [Eqs. (23) and (24)]. The latter are, however, only stable in the form of the thallium complexes [53]:

$$C_5H_5Tl + R\text{-}S\text{-}Cl \rightarrow C_5H_5SR + TlCl, \tag{21}$$

$$C_5H_5SR + TlOEt \rightarrow C_5H_4(SR)Tl + EtOH \tag{22}$$

$\{R = Me, Ph, \text{-}C_6H_4\text{-}4\text{-}Me, \text{-}C_6H_3(\text{-}2,4\text{-}NO_2)_2\}$.

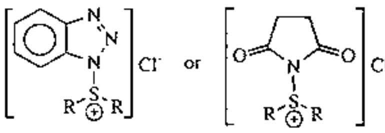
$$C_5H_4(SMe)Tl + MeI \rightarrow C_5H_4^- - {}^-SMe_2 + TlI \tag{23}$$

$$C_5H_4(SC_6H_4R')Tl + (Me_3O)BF_4 \xrightarrow{HBF_4} \rightarrow [C_5H_4S(Me)C_6H_4R'Tl]^+BF_4^- + Me_2O \tag{24}$$

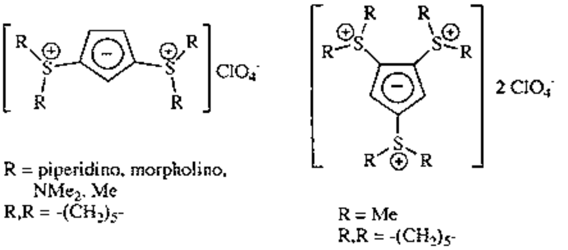
$(R' = H, Me)$.

Azasulfonium salts (**24**) react with unsubstituted C_5H_5Tl to give bis(sulfonio)-cyclopentadienides or tris(sulfonio)cyclopentadienides (**25**). Thallium salts of monosubstituted cyclopentadiene condense with the azasulfonium salts to form mono(sulfonio)cyclopentadienides [61].

Another electrophilic substitution reaction of C_5H_5Tl takes place with the "F^+" source 1-chloro-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane which generates 5-fluorocyclopentadiene [C_5H_5F] in situ, which could be trapped by suitable dienophiles, such as $(MeO_2CC)_2$, $CH_2=C(Cl)CN$, $CH_2=CHCO_2Me$, $MeCH=CHCHO$



24

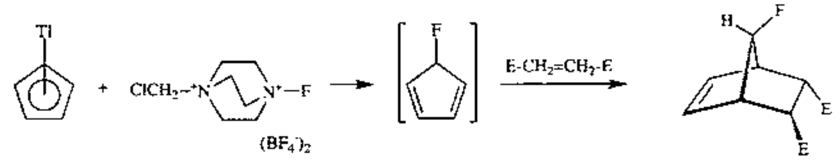


R = piperidino, morpholino, NMe$_2$, Me
R,R = -(CH$_2$)$_5$-

R = Me
R,R = -(CH$_2$)$_5$-

25

to give the respective Diels–Alder adduct [Eq. (25)] [59].



(25)

A major disadvantage of the applications reported here and in Table 10 for the cyclopentadienylthallium compounds is the discarding of the thallium salt side product, which should always be treated with caution and must be specially disposed of (e.g. heavy metal waste for special treatment) because of the poisonous nature of thallium. A large scale use or application of organothallium compounds in industry is, therefore, almost prohibitive.

As pointed out in Section 2.1, occasionally, identification of the organothallium compound was performed by utilizing it in a reaction with a transition metal salt as a ligand transfer agent. Successful formation of the organotransition metal compound was viewed as a proof for the existence of the organothallium reagent. Such was the case for isodicyclopentadienylthallium(I), $C_5H_3(C_5H_8)Tl$ [18], fluorenylthallium [123], pyrrolylthallium [123], (trifluoromethyl)cyclopentadienylthallium [14], and 1,2-azaborolylthallium [22].

The reaction between TlOH or Tl^+ and C_5H_6 in aqueous media which leads to the formation of C_5H_5Tl has been suggested as an analytical tool, either as a test for cyclopentadiene or thallium, *vice versa*, as it is very specific for both the identification of cyclopentadiene or thallium. Because of the low solubility of C_5H_5Tl in water, TlOH can still be precipitated quantitatively from a 3×10^{-5} wt.% solution with cyclopentadiene, when a ten-fold excess of KOH over TlOH is present [111].

Antiknock additive. C_5H_5Tl has been claimed in a patent as an antiknock additive [327].

Metallomesogenes. The syntheses of the thallium salts of the *p*-phenyl-substituted pentaphenylcyclopentadienyl ligands, $C_5\{C_6H_4\text{-}4\text{-}C(O)R\}_5Tl$ (R = Me, ^{n}Pr, nC_5H_{11}, nC_7H_{15}) and $C_5(C_6H_4\text{-}4\text{-}CO_2R)_5Tl$ (R = Et, nC_5H_{11}), has been driven by a desire to obtain discotic metallocenes or half-sandwich compounds, which may show anisotropic, liquid crystalline behavior [12,153]. Despite a statement on the mesogenic behavior of the amyl derivative, $C_5\{C_6H_4\text{-}4\text{-}C(O)nC_5H_{11}\}_5Tl$ [12,205], these expectations did not yet materialize by using a pentaphenylcyclopentadienyl backbone [328].

5.2. Thallium(I) compounds with ligands related to cyclopentadienyl

The applications of these complexes as ligand transfer agent are contained in Table 10. With respect to pyrrolylthallium, doubt may be expressed with respect to the products formulated from the reaction of the pyrrolyl compound with cyclopentadienyltitanium- or -zirconiumtrichloride. Based on the knowledge about the π-bonding capabilities of the unsubstituted pyrrolide ligand and the general stability of pyrrolyl (or aza-cyclopentadienyl) transition metal complexes [329], the mixed cyclopentadienyl(pyrrolyl)metal dichloride complexes with titanium and zirconium appear questionable.

Of major importance for the application as ligand transfer agents in this section are the hydrotris(pyrazolyl)borate thallium complexes. These are valued as a means of isolating and purifying the sterically more demanding tris(pyrazolyl)borate ligands. With increasing bulk of the pyrazolyl substituents, isolation of analytically pure samples of the sodium and potassium salts of the hindered tris(pyrazolyl)borate ligands is often problematic and conversion to crystalline thallium complexes by treatment with aqueous $TlNO_3$ or methanolic TlOAc in a metathesis reaction (method II, cf. Section 2.2.1) is often performed in order to obtain the ligands in pure form [15–17]. Subsequently, and because of their good solubility in hydrocarbon solvents, these thallium compounds are then used as ligand transfer agents just like the cyclopentadienyl derivatives. In comparison, this application aspect is, however, much more pronounced in TpTl chemistry than in CpTl. The tris(pyrazolyl)borate thallium complexes are not studied by themselves except perhaps for a recent NMR study [191]. The TpTl reagent can react with a transition- or main-group metal halide in a salt-elimination or metathesis reaction [Eq. (26)] with the formation of the Tp-metal moiety and thallous halide (TlX, as the thermodynamic driving force) and possibly elimination of additional ligands (e.g. CO) as the by-products [15,16,39,40], see also [330].

$$\mathrm{TpTl} + \mathrm{MXL}_y \rightarrow \mathrm{TpML}_z + \mathrm{TlX} + (y-z)L. \qquad (26)$$

In addition, TpTl reagents can also be reacted with dialkylmetal substrates, as was exemplified in the reactions of magnesium, zinc and cadmium dialkyls (MR_2) with $HB(3,5\text{-}R',R''\text{-}pz)_3Tl$ to give $\{HB(3,5\text{-}R',R''\text{-}pz)_3\}MR$ (Eq. (27)) [331–334]. Similarly, trimethylaluminum and $HB(3\text{-}^tBu\text{-}pz)_3Tl$ gave $HB(3\text{-}^tBu\text{-}pz)_3AlMe_2$ [335]. The driving force of these reactions is derived from the deposition of thallium metal, owing to the instability of TlR (see above: Section 2.1 and Section 4.2.1) [331–333].

$$\mathrm{MR_2 + HB(3,5\text{-}R',R''\text{-}pz)_3Tl \rightarrow HB(3,5\text{-}R',R''\text{-}pz)_3MR} \\ \mathrm{+ [TlR]_{decomposition}}, \qquad (27)$$

M = Mg, Zn, Cd; R = Me, Et, ^{i}Pr, ^{n}Bu, ^{t}Bu, CH_2SiMe_3, $CH=CH_2$, Ph.

R′ = ^{t}Bu, R″ = H; R′ = ^{t}Bu, R″ = Me; R′ = R″ = Me.

When the thallium complex HB(3-^{t}Bu-pz)$_3$Tl is reacted with Grignard reagents, RMgX, which offer both the chance of halide of alkyl metathesis [according to Eq. (26) *or* Eq. (27)], the latter (giving HB(3-^{t}Bu-pz)$_3$MgX) is favored for X = Cl and Br, only the iodo Grignard reagent prefers halide metathesis and formation of HB(3-^{t}Bu-pz)$_3$MgMe. The preference for alkyl metathesis is quite different from the behavior of the HB(3-^{t}Bu-pz)$_3$-potassium reagent which gives HB(3-^{t}Bu-pz)$_3$MgR as the principal products [332,336]. A listing of the applications for the TpTl compounds can be found in Table 10.

5.2.1. Recent results

The first alkylthallium(I) compound has just been unequivocally characterized [347]. Employing the bulky tris(trimethylsilyl)methyl ligand, the thallium derivative was prepared according to Eq. (28). In solution the compound is monomeric and decomposes slowly even at −50 °C, thereby being much less stable than the analogous gallium and indium complexes. No thallium–carbon coupling appeared to have been observed in the ^{13}C NMR spectrum in deutero-benzene. An X-ray structure of the red-violet, almost-black crystals of this alkylthallium compound (decays at 65 °C) showed a tetrameric arrangement in the solid state (Fig. 25) with quite long (in comparison to the indium analog) and uneven Tl–Tl contacts (range

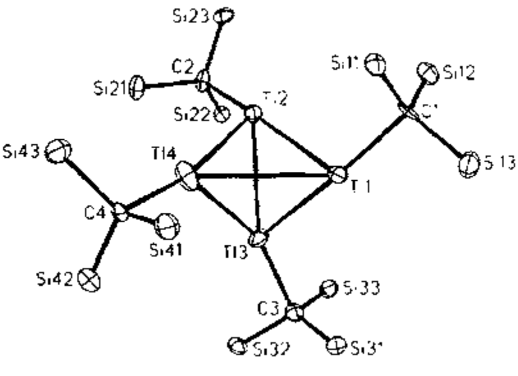


Fig. 25. Structure of the tetrameric unit of $(Me_3Si)_3CTl$ in the crystal (reprinted from Ref. [347] with permission from VCH Verlagsgesellschaft mbH, Weinheim, Germany).

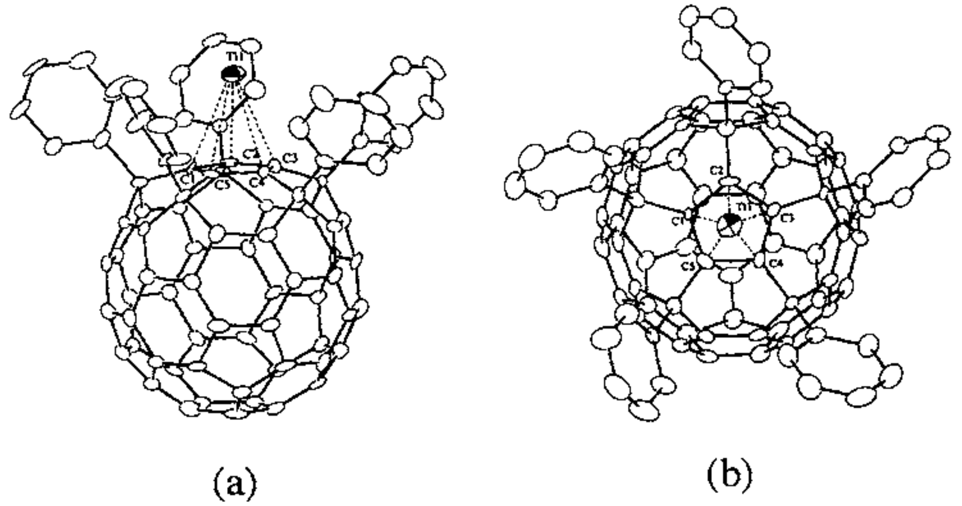


Fig. 26. View from the side (a) and from the top (b) of the molecular structure of $(\eta^5\text{-}C_{60}Ph_5)Tl \cdot 2.5$ THF [Tl–Cp(centroid) = 2.60 Å, Tl–C = 2.83–2.90 Å] (reprinted from Ref. [348] with permission, © 1996 American Chemical Society).

3.32–3.64 Å); Tl–C bond distances are 2.33 and 2.38 Å [347].

$$C_5H_5Tl + LiC(SiMe_3)_3 \cdot 2THF \xrightarrow{\text{toluene}} (Me_3Si)_3CTl + C_5H_5Li + 2THF. \qquad (28)$$

A thallium complex presented structural proof for the first pentahaptofullerene metal complex (transition metals were, so far, only found to bind η^2 across a C–C bond between two hexagons of a fullerene molecule) [348]. The key to this success was the synthesis of a pentaphenyl adduct of C_{60}, namely $C_{60}Ph_5H$, with one of the pentagons surrounded by phenyl groups and thereby isolated from the remaining 50 carbons as a cyclopenta*diene* moiety. Reaction of $C_{60}Ph_5H$ with TlOEt in THF then gave the thallium complex $(\eta^5\text{–}C_{60}Ph_5)Tl$, whose structure is illustrated in Fig. 26. From the side view of the structure it is evident that the thallium atom is buried in the cavity created by the phenyl rings, reminiscent of the structures of $C_5(CH_2Ph))_5Tl$ [8,213]. In its central part – involving the C_5-ring, the phenyl groups and the connecting carbon atoms (from which the fullerene sphere extends) – the $C_{60}Ph_5$ ligand can be compared with the $C_5(PhCH_2)_5$ ligand. Moreover, the chiral propeller array of the phenyl groups in $C_{60}Ph_5$ is also as found in the structure of decabenzylferrocene, $\{C_5(PhCH_2)_5\}_2Fe$ [205,349].

Acknowledgements

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