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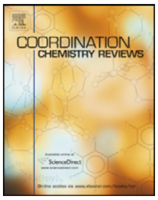

Review

Highly electrophilic main group compounds: Ether and arene thallium and zinc complexes

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Contents

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ABSTRACT

This review describes aspects of the chemistry of highly electrophilic compounds of thallium and zinc. Extremely weakly coordinating anions based on perfluorophenyl borates allow the synthesis and structural characterization of complexes in which cation–anion interactions are minimized. The metals are therefore able to coordinate weakly donating ligands without the structural distortions and limitations in coordination geometry that are always encountered when coordinating anions are present. This has led to the isolation of thallium mono-, bis- and tris-arene complexes, thallium–ferrocene multidecker structures and the determination of their bond energies. New types of ether and crown ether adducts, as well as the first examples of cationic alkylzinc derivatives have become similarly accessible. These ionic Zn compounds very effectively polymerize cyclic esters and epoxides. Arene coordination is also a feature of strongly Lewis acidic bis(perfluoroaryl)zinc compounds, which when combined with activated alkyl chlorides provide an excellent new type of initiator for the homo and copolymerization of isoalkenes. These systems have given rise to a new family of elastomer materials.

1. Introduction

The combination of metal ions and extremely weakly coordinating anions (WCAs) has proved particularly successful for the synthesis of highly electrophilic compounds. Coordinatively and electronically unsaturated organometallic systems show unprecedented reactivity and new insights into structure and bonding. This review attempts to illustrate this principle by describing some recent advances in the chemistry of electrophilic systems of thallium and zinc.

The degree of electrophilicity of a coordinatively unsaturated cationic metal complex, its ability to bind weakly coordinating ligands and its structure are strongly dependant on the nature of the counter anion. It is therefore appropriate to first consider these anions.

The combination of non-nucleophilic anions with cationic group 4 metal complexes has gained particular prominence in olefin polymerization catalysis where it has created new classes of soluble catalysts [1,2]. The often extremely high reactivity of these industrially very important systems strongly depends on the nature of the anion, and consequently much effort has been directed towards anion engineering. The chemistry of these "non-coordinating" or "super-weakly" coordinating anions [3] in the context of polymerization catalysis has been reviewed in some detail [4–10] and need not be repeated here. For catalysis with early transition metals, perfluoroarylborates have proved particularly effective, notably $[B(C_6F_5)_4]^-$ and $[Me–B(C_6F_5)_3]^-$ [11], the latter as the result of abstraction of a methyl ligand with $B(C_6F_5)_3$ [12,13]. Whereas the former has no dipole moment, the latter has a pronounced polarity and binds quite effectively to coordinatively unsaturated metal centres, giving zwitterionic complexes $L_nM(R)(\mu\text{-}Me)B(C_6F_5)_3$ [12,14]. Scheme 1 shows a number of perfluoroarylborate and -aluminate-based anions that have been

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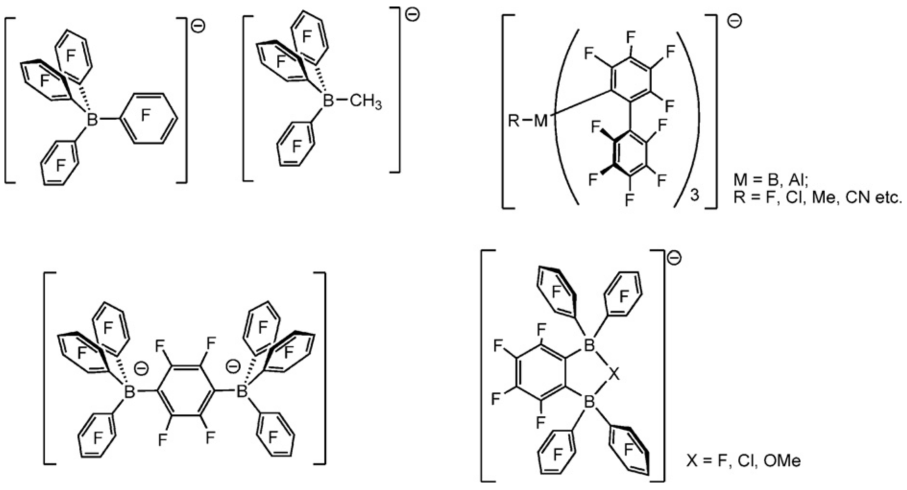
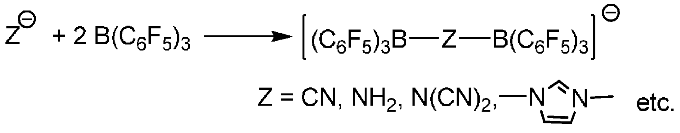


Scheme 1.

known to stabilize extremely electrophilic metal complexes. The design principle common to all are: (i) the need to delocalize the negative charge over as large a space as possible, (ii) chemical inertness, and (iii) resistance to one-electron-transfer reactions.

Some time ago we sought a simpler route to synthesize very non-nucleophilic anions by coordinating the strong Lewis acid $B(C_6F_5)_3$ to anionic bridging groups Z to give anions of the type $[Z\{B(C_6F_5)_3\}_n]^{x-}$ (Z = CN, $Ni(CN)_4$, NH_2) [15–17] (Eq. (1)), a strategy also pursued by workers at Dow [18]. These anions are readily accessible in high yields by reacting commercially available $B(C_6F_5)_3$ with KCN, $NaNH_2$ or similar linkers in diethyl ether, followed by transformation into the corresponding CPh_3^+ or $[H(OEt_2)_2]^+$ salts without prior isolation [15,17].



$$Z^{\ominus} + 2\,B(C_6F_5)_3 \longrightarrow \left[(C_6F_5)_3B{-}Z{-}B(C_6F_5)_3\right]^{\ominus} \qquad Z = CN,\ NH_2,\ N(CN)_2,\ \ldots\ \text{etc.} \tag{1}$$

The linear cyano-bridged anion $[CN\{B(C_6F_5)_3\}_2]^-$ has produced some of the most active ethylene polymerization catalysts ever reported [15] and has proved particularly effective in achieving very high molecular weight isobutene–isoprene copolymers if a metallocene/WCA combination is used as initiator in this cationic polymerization process [19]. Fig. 1 exemplifies the effect of WCAs in: (a) propene polymerization catalysis by a Ziegler-type catalyst (left) [16], and (b) as part of the activator system in the carbocationic isobutene polymerization (right). Evidently, the anion effects in these rather different reactions follow the same trend; in both cases the least coordinating anion gives the most successful systems.

The anion $[H_2N\{B(C_6F_5)_3\}_2]^-$ is of particular interest within the present context. It derives much of its chemical and thermal stability from hydrogen bonding between the NH_2 linker and neighboring C–F bonds (Fig. 2) [17,20] In terms of non-coordinating character and in catalysis, $[H_2N\{B(C_6F_5)_3\}_2]^-$ shows properties very similar to the "standard" anion $[B(C_6F_5)_4]^-$; both show extensive charge delocalization and are substantially more voluminous than most metal complex counter cations with which they may be paired (Fig. 1) [21]. However, the fact that $[H_2N\{B(C_6F_5)_3\}_2]^-$ has a dipole moment and shows directionality in its orientation towards the metal cation often leads to isolable crystalline materials, in contrast to $[B(C_6F_5)_4]^-$ which is almost spherical, most often disordered and tends to produce salts which are oils or glasses. For this reason the anion $[H_2N\{B(C_6F_5)_3\}_2]^-$ is preferred in our synthetic studies and has been used in most of the reactions reported here.

2. Thallium ether complexes

Thallium compounds of weakly coordinating anions attracted our interest primarily because thallium salts are frequently used as reagents for generating cationic metal complexes by halide abstraction; indeed $Tl[B(C_6F_5)_4]$ has been known for some time [22]. In the crystal, the thallium ion is stabilized by Tl···F contacts at varying distances ranging from 2.942(4) to 3.663(4) Å [23]. The coordination chemistry of thallium in the presence of very weakly coordinating anions had however not been investigated in detail, and it became apparent that many very simple compounds of thallium(I), such as ether complexes, had either not been made or not been structurally characterized. We therefore chose to briefly explore the bonding and structures of such compounds [24].

The reaction of thallium ethoxide with the strong Brønsted acid $[H(OEt_2)_2]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ in the presence of diethyl ether gave a compound with the composition $[Tl(OEt_2)_3][H_2N\{B(C_6F_5)_3\}_2]$ in 70% yield. The ^{19}F NMR spectrum showed three resonances at δ −133.5, −160.6 and −166.0, typical of a solvent-separated perfluorinated amidodiborate anion. Unlike $Tl[B\{3{,}5\text{-}C_6H_3(CF_3)_2\}_4]$ [25] and $Tl[B(C_6F_5)_4]$ [22], the thallium(I) salt of the amidodiborate could not be obtained free of Et_2O since the solvent molecules could not be removed even upon gentle heating under vacuum. This compound is very soluble in Et_2O and CH_2Cl_2 but dissolves only sparingly in aromatic hydrocarbons at room temperature. Recrystallization from a diethyl ether/light petroleum mixture at −26 °C gave colorless crystals of the tetra-ether adduct $[Tl(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$, which proved to be suitable for X-ray diffraction. The crystals are prone to ligand loss on exposure to vacuum. To the best of our knowledge, $[Tl(OEt_2)_4]^+$ is the first example of a structurally characterized thallium(I)–diethyl ether complex (Scheme 2). The thallium atom is disordered over three sites in the ratio ca. 85.0:11.5:3.5. In the principal Tl atom site, the metal is coordinated by four ether molecules in a distorted tetrahedral arrangement. The O–Tl–O angles range from 86.92(12)° to 132.97(12)°, in our view mainly due to packing forces, rather than to the effect of a sterically active lone pair. The thallium–oxygen bond lengths in the principal component are in the range 2.797–2.870 Å, with the Tl(1)–O(7) distance of 2.797(4) Å slightly shorter than the other three.

When the reaction of $[H(OEt_2)_2]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ with TlOEt was carried out in dichloromethane, microcrystalline $[Tl(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]\cdot CH_2Cl_2$ was obtained.

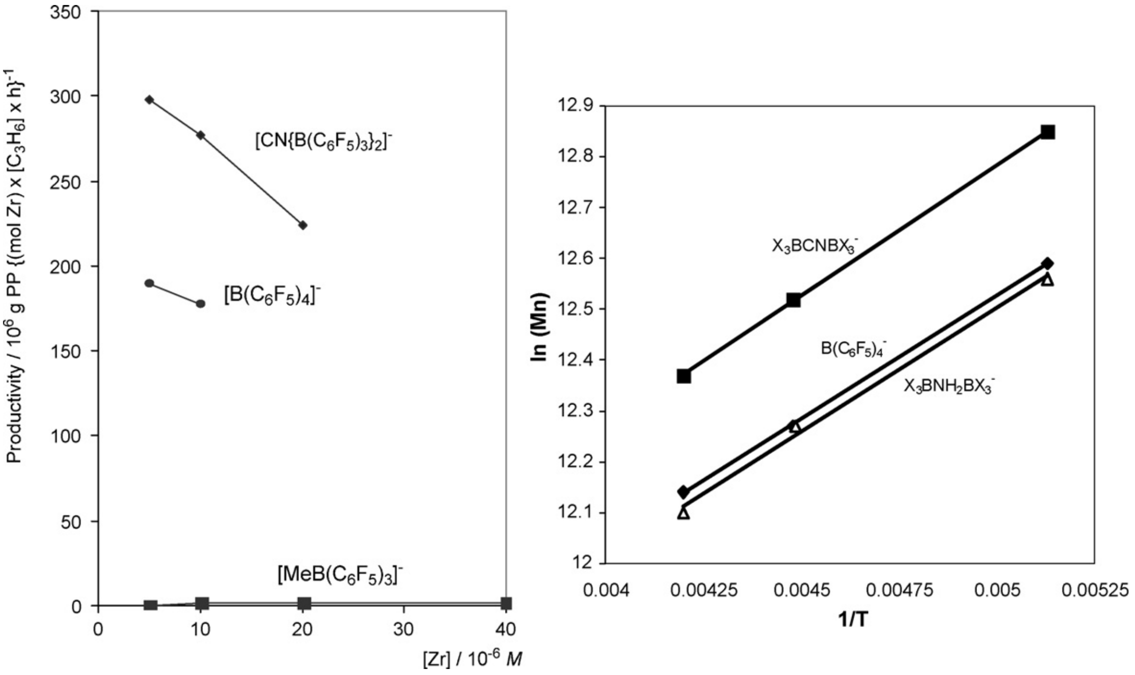
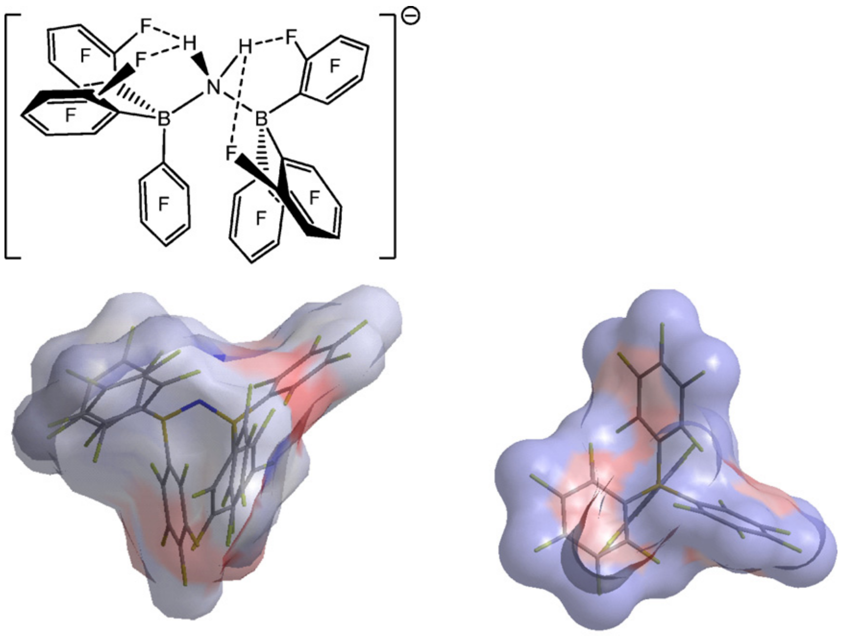


Fig. 1. Example of anion effects in polymerization processes. Left: dependence of propene polymerization productivity on the nature of the counter anion and the concentration of the zirconium catalyst (data from Ref. [16]). Right: temperature dependence of the number-average molecular weight M_n of isobutene/isoprene copolymers initiated with $[Cp'_4Zr_2H_3]^+[borate]^-$ as a function of the counter anion ($X = C_6F_5$) (data from Ref. [19]). Reproduced by permission. Copyright American Chemical Society.

The attempted recystallization of this product at −26 °C for several days gave colorless blocks of a hydrolysis product, $[Tl_4(\mu^3\text{–}OH)_2][H_2N\{B(C_6F_5)_3\}_2]_2{\cdot}4CH_2Cl_2$ in low yield (Scheme 3). The IR spectrum of this compound showed diagnostic OH and NH_2 bands at 3610 and 3565 cm^{-1} (OH) and 3384 and 3345 cm^{-1} (NH_2).

The crystallographic identification of this product showed that it contained the unusual hydroxyl-bridged dication, $[Tl_4(\mu^3\text{–}OH)_2]^{2+}$, consisting of a central $Tl_2(OH)_2$ core with both oxygen atoms coordinated to the two bridging and to a terminal thallium atoms. The O–Tl distances to the bridging Tl atoms are noticeably longer than to the terminal ones. There are also various C–F···Tl and C–F···H–O contacts; e.g. O(1)–H(1)···F(5^E) shows a short distance of 2.30 Å. The thallium atoms are four-coordinate; the terminal ones have contacts to two F atoms of the neighboring counter anion and one Cl atom from a dichloromethane molecule, while the two bridging Tl atoms show strong interactions to two F atoms each.

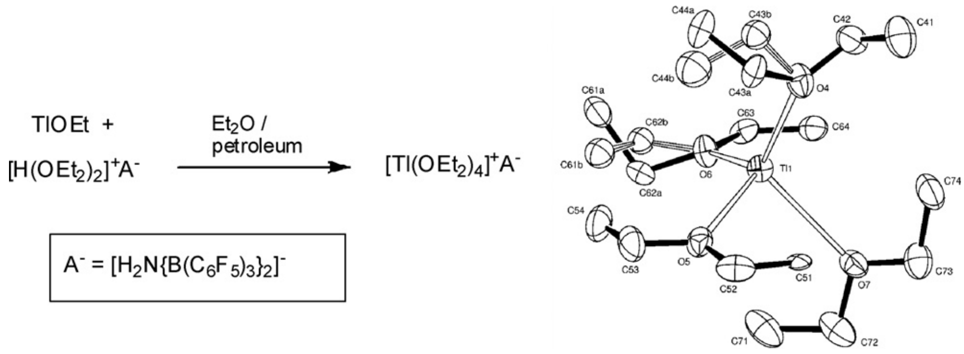
A number of related ether complexes are readily accessible; for example salts of $[Tl(OEt_2)_2(DME)]^+$,



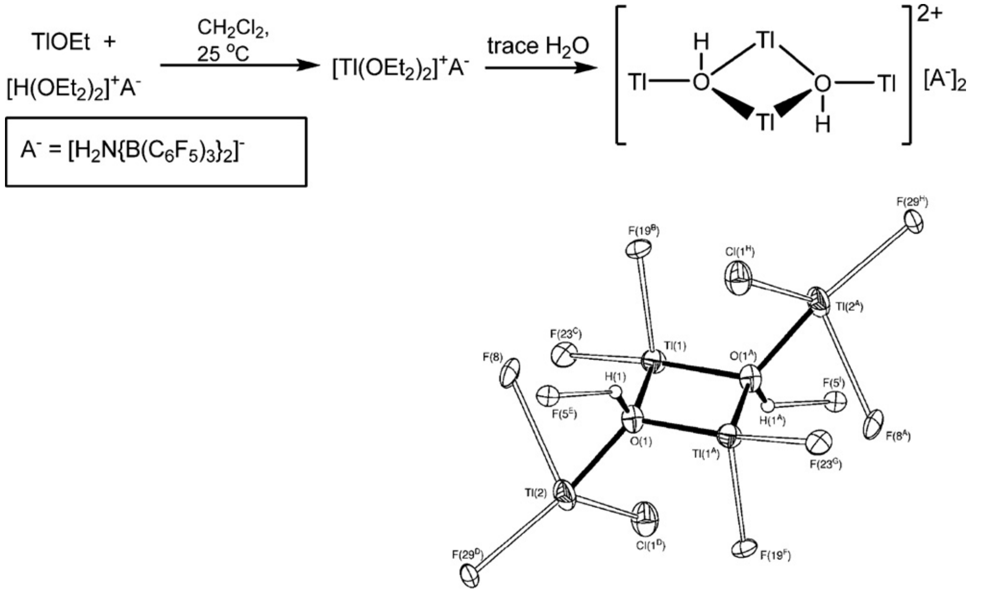
$[H_2N\{B(C_6F_5)_3\}_2]^-$, volume 621 A^3

$[B(C_6F_5)_4]^-$, volume 405 A^3

Fig. 2. Structure and Van der Waals volumes of the $[H_2N\{B(C_6F_5)_3\}_2]^-$ anion in comparison to $[B(C_6F_5)_4]^-$.



Scheme 2. The structure of the $[Tl(OEt_2)_4]^+$ with an indication of the disorder. There are no close contacts to the counter anion.



Scheme 3. Synthesis and structure of the $[Tl_4(\mu^3\text{–}OH)_2]^{2+}$ dication, showing contacts to F and Cl atoms of the counter anion and dichloromethane of solvation, respectively.

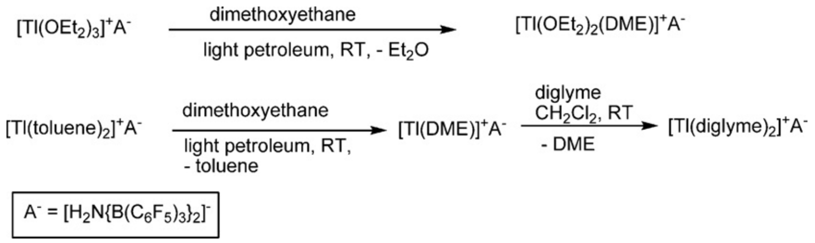
$[Tl(DME)]^+$, and $[Tl(diglyme)_2]^+$ were made according to Scheme 4.

Of potentially more interest are crown ether complexes. Compounds of that type have attracted attention for example for the recognition of Tl^+ by fluorogenic calixarene derivatives [26] and because of the high cation binding ability of benzo-crown ethers [27]. Thallium complexes of crown ethers exist either as sandwich-like 1:2 adducts $[Tl(crown)_2]^+$, or 1:1 complexes $[Tl(crown)]^+$. In the latter the thallium atom is usually displaced out of the plane defined by the oxygen atoms, a phenomenon referred to as the "sunrise conformation". This contrasts with the structures of the corresponding complexes of K^+ and Pb^+; these ions have similar ionic radii but are located within the ether–oxygen plane.

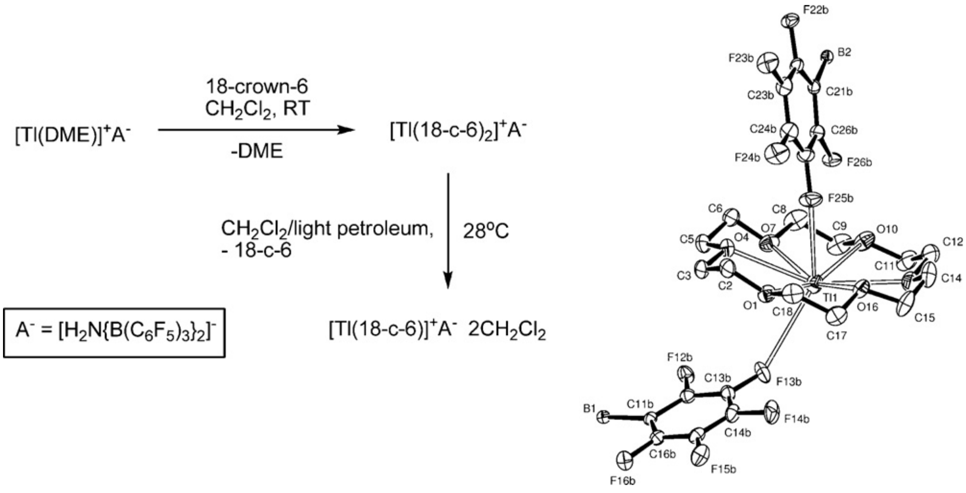
The ligand exchange reaction of $[Tl(DME)][H_2N\{B(C_6F_5)_3\}_2]$ with 18-crown-6 in dichloromethane gives the 1:2 complex $[Tl(18\text{-crown-}6)_2][H_2N\{B(C_6F_5)_3\}_2]$. On recrystallization from a CH_2Cl_2/light petroleum mixture, however, single crystals of the 1:1 adduct $[Tl(18\text{-crown-}6)][H_2N\{B(C_6F_5)_3\}_2]\cdot 2CH_2Cl_2$ were isolated (Scheme 5).

Whereas $[Tl(OEt_2)_4]^+$ was four-coordinate without close contacts to the counter anion, the metal centre in $[Tl(18\text{-crown-}6)][H_2N\{B(C_6F_5)_3\}_2]$ is eight-coordinate, including two interactions to meta-F atoms of neighboring anions of 3.111(2) and 3.105(2) Å. The F···Tl···F arrangement is bent, 126.86(5)°.

The structures of thallium crown ether complexes have been studied in some detail, not least in respect of the possible stereochemical role of the "inert" ion pair of Tl^+. This is in spite of the very significant relativistic stabilization of the $6s^2$ level, which reduces s–p mixing [28]. A number of early reports have



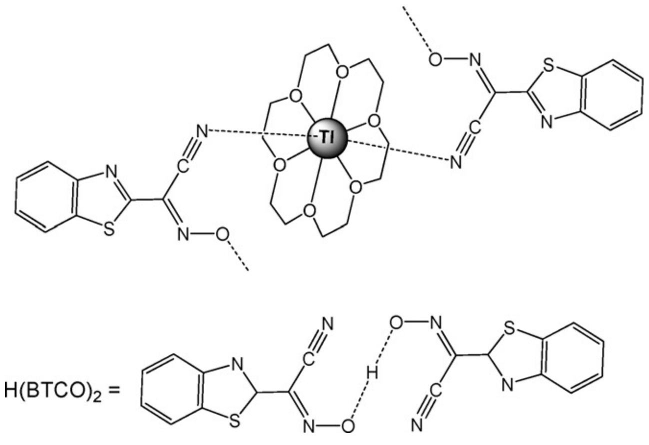
Scheme 4. Syntheses of thallium ether complexes.



Scheme 5. Synthesis of thallium crown ether complexes and the partial structure of $[Tl(18\text{-crown-}6)][H_2N\{B(C_6F_5)_3\}_2]\cdot 2CH_2Cl_2$ showing the cation–anion close contacts.

correlated distortions in the structure of thallium crown ether complexes with the effect of a stereochemically active lone pair. For example, [Tl(18-crown-6)][TCNQ] consists of two tetracyanoquinodimethanide radical anions bridging two $[Tl(18c6)]^+$ cations, in an arrangement that evidently involves significant Tl^+-anion Coulomb interactions [29]. The 26.4° tilt angle of the oxygen planes in $[Tl(12c4)_2]^+$ was also ascribed to the thallium electron pair effect, even though this distortion was absent in the closely related $[Pb^{II}(15c5)_2]^{2+}$ ion [30]. A survey of a number of thallium crown ether complexes shows that although the thallium atom is almost invariably displaced out of the crown ether plane, the extent of this displacement is highly variable and ranges from 1.34 Å in $[Tl(18c6)_2][TlI_4]\cdot 2H_2O$ [31] to less than half that value in $[Tl(18c6)][H_2N\{B(C_6F_5)_3\}_2]$ [24]. One example has been reported, $[Tl(18c6)][H(BTCO)_2]$ (Scheme 6), which showed no displacement of the metal out of the crown ether plane [32].

Table 1 summarizes the displacement of the thallium atoms from the O_6-plane of the crown ether ligands for a representative number of such complexes. Although one might have expected the distortion (due either to the thallium lone pair or repulsive interactions with the oxygen lone pairs) to be most prominent in cases where the anion interacts least with the metal centre, the opposite is found, and the displacement is smallest in the compound that contains the least nucleophilic anion, $[Tl(18c6)][H_2N\{B(C_6F_5)_3\}_2]$ (0.56 Å). This seems to indicate that electrostatic and bonding interactions in these compounds are a major if not the dominant cause of the observed displacements.



Scheme 6. Solid-state structure of $[Tl(18c6)][H(BTCO)_2]$.

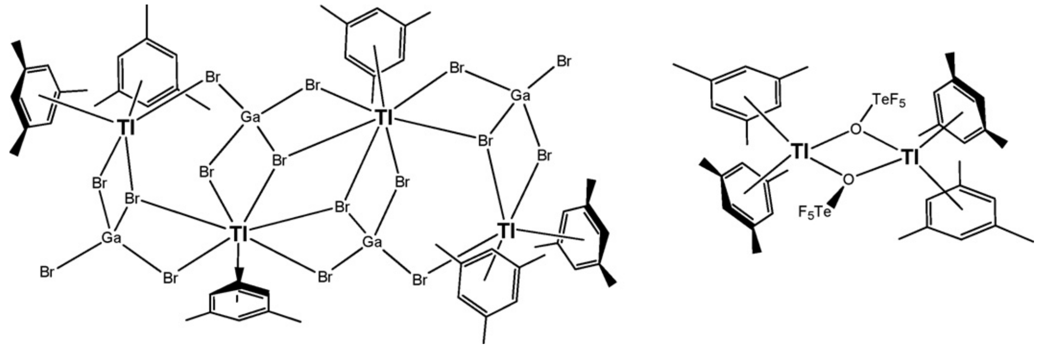
3. Thallium arene complexes

Thallium binds only weakly to π-ligands such as aromatic compounds, and such complexes can only be isolated with relatively weakly coordinating anions. The first examples, the benzene adducts $(C_6H_6)_2\cdot TlAlCl_4$ and $C_6H_6\cdot 2(TlAlCl_4)$, were reported by Amma and coworkers in the late 1960s [37], but these compounds could only be identified by elemental analysis. In 1985 Schmidbaur described the first structurally characterized Tl(I) arene complex, $[(mes)_6Tl_4][GaBr_4]_4$ [38], which consists of a tetrameric $[TlGaBr_4]_4$ framework where two $Tl(mes)^+$ and two $Tl(mes)_2{}^+$ cations are bridged by four $[GaBr_4]^-$ anions (mes = mesitylene, 1,3,5-$C_6H_3Me_3$) (Scheme 7). The thallium atoms in this framework may be considered as five- and seven-coordinate (Scheme 7). In both cations the mesitylene ligands are η^6-bonded, with Tl···centroid distances between 2.94 and 3.03 Å. Schmidbaur's initial discovery was rapidly followed by Strauss' characterization of $[TlOTeF_5(mes)_2]_2\cdot mes$ (Scheme 7) and $[Tl(mes)_2][B(OTeF_5)_4]$ (Fig. 3) [39,40], two complexes where the mesitylene molecules are also η^6-coordinated to the metal ions with $Tl\cdots C_{arene}$ distances in the regions of 3.12–3.52 and 3.12–3.22 Å, respectively. More recently, Frank et al. characterized dimeric complexes $[Tl(arene)_2(MCl_4)]_2$ (M = Al, arene = mesitylene, 1,2,4-trimethylbenzene; M = Ga, arene = 1,2,4-trimethylbenzene) which all exhibit $Tl\cdots C_{arene}$ distances in the range of 3.23–3.41 Å [41].

Several complexes involve less highly substituted arenes. The paracyclophane complex $[Tl(p\text{-}C_6H_4CH_2CH_2)_2][GaCl_4]$ contains one-dimensional $Tl\cdots(p\text{-}C_6H_4CH_2CH_2)\cdots Tl\cdots(p\text{-}C_6H_4CH_2CH_2)$ stacks formed via η^6-coordination of the outer side of the benzene rings to the thallium atoms (Tl···centroid = 2.95 Å) [42].

Table 1
Distances of Tl^+ from the least-squares plane defined by O atoms in crown ethers.

Compound	Out-of-plane displacement	Refs.
$[Tl(18c6)_2][TlI_4]\cdot 2H_2O$	1.34(1) Å	[31]
$[Tl(18c6)][Cl_3CC(O)NP(O)(OMe)_2]$	1.13 Å	[33]
$[(Tl@18c6)_4CuBr_4][TlBr_4]_2$	1.10 Å	[34]
$[(Tl@18c6)_4MnCl_4][TlCl_4]_2$	0.93 Å	[35]
$[(Tl@18c6)_4CuCl_4][TlCl_4]_2\cdot 0.25H_2O$	0.92 Å	[36]
$[Tl(18c6)][TCNQ]$	0.89 Å	[29]
$[Tl(18c6)][ClO_4]$	0.75 Å	[28]
$[Tl(18c6)][TlI_4]$	0.66 Å	[28]
$[Tl(18c6)][H_2N\{B(C_6F_5)_3\}_2]\cdot 2CH_2Cl_2$	0.562 Å	[24]
$[Tl(18c6)][H(BTCO)_2]$	0	[32]



Scheme 7. Structures of thallium mesitylene complexes with $GaBr_4^-$ and $OTeF_5^-$ anions [38,39].

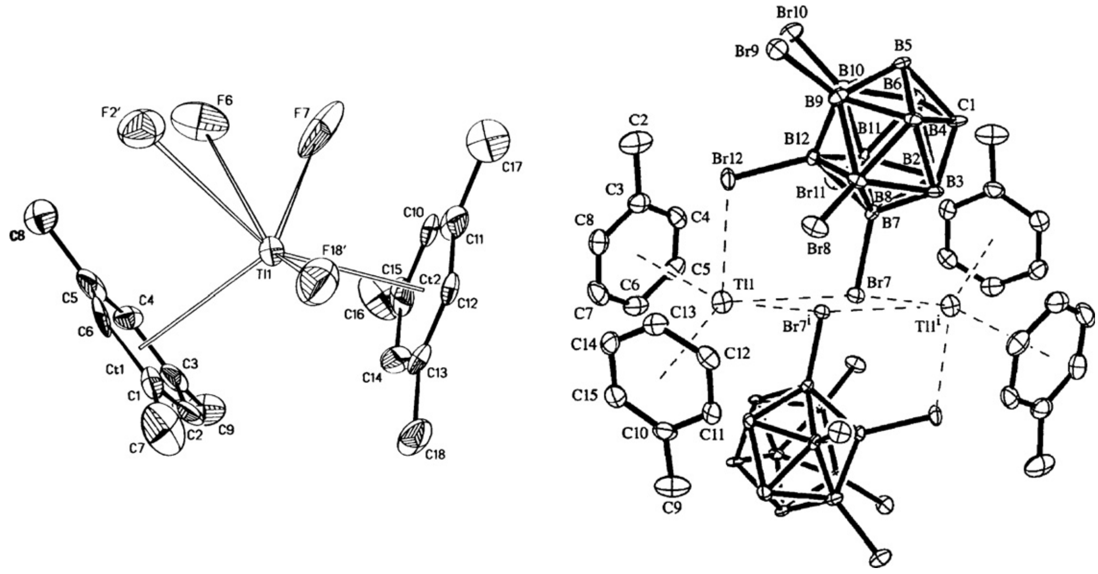
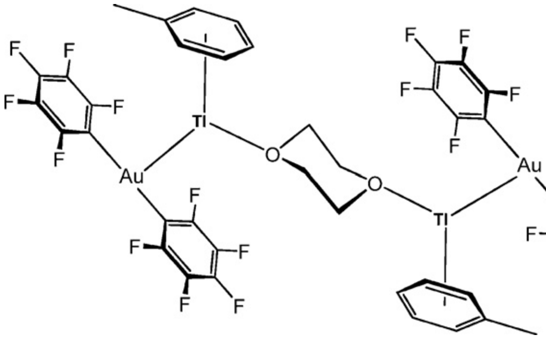


Fig. 3. Coordination environment of thallium in $Tl(mes)_2\{B(OTeF_5)_4\}$ [40] (left) and $[Tl(toluene)_2][CB_{11}H_6Br_6]$ [44] (right). Reproduced by permission. Copyright (1987) American Chemical Society (Ref. [40]) and International Union of Crystallography (1997) (Ref. [44]).

A number of thallium–toluene complexes have been characterized. Hawthorne described the structure of $Tl[Al(C_2B_9H_{11})_2]\cdot(2/3)$toluene in which thallium is supported by coordination to toluene ($Tl\cdots C_{arene} = 3.17–3.23$ Å) as well as by close contacts to H–B and H–C bonds of the carboranyl anion [43]. Reed prepared $[Tl(toluene)_2][CB_{11}H_6Br_6]$, a dimer where two of the bromine atoms of each halocarborane anion coordinate to thallium, one of them bridging two Tl atoms (Fig. 3) ($Tl\cdots C_{arene} = 3.21–3.50$ Å) [44]. The gold–thallium complex (η^6-toluene)$TlAu(C_6F_5)_2$(dioxane) (Scheme 8) contains thallium in a trigonal-planar geometry, with a $Tl–Ct_{tol}$ distance of 3.079 Å and a remarkably short Tl–Au bond of 2.8935(3) Å; the compound exhibits blue luminescence [45].

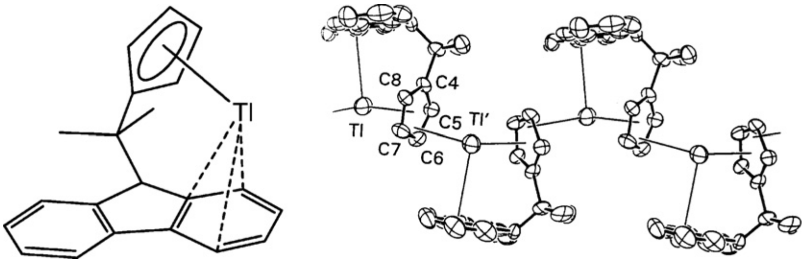


Scheme 8.

In addition to these salts, there are also several cases of intramolecular Tl(I)···arene interactions, i.e. where the arene is part of a ligand framework covalently bound to the metal [46–56]. An example is the thallium cyclopentadienide $Tl(C_5H_4)CMe_2$(1-fluorenyl) which forms either chains or layers constructed from Tl–Cp and Tl–C_6 π-interactions (Scheme 9) [47].

All these thallium(I) arene adducts display significant stabilizing Tl···X (X = halogen or oxygen) interactions with the counter anion which profoundly influence the thallium coordination geometry and the structure of the salts in the solid-state. We therefore undertook a study of the structure of thallium arene complexes in which cation–anion interactions were minimized. The chemistry of arene complexes of gallium has recently been reviewed [57].

Passing dry argon through warm (75 °C) toluene suspensions of $[Tl(Et_2O)_x][H_2N\{B(C_6F_5)_3\}_2]$ leads to loss of diethyl ether and formation of a solid of composition $[Tl(toluene)_2][H_2N\{B(C_6F_5)_3\}_2]$. Recrystallization from toluene gave $[Tl(toluene)_3][H_2N\{B(C_6F_5)_3\}_2]$, to the best of our knowledge the first example of a tris-toluene complex of thallium. The metal centre is surrounded by three π-bonded arenes in a trigonal-planar environment, as indicated by the sum of the centroid–Tl–centroid



Scheme 9. Chain modification of Tl(C_5H_4)CMe_2(1-fluorenyl) showing intramolecular arene–thallium interactions [47]. Reproduced by permission. Copyright (1993) Wiley-VCH.

angles of 359.7°. The average Tl–centroid distance is 2.966 Å. These Tl–toluene distances compare well with the shortest observed so far; the data are given in Table 2 for comparison. The nearest fluorine atom of the anion is further than the sum of the van der Waals radii of F and Tl, and there is no appreciable cation–anion interaction (Scheme 10).

Similarly, warming the thallium ether complexes to 75 °C in the presence of a large excess of hexamethylbenzene followed by recrystallization from dichloromethane gave the sandwich complex [Tl(C_6Me_6)$_2$][$H_2N\{B(C_6F_5)_3\}_2$]·1.5CH_2Cl_2. Previous attempts at isolating a thallium(I)–hexamethylbenzene complex have been reported to have failed [38a]. Although subsequent DFT calculations showed an energetic preference for the tris-arene adduct, only two arene ligands are coordinated, undoubtedly due to the bulk of C_6Me_6.

The structures of the toluene and hexamethylbenzene complexes are shown in Fig. 4. The C_6Me_6 molecules are η^6-coordinated, with very short Tl···centroid distances of 2.789 and 2.855 Å (cf. Table 2). Remarkably, neither structures shows any close contacts between thallium and the anions, that is to say, the Tl···F distances are significantly (ca. 0.2 Å) longer than the sum of the van der Waals radii of Tl and F (3.35 Å). This provides the structural data

Table 2
Geometric parameters for Tl(I)–arene complexes.

Compound	Anion A	Tl^+–A interaction	Closest Tl···A distance (Å)	Tl···Ctr[a] (Å)	Tl···C_{ring} (Å)	Refs.
[Tl(toluene)$_3$]A	$H_2N\{B(C_6F_5)_3\}_2$	No	3.43	3.01 2.95 2.94	3.16–3.35	[24]
[Tl(C_6Me_6)$_2$]A·2.5CH_2Cl_2	$H_2N\{B(C_6F_5)_3\}_2$	No	3.53 3.55	2.79 2.85	3.11–3.15 3.15–3.20	[24]
[Tl(C_6Me_6)]A·2CH_2Cl_2	$H_2N\{B(C_6F_5)_3\}_2$	Yes	3.15	2.723	2.99–3.13	[58]
[Tl_2($FeCp_2$)$_3$][A]$_2$·5CH_2Cl_2	$H_2N\{B(C_6F_5)_3\}_2$	Yes	3.03 3.26 3.18	2.92 2.93	3.07–3.26 3.05–3.28	[24]
[Tl(Cp_2Fe)]A·CH_2Cl_2	$H_2N\{B(C_6F_5)_3\}_2$	Yes	3.19	2.794	2.97–3.13	[58]
[Tl_4(mes)$_6$][A]$_4$[c]	$GaBr_4$	Yes	3.35	2.94 3.01 3.03		[38]
[Tl(A)(mes)$_2$]$_2$·mes[c]	$OTeF_5$	Yes	2.69 2.70		3.35–3.43 3.13–3.52	[39]
[Tl(mes)$_2$][A][c]	B($OTeF_5$)$_4$	Yes	2.69 2.70 2.71		3.12–3.22 3.14–3.21	[40]
Tl[A]·(2/3)tol[b]	Al($C_2B_9H_{11}$)$_2$	Yes	2.75 2.79		3.17–3.24	[43]
[Tl(pcp)$_2$][A][d]	$GaCl_4$	Yes	3.28 3.37	2.95	3.16–3.44	[42]
[Tl(mes)$_2$]$_2$[A]$_2$	$AlCl_4$	Yes	3.21 3.29	2.94 3.01	3.16–3.34 3.25–3.39	[41a]
[Tl(tmb)$_2$]$_2$[A]$_2$[e]	$AlCl_4$	Yes	3.36 3.34	2.96 3.06	3.23–3.29 3.30–3.41	[41b]
[Tl(tmb)$_2$]$_2$[A]$_2$[e]	$GaCl_4$	Yes	3.33	2.97 3.07	3.25–3.30 3.30–3.41	[41b]
[Tl(tol)$_2$][A][b]	$CB_{11}H_6Br_6$	Yes	3.39 3.42 3.59	2.99 3.09	3.21–3.35 3.27–3.50	[44]

[a] Ctr = centroid.
[b] tol = toluene.
[c] mes = 1,3,5-$Me_3C_3H_6$.
[d] pcp = [2,2]paracyclophane.
[e] tmb = 1,3,4-$Me_3C_3H_6$.

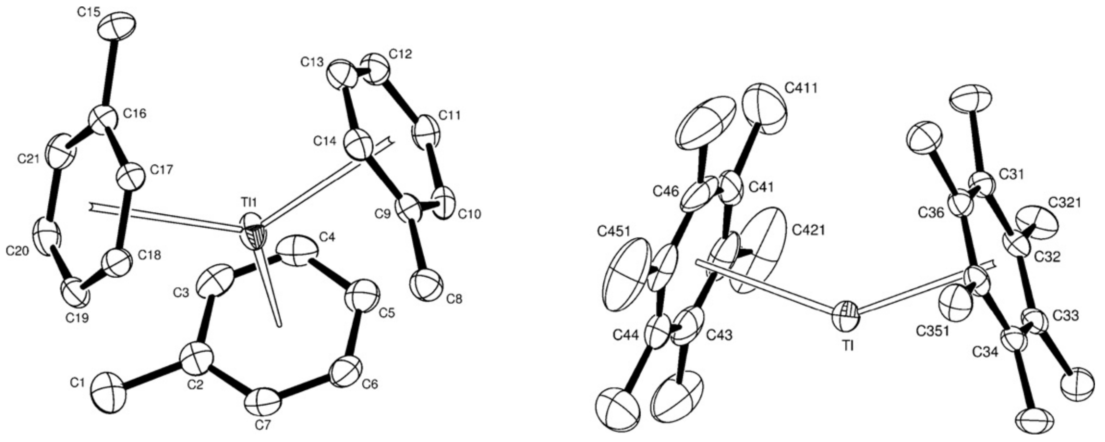
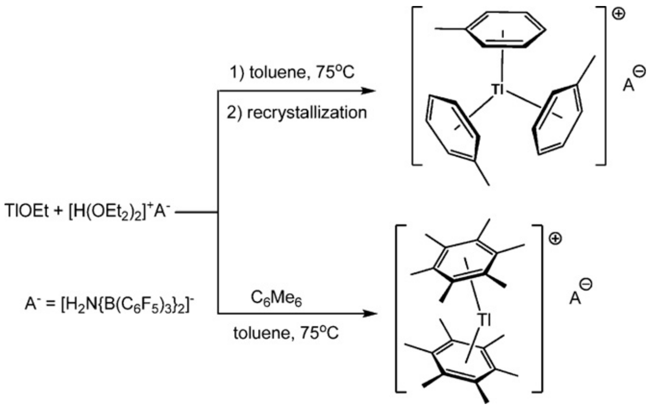


Fig. 4. Structures of $[Tl(toluene)_3]^+$ (left) and $[Tl(C_6Me_6)_2]^+$ (right). Reproduced by permission from [24]. Copyright (2007) American Chemical Society.



Scheme 10.

for calculations to probe the thallium–arene bonding with minimal interference by the anion. The thallium sandwich has a bent geometry, with a Ctr(1)–Tl–Ctr(2) angle of 142.4°, rather larger than the corresponding angle in $[Tl(toluene)_2][CB_{11}H_6Br_6]$ (111.8°) [44]. The wider angle is likely due to the lack of interaction between Tl^+ and the anion, whereas in $[Tl(toluene)_2][CB_{11}H_6Br_6]$ there are three additional Tl···Br contacts.

Passing argon through a warm solution of $[Tl(C_6Me_6)_2][H_2N\{B(C_6F_5)_3\}_2]\cdot 1.5CH_2Cl_2$ in toluene heated to 75 °C, followed by drying in vacuo, allowed the isolation of the half-sandwich complex $[Tl(C_6Me_6)][H_2N\{B(C_6F_5)_3\}_2]$ [58] which crystallized with two molecules of CH_2Cl_2. Here the hexamethylbenzene is bound even tighter, and the Tl–centroid distance of 2.723 Å is the shortest reported to date. In the crystal the coordination sphere of $[(C_6Me_6)Tl]^+$ is completed by a contact to a chlorine atom of CH_2Cl_2 (3.448(4) Å) and five contacts to fluorine atoms of the anion at distances of 3.154(5)–3.325(5) Å but without any

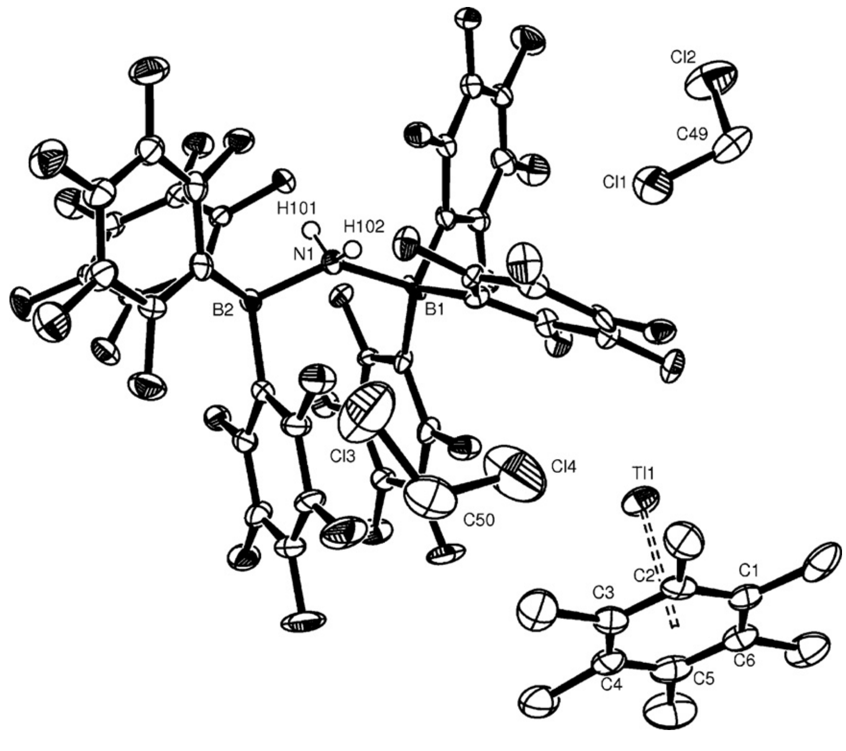


Fig. 5. Solid-state structure of the half-sandwich complex $[Tl(C_6Me_6)]$–$[H_2N\{B(C_6F_5)_3\}_2]\cdot 2CH_2Cl_2$. Reproduced by permission from Ref. [58]. Copyright (2007) American Chemical Society.

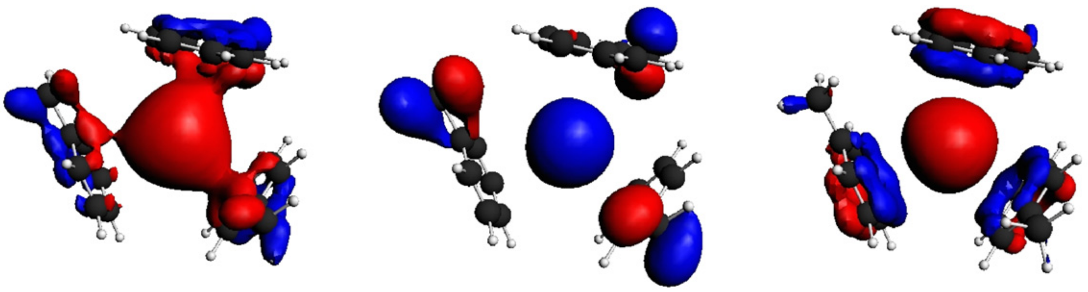


Fig. 6. Molecular orbitals in $[Tl(tol)_3]^+$. Left: bonding between the Tl and the in-phase combination of the toluene π_1 orbitals. Centre: thallium–toluene non-bonding. Right: anti-bonding between Tl and the in-phase combination of the toluene π_1 orbitals. Reproduced by permission from Ref. [24]. Copyright (2007) American Chemical Society.

apparent directional nature. This complex is the first example of a discrete half-sandwich complex of thallium (Fig. 5).

Density functional theory calculations on the thallium arene complexes showed that the observed structures represent very shallow energy minima, i.e. there are no electronic preferences, and the geometry of the complexes is determined by primarily if not exclusively steric interactions. The Mulliken charge for Tl in $[Tl(tol)_3]^+$ is +0.90, remarkably close to the formal oxidation state, and indicates that the overall charge of this complex is very much localized on the metal atom. Arene bonding is therefore mainly electrostatic in nature. The computed interaction energy between the three toluene ligands and the Tl^+ ion in $[Tl(tol)_3]^+$ is 221 kJ mol^{-1}, i.e. 73.7 kJ mol^{-1} per toluene. Fig. 6 shows representative molecular orbitals.

The computed interaction energy in $[Tl(C_6Me_6)_2]^+$ is larger, 243.4 or 121.7 kJ mol^{-1} per arene, in line with the observed shorter Tl–Ctr(C_6Me_6) distances. The mono-arene complex $[Tl(C_6Me_6)]^+$ shows an even higher interaction energy, 163 kJ mol^{-1} [58]. Varying the Ctr–Tl–Ctr angle in $[Tl(C_6Me_6)_2]^+$ in an effort to probe whether a linear or bent geometry is the most stable revealed a very flat potential energy surface, again confirming the absence of any directional electronic influences (Fig. 7). The deviation from linearity in the crystal structure is therefore likely due to packing forces.

Overall there is an energetic preference for thallium coordinating three arene molecules. $Tl(tol)_2{}^+$ plus an isolated toluene ligand was calculated to be 50 kJ mol^{-1} less stable than $[Tl(tol)_3]^+$. On the other hand, $[Tl(C_6Me_6)_2]^+$ plus an isolated C_6Me_6 molecule was only 28 kJ mol^{-1} less stable than $[Tl(C_6Me_6)_3]^+$. Hence, it is favorable for both systems to coordinate three arene rings, but less so for the bulkier C_6Me_6 system. Although it is possible $[Tl(C_6Me_6)_3][H_2N\{B(C_6F_5)_3\}_2]$ could have been formed as initial product that lost C_6Me_6 during work-up, there is as yet no evidence for this.

The reaction of thallium(I) with ferrocenes can take two courses: redox reactions, i.e. electron transfer, or complex formation. The first is illustrated by the reaction of $[Tl(toluene)_n][H_2N\{B(C_6F_5)_3\}_2]$ with $Fe(C_5Me_5)_2$, which leads to thallium metal and the corresponding $[Fe(C_5Me_5)_2]^+$ salt. The latter occurs with ferrocene itself. Thus adding ferrocene to $[Tl(toluene)_2][H_2N\{B(C_6F_5)_3\}_2]$ in dichloromethane at room temperature (Scheme 11) gave a product of the composition $[Tl_2(FeCp_2)_3][H_2N\{B(C_6F_5)_3\}_2]_2 \cdot 5CH_2Cl_2$ [24].

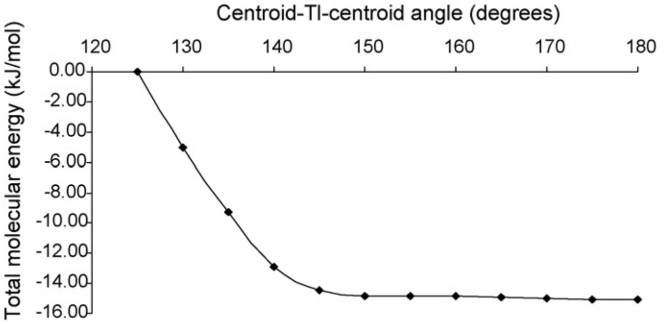
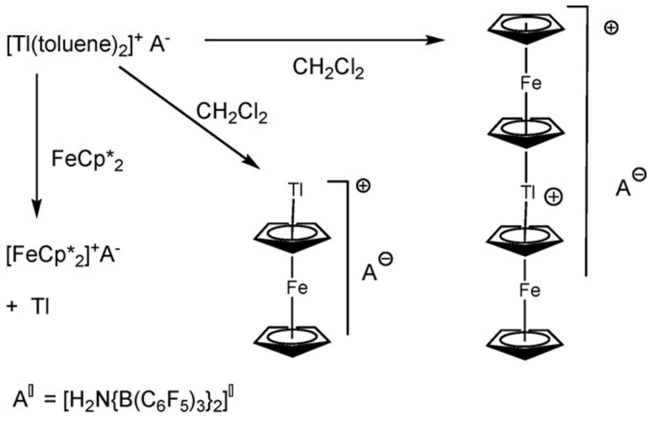


Fig. 7. Total molecular energy in $[Tl(C_6Me_6)_2]^+$ as a function of the Ctr–Tl–Ctr angle. The energy of the molecule was arbitrarily set to 0 kJ mol^{-1} for ⟨Ctr–Tl–Ctr = 125°. Reproduced by permission from Ref. [24]. Copyright (2007) American Chemical Society.



Scheme 11.

The crystal structure (Fig. 8) showed that the compound did not contain a multidecker $[Fc–Tl–Fc–Tl–Fc]^{2+}$ dication but rather a 1:1 mixture of $[Tl(Fc)_2]^+$ and $[Tl(Fc)]^+$ (Fc = $FeCp_2$), with sandwich and half-sandwich structures, respectively. There are also weak interactions with the anion, which give the $[Tl(Fc)_2]^+$ cation a square-planar geometry. The half-sandwich compound $[Tl(Fc)][H_2N\{B(C_6F_5)_3\}_2]$ has also been obtained in pure form and structurally characterized (Fig. 9) [58]. These ferrocene adducts may therefore be seen as models for the pre-complex that must be formed prior to electron transfer with more easily reduced ferrocenes.

These compounds represent the first examples of thallium–metallocene π-complexes; the structures resemble those recently reported for the mixed-valence Ga(I, III) complex $[Ga(Fc)][GaCl_4]$ (Scheme 12) [59].

The computed interaction energy between the thallium atom and ferrocene was found to be 129 kJ mol^{-1}, significantly less than the binding energy for hexamethylbenzene, a consequence of the lower donor strength of ferrocene.

4. Zinc complexes

Whereas thallium salts with sufficient electrophilic character to effectively bind arenes are readily accessible, related species of metals like zinc and magnesium proved more elusive. The main reason is that highly electrophilic cationic species of these lighter elements have a strong tendency to attack counter anions of the perfluoroarylborate type. Lack of π-ligands and coordinative unsat-

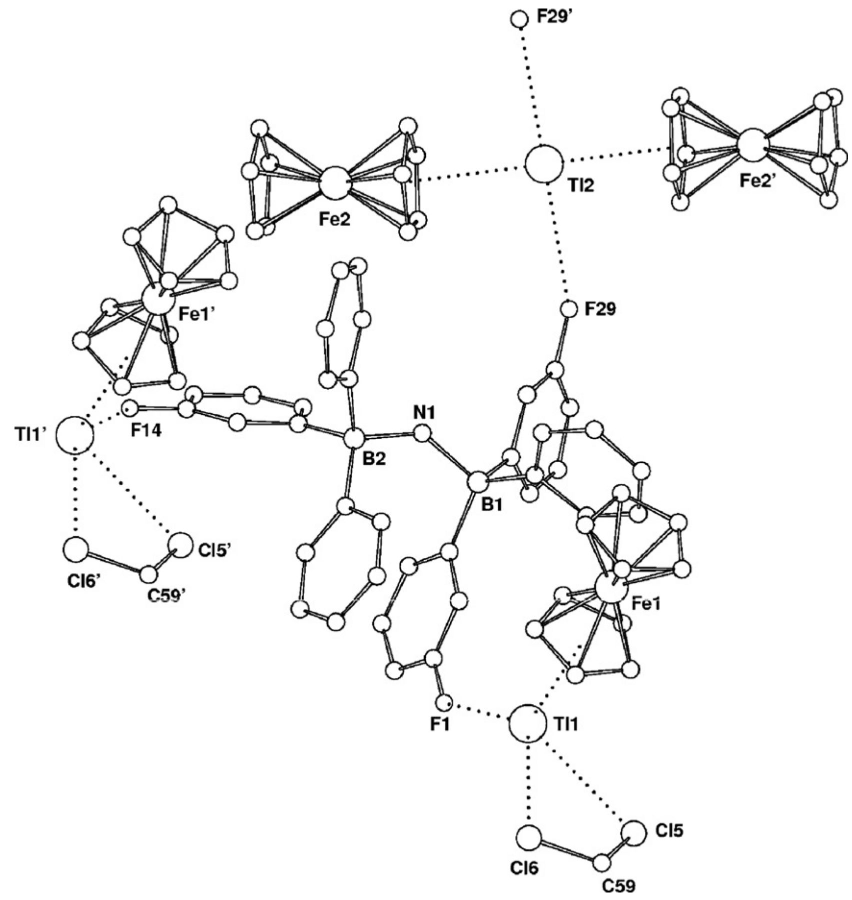


Fig. 8. Crystal structure of $[Tl_2(FeCp_2)_3][H_2N\{B(C_6F_5)_3\}_2]_2{\cdot}5CH_2Cl_2$ showing the positions of the $[Tl(Fc)_2]^+$ and $[Tl(Fc)]^+$ cations. The Tl(2)–F(29) distance of 3.1833(3) Å is slightly shorter than the sum of the van der Waals radii (3.35 Å). Reproduced by permission from Ref. [24]. Copyright (2007) American Chemical Society.

uration facilitate this process. For example, while the reaction of $MeAlCp_2$ with $B(C_6F_5)_3$ gives salts of the cationic aluminium sandwich $[AlCp_2][MeB(C_6F_5)_3]$ which acts as a powerful initiator for the polymerization of isobutene [60], the reaction of $AlMe_3$ with $B(C_6F_5)_3$ readily leads to alkyl/aryl exchange to give $Al(C_6F_5)_3$ [61]. The same product is obtained from the reaction of aluminium alkyls with $[CPh_3][B(C_6F_5)_4]$ [62]. Similarly, zinc alkyls ZnR_2 (for R = Me, Et) react with $B(C_6F_5)_3$ to give BMe_3 and $Zn(C_6F_5)_2$. Ion pairs or zwitterions of the type $XZn(\mu\text{-}Me)B(C_6F_5)_3$ (X = Me or C_6F_5) could not be detected.

On the other hand, there was evidence for such zwitterions in the reaction between $ZnMe_2$(TMEDA) and $B(C_6F_5)_3$

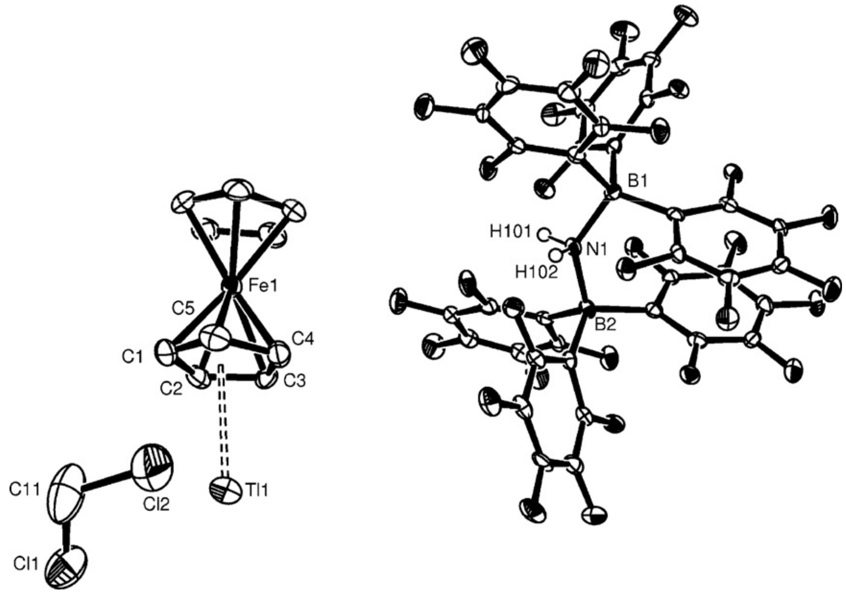


Fig. 9. Structure of $[Tl(Fc)][H_2N\{B(C_6F_5)_3\}_2]{\cdot}CH_2Cl_2$. Reproduced by permission from Ref. [58]. Copyright (2007) American Chemical Society.

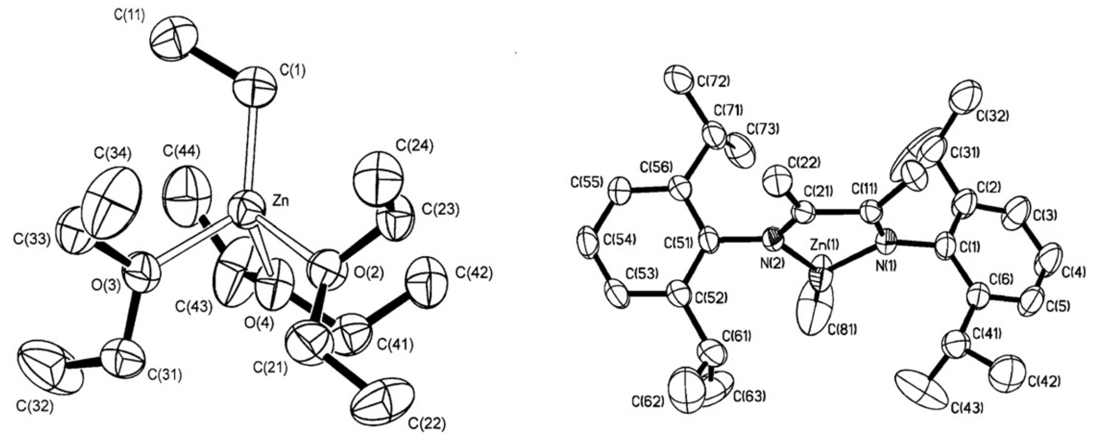


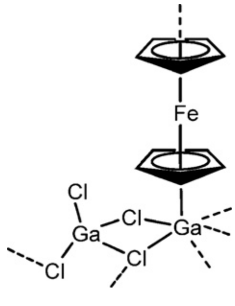
Fig. 10. Solid-state structures of the cationic zinc complexes $[EtZn(OEt_2)_3]^+$ and $[MeZn(DAD)]^+$ [66,68]. Reproduced by permission from Refs. [66] and [68]. Copyright American Chemical Society 2001 (Ref. [66]) and Royal Society of Chemistry 2002 (Ref. [68]).

in dichloromethane-d_2 at −70 °C where (TMEDA)ZnMe(μ-Me)B$(C_6F_5)_3$ could be identified. On warming to room temperature the signals for (TMEDA)ZnMe(μ-Me)B$(C_6F_5)_3$ broadened and merged with those of ionic $[MeB(C_6F_5)_3]^-$ and $[ZnMe(TMEDA)]^+$ cation as well as excess $ZnMe_2$(TMEDA) [63].

There was a reasonable expectation that arene-stabilized ions such as $[MeZn(\eta\text{-}C_6Me_6)]^+$ might be detectable since these are isoelectronic to the well-known MeZnCp [64,65]. Studying the reaction of $ZnMe_2$ with $[CPh_3][B(C_6F_5)_4]$ in the presence of excess C_6Me_6 did indeed indicate a slower aryl transfer than without the arene, although conclusive evidence for an intermediate with π-bonded arene was not obtained [66].

In the presence of Lewis bases, cationic zinc complexes are of course readily isolable. For example, the reaction of ZnR_2 with $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$ in diethyl ether gives the compounds $[RZn(OEt_2)_3]^+[B(C_6F_5)_4]^-$ (R = Me, Et or Bu^t) in quantitative yield [66] (Fig. 10). Similar reactions give access to cationic magnesium and zinc alkyls and amides, such as $[(Et_2O)_3Mg^nBu]^+$, $[(Et_2O)_3MgN(SiMe_3)_2]^+$ and $[(Et_2O)_3ZnN(SiMe_3)_2]^+$ [67]. All these complexes are tetrahedral. Three-coordinate, trigonal-planar zinc cations are obtained in the presence of the bulky diazadiene DAD = $(MeC{=}N\text{-}C_6H_3Pr_2^i\text{-}2,6)_2$, e.g. from the reaction of ZnR_2 and $[DADH][B(C_6F_5)_4]$ [20,68]. Both these three- and four-coordinate main group cations are highly effective catalysts for the ring-opening polymerization of ε-caprolactone, propylene oxide and cyclohexene oxide, most probably via a cationic polymerization mechanism.

As referred to above, the reaction of $B(C_6F_5)_3$ with $ZnMe_2$ is a facile route to $Zn(C_6F_5)_2$. This compound is a moderately strong Lewis acid, and recrystallization from toluene affords an arene adduct, $Zn(C_6F_5)_2$·toluene [63]. By contrast, crystallization of $Zn(C_6F_5)_2$ from benzene has been reported to give a benzene-free product [69]. The toluene molecule can easily be exchanged for more electron-rich arenes such as hexamethylbenzene. An even bulkier zink perfluoroaryl, bis(2-perfluorobiphenylyl)zinc, was obtained from EtZnCl and $LiC_6F_4\text{-}2\text{-}C_6F_5$. This, too, forms a toluene complex, $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2$·toluene (Scheme 13) [70].



Scheme 12.

Although the Zn^{2+} ion and many zinc(II) compounds are known for their behaviour as Lewis acids and the ability to readily bind polar molecules, well-characterized complexes of zinc coordinated to neutral C═C π-systems are remarkably rare. Pioneering studies on the system $Zn(SbF_6)_2$/arene in liquid SO_2, led to the isolation of compounds of composition $Zn(SbF_6)_2$·arene for electron-rich arenes (C_6HMe_5 and C_6Me_6) which contained labile zinc–arene interactions [71]. Weak intramolecular interactions between metal centres and aryl substituents have for example been found in $Zn(SC_6H_3\text{-}2,6\text{-}Ar_2)_2$ (Ar = 2,4,6-$R_3C_6H_2$, R = Me or Pr^i) [72]. However, simple, structurally characterized arene complexes of zinc remained elusive until now.

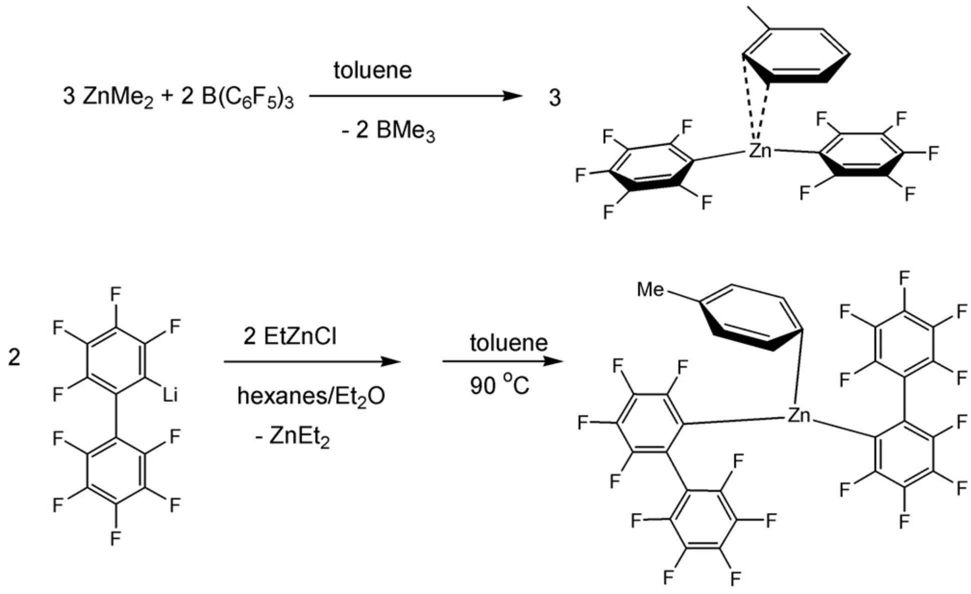
The structure of $Zn(C_6F_5)_2$·toluene (Fig. 11) is essentially T-shaped, with an almost linear aryl–Zn–aryl core (C(1)–Zn–C(11) 162.35(6)°) [70] The toluene molecule is predominantly bonded via the *ortho*-C atom and best described as η^2-coordinate, with closest Zn–C(toluene) distances of 2.784(2) and 2.6847(15) Å, that is 0.74 and 0.84 Å longer, respectively, than the average Zn–C_6F_5 bonds.

By contrast, the toluene ligand in $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2$·toluene is bonded to the metal centre via the *para*-C atom, and the Zn–C(toluene) bond length is significantly shorter, 2.524(3) Å. The C(1a)–Zn–C(1b) angle is more acute, 153.26(11)° (Fig. 11).

However, MO calculations on these molecules revealed remarkably little difference between the zinc–arene bonding modes [70]. In both cases there is comparatively little Zn–toluene covalent bonding. The zinc–toluene bonds are weak, much weaker than the thallium–toluene bond energies discussed above, only 25.4 kJ mol^{-1} in $Zn(C_6F_5)_2$·toluene and 27.9 kJ mol^{-1} in $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2$·toluene. The calculations also showed very similar orbital delocalizations in both molecules. The differences in hapticity that one so readily asserts on the basis of crystallographic bond distances are not reflected in the orbital overlap and may in fact be rather less important than is generally assumed.

Yet another zinc arene complex was obtained by reacting $[EtZnCl]_\infty$ [73] with $B(C_6F_5)_3$ in toluene in the presence of hexamethylbenzene. Crystalline $[Zn(\mu\text{-}Cl)(C_6F_5)(\eta\text{-}C_6Me_6)]_2{\cdot}CH_2Cl_2$ was isolated (Scheme 14). Here the arene ligand shows a tendency towards η^3-bonding (Zn(1)–C(7) 2.448(3) Å, Zn(1)–C(8) 2.714(3) Å, Zn(1)–C(12) 2.767(3) Å) (Fig. 12) [74].

$Zn(C_6F_5)_2$ gains importance because of its unexpected role as an initiator for the carbocationic polymerization of isobutene (IB) and



Scheme 13. Synthesis of zinc toluene complexes.

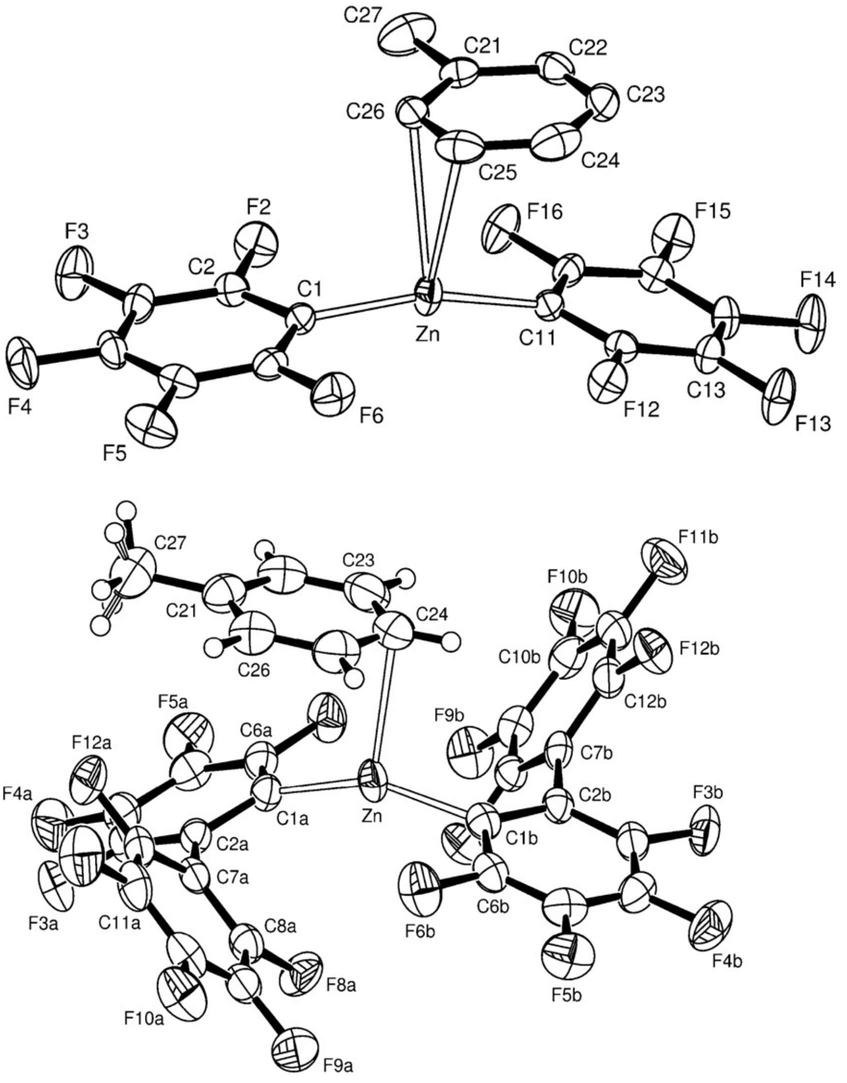
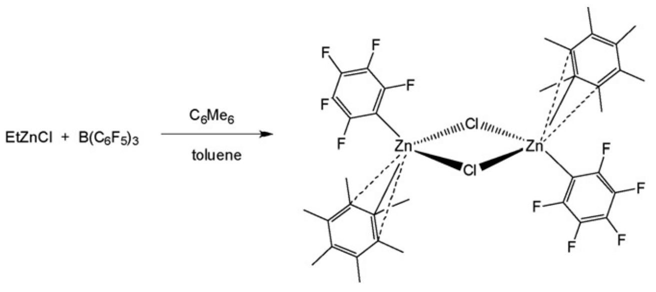


Fig. 11. Molecular structure of $Zn(C_6F_5)_2$·toluene (top) and of $Zn(C_6F_4\text{-}2\text{-}C_6F_5)_2$·toluene (bottom). Reproduced by permission from Ref. [70]. Copyright (2007) American Chemical Society.



Scheme 14.

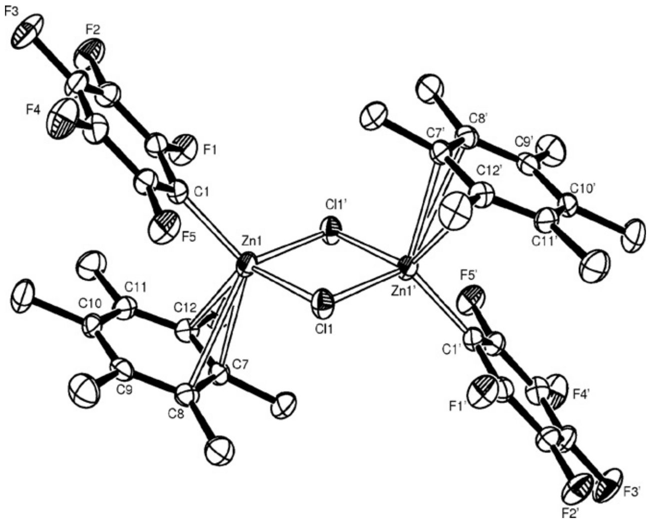


Fig. 12. Molecular structure of $[Zn(\mu\text{-}Cl)(C_6F_5)(\eta\text{-}C_6Me_6)]_2$. Reproduced by permission from Ref. [74]. Copyright (2008) Elsevier.

its copolymerization with isoprene (IP) (Scheme 15). The propagating species is a carbocation which must by necessity be associated with a counter anion. The kinetics of this polymerization are therefore dictated by the strength of the ion pairing, and systems that produce anions that are only weakly coordinating and resistant to electron-transfer reactions will give high reactivity.

IB/IP copolymers are known as IIR rubbers and used predominantly in tyre manufacture because of their excellent gas barrier properties and their ability to cross-link to unsaturated polymers, notably polybutadiene. Industrially these polymerizations are initiated by an $AlCl_3/H_2O$ slurry (i.e. a proton source) in chloromethane solvent at low temperatures (ca. −100 °C). Under such conditions, IP is a powerful retardant, and its incorporation is typically limited to 2–2.5 mol%. Copolymers with increased IP content, and hence increased main chain unsaturation, can be desirable to improve cross-linking in polymer composites.

Many Lewis acidic metal halides have been used as initiators [75,76]. More recently, organometallic Lewis acids paired with very weakly coordinating anions have been more intensely explored, such as $MeAlCp_2/B(C_6F_5)_3$ [59] $[SiMe_3][B(C_6F_5)_4]$ [77], $Cp^*TiMe_3/B(C_6F_5)_3$ [78] and $(Cp^R)_2ZrX_2'/[CPh_3][B(C_6F_5)_4]$ (X = Me, H) [19,79,80]. However, little attention has been paid to zinc-based systems. There is an early report on the use of ZnI_2 and zinc dust in the presence of tert-butyl iodide for isobutene polymerizations [81]; however, other zinc Lewis acids, and most notably $ZnCl_2$, are totally ineffective.

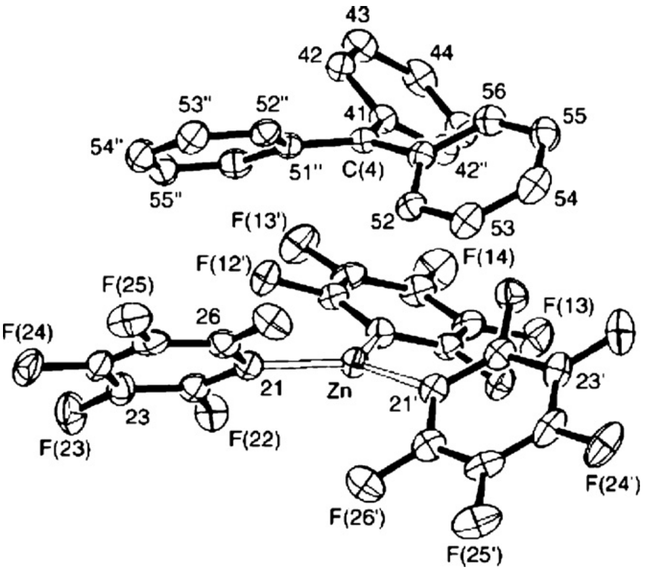


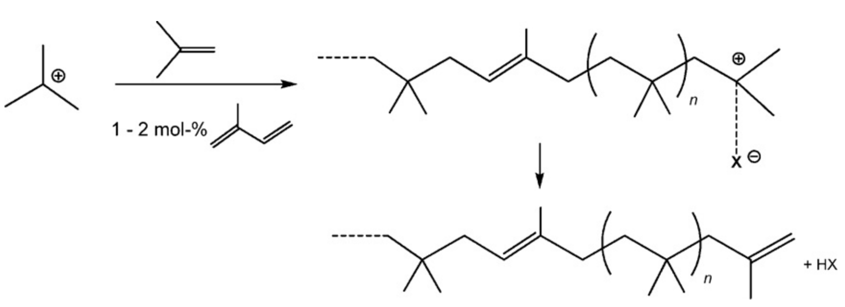
Fig. 13. Crystal structure of $[CPh_3][Zn(C_6F_5)_3]$. Reproduced by permission from Ref. [82]. Copyright (2004) Wiley-VCH.

In order to act as an initiator for IB (co-)polymerizations, the Lewis acidic precursor must be able to generate a carbocation. It must also produce a counter anion that is non-nucleophilic and stable in the presence of carbocations and under acidic conditions. The reaction of $Zn(C_6F_5)_2\cdot$toluene with activated alkyl chlorides was therefore investigated, in order to ascertain whether the compound was sufficiently Lewis acidic to generate carbocations by chloride abstraction.

The reaction of $Zn(C_6F_5)_2\cdot$toluene with Ph_3CCl gives a mixture of products from which crystalline $[CPh_3][Zn(C_6F_5)_3]$ could be isolated. This is to our knowledge the first example of an organometallic zincate anion of sufficiently low nucleophilicity to give stable salts with a carbocation (Fig. 13) [82].

Mixtures of $Zn(C_6F_5)_2\cdot$toluene with tert-alkyl or acyl halides in the presence of IB and IP at low temperatures (typically −35 to −90 °C) lead to rapid polymerization. This process can be assumed to involve formation of a carbocation stabilized by a perfluoroaryl zincate anion (Eq. (2)):

$$Zn(C_6F_5)_2 + R\text{–}X \rightleftharpoons R^+[ZnX(C_6F_5)_2]^- \tag{2}$$



Scheme 15.

Remarkably, these systems are not only very effective initiators, but they also allow the incorporation of much higher concentrations of isoprene than was hitherto possible with industrial catalysts, up to ca. 15 mol%, without significant gel formation [83]. These are new types of materials that are not accessible with the classical Al-based systems.

5. Conclusions

Very weakly coordinating anions and/or strongly electron withdrawing substituents such as pentafluorophenyl impart a degree of electrophilicity on coordinatively unsaturated metal systems that enables even extremely poor donor ligands to be coordinated. Synthetic, spectroscopic and computational studies have allowed us to obtain a detailed picture of fundamental aspects of the interactions of metal ions with weak π-ligands such as arenes. Naturally, this high reactivity is readily exploited in catalysis and, as the examples of electrophilic zinc catalysts have shown, provides subtle changes in ion pairing that give unexpected access to new types of copolymer materials, such as high-isoprene butyl rubber. These examples demonstrate the intimate relationship between fundamental structural and bonding studies and industrial applicability.

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