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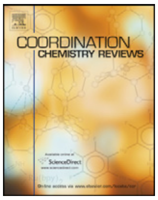

Review

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

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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.

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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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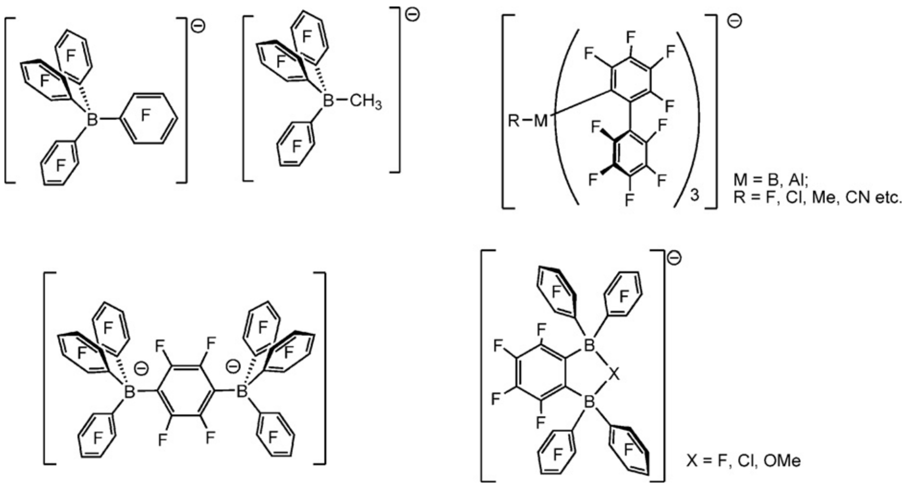
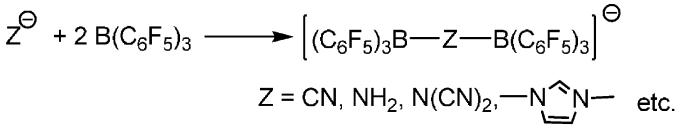


Scheme 1.

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].



$$Z^{\ominus} + 2\,B(C_6F_5)_3 \longrightarrow \left[(C_6F_5)_3B{-}Z{-}B(C_6F_5)_3\right]^{\ominus} \qquad (1)$$

Z = CN, NH₂, N(CN)₂, —N⌒N— etc.

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.

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