Abstract. The importance of weakly-coordinating anions in homogeneous catalysis was recognised as early as the 1970s. The traditional anions, such as BF$_4^-$, PF$_6^-$ and ClO$_4^-$, still display significant interaction with cationic transition-metal catalysts and proved, e.g., incompatible with highly reactive metallocene catalysts developed for olefin polymerisation. Therefore, the use of more stable and less coordinating counterions was investigated. This resulted in the preparation, amongst others, of a broad range of compounds based on the tetraphenylborate anion. In this chapter, the development of tri- and tetraarylborate anions and the use of these anions in catalysis are reviewed. Special attention is given to the enhancement of the solubility of transition-metal complexes in apolar solvents through the use of lipophilic tetraarylborate anions.
2.1 Introduction

The role of weakly-coordinating anions in the preparation of highly active cationic catalysts was recognised early on in homogeneous catalysis.\(^1\) However, little attention was paid to the differences between the various weakly-coordinating anions and their effect on the activity and selectivity of transition-metal catalysts.\(^{1c,f}\) With the discovery of metallocene-based olefin polymerisation catalysts and the quest for isolation of intrinsically unstable cations, such as germyl and trialkylsilylium cations, the conventional weakly-coordinating anions were found to be unsuitable, because they could interact with such reactive cations.\(^2\) This has led to the development of ever more stable, but also more weakly-coordinating, anions, such as carboranes, tetraphenylborates, C\(_{60}\)^-, pentafluorooxotellurates and aluminates.\(^3\)

Of the large range of anions available to date, the tetraphenylborate anion and its wide range of derivatives might be considered the most successful ones, as they can be readily functionalised and have been employed successfully in a wide variety of applications. For example, tetraarylborate derived anions have been used as counterions in catalysis and synthesis,\(^3,4\) but also as analytical reagents,\(^5,6\) radiation sensitive registration materials,\(^7\) fungicides,\(^8\) perspiration inhibitors,\(^9\) dental adhesives,\(^10\) anion exchangers,\(^11\) in cation-sensing membranes and electrodes,\(^12\) and as non-aqueous electrolytes.\(^13\) In this chapter, the characteristics that make this family of anions so interesting, the general methods for their synthesis and their use in catalysis are discussed. Special attention will be given to the properties, \(e.g.,\) solubility in apolar solvents and high stability, which make them of interest for application in novel reaction media, such as supercritical carbon dioxide, ionic liquids and perfluorinated solvents.

2.2 A Short History of the Tetraphenylborate Anion

Sodium tetraphenylborate (Na[1]) was first prepared by Wittig \textit{et al.} who immediately recognised the potential of its high stability.\(^14\) Its synthesis involved the reaction of triphenylborane with phenyllithium.\(^14a\) An alternative synthetic procedure, based on a reaction of phenylmagnesiumhalide with boron trifluoride (Scheme 1), was reported shortly afterwards\(^14b\) and has since remained the most widely employed route for the preparation of tetraphenylborate derived anions.
The initial interest in the tetraphenylborate anion was aroused by the poor solubility of its potassium salt, which was exploited as a means for estimating the concentration of potassium in aqueous solutions. However, within a short period of time, interest in the use of tetraaryloboron compounds widened considerably, and it is still very much a subject of research today. The use of the tetraphenylborate anion and the ever-continuing development of new derivatives stems from the desire to develop an anion which is as weakly coordinating as possible. It was discovered as early as the 1960s, that conventional ‘non-coordinating’ anions, e.g., $\text{BF}_4^-$, $\text{PF}_6^-$, $\text{ClO}_4^-$, $\text{SbF}_6^-$, can coordinate to a cation in many fashions in the absence of water. Single crystal structure determinations, IR and NMR spectroscopy provided evidence for this coordinating behaviour. More recently, the use of multidimensional NMR spectroscopy has allowed the study of the position of $\text{BF}_4^-$ and $\text{PF}_6^-$ anions in palladium- and platinum-diimine-complexes in solution. Using this technique, inter-ionic $\text{H} \cdots \text{F}$ interactions and contact ion-pair formation were detected. Similar studies revealed the positioning of $\text{BF}_4^-$ and $\text{PF}_6^-$ at the back of the bipyridine ligand in $[\text{Ir(H)}_2(\text{bipy})(\text{PPh}_3)_2]X$ complexes (Figure 1).
A severe limitation of the use of BF$_4^-$, PF$_6^-$, SbF$_6^-$, and even [B(OTeF$_5$)$_4$]$^-$, is their instability towards attack by strong electrophilic cations which can abstract F$^-$. This property makes these ions incompatible for use in combination with strong Lewis bases. However, anions with a low overall charge, delocalisation of the negative charge, large size and the presence of only weakly basic sites, *e.g.*, H and F, on the periphery of the anion are likely to have reduced coordinating-power and nucleophilicity. It is the tetraphenylborate anion that combines all of these properties in a single ion, and which therefore is an attractive alternative in cases where BF$_4^-$ and PF$_6^-$ prove to be too reactive.

In 1969 it was recognised by Haines *et al.* that under certain conditions the tetraphenylborate anion is not truly non-coordinating anion either (Figure 2). He found that the tetraphenylborate anion has the ability to interact via its phenyl rings through $\eta^2$, $\eta^3$- or $\eta^6$-coordination. The most often encountered interaction between the tetraphenylborate anion and a cation is via a single phenyl-group in an $\eta^6$-fashion, although up to four phenyl-groups can coordinate simultaneously, *e.g.*, in $\{(C_2H_4)_2Rh(\eta^6-Ph)\}_4B\}(O_3SCF_3)_3$ and $\{(\eta^5-C_5Me_5)Ru(\eta^6-Ph)\}_4B\}(O_3SCF_3)_3$. Although such zwitterionic complexes have found applications as catalysts in the hydroboration ([Rh(\eta^6-PhBPh$_3$)(dppe)]), hydrocarbonylation, hydroformylation, silylformylation, and hydrogenation ([Rh(\eta^6-PhBPh$_3$)(COD)]) of alkenes, this coordinating behaviour of the tetraphenylborate anion is considered to be undesirable, as it results in reduced electrophilicity of the transition-metal centre, and often in reduced catalytic activity compared to ionic catalysts.

Besides its tendency to coordinate, the stability of [BPh$_4$]$^-$ is also not optimal; metallation at the phenyl ring, phenyl transfer to a metal or an organic substrate, photolytic instability and electrochemical oxidation have all been reported. Furthermore, transition-metal-catalysed transfer of the phenyl group is facile enough to allow the use of sodium tetraphenylborate as a reagent in cross-coupling reactions. In order to reduce the
coordinating ability and the reactivity of $[\text{BPH}_4]$ and to increase the hydrophobicity and the solubility of its complexes in organic (apolar) solvents, a wide range of derivatives has been prepared, most notably fluorine-substituted compounds. The development of tetraphenylborate derivatives with enhanced stability received a huge impulse at the end of the 1980s by the discovery that trityl-, anilinium- and oxonium tetraphenylborate salts as well as boranes are efficient co-catalysts for metallocene-catalysed olefin polymerisation. The lipophilicity of these fluorine-substituted borate anions makes them interesting as counterions for use in perfluorinated solvents and supercritical carbon dioxide, where they aid in the solvation and dissociation of the catalysts’ ions. In the following sections, the application of anionic tetraphenylborate and alkyltriphenylborate derivatives is discussed, with emphasis on the properties that make them interesting as counterions for catalysis in unconventional reaction media. The overview will limit itself to complexes and (pre)catalysts in which the presence of an arylborate anion was unequivocally established, the wide variety of borate counterions formed in situ during catalysis falling outside the scope of this chapter.

2.3 Tetraarylborates as Analytical Reagents

After the success of sodium tetraphenylborate as a reagent for the determination of cation concentrations in water, the development of alkyl- and aryl-substituted tetraarylborate anions received attention in an attempt to increase the sensitivity and selectivity for alkali-metals. Increased steric bulk of the anion was expected to reduce the aqueous solubility of the corresponding salts, especially of salts with large alkali-metal cations, thus enhancing selectivity for the larger metal ion. The first derivatives prepared with this goal in mind were the tetrakis($o$-tolyl)borate (2), tetrakis($m$-tolyl)borate (3) and tetrakis($p$-tolyl)borate (4) anions, prepared by reaction of $o$-, $m$- or $p$-tolyl lithium with the corresponding tritolylboranes. A simplified preparation was described more recently (Scheme 2).

![Scheme 2. Preparation of methyl-substituted borates from tolylmagnesiumbromide and KBF$_4$.][32]

The solubility of the corresponding borate salts in water, as well as their stability, increases in the order $p < m < o$-tolylborate, but the overall stability in water is low. For example, lithium tetrakis($p$-tolyl)borate starts to decompose immediately upon dissolution. To improve the stability of the tetraarylborate salts, sterically more demanding substituents, in
the form of additional phenyl groups, were introduced around the boron atom (Figure 3),\textsuperscript{33} and a range of bisborate anions was developed (Figure 4).\textsuperscript{33b} Besides improved stability, these sterically encumbered anions were expected to decrease the aqueous solubility of the corresponding alkali-metal salts even further. However, the solubility of the alkali-metal salts of the substituted borate anions did not differ significantly from that of the corresponding tetraphenylborate salts, and therefore sodium tetraphenylborate remained the most suitable agent for the determination of alkali-metal concentrations in aqueous media.

![Chemical structures](image)

**Figure 3.** A family of aryl-substituted tetraarylborate anions, developed for the precipitation of alkali-metals from aqueous solutions.
Figure 4. Bisborate anions developed in order to reduce the solubility of alkali-metal salts in aqueous media.

Another application for alkyl-substituted tetraarylborate anions is their use in cation-sensing membranes. The successful use of $[\text{B}(\text{C}_6\text{H}_4\text{Cl-4})_4]$ in membranes that are selective for large metal ions sparked the interest for the use of substituted borate anions in this field of chemistry. Therefore, a range of lipophilic meta-alkyl-substituted tetraarylborate anions was prepared (Figure 5).12a

Figure 5. Meta-substituted borates developed for use in cation sensing membranes.

The meta-position was chosen as the site for the introduction of the substituents as previous results had shown that this yields anions with (kinetically) more stable B-C bonds.12a Furthermore, the salts Cs[\text{B}(\text{C}_6\text{H}_4\text{Me-3})_4], Cs[\text{B}(\text{C}_6\text{H}_4\text{Et-3})_4], Cs[\text{B}\{\text{C}_6\text{H}_4(\text{nPr})-3\}_4] and Cs[\text{B}\{\text{C}_6\text{H}_4(\text{nBu})-3\}_4] were prepared as these were found to be more stable than the corresponding sodium salts, which are prone to decomposition. The solubility of these cesium salts in a number of solvents was explored (Table 1). Increased solubility in organic solvents was observed upon increase of the length of the alkyl groups. However, also in this case, cesium tetraphenylborate itself proved to be the most soluble of the salts explored.
Table 1: Solubility of cesium tetrakis{m-(R)phenyl}borates in polar solvents.

<table>
<thead>
<tr>
<th>-R</th>
<th>acetone (10^{-2} M)</th>
<th>acetonitrile (10^{-2} M)</th>
<th>water (10^{-4} M)</th>
</tr>
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<tbody>
<tr>
<td>H</td>
<td>2.7</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>methyl</td>
<td>0.2</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>ethyl</td>
<td>2.4</td>
<td>0.9</td>
<td>5</td>
</tr>
<tr>
<td>&quot;propyl</td>
<td>1.3</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>&quot;butyl</td>
<td>2.2</td>
<td>1.2</td>
<td>4</td>
</tr>
</tbody>
</table>

Because low stability, and in particular protonolysis, hampered the effectiveness of \([\text{BPh}_4]^-\) (and the alkyl- and aryl-substituted derivatives thereof) as analytical agents, another approach was followed in order to reduce the lability of tetraarylborate anions. Since the introduction of substituents with an inductive electron-withdrawing effect significantly lowers reactivity, the anions tetrakis(3-fluorophenyl)borate (20), tetrakis{3-(trifluoromethyl)phenyl}borate (21), tetrakis{4-(trifluoromethyl)phenyl}borate (22) and tetrakis(4-fluorophenyl)borate (23) were prepared. Their stability was found to increase in the order 23 < 22 < 21 < 20, but the effectiveness of these anions as analytical reagents has not been reported on.

2.4 Phase-Transfer Catalysis

2.4.1 Fluorine-Substituted Tetraarylborate Anions

Besides the enhanced stability achieved by the introduction of fluorine substituents in tetraarylborate anions, the presence of such hydrophobic moieties also increases the solubility of these anions in organic solvents. The introduction of even a single fluorine substituent already induces a significant increase in solubility in non-coordinating solvents such as CH\(_2\)Cl\(_2\), toluene and cyclohexane. Due to both the enhanced stability and solubility of the fluorine-substituted tetraarylborate anions, the tetrakis{3,5-(trifluoromethyl)phenyl}borate anion (TFPB, 24) (Scheme 3) was designed by Kobayashi et al. to fully exploit these effects. Whereas \([\text{BPh}_4]^-\) is chemically labile, especially in the presence of acids or oxygen, the strongly electron-withdrawing effect of the two trifluoromethyl-substituents in TFPB suppresses electrophilic attack on the ipso-carbon. This results in an anion that is more stable than tetraarylborate anions with a single CF\(_3\)-substituent. The latter are still prone to reaction with acid or oxygen, whereas TFPB is unreactive. Furthermore, the fluorine-substitution of the tetraphenylborate anion reduces its tendency towards \(\pi\)-coordination through the phenyl groups.
Scheme 3. Preparation of tetrakis{3,5-bis(trifluoromethyl)phenyl}borate.

The solubility of the fluorine substituted borate anions in dichloromethane and toluene increases in the order $23 < 21 << 24$. Furthermore, the partitioning of various alkali metal tetraarylborate salts in water/CH$_2$Cl$_2$ and water/toluene biphasic systems was studied. This revealed that in a water/CH$_2$Cl$_2$ system, partitioning of the borate salts in favour of the organic solvent is more pronounced for TFPB ($C_{org}/C_{aq} \sim 10^3$) than for [BPh$_4$], [B(C$_6$H$_4$F-4)$_4$] and [B{C$_6$H$_4$(CF$_3$)-3}$_4$] ($C_{org}/C_{aq} \sim 0.10$) whereas this difference is much less distinct in a water/toluene system.

The increased solubility of TFPB in hydrocarbon solvents improves its ability to extract organic and inorganic cations from aqueous solutions, a feature also observed, but to a lesser extent, for [BPh$_4$]. This led to the extensive use of the tetrakis{3,5-bis(trifluoromethyl)phenyl}borate anion as a more stable and more effective alternative to [BPh$_4$] in phase-transfer catalysis in organic media of low polarity. Applications as catalyst for azo couplings, Friedel-Crafts alkylations, electron-transfer and sulfonium ylide formation have been described by Kobayashi et al.

2.4.2 Higher Derivatives of Tetrakis{3,5-bis(trifluoromethyl)phenyl}borate

The successful application of TFPB salts in phase-transfer catalysis led to the exploration of homologous anions containing a larger number of fluorine-containing groups. This was expected to result in derivatives with increased solubility in apolar organic solvents. An extensive library of fluorinated tetraarylborate anions (25-31) was prepared (Figure 6). The solubility of the corresponding tetramethylammonium salts and that of a small number of sodium salts in halocarbon solvents was reported (Table 2). From these studies it can be deduced that an increase in the number of fluorinated groups enhances the solubility of the borate salts in these non-coordinating solvents. The efficiency of these TFPB derivatives as phase-transfer catalysts has not been reported.

The acid stability of TFPB proved higher than for the anions with an increased number of fluorinated groups. Since the electron-withdrawing properties of CF$_3$ are most pronounced in the derivatives 25-31, the higher stability of TFPB is not fully understood.
Figure 6. Derivatives of [BPh₄]⁻ with an increased number of fluorinated groups per anion.⁴₀

Table 2: Solubility of tetramethylammonium perfluoroalkyl-substituted tetraarylborates.⁴₀

<table>
<thead>
<tr>
<th>anion</th>
<th>CH₂Cl₂ (10⁻² M)</th>
<th>CHCl₃ (10⁻⁴ M)</th>
<th>(CBrF₂)₂ (10⁻⁴ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFPB</td>
<td>2.0</td>
<td>1.4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>21</td>
<td>14</td>
<td>5.0</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>25</td>
<td>4.7</td>
<td>7.6</td>
<td>1.3</td>
</tr>
<tr>
<td>26</td>
<td>14</td>
<td>6.6</td>
<td>2.0</td>
</tr>
<tr>
<td>27</td>
<td>12</td>
<td>5.0</td>
<td>18</td>
</tr>
<tr>
<td>28</td>
<td>0.06</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>29</td>
<td>7.7</td>
<td>31</td>
<td>2.2</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
<td>36</td>
<td>4.5</td>
</tr>
<tr>
<td>31</td>
<td>0.4</td>
<td>0.2</td>
<td>14</td>
</tr>
</tbody>
</table>
2.5 Olefin Polymerisation Catalysed by Early Transition-Metal Complexes

2.5.1 Early Work on Tetraarylborate Anions in Olefin Polymerisation

Early transition-metal metallocenes are among the most active homogeneous olefin polymerisation catalysts known to date. In their active form, these catalysts consist of a metallocene cation and a weakly-coordinating anion. This ion-pair is formed when the catalyst precursor reacts with a Lewis acid co-catalyst. The use of aluminum alkyls such as methylaluminoxane (MAO) as co-catalysts has long been an established activation route. However, despite its high effectiveness, MAO has largely remained a ‘black box’ as far as structure and properties are concerned. Well defined alternatives for the aluminoxanes as activators for the metallocene catalysts were found in triarylboranes and tetraarylborate salts.

Turner et al. reported the first use of tetraarylborate salts in combination with metallocenes. The combination of [Cp*₂ZrMe₂] with [⁴Bu₄N][BPh₄], [⁴Bu₄N][B(C₆H₄Me-4)₄] and [⁴Bu₄N][B(C₆H₄Et-4)₄] yielded zwitterionic complexes with the borate anion metallated at the meta-position of one of its aryl rings. These complexes showed modest activity in the polymerisation of ethylene, while the borate anion was easily degraded. Also described was the use of tetrakis(4-fluorophenyl)borate salts in the activation of [Cp*₂ZrMe₂] and [Cp*TiMe₃], but this proved ineffective as Zr-F interactions and other processes led to deactivation of the catalysts. Increasing the fluorine substitution, with the fluorine content increasing in the series [B(C₆H₄F-x)₄] (23) < [B(C₆H₃F-x)₄] (32) < [B(C₆H₂F₃-x)₃] (33), and, for example, [B{C₆F₄(CF₃)-x}] (34) and [B(C₆F₅)₄] (35), improves the effectiveness of the corresponding anilinium tetraarylborate salts as co-catalysts in these early transition-metal catalysed polymerisation reactions (Table 3). Interestingly, the use of TFPB, with two CF₃-substituents but no fluorine substituents on the phenyl ring, in combination with early transition-metal catalysts has received little attention. This seems to be

<table>
<thead>
<tr>
<th>borate anion</th>
<th>catalytic activity (kg/g Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[B(C₆H₅)₄]</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>32</td>
<td>5</td>
</tr>
<tr>
<td>33</td>
<td>10</td>
</tr>
<tr>
<td>34</td>
<td>20</td>
</tr>
<tr>
<td>35</td>
<td>250</td>
</tr>
</tbody>
</table>

Conditions: Cp*TiMe₃: 5 × 10⁻⁷ mol, co-catalyst [PhNMe₂H][X]: 5 × 10⁻⁷ mol, TIBA: 3 × 10⁻⁶ mol, T = 70 °C.
due to the instability of this anion towards attack by the highly electrophilic metal centres on its aryl rings, as has been observed in a reaction of $[\text{Ph}_3\text{C}][\text{TFPB}]$ with $[\text{Cp}_2\text{ZrMe}_2]$. Nevertheless, the anilinium salt of TFPB could be used in combination with $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{TiMe}_2]$ and $[\text{Ind}_2\text{TiMe}_2]$ (Ind = indenyl), resulting in active ethylene polymerisation catalysts. However, active catalysts from reaction of TFPB salts with Zr and Hf precursors have not been reported so far.

A more effective co-catalyst in comparison with the partly fluorinated anions was found in tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$). This activator reacts as a Lewis acid with catalyst precursors of the type $[\text{L}_2\text{MR}_2]$, forming ion pairs $[\text{L}_2\text{MR}]^+[\text{RB}(\text{C}_6\text{F}_5)_3]$ (L = ligand, R = alkyl or phenyl), which are highly active olefin polymerisation catalysts. Still, considerable interaction between the thus formed tetraaryl- or alkyltriarylborate anions and the cationic, catalytically active, metallocene centre were observed. Using dynamic NMR techniques, borane dissociation and ion-pair symmetrisation could be observed (Scheme 4), the dissociation being enhanced with increasing solvent polarity. Despite the high efficiency of this borane co-catalyst in activating metal-alkyl-complexes, subsequent interaction between the resulting anions and the metal centre hampers the catalyst activity. This has stimulated the development of co-catalysts based on even more weakly-coordinating anions.

![Scheme 4](image-url)
2.5.2 The Tetrakis(pentafluorophenyl)borate Anion

This search for an anion with even weaker interactions and increased resistance to electrophilic cations led to the rediscovery of the tetrakis(pentafluorophenyl)borate anion (PFPB, 35). The synthesis of Li[PFPB] was first reported in 1963 (Scheme 5), but the anion received little attention until its use as counterion in polymerisation was investigated. The trityl and trialkylammonium salts of PFPB proved to be very efficient co-catalysts for the activation of metallocenes, e.g., [(Cp’)2TiMe][PFPB] proved 3300 times more active in ethylene polymerisation than the corresponding [(Cp’)2TiMe][BPh4]. The tendency of less fluorinated borates to undergo F- abstraction or aryl-transfer is non-existent in the case of PFPB. Moreover the use of PFPB yields more active catalysts. For example, the activity of bis-Cp metallocene catalysts increases in the order BF4- ~ [B(C6H5)4]- << X-MAO (X = Cl, Me) < [MeB(C6F5)3] < [B(C6F5)4]-, reflecting the decrease of the anion coordination strengths in this series. Furthermore, catalysts equipped with [B(C6F5)4]- proved to be more effective in the polymerisation of propylene (with dimethylzirconocenes) and styrene (with Cp*TiMe3, see Table 3) than metallocenes activated by B(C6F5)3.

\[
\text{B(C6F5)3} + \text{Li(C6F5)} \rightarrow \text{Li[B(C6F5)4]} \]

Scheme 5. Preparation of lithium tetrakis(pentafluorophenyl)borate.

2.5.3 Development of Fluorous Triarylborane and Borate Derivatives Directed at Increasing the Solubility and Reactivity of Metallocene Polymerisation Catalysts

Metallocene complexes activated with B(C6F5)3, and especially PFPB salts, are highly active in the polymerisation of olefins. However, they are only sparingly soluble in toluene and even less soluble in \(\alpha\)-olefins and hydrocarbons. Furthermore, as they are difficult to crystallise, the characterisation of the catalytically active species is difficult. Complexes prepared with these activators suffer from poor thermal stability, resulting in short catalyst lifetimes. In order to achieve improved solubility, thermal stability, characterisability, as well as catalytic efficiency, a range of functionalised fluoroarylborates has been prepared.

Tris(pentafluorophenyl)borate Derivatives

With the goal of improving the solubility of metallocene complexes in apolar solvents, a range of anionic substituents were introduced in B(C6F5)3. Hydroxy-, mercapto-, silanol- and oxime-derivatives of the PFPB anion were prepared (Scheme 6). The complex [(Ind)2ZrMe][38] proved soluble in 1-hexene/toluene (80:1) and 1-hexene/hexane (40:1) mixtures in concentrations up to \(1 \times 10^{-3}\) M, and was activity in the polymerisation of 1-hexene under in these solution. However, no tests in neat monomer were reported.
Scheme 6. Borate anions prepared in the search for increased solubility of ionic metallocene catalysts in neat olefins.55

Tetrakis{4-(tert-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl}borate and Tetrakis{4-(triisopropylsilyl)-2,3,5,6-tetrafluorophenyl}borate Anions

The study of ion-pairing behaviour of metallocene cations with \([\text{B(C}_6\text{F}_5)_4]\) anions was encumbered by the difficulty of isolating the corresponding complexes, as they suffer from poor solubility, thermal stability and crystallinity. Therefore, derivatives of \([\text{B(C}_6\text{F}_5)_4]\) containing silyl functionalities were designed to enhance solubility (Scheme 7).56 As the silyl substituents sterically protect the inner sphere of the anion and help in the delocalisation of the negative charge on the anion through the \(\pi\)-accepting silicon atom, they also help to stabilise the anion. Fluorine substitution of the aryl ring was maintained to ensure \(\delta\)-delocalisation of the negative charge.

Scheme 7. Preparation of lithium silyl-substituted tetrakis(2,3,5,6-tetrafluoroaryl)borate salts.56
The reaction [Ph$_3$C][44] and [Ph$_3$C][45] with a [Cp$_2$ZrMe$_2$], [(1,2-Me$_2$Cp)$_2$ZrMe$_2$], [{(Me$_4$Cp)SiMe$_2$(BuN)}ZrMe$_2$] and [(Cp’)$_2$ZrMe$_2$] resulted in benzene soluble ionic metallocene complexes. Furthermore, [{(Me$_4$Cp)SiMe$_2$(BuN)}ZrMe][45] even displayed solubility in pentane. As the corresponding [B(C$_6$F$_5$)$_4$]$^-$ complexes are only poorly soluble in these solvents,$^{56a}$ the silyl substituents significantly increase the solubility of these metallocene complexes in apolar solvents.

The coordinating strength of the borate anions 44 and 45 was investigated using NMR techniques and proved to be in between that observed for [MeB(C$_6$F$_5$)$_3$]$^-$ and [B(C$_6$F$_5$)$_4$]$^-$.$^{59}$ Furthermore, the results of polymerisation of ethylene and propylene catalysed by [Cp$_2$ZrMe]$^+$, [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$, [{(Me$_4$Cp)SiMe$_2$(BuN)}ZrMe]$^+$ or [(Cp’)$_2$ZrMe]$^+$ seemed to be independent of whether the anion 44, 45 or [B(C$_6$F$_5$)$_4$]$^-$ was used. The only major difference between the metallocenes activated by [Ph$_3$C][44] and [Ph$_3$C][45], or by [Ph$_3$C][PFPB], was the increased stability of the former two. This made it possible to isolate the catalytically active species, whereas the corresponding [B(C$_6$F$_5$)$_4$]$^-$ catalysts had to be generated in situ. Nevertheless, the isolation of Zr and Th complexes of the silyl-substituted anions still proved difficult and thermal lability remains an issue, as was more recently reported for [Me$_2$Si(Ind)$_2$ZrMe][45].$^{57}$ The reaction of [H(OEt)$_2$][44] with [Cp’$_2$Zr(H)$_2$]$_2$, yielding [Cp’$_4$Zr$_2$(H)$_3$][44], was also reported.$^{58}$ This compound was prepared as a model for [Cp’$_4$Zr$_2$(H)$_3$][B(C$_6$F$_5$)$_4$], which is active in the co-polymerisation of isobutene and isopropene. However, the activity in olefin polymerisation of [Cp’$_4$Zr$_2$(H)$_3$][44] itself was not investigated.

**Tetrakis{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}borate** and **Tetrakis{3-(trifluoromethyl)-2,4,5,6-tetrafluorophenyl}borate Anions**

To arrive at even less coordinating anions, salts of tetrakis{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}borate (46)$^{59}$ and tetrakis{3-(trifluoromethyl)-2,4,5,6-tetrafluorophenyl}borate (34)$^{43}$ were prepared (Scheme 8). High solubility of various ion pairs containing 46, reduced coordinating abilities, and added stability due to the perfluorinated nature of the ligand framework of 46 were all claimed.$^{59}$ However, these qualities have not been quantified. When [Ph$_3$C][46] was used as a co-catalyst with [(C$_2$H$_4$)(Ind)$_2$ZrMe$_2$], the performance of the resulting catalyst in the polymerisation of ethylene appeared to be inferior to that observed for the complex activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or MAO. On the other hand, the thermal stability of the activated complex was improved, while no catalyst decomposition was observed below 0 °C in toluene.$^{59}$

The anilinium salt of tetrakis{3-(trifluoromethyl)-2,4,5,6-tetrafluorophenyl}borate (34) was used in combination with [Cp’TiMe$_2$] in the polymerisation of styrene (Table 3).$^{43}$ The resulting catalyst was an order of magnitude less active than its [Cp’TiMe$_2$][PFPB] analogue.
Scheme 8. Synthesis of lithium tetrakis{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}borate.

Tris(pentafluorophenyl)(2-perfluorobiphenyl)borate Anion
Attempts by Marks et al. to synthesise an anionic derivative of tris(2,2',2"-perfluorobiphenyl)borane, which was prepared as an activator for dialkyl-metallocenes, did not yield the desired compound. Instead, the trityl tris(pentafluorophenyl)(2-perfluorobiphenyl)borate salt ([Ph₃C][47]) was isolated (Scheme 9).⁴d This salt was employed as a co-catalyst with [(1,2-Me₂C₅)₂ZrMe₂] in ethylene polymerisation. The performance of the resulting catalyst was found to be comparable to that achieved with the corresponding [Ph₃C][PFPB] activated complex.

Scheme 9. Preparation of tris(pentafluorophenyl)(2-perfluorobiphenyl)borate.⁴d

Bis(octafluoro-2,2'-biphenyl)borate Anion
The bis(2,2'-octafluorobiphenyl)borate anion (48) was designed for the preparation of supported olefin polymerisation catalysts (Scheme 10).⁴d,60 Both its anilinium and trityl salts were synthesised, and proved to be efficient co-catalysts for an unspecified dimethylzirconium complex. Preliminary results indicated that [Ph₃C][48] and [PhNMe₂H][48] are more effective co-catalysts than the corresponding [B(C₆F₅)₄]⁻ salts.⁴d A
related anion (49) was also claimed for a similar purpose, but the nature of the salt used as co-catalyst, nor its synthesis, were reported.60a

Scheme 10. Bis-biphenylborate anions for the preparation of supported catalysts.

2.5.4 Bi-functional Borate Anions

In the quest for more stable and weakly-coordinating anions, a number of bi-functional borate anions has been prepared (Scheme 11). In these bi-functional anions, two boron centres are linked through an extended π-system, resulting in enhanced delocalisation of the negative charge compared to ‘mono’-borates. This was expected to result in higher stability. As high stability and low coordination strength are interesting features for anions in early transition-metal-catalysed olefin polymerisation, the anions 50-56 (Scheme 11) were tested for this purpose.4d,61 The reaction of trityl and anilinium salts of the bisborate anions with metallocenes yielded catalysts active in the polymerisation of ethylene61a-c,e and propylene.61g However, none of the bisborate containing catalysts exhibited better polymerisation rates than the corresponding [B(C6F5)4]+ complexes.61c Furthermore, [Ph3C][53] yielded inactive complexes because of F-transfer.61e Other examples of bi-functional borate anions (57-61) have also been reported (Scheme 12).4d,61f However, these remain untested in catalysis.
Scheme 11. Bi-functional borate salts that have been used as co-catalysts in metallocene-catalysed olefin polymerisation.
2.5.5 Linking Boranes through Monoanionic, Coordinating, Molecules: [(C₆F₅)₃B-LN-B(C₆F₅)₃]⁻-Type Anions

In the search for borate anions with ever higher stability, increased solubility and reduced coordinating strength in comparison with PFPB, ever more complex structures were devised. As the synthesis of such large and complex perfluoroarylborate salts is both costly and synthetically laborious, the generation of bulky anions through more straightforward methods was independently studied by the research groups of Bochmann and LaPointe. They constructed large anions with multiple boron centres from commercially available B(C₆F₅)₃ units and small, anionic, bifunctional ligands (Scheme 13).
Examples of anions obtained using this approach are: $[\text{CN}(\text{B}(\text{C}_6\text{F}_5)_3)_2]^{-}$ (62), $[\text{M}(\text{CNB}(\text{C}_6\text{F}_5)_3)_3]^{-2}$ (M = Ni (63), Pd (64)), $[\text{imidazolide}{\text{B}(\text{C}_6\text{F}_5)_3}_2]^{-}$ (65) and its azide (66), dicyanamide (67), tetra(imidazoyl)borate (68), benzotriazolide (69), 5,6-dimethylbenzimidazolide (70), benzimidazolide (71), 4,5-dichloroimidazolide (72), 4,5-dimethylimidazolide (73), 4,5-diphenylimidazolide (74), 1,2,4-triazolide (75) and 4,4-dimethylimidazolinide (76) analogues. The trityl salts of 62, 63 and 64 were tested as co-catalysts for the polymerisation of ethylene using $[\text{Cp}_2\text{ZrMe}_2]$, $[\{\text{rac-Me}_2\text{Si}(\text{indenyl})\}_2\text{ZrMe}_2]$ and $[\{1,3-(\text{SiMe}_3)_2\text{C}_5\text{H}_3\}_2\text{ZrMe}_2]$ as catalyst-precursors.
While using these co-catalysts, similar activities were observed for all catalysts prepared. This was caused by mass-transport limitations of ethylene and prevented any meaningful analysis of anion effects on the polymerisation rates. Similar tests in the polymerisation of propylene, which were not mass-transport limited under the investigated conditions, showed that 62 is the most effective anion in the series 62, PFPB, 63 and [MeB(C6F5)3]. Reduced cation-anion association, which is the result of increased charge-delocalisation through the large π-system in 62, was proposed as an explanation for its efficiency as weakly-coordinating anion. The 2 charge of 63 induced lower activity and lower solubility of the corresponding complexes in toluene in comparison with the corresponding compounds with either 62 or PFPB as it results in stronger ion-ion interactions. Furthermore, the use of [HNMe(C18H37)2][65] as a co-catalyst with [{Me2Si(η5-Me4C5)(tBuN)}TiMe2] yielded a catalyst with increased activity in the co-polymerisation of ethylene and 1-octene in comparison with [{Me2Si(η5-Me4C5)(BuN)}TiMe][MeB(C6F5)3]. Disappointingly, the anions 62 and 63 were prone to slow decomposition when in solution through the dissociation of the anionic components.

2.5.6 Supported Borates as Co-catalysts in Olefin Polymerisation

A number of methods have been devised to attach B(C6F5)3 or PFPB to a backbone, thus creating supported borate anions. The idea of generating such poly-anionic materials, which can be used as activators in metallocene-catalysed polymerisation, stems from the search for better polymer morphology, e.g., the formation of beads instead of powders. The use of a co-catalyst immobilised on the surface of a particle could result in the formation of a supported catalyst, which can be employed in slurry polymerisation. When compared to homogeneous metallocene catalysts, such a catalyst would allow better control over the size of the polymer particles produced. Furthermore, the increase in steric bulk that ensues from the creation of such a supported co-catalyst could help in reducing cations-anions association, thus enhancing catalyst activity.

Dendrimer-Supported Borate Anions

With the aim of making anions that are sterically demanding, poly-anionic carbosilane dendrimers were prepared (Scheme 14). These dendrimers, which are well-defined and highly branched molecules, have been functionalised with [RB(C6F5)3]+ anionic groups on their periphery. The carbosilane backbone appeared suitable for use as a core for stable anions, as the C-Si bonds are chemically inert, making side reactions with the support during catalysis unlikely. The stable anilinium salts of 77, 78 and 79 were used as co-catalysts with [[Ind2ZrMe2] and [Cp2ZrMe2] in the homo-polymerisation of ethylene and propylene, and in the co-polymerisation of ethylene/propylene and ethylene/1-hexene mixtures. In these reactions, these poly-borate salts proved themselves to be among the most active co-catalysts to date. For example, in combination with [Cp2ZrMe2] the polymerisation rate for ethylene is an order of magnitude higher than for the corresponding [PhNMe2H][PFPB] activated...
catalyst. No degradation of the poly-borate anions was observed during these reactions and high polymerisation activity in aliphatic solvents such as \( n \)-hexane was observed with the salts of 77 and 78. This is an indication for the high solubility of the salts of these anion in these solvents. The effects of the use of these supports on polymer morphology was not reported.

\[
\text{Scheme 14. Carbosilane dendrimers used as a backbone for borate anions.}
\]

Silica-Supported Borate Anions and Silsesquioxane Model Systems

Work on silica-supported anions has remained mostly confined to the patent literature with reports focusing on the immobilisation of \( \text{B}(\text{C}_6\text{F}_5)_3 \) on a silica surface. This creates a supported four-coordinated borate anion, which behaves very much like the free PFPB anion. The most successful route for immobilisation has been the mixing of the silica support with borane in the presence of an amine (Scheme 15). Addition of a dialkylzirconium catalyst precursor to thus immobilised borate anions yields catalysts with activity in the slurry-phase polymerisation of various alkenes. During catalysis the presence of the amine is required as the attachment of \( \text{B}(\text{C}_6\text{F}_5)_3 \) to the support is otherwise reversible. Trityl salts of
the silica-supported anions were prepared by reaction of butyllithium and $B(C_6F_5)_3$ with silica, followed by metathesis with $Ph_3CCl^{65b}$ or by ion exchange with $[Ph_3C][B(C_6F_5)_4]$. The stability of the B-O bond was investigated using $B(C_6F_5)_3$ grafted on silsesquioxanes, which have proven to be realistic models for the silica surface. Anilinium and triethylammonium salts of $\{[(c-C_5H_9)Si_8O_{13}B(C_6F_5)_3]\}$ (81) and $\{[(c-C_5H_9)Si_7(OH)_{10}B(C_6F_5)_3]\}$ (82) were prepared. The B-O bonds in these salts displayed a limited stability toward both Brønsted and Lewis bases. Furthermore, B-O bond breaking by hydrolysis or alcoholysis was also facile. $[Cp_2Zr(CH_2Ph)_2]$ activated by $[PhNMe_2H]$ rapidly transformed into the inactive silsesquioxane complex $\{[(c-C_5H_9)_2Si_8O_{13}ZrCp_2][PhCH_2B(C_6F_5)_3]\}$. The subsequent breaking of the B-C bond leads to the formation of physisorbed $B(C_6F_5)_3$, which then acted as co-catalyst and was responsible for the polymerisation activity observed.

A second approach followed for the preparation of silica-supported metallocones is the reaction of $B(C_6F_5)_3$ with the silanol-groups of silica. This yields a zwitterionic intermediate, which reacts with $[Cp_2ZrMe_2]$ to form an immobilised catalyst. However, thus immobilised $[Cp_2ZrMe_2]$ was active only in the presence of MAO. As the aluminumalkyl co-catalyst causes cleavage of the Si-O bonds, thus releasing the catalyst into solution, the observed polymerisation activity is most likely caused by catalyst in solution. A third method employed for the synthesis of silica-supported borate anions is the tethering of $B(C_6F_5)_3$ via a linker. Anilinium $\{4-(trichlorosilyl)-2,3,5,6$-tetrafluorophenyl$\} tris$(pentfluorophenyl$) borate, $[PhNMe_2H][81]$, was reacted with silica (Scheme 16). The resulting supported anilinium borate has been used as co-catalyst with $[Ind_2ZrCl_2]$, in the presence of triisobutylaluminum, yielding a catalytic system that is active in ethylene and propylene polymerisation. In a similar fashion, triethylammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate and related compounds were reacted with MAO-treated silica, yielding supported anions which were used for the preparation of supported metalloocene catalysts.
**Alumina-Supported Borates**

Fully hydroxylated alumina was used as a support for borate anions. Reaction of B(C₆F₅)₃ with the alumina yields a zwitterionic species which reacts with [Cp₂ZrMe₂] to form a supported catalyst. In contrast to silica treated in an identical fashion, this catalyst was active without addition of MAO. The activity of the immobilised catalyst was reported to be much higher than that achieved with a mixture of [Cp₂ZrMe₂], MAO and alumina.⁶⁵f

**Polymer-Supported Borates**

Another class of materials that can be used as an anionic support for polymerisation catalysts in slurry-phase polymerisation are borane-substituted (co-)polymers. B(C₆F₅)₃ has been attached to various polymer surfaces in order to create supported metallocene catalysts. An illustrative example is the use of lightly cross-linked polystyrene beads functionalised with a hafnium catalyst (Scheme 17).⁶³ The open structure of this polymer, combined with its high polarity relative to the reaction medium resulted in a homogeneous distribution of the cation-anion pairs throughout the polymer matrix. This means that polymerisation took place inside the particle, whereas with other supported catalysts this occurs on the outside. Excellent activity, very low catalyst leaching and the formation of discrete spherical polymer beads with a diameter in the millimetre range were the result.
Other polymers that were used as anionic supports were prepared through the co-polymerisation of trialkylammonium tris(pentafluorophenyl-4-vinyl)phenylborates with styrene and 2,3,4,5,6-pentafluorostyrene (Figure 7), the co-polymerisation of ammonium tris(pentafluorophenyl-4-vinyl)phenylborates and ammonium tris(pentafluorophenyl)-norbornenes or the introduction of $\text{B(C}_6\text{F}_5)_3$ after lithiation of a preformed polymeric core, e.g., (chloromethyl)polystyrene and poly(divinyl)benzene.

![Figure 7. Examples of co-polymers used as anionic catalyst supports.](image)

### 2.6 Olefin Polymerisation Catalysed by Late Transition-Metal Complexes using Borate Salt Co-Catalysts

Following the discovery of $\text{B(C}_6\text{F}_5)_3$ and $[\text{B(C}_6\text{F}_5)_4]^-$ as efficient activators for early transition-metal polymerisation catalysts, a separate breakthrough was reported involving the development of efficient polymerisation catalysts based on late transition-metal complexes. The latter complexes are less oxophilic than early transition-metal complexes, and therefore rather than form high molecular weight polymers they tend to dimerise or oligomerise olefins. However, Brookhart et al. discovered that nickel and palladium complexes with bulky diimine ligands (Scheme 18), when activated through protonolysis by a co-catalyst, are active in both the homo- and co-polymerisation of ethylene and $\alpha$-olefins. These catalysts were also the first transition-metal complexes capable of co-polymerising functionalised monomers, such as alkyl acrylates and methylvinylketone, substrates that are not compatible with the more oxophilic metallocene catalysts.

#### 2.6.1 TFPB as Anion for Late Transition-Metal Polymerisation Catalysts

For the activation of late transition-metal dialkyl-diimine-complexes a new co-catalyst was required as the trityl and ammonium borates, that are commonly used in the
activation of dialkyl metallocenes, are generally not capable of activating these catalyst precursors. This resulted in the development of the [H(OEt₂)₂]⁺ salt of TFPB, which can be prepared from Na[TFPB] and HCl in diethyl ether. Whereas the TFPB anion was instable in the presence of highly electrophilic early transition-metals, cationic late transition-metal complexes proved unreactive towards this anion. This resulted in numerous applications of TFPB in catalysis.

Besides the Brookhart-type polymerisation catalysts, other examples of late transition-metal complexes activated by [H(OEt₂)₂][TFPB] are [Cp⁺(C₂H₄)Rh{CH₂CH₂(µ-H)}][TFPB] (dimerisation of methyl acrylate), [Cp⁺(P(OMe)₃)Co{CH₂CH₂(µ-H)}][TFPB] (polymerisation of ethylene), [(dppp)Pd((C(O)Me)(CO))][TFPB] (co-polymerisation of CO and ethylene) and [(N’N)Pd(Me)(MeCN)][TFPB] (N’N = 2,2'-bipyridine or 1,10-phenanthroline, co-polymerisation of CO and tert-butylstyrene). Both the [H(OEt₂)₂]⁺ and [PhNMe₂H]⁺ salts of TFPB were used to activate [Ni(C₁₂H₁₈)], yielding complexes that are active in the 1,4-cis-polymerisation of butadiene. In this example, the oxonium and the anilinium salts proved to be equally efficient co-catalysts. Furthermore, [PhNMe₂H][TFPB] was used in combination with [(N’N)NiMe₂] (N’N = {2,6-(Pr)₂}C₆H₄-N=C(Me)C(Me)=N{2,6-(Pr)₂}C₆H₄), yielding a catalyst active in the polymerisation of ethylene.

Despite the fact that the TFPB anion proved to be highly stable in the presence of late transition-metal catalysts, some examples of its coordination and decomposition have been reported. When trans-{[(PPh₃)₂Pt(Me)(OEt₂)][TFPB]} is refluxed in toluene, transfer of two 3,5-bis(trifluoromethyl)phenyl groups to the metal centre was observed (Figure 8). Furthermore, π-bonding of the aryl group was observed in [Ag(η⁴-TFPB)(2,2'-bipy)], [Ag(η⁴-TFPB)(I₂C₆H₄)] and [Rh(η⁴-TFPB)(COD)].
2.6.2 Other Tetraarylborate Anions as Activators for Late Transition-Metal Polymerisation Catalysts

In the field of late transition-metal-catalysed polymerisation, less attention has been given to the influence of the anion on the reaction than for early transition-metal catalysts. Whereas, the use of metallocenes resulted in the development of a broad range of substituted borate co-catalysts, in the case of the Brookhart-type catalysts little variation in the anions has been attempted. The following examples are exceptions where (in addition to TFPB) other borate anions were also employed.

Tetrakis(pentafluorophenyl)borate (PFPB) and Tetrakis{4-(α,α’-bis-(pentafluorophenyl)-fluoromethyl)-2,3,5,6-tetrafluorophenyl}borate Anions

PFPB was used in the nickel complex [Ni(C12H19)][B(C6F5)4] which proved an efficient catalyst for the polymerisation of 1,4-butadiene. Its activity in this reaction was comparable to that observed for [Ni(C12H19)][PF6]. In further examples, [(dppp)PdMe(THF)][B(C6F5)4] and [{Ph2Si(CH2PPh2)2}PdMe(THF)][B(C6F5)4] proved active in the co-polymerisation of CO and ethylene.

Expanding the range of para-substituted tetrakis(perfluorophenyl)borate anions for use with metallocene catalysts, Brant et al. prepared [PhNMe2H][B{C6F4(C(C6F5)2F)-4}4] (Scheme 19). However, as attempts to obtain Group 4 metallocene cations stabilised by [B{C6F4(C(C6F5)2F)-4}4] were unsuccessful, the performance of [PhNMe2H][B{C6F4(C(C6F5)2F)-4}4] as co-catalyst for [(N=N)NiMe2] (N=N = (2,6-(2’Pr)2C6H3)N=C(Me)C(Me)=N(2,6-(2’Pr)2C6H3)) in the polymerisation of ethylene was investigated. The activity and the molecular weight of the polymer obtained were lower than those achieved with this complex activated with the corresponding anilinium TFPB and PFPB salts.
**Tetakis(pentafluorophenoxy)borate Anion**

The synthesis of borates and boranes with a perfluoroaryl framework will be a serious challenge on industrial scale as it entails the use of fluorinated Grignard or lithium compounds, which can **explode spontaneously** when working at room temperature.\(^8^1\) This danger exists especially when ortho-fluorine substituents are present, as is the case in many of the syntheses described herein. Therefore, the design of anions that are less cumbersome to prepare, but equally efficient as weakly-coordinating counterions, has attracted some attention. Trimethylammonium tetakis(pentafluorophenoxy)borate was prepared using a straightforward procedure, eliminating hazardous intermediates (Scheme 20).\(^8^2\) Reaction of \([\text{Me}_3\text{NH}][\text{B(OC}_6\text{F}_5)_4]\) with \([\{2,6\text{-bis(1-(2,6-diisopropyliminophenyl)ethyl)pyridine}\}\text{Fe(II)Cl}_2]\) yielded a highly active olefin polymerisation catalyst, which displayed reaction rates more than twice as high as observed with the corresponding catalyst activated with \([\text{PhNMe}_2\text{H}][\text{B(C}_6\text{F}_5)_4]\).\(^8^2\) However, a rapid decline in activity during catalysis was observed, indicating decomposition of the catalytic species when using the borate anion \(^8^6\). Furthermore, \(^8^6\) proved incompatible with zirconocenes because of the high oxophilicity of these complexes.\(^8^2\)

**Scheme 20.** A safe way to prepare a highly efficient borate co-catalyst.
2.7 The Use of Substituted Tetraarylborate Anions in other Catalytic Processes

2.7.1 Hydrogenation

Although in most cationic hydrogenation catalysts traditional anions such as BF$_4^-$, PF$_6^-$, triflates or tosylates are used,$^{11}$ some examples of catalysts with tetraarylborate anions have been reported. Enantioselective hydrogenation of (E)-1,2-diphenyl-1-propene is catalysed by [(P’N)Ir(COD)][TFPB] (P’N = phosphanodihydrooxazole, Figure 9),$^{83}$ which showed better catalytic performance than the corresponding PFPB,$^{30}$ SbF$_6^-$, BF$_4^-$, PF$_6^-$, BPh$_4^-$, OTf$^-$ and halides complexes. HOESY NMR studies, in which the PF$_6^-$ and TFPB complexes were compared, revealed marked difference in the interaction of these anions with the cation.$^{83b}$ Whereas close contact ion-pairs between the TFPB anion and the cation were not detected, a regioselective interaction of the anion with the cation at the oxazoline ring was detected with PF$_6^-$, indicating tight ion pairing.

![Figure 9.](image)

Figure 9. [Ir(COD)(phosphanodihydrooxazole)][TFPB], an enantioselective hydrogenation catalyst.

The activation of [Cp(CO)$_2$(PR)$_3$MH] (R = phenyl, cyclohexyl or methyl, M = W, Mo) with [Ph$_3$C][TFPB] yields complexes that are active in the hydrogenation of acetone and 3-pentanone.$^{84}$ Their catalytic performance was compared with that of the corresponding BF$_4^-$, PF$_6^-$ and OTf$^-$ complexes. This demonstrated that the TFPB-equipped complexes have the highest catalytic activity. In a further example, [’Bu$_3$NH][PFPB] was used as co-catalyst in combination with [(Cp’)$_2$ThR$_2$] (R = Me or CH$_2$C$_6$H$_5$), resulting in the formation of hydrogenation catalysts for 1-hexene that were 4100 times more active than the corresponding [BPh$_4^-$] analogues.$^{52a}$ The related complex [(Cp’)$_2$Th(CH$_3$)][’BuCH$_2$CH[B(C$_6$F$_5$)$_2$]$_2$(µ-H)] was prepared as well, but its activity only slightly exceeded that of the PFPB analogue.$^{61}$

2.7.2 Hydrosilylation

Intramolecular hydrosilylation of alkenyl-silanes and alkenyl-silyl-ethers can be used for the preparation of five-membered silicon containing heterocycles. Application of cationic Pd(II) complexes in conjunction with a weakly-coordinating anion yielded efficient catalysts
for this reaction. The use of \([H(OEt_2)_2][TFPB]\) to activate \([(N\textsuperscript{\&}N)Pd(Me)_2]\) (\(N\textsuperscript{\&}N = 1,10\)-phenantroline, 2,2’-bipyridine or neocuprine) resulted in the formation of catalysts active in the intramolecular hydrosilylation of 4-pentenyl- and 5-hexenyl-silanes (Scheme 21).85

![Scheme 21. Palladium catalysts for the intramolecular hydrosilylation of alkenyl-silanes and alkenyl silyl-ethers.](image)

### 2.7.3 Diels-Alder Reactions

TFPB has also been used as counterion for organic cationic catalysts, e.g., idinium cations86 and oxazaborinane cations (Figure 10),87 which display activity as catalysts for Diels-Alder reactions. When using idinium, TFPB proved to be a much more efficient anion than either BF\textsubscript{4}\textsuperscript{-} (sparsely soluble salt) or \([BPh_4]\textsuperscript{-} (strong ion-pairing). Furthermore, reaction of Na[TFPB] with [CpRu(biphop-F)I] (biphop-F = 1,2-bis{bis(pentafluorophenyl)phosphanylxy}-1,2-diphenylethane, Figure 10) afforded complex [CpRu(biphop-F)][TFPB], which is also active in the Diels-Alder reaction.88 Studies of this Diels-Alder reaction showed that the activity, but not the selectivity, of the cationic ruthenium-catalyst was highly dependent on the nature of the anion, with the rate increasing in the series OTf\textsuperscript{-} < BF\textsubscript{4}\textsuperscript{-} < PF\textsubscript{6}\textsuperscript{-} < SbF\textsubscript{6}\textsuperscript{-} < TFPB.

### 2.7.4 Halogenation

Recently, the use of [Cp\textsubscript{2}Fe][TFPB] as catalyst for the direct halogenation of aromatics was reported.89 This reaction was carried out in the presence of ZnO and makes use of either ICl and Br\textsubscript{2} for iodination or bromination, respectively.
2.7.5 Photopolymerisation

The borate anions PFPB, 52 and 65 were used as weakly-coordinating anions in the iodonium-catalysed photopolymerisation of epoxy silicones (Figure 11). The salts of PFPB and 65 were the most active and most soluble photoacid generators of the group tested, which also comprised the anions 7,8,9,10,11,12-hexabromocarborane, tetrakis(pentafluorophenyl)gallate, SbF$_6^-$ and Cl$^-$. The di-anion 52 proved less efficient as the higher charge density reduced the solubility of the corresponding iodonium salt in silicones.

![Figure 11. Iodonium salts used as catalyst for photopolymerisation of silicones (X = PFPB or 65).](image)

2.8 Catalysis in Supercritical Carbon Dioxide

Because of its high lipophilicity, TFPB has also found application as solubility-enhancing counterion in supercritical carbon dioxide (scCO$_2$). This solvent has emerged as a substitute for organic solvents, because of the current view that its low toxicity and chemical inertness make it an environmentally friendly alternative to solvents currently employed. As scCO$_2$ is highly apolar, most catalysts, in particular the ionic ones, dissolve only poorly in this medium. Their solubility can be enhanced by the introduction of lipophilic groups, and the use of lipophilic TFPB, in particular, has proved very effective in the solubilisation of cationic transition-metal complexes in scCO$_2$. For example [Rh((R,R)-Et-Duphos)(COD)][TFPB] ($(R,R)$-Et-DuPhos = (R,R)-1,2-bis(trans-2,5-diethylphospholano)benzene, Figure 12) proved to be an active catalyst for the asymmetric hydrogenation of $\alpha$-enamides. The enantiomeric
excess achieved (> 90%) was similar to that achieved in conventional solvents, while the ee’s achieved in the hydrogenation of β,β-disubstituted enamides were at the time the highest reported (> 85%).

Figure 12. Rhodium-Duphos-complexes that were employed as catalysts in asymmetric hydrogenation in scCO₂.

In another example, the application of [(4S)-2-{2-(diphenylphosphanylidiphenyl)-4-isopropyl-4,5-dihydrooxoazole}iridium][TFPB] (Figure 9) in the asymmetric hydrogenation of imines in scCO₂ resulted significantly improved catalyst performance in comparison with that achieved with the corresponding PF₆⁻ complex. Enantioselectivity was in the order of 80%, whereas ee’s in the range of 20-40% were observed with the conventional catalyst in CH₂Cl₂. Besides improving catalyst performance, the use of TFPB as solubilising moiety proved more effective than use of a phosphanyl ligand that had been functionalised with two –(CH₂CH₂C₆F₁₃) (fluorous) functionalities.⁹³

Another example of the successful use of TFPB counterions in scCO₂, is the activation of Wilke’s catalyst (Figure 13) with Na[TFPB]. This yielded a catalyst active in the hydrovinylation of styrene.⁹⁴ Furthermore, this complex was also employed in a solvent system that combined the use of scCO₂ with that of the ionic liquid [EMIm][TFPB] (EMIm = 1-ethyl-3-methylimidazolium) as non-volatile liquid phase. This enabled the development of a continuous flow catalytic system, with excellent catalyst retainment and only a slight decrease in activity after 61 hours of continuous operation.⁹⁴b

A last example of the TFPB facilitated catalysis in scCO₂ is that of [(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(OEt₂)][TFPB] in the (co-)polymerisation of ethylene and 1-hexene.⁹⁵ The performance of this catalyst under supercritical conditions was similar to that in CH₂Cl₂.

2.9 Concluding Remarks

The recent interest in homogeneous cationic single site catalysts, and especially the use of early transition-metal metallocenes, in olefin polymerisation has sparked the interest in
the influence of the anion on catalyst performance. This has led to the development of a broad spectrum of tetraarylborate anions and derivatives thereof. Despite the diversity of anions reported, their preparation follows a rather uniform synthetic approach, often entailing the reaction of aryl lithium or -Grignard compounds with a trihalo- or triaryl-boranes at some stage during the synthesis.

Although anion effects on catalyst activity and selectivity have been widely investigated in olefin polymerisation, the formulation of a general trend is still a difficult task. It is clear that, in general, a reduction in the coordinating strength of the anion and an increase in its stability improve the activity and robustness of a catalyst. Nevertheless, many examples are encountered where, despite an increase in the size of the anion and an increase in the fluorine content, no significant influence on the catalyst performance could be discerned. Therefore, TFPB and PFPB remain the most widely employed counterions, because they combine a relatively straightforward synthesis with the best catalyst activity in all but a few examples. Furthermore, despite the performance gains achieved in polymerisation, the application of these weakly-coordinating anions in other fields of homogeneous catalysis has so far remained limited.

The use of large and weakly-coordinating anions as solubilising agents for highly apolar solvents, such as scCO₂ and perfluorinated solvents has hardly been explored. Yet, as shown by the few reported examples, introduction of fluorine substituents as well as alkyl substituents in borate anions often results in enhanced solubility of the corresponding borate salts and ionic metal complexes in non-coordinating and/or apolar solvents. Further exploration of the use of tetraarylborate anions with a highly fluororous character could be highly rewarding, as it might yield improved solubility of transition-metal complexes in such non-conventional solvents and allow studies into the solvent effects of these unique media on the performance of ionic homogeneous catalysts.
References and Notes


(50) A search in Chemical Abstracts revealed 7 papers mentioning the synthesis and/or use of the tetrakis(pentafluorophenyl)borate anion, none of which concern catalysis, between 1964 and 1988. Since then, over 1600 papers referring to the use of this anion have been published.


Arylborate Anions; Versatile Counterions in Homogeneous Catalysis with Potential for Use...


