

Role of $B(C_6F_5)_3$ in catalyst activation, anion formation, and as C_6F_5 transfer agent^{*,**}

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Abstract: The versatile reactivity of $B(C_6F_5)_3$ in alkene polymerization reactions is summarized. Adduct formation with basic anions such as CN^- and NH_2^- gives extremely weakly coordinating diborates, which are the basis of some of the most active polymerization catalysts known to date. By contrast, the reaction of $B(C_6F_5)_3$ with zirconium half-sandwich complexes leads to extensive C_6F_5 transfer, including the surprising formation of borole-bridged tripledecker complexes. Main group alkyls undergo such C_6F_5 exchange reactions very readily unless donor ligands are present. Borate salts of new three-coordinate zinc alkyl cations proved to be highly effective catalysts for the ring-opening polymerization of epoxides and lactones.

INTRODUCTION

Tris(perfluorophenyl)borane is known for its chemical stability and is now finding widespread application as an activator of metallocene-based polymerization catalysts. Unlike boron halide-based Lewis acids of comparable acid strength, it is largely resistant to hydrolysis, and in contrast to most boron aryls does not react with aggressive electrophiles such as bromine. The compound was first described in 1963 by Stone et al. [1] who also demonstrated most of these characteristics and showed that the reaction with LiC_6F_5 produces a very stable tetraarylborate, $[B(C_6F_5)_4]^-$ [2].

In 1991, Marks et al. showed that $B(C_6F_5)_3$ was capable of abstracting methyl ligands from zirconocene dimethyls, to give zwitterionic products $L_2ZrMe(\mu-Me)B(C_6F_5)_3$ which were capable of acting as highly efficient ethylene polymerization catalysts [3]. Alongside other methods such as protolysis by HNR_3^+ [4] or alkyl abstraction by CPh_3^+ salts of tetraaryl borates [5], alkyl abstraction by $B(C_6F_5)_3$ proved to be a convenient method for generating cationic organometallic electrophiles [6]. Activation of metallocenes by $B(C_6F_5)_3$ is now used in some industrial polymerization processes.

Our interest in the chemistry of $B(C_6F_5)_3$ was twofold: its Lewis acidity makes this compound ideal as a source of new, conveniently prepared “super-weakly” coordinating anions, and in view of its large-scale industrial application, we wished to explore its reactivity toward other components of polymerization catalyst systems in order to gain some understanding of possible catalyst deactivation pathways and the reasons for catalyst decay and lifetime limitations.

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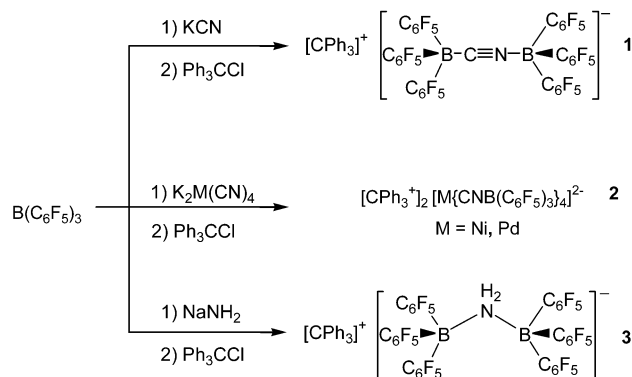
^{**}Dedicated to Prof. Walter Siebert on the occasion of his 66th birthday.

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WEAKLY COORDINATING ANIONS DERIVED FROM $B(C_6F_5)_3$

The importance of the counteranion in the ion pair $[L_nMR]^+X^-$, where $[L_nMR]^+$ = catalytically active metal alkyl, has been amply demonstrated [3–6]. Significant synthetic effort continues to be invested in devising very weakly coordinating anions or activators leading to such anions. Apart from the more commonly used anions $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$, examples include variously substituted perfluoroarylborates [7], chelating diboranes [8], dendrimer-supported anions [9], alkoxymetallates [10], and halogenated carboranyl anions [11].

In devising anions of very low nucleophilicity, delocalization of the negative charge over several centers is an attractive strategy. Such borate anions can be made by reacting $B(C_6F_5)_3$ with basic anions capable of functioning as bridging groups. Thus, the reaction of $B(C_6F_5)_3$ with KCN in Et_2O followed by treatment with Ph_3CCl in CH_2Cl_2 gives rise to $[CPh_3]^+[(C_6F_5)_3B-CN-B(C_6F_5)_3]^-$ (**1**) in a one-pot procedure (Scheme 1). As an activator for metallocene-based polymerization catalysts, compound **1** has several practical advantages over the commonly employed $[CPh_3][B(C_6F_5)_4]$; most importantly, it avoids the use of hazardous LiC_6F_5 , which is prone to detonate on warming above $-20\text{ }^\circ\text{C}$ [12]. $[CPh_3][B(C_6F_5)_4]$ is frequently very difficult to crystallize and purify and is air-sensitive; by contrast, $B(C_6F_5)_3$ is commercially available, can be made by safe alternative routes [13]; compound **1** can easily be purified by crystallization and as solid proved to be air-stable for extended periods of time. Similarly, the reaction of $B(C_6F_5)_3$ with cyanometallates $[M(CN)_4]^{2-}$ gives the dianions $[M\{CNB(C_6F_5)_3\}_4]^{2-}$ (**2**, $M = Ni$ or Pd). These, too, form stable CPh_3^+ salts suitable for metallocene catalyst activation [14,15]. A third type of anion is obtained from sodium amide and $B(C_6F_5)_3$ in diethyl ether, which gives salts of the amido-bridged diborate $[H_2N\{B(C_6F_5)_3\}_2]^-$ (**3**) [16]. Conceptually, similar anions have been reported by Dow, such as diborate anions containing imidazole-bridges [17].



Scheme 1

A comparison of the structures of **1** and **3** is instructive and may explain the differences in the behavior of these anions in polymerization catalysis. **1** is linear, with the bridging cyano moiety well shielded by the pentafluorophenyl substituents. The anion in **3** is, of course, bent, with a B–N–B angle of $134.3(2)^\circ$ (Fig. 1). Rather unexpectedly, the polarity of the B–NH₂–B moiety leads to significant intramolecular N–H⋯F hydrogen bonding, with one N–H hydrogen atom showing close contacts to two and the other to three F-atoms. One distance of the former, H(52)⋯F(82), is particularly short [$1.90(2)\text{ \AA}$] and correlates with the N–H⋯F arrangement approaching linearity [$155(2)^\circ$]. The other H⋯F distances range from $2.18(2)$ to $2.42(2)\text{ \AA}$, with very much smaller N–H⋯F angles of 115 – 127° . Cooling CD_2Cl_2 solutions of **1** to $-90\text{ }^\circ\text{C}$ leads to a splitting of the *o*-F signal ($\delta -135.4$ at $25\text{ }^\circ\text{C}$) into five components (ratio 1:2:1:1:1), indicative of hindered rotation. One of these signals is high-field shifted, to $\delta -141.8$. The complexity of the low-temperature spectra support the notion that H-bonding persists in solution. Generally, H⋯F bonding in organofluorine compounds is very rare and weak [18].

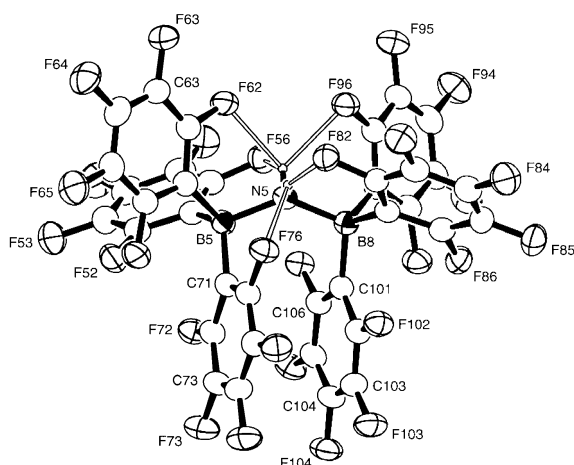


Fig. 1 Structure of the $[H_2N\{B(C_6F_5)_3\}_2]^-$ anion in $[Na(OEt)_4][H_2N\{B(C_6F_5)_3\}_2]$, showing the atomic numbering scheme. Open lines indicate $H\cdots F$ hydrogen bonding.

Here, it is evidently energetically important and may explain our failure to synthesize anions with NMe_2 , PMe_2 , or PCy_2 bridges where such hydrogen bonding is not possible.

Metallocene dialkyls activated with **1** or **3** give extremely active olefin polymerization catalysts. For example, mixtures of *rac*-(SBI)ZrMe₂/AlBu^{*i*}₃/1 (1:100:1) [SBI = Me₂Si(1-Ind)₂] in toluene under 7 bar ethene pressure at an initial temperature of 60 °C gave productivities in the order of 7.6×10^8 g PE (mol Zr)⁻¹ h⁻¹ bar⁻¹. This corresponds to a time-averaged turnover number of 53 000 s⁻¹, the highest reported to date for a polymerization catalyst.

A proper assessment of such high-activity catalysts proved problematic. Catalyst activity depends on many factors, and although it is common to draw a direct correlation between the ligand structure and the productivity observed under a given set of conditions, mass-transport limitation frequently prevails. The problem is exemplified in Fig. 2, which shows a steep increase in the activity of a given cat-

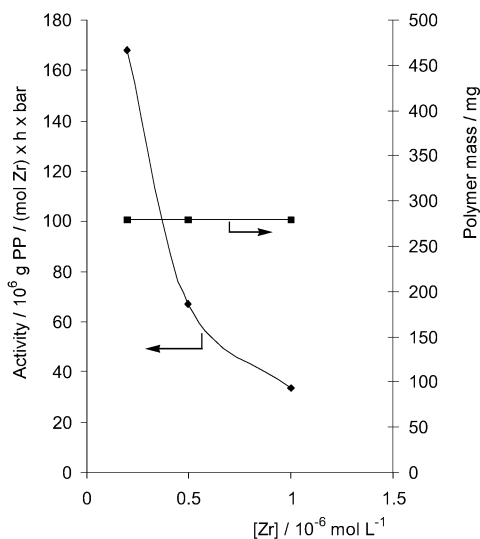


Fig. 2 Changes in apparent catalyst activity with concentration as a consequence of mass-transport limitation.

alyst with increasing dilution. In fact, under all three conditions, essentially identical amounts of polymer were obtained, indicating that the productivity was limited by the amount of monomer available to the catalyst. In other words, none of these figures can be regarded as measure of the actual activity of this catalyst system.

Propene polymerizations, by contrast, are slower, and it can be shown that even with high activity catalyst polymer yields increase linearly with catalyst concentration. Experiments reducing the catalyst concentration by a factor of 10 gave very similar productivity values, i.e., were not monomer limited. Using such a protocol for a number of different activators, it is possible to quantify the contribution of the counteranion to the activation barrier of propene polymerizations (Fig. 3). The extrapolation of productivity graphs to zero catalyst concentration gives the “intrinsic” catalyst activity that is characteristic for a given anion and reaction temperature, but independent of catalyst concentration. There is a clear decrease within the series of counteranions, in the order $[\text{CN}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^- < [\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^- \approx [\text{B}(\text{C}_6\text{F}_5)_4]^- < [\text{Ni}\{\text{CNB}(\text{C}_6\text{F}_5)_3\}_4]^{2-} \ll [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$. The activities of $\text{B}(\text{C}_6\text{F}_5)_3$ activated zirconocenes, i.e., those containing the more strongly coordinating $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion, were so low that much longer reaction times were required to obtain measurable amounts of polymer. The linear cyanodiborate **1** reduces the activation barrier by about 1 kcal/mol compared to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Fig. 4).

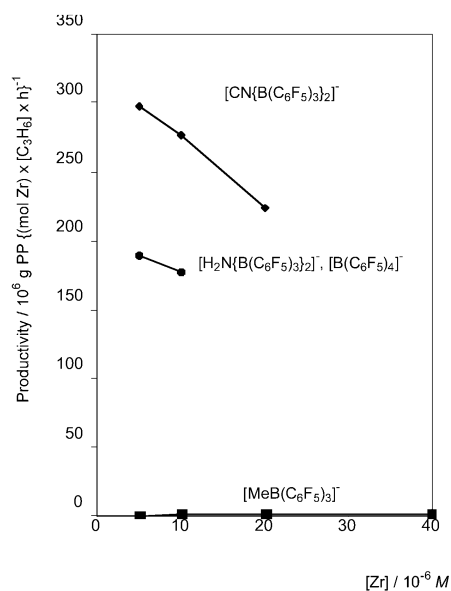


Fig. 3 Productivity of the catalyst $\text{rac}-(\text{SBI})\text{ZrMe}_2/\text{AlBu}_3^i/\text{CPh}_3^+\text{X}^-$ as a function of $[\text{Zr}]$ and X.

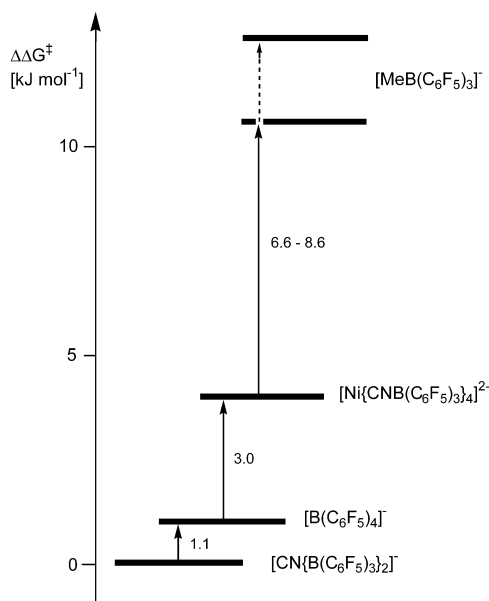


Fig. 4 Contributions of different counteranions to the activation energy of propene polymerizations with zirconocene catalysts.

For a given anion, the activities of different zirconocenes can be compared. The results are occasionally surprising; for example, while the cyanodiborate anion gives the highest activities at 25 °C, the more stable $[H_2N\{B(C_6F_5)_3\}_2]^-$ is more suitable for reactions at 60 °C (Fig. 5).

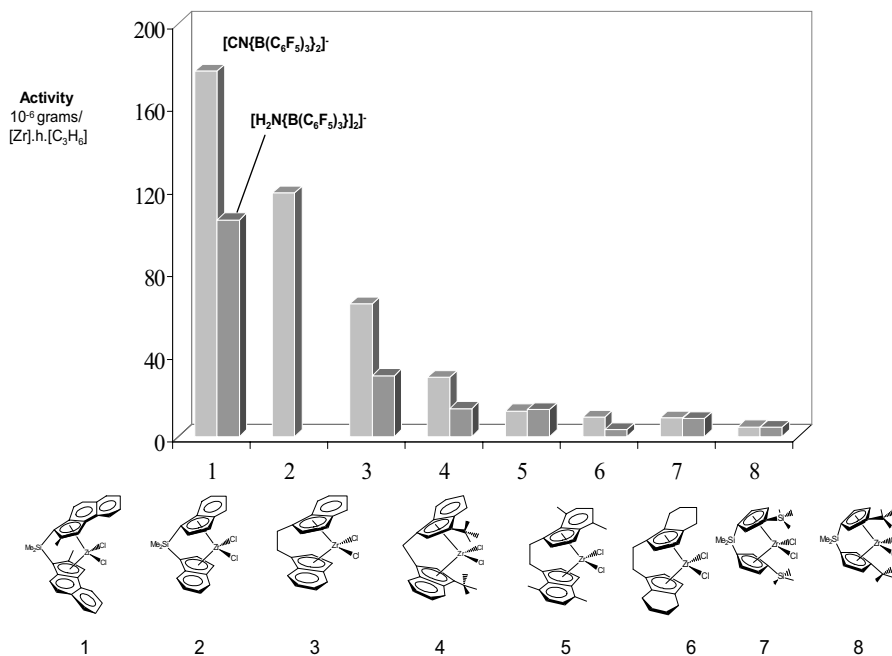


Fig. 5 Effect of the counter anion on the propene polymerization activity of zirconocene catalysts. Conditions: toluene, 20 °C, reaction time, 60 s.

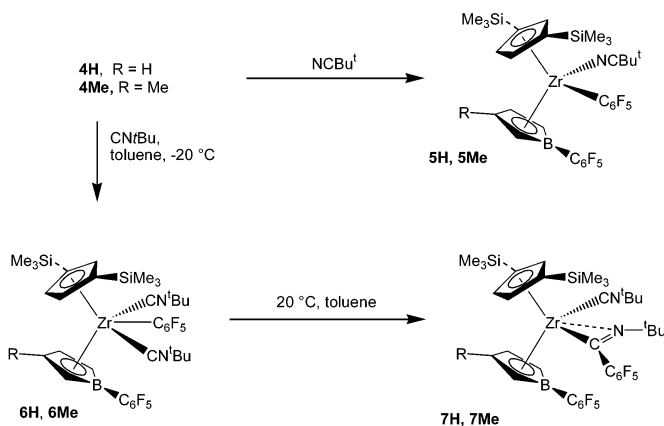
BOROLE COMPLEXES

Whereas $B(C_6F_5)_3$ reacts cleanly with zirconocene complexes, the reactivity with zirconium half-sandwich compounds is rather unexpected. For example, we showed some time ago that the zirconium diene complexes $Cp''Zr(\eta^3\text{-crotyl})(\eta^4\text{-butadiene})$ and $Cp''Zr(\eta^3\text{-allyl})(\eta^4\text{-isoprene})$ react with $B(C_6F_5)_3$ to produce the borole complexes $Cp''Zr(C_6F_5)(OEt_2)\{\eta^5\text{-}C_4H_3\text{-}3\text{-}R\text{-}1\text{-}B(C_6F_5)\}$ (**4H**, $R = H$; **4Me**, $R = Me$) as the products of successive C–H activation steps within the metal coordination sphere [$Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$] [19]. This reaction seems to be specific to bulky cyclopentadienyl ligands such as Cp'' .

Mixtures of mononuclear borole complexes **4** with an excess of trimethylaluminium show good activity as ethene polymerization catalysts, most probably following zirconium C_6F_5/CH_3 exchange. This differs from the behavior of other neutral zirconium alkyl complexes, which have little propensity for alkene binding and consequently are inactive or show low activity.

The reactivity of the Zr- C_6F_5 moiety with alkylating agents was explored, in an effort to generate isolable 14-electron zirconium alkyl complexes that might be suitable as single-component catalysts for olefin polymerizations. While $SnMe_4$, $Sn(\text{allyl})_4$, and $B(\text{allyl})_3$ failed to react with **4H** and **4Me**, Grignard reagents such as benzyl- and allylmagnesium chloride gave products that indicated an exchange of the B- C_6F_5 as well as the Zr- C_6F_5 substituents. With $LiMe$ or $ZnMe_2$ there was evidence for preferential methylation on zirconium to give yellow solids. However, none of these reactions gave a clean isolable product.

However, the Zr- C_6F_5 bond readily reacts with nitriles and isocyanides [20]. Thus, treatment of toluene solutions of **4H** and **4Me** with pivalonitrile produces a rapid color change from red to deep purple or blue, to give $Cp''Zr(C_6F_5)(NCBu^t)\{\eta^5\text{-}C_4H_3\text{-}3\text{-}R\text{-}1\text{-}B(C_6F_5)\}$ (**5H**, $R = H$; **5Me**, $R = Me$) (Scheme 2). Unlike the ether adducts, where the diethyl ether ligand readily dissociates in benzene solution, the nitrile ligand remains coordinated. As in the case of **4Me**, the methyl substituent on the borole ligand in **5Me** leads to the formation of two diastereomers in an approximate ratio of 1:0.6 at room temperature. The ^{19}F NMR spectra at room temperature show two peaks for the *ortho*-F of the Zr- C_6F_5 ligand, indicative of hindered rotation. By contrast, the borole- C_6F_5 group shows only one *o*-F peak at this temperature. As with **4H** and **4Me**, the ^{11}B NMR spectra of **5** show broad peaks around δ 30 to 40, which are high-field-shifted by some 10 to 20 ppm compared to C_6H_5 -substituted boroles [21], evidently a reflection of the stronger electron-withdrawing characteristics of the perfluorophenyl substituent.



Scheme 2

Treatment of solutions of **4H** and **4Me** in toluene- d_8 at -20 °C with 4 equiv of *t*-butyl isocyanide gives the yellow *bis*-isocyanide adducts $Cp''Zr(C_6F_5)(CN^tBu)_2\{\eta^5-C_4H_3-3-R-1-B(C_6F_5)\}$ (**6H**, **6Me**). The 1H NMR spectrum for **6H** shows a sharp singlet at δ 0.79 representing 18 protons, while for the C_1 symmetric **6Me** there are two singlets at δ 0.83 and 0.84 (ratio 1:1) for the two inequivalent isocyanide ligands. The *o*-F signals of the Zr- C_6F_5 group in the ^{19}F NMR spectra are at very low field (δ -98.7 and -99.3 for **6H** and δ -97.7 and -99.5 for **6Me**) and clearly show hindered rotation.

Complexes **6** are not thermally stable. There is slow insertion of isocyanide into the Zr- C_6F_5 bond, and after 1 h at room temperature the bright yellow iminoacyl derivatives $Cp''Zr\{C(N^tBu)C_6F_5\}(CN^tBu)\{\eta^5-C_4H_3-3-R-1-B(C_6F_5)\}$ (**7H**, **7Me**) are isolated. The iminoacyl ligand is η^2 -bonded, as confirmed by a crystallographic study of **7H**. Such migratory insertion reactions are common for organometallic zirconium complexes [22], however we believe that this represents the first crystallographically characterized example involving an insertion into the rather stable Zr- C_6F_5 bond. There is no evidence for further insertions, even in the presence of excess isocyanide.

The crystal structure of **7H** (Fig. 6) shows an "N-inside" orientation of the η^2 -iminoacyl ligand. There are two independent molecules in the unit cell, with Zr–N distances of 2.279(4) Å and 2.266(4) Å and Zr–C distances of 2.252(4) Å and 2.264(4) Å, while the Zr–C(isocyanide) bond is longer, 2.362(4) Å and 2.364(4) Å. As expected, the Zr–C \equiv N– unit is linear. The C \equiv N bond lengths of 1.150(5) Å and 1.140(5) Å are very similar to the C–N distance in the free isonitrile.

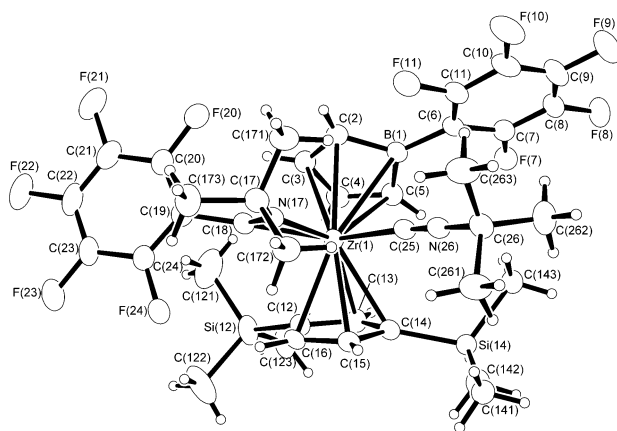
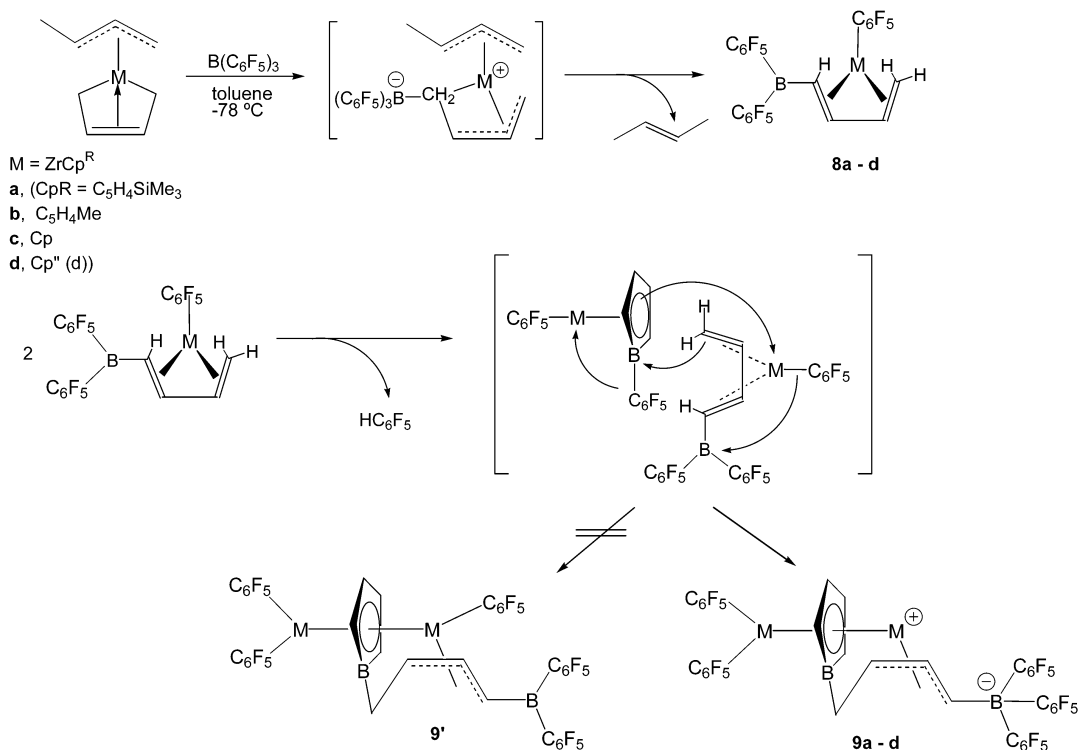


Fig. 6 Molecular structure of $Cp''Zr\{C(N^tBu)C_6F_5\}(CN^tBu)\{\eta^5-C_4H_4B(C_6F_5)\}$ (**7H**).

The reaction of $B(C_6F_5)_3$ with zirconium diene complexes carrying smaller cyclopentadienyl ligands or at slightly elevated temperatures takes a remarkably different course. The reaction of $Cp^RZr(\eta^5\text{-crotyl})(\eta^4\text{-butadiene})$ ($Cp^R = C_5H_4SiMe_3$ (**a**); C_5H_4Me (**b**); Cp (**c**); Cp'' (**d**)) with $B(C_6F_5)_3$ in toluene at room temperature over about 48 h, or warming to 50 °C for 2 h, does not lead to mononuclear borole complexes but generates the borole-bridged tripledecker complexes $Zr_2(Cp^R)_2(C_6F_5)_2\{\mu-\eta^5:\eta^5-C_4H_4BCH_2-\eta^3,\kappa F-CHCHCHB(C_6F_5)_3\}$ (**9a–d**) as red to orange solids (Scheme 3). The conversion is essentially quantitative. The reaction proceeds via the boryldiene compounds $Cp^RZr(C_6F_5)\{\eta^4-CH_2CHCHCHB(C_6F_5)_2\}$ **8** as intermediates, although compounds **9** are best made in one-pot reactions from the zirconium diene precursors.

The reaction sequence leading to **9** is shown in Scheme 4. It involves two boryldiene molecules **8** which react with redistribution of the C_6F_5 substituents of their $-B(C_6F_5)_2$ moieties to give a borole and a borate. One C–H activation step is involved which leads to the formation of one equivalent of pentafluorobenzene. As a result of these rearrangements, one of the original $B(C_6F_5)_3$ molecules has lost all of its C_6F_5 substituents.



Scheme 3

The ¹¹B NMR spectra of **9a–d** consist of a sharp signal at δ –12 to –13 for the borate and a broad signal around δ 0 to 3 for the borole ligand. The ¹⁹F NMR spectra for all three complexes show a signal in the region δ –215 to –225, which is indicative of the coordination of one of the *ortho*-F atoms of the butenyl-B(C₆F₅)₃ moiety to the metal center. Erker and coworkers previously found a similar ¹⁹F NMR chemical shift in the related complex Cp₂Zr{ η^3 -CH₂CHCHCH₂B(C₆F₅)₃} (δ –213.2) [23]; however, in that case the Zr...F interaction is rather weak ($\Delta G^\ddagger = 8.1$ kcal mol^{–1}). By contrast, **9a–d** show well-resolved *o*-F signals even at room temperature and a coalescence temperature of 68 °C, with a much stronger Zr–F bond ($\Delta G^\ddagger = 13.2$ kcal mol^{–1}).

In agreement with these findings, the crystal structure of **9d** (Fig. 7) revealed an unusually short Zr–F distance of 2.355(3) Å [24] when compared to related species with Zr...F coordination, for example, [NEt₄]₂[{C₅H₄B(C₆F₅)₃}Zr(μ -Cl)Cl₂]₂ [2.430(2) Å] [25], (C₅Me₅)Zr(C₆F₅)₃{ η^4 -C₄H₅B(C₆F₅)₂} [2.4292(15) Å] [26], and Cp₂Zr{ η^3 -C₄H₆B(C₆F₅)₃} [2.423(3) Å] [23].

Although a number of triple-decker complexes featuring a central borole ligand are known [27], compounds **9** are the first examples for a group 4 metal. Whereas the formation of the mononuclear borole complex Cp"Zr(C₆F₅)₃(OEt₂){ η^5 -C₄H₃-3-R-1-B(C₆F₅)} was specific to Cp", the triple-decker complexes form readily for a variety of Cp ligands. Apparently, the sterically highly hindered Cp" ligand is needed for the formation of **4**, while the triple-decker compounds **9** are formed in high yield even with unsubstituted cyclopentadienyl derivatives.

Ethene polymerization

Activating the mononuclear borole complex **4Me** with either AlMe₃ or MAO in ratios from 1:15 to 1:40 gives catalyst with good ethene polymerization activity. By contrast, mixtures of **9d** with AlMe₃ (Al:Zr = 30:1) at 25 and 60 °C under 1 bar ethene failed to produce any polymerization. NMR experi-

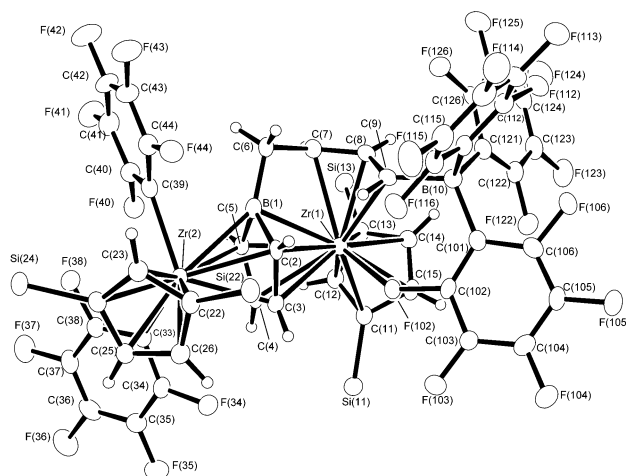
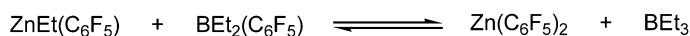
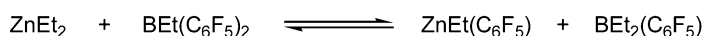
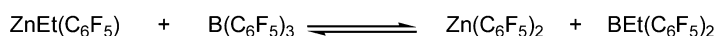
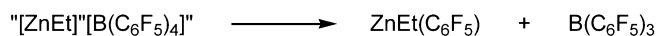


Fig. 7 Molecular structure of triple-decker complex **9d**.

ments show that under such conditions **9d** does not react with $AlMe_3$, in contrast to **4Me**/ $AlMe_3$ where $Zr-C_6F_5/Me$ exchange takes place. Treatment of the sterically less hindered compounds **9a** and **9b** with MAO resulted in higher activities, up to ca. 6×10^5 g PE (mol M) $^{-1}$ h $^{-1}$ bar $^{-1}$. The molecular weight distributions are broader than is typical for metallocenes. This may be due to nonuniform active species generation under these mild conditions.

BORATE SALTS OF ZINC COMPLEXES

Whereas aryl exchange reactions between $B(C_6F_5)_3$ and transition-metal alkyls are the exception rather than the rule, they become the dominant pathway with main group metal alkyls. This is typified by the chemistry of dialkyl zinc compounds. For example, the reaction of $ZnEt_2$ with $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ in noncoordinating solvents rapidly leads to alkyl/ C_6F_5 exchange and formation of $Zn(C_6F_5)_2$ (Scheme 4). If toluene is used, the crystalline toluene solvate $Zn(C_6F_5)_2(\text{toluene})$ is formed. The arene is presumably bound to the Lewis acidic metal center via its π -system. Treatment of solutions of $Zn(C_6F_5)_2(\text{toluene})$ with more electron-rich arenes leads to arene exchange. A series of complexes $Zn(C_6F_5)_2(\text{arene})$ can be made in this way (arene = C_6Me_6 , $C_6H_3Me_3$, $C_6H_5Bu^t$, naphthalene,



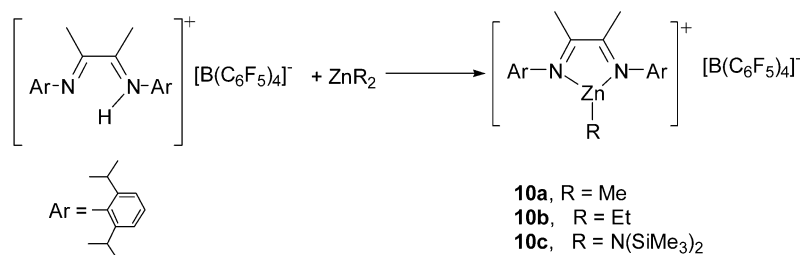
Scheme 4

etc.) The reaction of $B(C_6F_5)_3$ with zinc dialkyls is a very convenient salt-free method for the preparation of $Zn(C_6F_5)_2$ [28]. The chemistry mirrors that of $B(C_6F_5)_3$ with aluminium alkyls [29]. The reaction of $Zn(C_6F_5)_2$ (toluene) with $[CPh_3][B(C_6F_5)_4]$ in toluene leads to zinc cations, presumably $[C_6F_5Zn(toluene)]^+$, which are still reactive enough to attack $[B(C_6F_5)_4]^-$ and lead to C_6F_5 exchange, while hexamethylbenzene complexes appear more stable. However, none of these arene-stabilized zinc cations could be isolated. Although the cations $[C_6F_5-Zn(\eta^6\text{-arene})]^+$ would be isoelectronic to the well-known neutral cyclopentadienyls $RZn(\eta^5\text{-Cp})$, no such species could be identified with certainty.

In the presence of donor ligands such as ether solvent, the reaction of ZnR_2 ($R = \text{Me, Et, Bu}^t$) with $B(C_6F_5)_3$ takes a different course, and C_6F_5 exchange is suppressed. Thus, ZnR_2 and $B(C_6F_5)_3$ in diethyl ether give crystalline $[RZn(OEt)_2]^+[RB(C_6F_5)_3]^-$. Similarly, alkyl abstraction with $[CPh_3][B(C_6F_5)_4]$ gives the corresponding stable $[B(C_6F_5)_4]^-$ salts. The crystal structures of the Et and Bu^t complexes show tetrahedrally coordinated zinc cations [28].

Zinc complexes of sterically hindered ligands have attracted considerable attention in recent years as catalysts for the formation of polyesters. Examples include aryloxides [30], carboxylates [31], and bulky diketiminato complexes [32] which catalyze the alternating copolymerization of cyclohexene oxide with carbon dioxide to give polycarbonates. Several neutral zinc diketiminato [33], tris(pyrazolato)borate [34] and iminophenolato [35] complexes were found to be active for the ring-opening polymerization of lactides, but unreactive toward the homopolymerization of propene oxide (PO) and even cyclohexene oxide (CHO). We decided to investigate the chemistry of cationic zinc alkyl complexes in the presence of $B(C_6F_5)_3$ and tetra(perfluoroaryl)borates.

Treatment of ZnR_2 [$R = \text{Me}$ (**a**); Et (**b**); $N(\text{SiMe}_3)_2$ (**c**)] with borate salts of protonated diazadienes, $[DADH]^+[B(C_6F_5)_4]^-$, give the compounds $[RZn(DAD)][B(C_6F_5)_4]$ (**10a–c**), respectively (Scheme 5) [$DAD = (\text{MeC}=\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6})_2$]. There was no indication for the formation of the methyl-bridged binuclear cation $[\{(DAD)ZnMe\}_2(\mu\text{-Me})]^+$, even at -80°C .



Scheme 5

The X-ray crystal structure of **10a** confirmed the trigonal-planar coordination geometry of the metal center (angle sum 359.6°) (Fig. 8). The Zn–N distances of, on average, $2.040(2) \text{ \AA}$ are longer than those of the neutral diketiminato complexes $\{\text{HC}(\text{MeC}=\text{NAr})_2\}ZnX$ ($X = NPr^i_2, OBU^t$), while the N(1)–Zn–N(2) angle is more acute, $80.10(8)^\circ$. Although a number of three-coordinate neutral and anionic zinc alkyl complexes are known [32–34], complex **10a** appears to be the first structurally characterized example of a cationic zinc center in such a low coordination number.

Complexes **10** catalyze the polymerization of epoxides and ϵ -caprolactone under mild conditions. The rapid polymerization of CHO generates a significant exotherm which was moderated by dilution with toluene and ice bath cooling. The polymer molecular weight increases with time, with a polydispersity of about 2. The polymerization of PO proceeds more slowly, producing polymers with molecular weights of $30\text{--}40\,000 \text{ g mol}^{-1}$, regardless of reaction time. The polymerization of ϵ -caprolactone at room temperature was slow but accelerated on heating to 60°C . The resulting polymer gave M_w values of up to 40 000, with polydispersities close to 1 (Table 1). Methyl methacrylate was slowly polymerized at 25°C to give polymer with 70 % syndiotacticity.

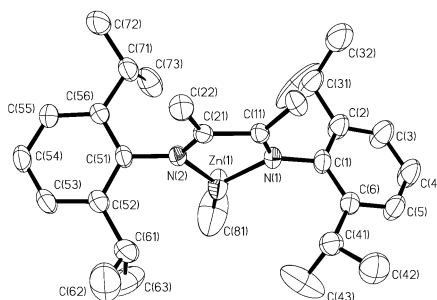


Fig. 8 Structure of the $[MeZn(DAD)]^+$ cation in **10a**. Ellipsoids are drawn at 40 % probability.

Table 1 Ring-opening polymerizations catalyzed with complex **10a**.

Monomer	Time	Temp. °C	Conv (%) ($kg \cdot mol^{-1} h^{-1}$)	Activity	M_w	M_w/M_n
CHO ^a	2 min	0	28.7	8493	113 000	2.3
CHO ^a	5 min	0	54.3	6419	177 000	1.8
PO ^b	1 h	23	0.8	4.76	33 000	6.4
PO ^b	24 h	23	51.6	12.49	35 000	1.9
CL ^c	0.5 h	60	4.4	10.1	23 000	2.0
CL ^c	1 h	60	12.7	14.7	40 000	1.1

^aCHO:Zn = 10000:1, 10 μ mol of **10a** in 50.5 mL toluene precooled to 0 °C.

^bPO:Zn = 10000:1, 25 μ mol **10a**.

^c10 mL CL, 93.5 μ mol of **10a**, 40 mL toluene at 60 °C. Reactions were terminated by quenching with HCl/MeOH.

CONCLUSION

Tris(pentafluorophenyl)borane has proved to be a remarkably versatile reagent. Originally chosen for its chemical stability and employed primarily as a powerful Lewis acid for the activation of metallocene catalysts for the polymerization of olefins, it has now been shown to be capable of undergoing a number of intriguing C_6F_5 transfer reactions. Its reaction with basic anions such as CN^- and NH_2^- affords new families of remarkably stable diborate anions $[X\{B(C_6F_5)_3\}_2]^-$ which in combination with zirconocenium cations give some of the most active alkene polymerization catalysts reported to date.

With transition-metal alkyls, alkyl/ C_6F_5 exchange reactions are the exception rather than the norm, although in the case of zirconium half-sandwich complexes, such reactions proceed under remarkably smooth conditions. The transformation of $B(C_6F_5)_3$ into the new borole $C_4H_4BC_6F_5$ leads to neutral 14-electron complexes that show good activity as polymerization catalysts, while under slightly more forcing reaction conditions borole-bridged tripledecker complexes are formed in high yield. These complexes are examples for extensive C_6F_5 rearrangement, such that the boron in the bridging borole ligand has lost all of its original three C_6F_5 substituents. These reactions represent catalyst deactivation pathways.

With main group metals such as zinc and aluminium alkyl/ C_6F_5 transfer is very facile, unless donor ligands are present. The reaction of ZnR_2 with $B(C_6F_5)_3$ in hydrocarbon solvents is an excellent route to $Zn(C_6F_5)_2$. Evidently, perfluoroarylborates anions are not stable enough to withstand electrophilic attack by $[RZn]^+$ intermediates. By contrast, C_6F_5 transfer reactions are suppressed by *N*- and *O*-donors, and four- and even three-coordinate zinc alkyl cations can be isolated. These are highly active catalysts for the ring-opening polymerization of epoxides and lactones.

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