[H(OEt$_2$)$_2$]$^+$ and [Ph$_3$C]$^+$ Salts of the Borate Anions [B(CF$_3$)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$, and [B(CN)$_4$]$^-$

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The reaction of gaseous HCl with K[B(CF$_3$)$_4$] in diethyl ether gave the oxonium acid [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] as a stable salt at room temperature. Syntheses of [Ph$_3$C][B(CF$_3$)$_4$] and [Ph$_3$C][(CF$_3$)$_3$BCN] were accomplished from the corresponding potassium salts and Ph$_3$CCl. The metathesis reaction of Ag[B(CN)$_4$] with trityl bromide resulted in formation of [Ph$_3$C]-[B(CN)$_4$]. Treatment of Cp$_2$ZrMe$_2$ with [H(OEt$_2$)$_2$][B(CF$_3$)$_4$], [Ph$_3$C][B(CF$_3$)$_4$], [Ph$_3$C][(CF$_3$)$_3$-BCN], and [Ph$_3$C][B(CN)$_4$], monitored by NMR spectroscopy, showed the formation of [Cp$_2$ZrMe(OEt$_2$)]$^+$, [(Cp$_2$ZrMe)$_2$-μ-Me]$^+$, [Cp$_2$ZrMe]$^+$, Cp$_2$ZrMe{NCB(CF$_3$)$_3$}, and Cp$_2$Zr{NCB-(CN)$_3$}$_2$, respectively. Attempted polymerizations of propene with catalysts generated in situ from *rac*-Et(1-Ind)$_2$ZrMe$_2$ and [H(OEt$_2$)$_2$][B(CF$_3$)$_4$], [Ph$_3$C][B(CF$_3$)$_4$], or [Ph$_3$C][B(CN)$_4$] yielded only little to no polymer, possibly due to the low solubility of the catalysts in the reaction medium.

Introduction

Recently we reported the synthesis of salts of the weakly coordinating tetrakis(trifluoromethyl)borate anion, [B(CF$_3$)$_4$]$^-$,[1] by fluorination of the tetracyanoborate anion, [B(CN)$_4$]$^-$,[2] in anhydrous HF using either ClF or ClF$_3$ as fluorinating agent.[1,3] The ability of [B(CF$_3$)$_4$]$^-$ to stabilize unusual cations was demonstrated by the formation of [Ag(CO)$_4$]$^+$,[1] and furthermore Li[B(CF$_3$)$_4$] was shown to be an excellent conducting salt for lithium ion batteries.[3] Tetracyanoborates are now easily accessible by heating a mixture of K[BF$_4$], KCN, and LiCl.[4] In contrast to the [B(CF$_3$)$_4$]$^-$ anion, [B(CN)$_4$]$^-$ exhibits a rich coordination chemistry.[5−7] While the [B(CN)$_4$]$^-$ anion has four and [B(CF$_3$)$_4$]$^-$ has practically no coordination site, the related tris(trifluoromethyl)cyanoborate anion, [(CF$_3$)$_3$BCN]$^-$, can coordinate via its cyano ligand.[8] The synthesis of salts of the [(CF$_3$)$_3$BCN]$^-$ anion

was achieved by isomerization of the [(CF$_3$)$_3$BNC]$^-$ anion[8] or by dehydration of [(CF$_3$)$_3$BC(O)NH$_2$]$^-$ with phosgene in the presence of triethylamine.[9]

The influence of the counteranion on the polymerization behavior of cationic group 4 metallocene complexes in the homogeneous Ziegler−Natta catalysis is subject to detailed investigations, and the pivotal role of the anion depending on its stability, coordinating ability, and influence on the solubility of the ion pair is widely recognized.[10−13] A general procedure for the formation of the catalytically active species, for example, [Cp*$_2$ZrMe]$^+$, is the abstraction of a Me$^-$ ligand from a suitable metallocene complex by methylalumoxane (MAO), trityl salts, [Ph$_3$C]X, or a proton source, e.g., [H(OEt$_2$)$_2$]$^+$ salts.[10,11,13]

In this study we report the syntheses of the new salts [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] and [Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$, [B(CN)$_4$]$^-$). Reactions of Cp$_2$ZrMe$_2$ with the potential cocatalysts in deuterated dichloromethane or toluene were monitored by NMR spectroscopy, and furthermore the polymerization of propene with *rac*-Et-(1-Ind)$_2$ZrMe$_2$ and [H(OEt$_2$)$_2$][B(CF$_3$)$_4$], [Ph$_3$C][B(CF$_3$)$_4$], or [Ph$_3$C][B(CN)$_4$] was studied.

Results and Discussion

[H(OEt$_2$)$_2$][B(CF$_3$)$_4$]. Similar to the syntheses of other [H(OEt$_2$)$_2$]$^+$ salts with [B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^-$,[14]

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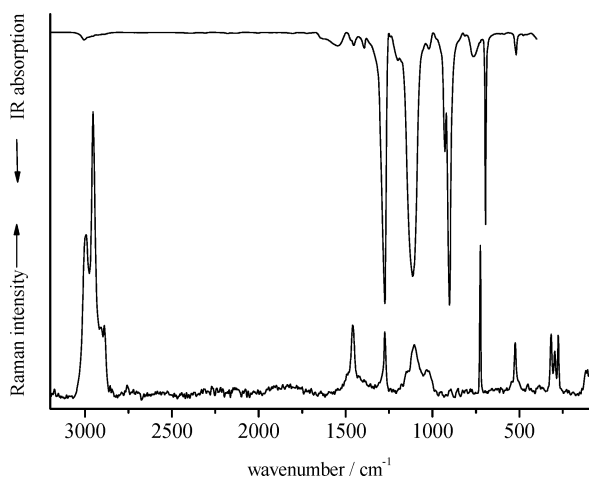(9) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. *J. Am. Chem. Soc.* **2002**, *124*, 15385.
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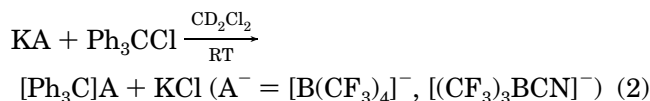**Figure 1.** IR and Raman spectrum of [H(OEt$_2$)$_2$][B(CF$_3$)$_4$].

[B(C$_6$F$_5$)$_4$]$^-$,[15] [(C$_3$H$_3$N$_2$){B(C$_6$F$_5$)$_3$}$_2$]$^-$,[16] or [HCB$_{11}$-H$_5$Cl$_6$]$^{-17}$ as counteranions, the preparation of [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] was achieved in a metathesis reaction according to eq 1.

$$K[B(CF_3)_4] + HCl + 2 \ Et_2O \xrightarrow[-30 \ °C]{Et_2O}$$
$$[H(OEt_2)_2][B(CF_3)_4] + KCl \ (1)$$
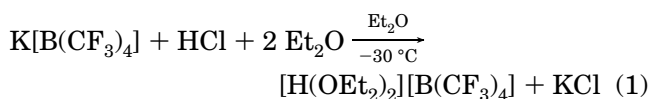
Potassium chloride and [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] precipitated quantitatively from the diethyl ether solution. The insolubility of [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] is contrary to the behavior of [H(OEt$_2$)$_2$][HCB$_{11}$H$_5$Cl$_6$][17] or [H(OEt$_2$)$_2$]-[B(C$_6$F$_5$)$_4$],[15] which can be recrystallized from Et$_2$O. However, the [B(CF$_3$)$_4$]$^-$ salt is soluble in methylene chloride and can be extracted from the salt mixture. The hygroscopic salt melts at 68 °C, whereas for [H(OEt$_2$)$_2$]-[B(C$_6$F$_5$)$_4$] a melting point of 148 °C was reported.[15] According to DSC measurements decomposition of [H(OEt$_2$)$_2$][B(CF$_3$)$_4$] takes place at 172 °C.

The ^{11}B, ^{13}C, and ^{19}F NMR chemical shifts and coupling constants of the anion in CD$_2$Cl$_2$ solution are nearly identical to those of K[B(CF$_3$)$_4$] measured in CD$_3$-CN.[1] The ^{1}H and ^{13}C NMR spectroscopic data of the cation are in agreement with values reported for other [H(OEt$_2$)$_2$]$^+$ salts.[14–17] Characteristic is the high ^{1}H NMR resonance frequency at 16.3 ppm.[14–17] The salt is also characterized by IR and Raman spectroscopy (Figure 1), and most of the anion bands are easily assigned by comparison to those reported for K[B(CF$_3$)$_4$].[1] The remaining bands are similar to those found for [H(OEt$_2$)$_2$]$^+$ salts with carborate counteranions.[17]

[Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$, [B(CN)$_4$]$^-$). The syntheses of the salts [Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$) are straightforward starting from the corresponding potassium salts and trityl chloride (eq 2).

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$$KA + Ph_3CCl \xrightarrow[RT]{CD_2Cl_2}$$
$$[Ph_3C]A + KCl \ (A^- = [B(CF_3)_4]^-, \ [(CF_3)_3BCN]^-) \ (2)$$

However, the corresponding tetracyanoborate salt cannot be prepared from Ph$_3$CCl and K[B(CN)$_4$]. The synthesis of [Ph$_3$C][B(CN)$_4$] was achieved by reacting silver tetracyanoborate with trityl bromide (eq 4).

$$Ag[B(CN)_4] + Ph_3CBr \xrightarrow[RT]{CH_3CN}$$
$$[Ph_3C][B(CN)_4] + AgBr \ (3)$$
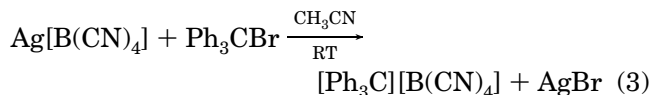
According to DSC measurements the three salts melt with decomposition at 125 °C ([Ph$_3$C][(CF$_3$)$_3$BCN]), 158 °C ([Ph$_3$C][B(CN)$_4$]), and 235 °C ([Ph$_3$C][B(CF$_3$)$_4$]). A comparison with the respective decomposition temperatures of the potassium salts (320 °C (K[B(CF$_3$)$_4$]), 370 °C (K[(CF$_3$)$_3$BCN]), 510 °C (K[B(CN)$_4$]))[1,2,8] indicates that there is no simple correlation between the thermal stabilities of different salts with the three borate anions.

The NMR spectroscopic data of the anions in [Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [B(CN)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$) dissolved in CD$_2$Cl$_2$ are identical to those reported previously for solutions of other salts.[1,2,8] The presence of the solvated trityl cation in the CD$_2$Cl$_2$ solutions was also confirmed by NMR spectroscopy. Even in the case of [Ph$_3$C]-[B(CN)$_4$] and [Ph$_3$C][(CF$_3$)$_3$BCN] the NMR data proved the ionic nature of the compounds and the lack of coordination of the cyano nitrogen atom to the carbocation. [Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [B(CN)$_4$]$^-$) also were characterized by IR spectroscopy, and the spectra are displayed in the Supporting Information in Figures S1 and S2. No Raman spectra could be acquired due to decomoposition in the Nd:YAG laser beam. The anion bands are easily assigned by comparison with similar spectra of the respective potassium salts (Tables S1 and S2).[1,2] For [Ph$_3$C][B(CN)$_4$] only one weak band in the characteristic region for ν(CN) was observed at 2221 cm^{-1}. This value is comparable to that measured for [^{n}-Bu$_4$N][B(CN)$_4$] (2222 cm^{-1}),[2] indicating a similar, very weak interaction between cations and anions in the solid state, in contrast to M[B(CN)$_4$] (M = K, Ag), where higher wavenumbers (K$^+$: 2234 cm^{-1}, Ag$^+$: 2257 cm^{-1}) and hence stronger interactions were found.[2] The band positions of the [Ph$_3$C]$^+$ cation are summarized in Table S3 and compared to values reported for [Ph$_3$C][BF$_4$].[18]

In addition Ph$_3$CCl was reacted with K[(CF$_3$)$_3$BNC] to study the difference in the coordination chemistry of the −CN versus the −NC substituent toward [Ph$_3$C]$^+$. The product (CF$_3$)$_3$BNCCPh$_3$ is a molecular complex, as demonstrated by its NMR spectroscopic properties. The ^{1}H and ^{13}C NMR signals of the Ph$_3$C fragment are shifted to lower frequencies in comparison to the trityl cation. The strong interaction between [Ph$_3$C]$^+$ and [(CF$_3$)$_3$BNC]$^-$ is also demonstrated by comparison with the ^{11}B and ^{19}F NMR chemical shifts of K[(CF$_3$)$_3$BNC][8] (δ(^{11}B) = −17.5 ppm, δ(^{19}F) = −67.0 ppm) versus (CF$_3$)$_3$-BNCCPh$_3$ (δ(^{11}B) = −14.4 ppm, δ(^{19}F) = −66.4 ppm). Another indication for the different bonding situations are the colors: [Ph$_3$C]X (X = [B(CF$_3$)$_4$]$^-$, [(CF$_3$)$_3$BCN]$^-$) exhibit the typical yellow to orange color of the [Ph$_3$C]$^+$ cation, in contrast to the covalently bonded (CF$_3$)$_3$-

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Table 1. Crystallographic Data of [Ph₃C][B(CN)₄] at 173(2) K

empirical formula	$C_{23}H_{15}BN_4$
fw [g mol^{-1}]	358.20
cryst size [mm]	$1.3 \times 1.3 \times 1.5$
cryst syst	trigonal
space group	$R\bar{3}$
a, b [Å]	12.618(2)
c [Å]	21.220(4)
V [Å^3]	2925.9(9)
Z	6
ρ_{calc} [g cm^{-3}]	1.220
μ [mm^{-1}]	0.074
data collection range [deg]	$2.10 < \theta < 25.99$
no. of reflns collected/unique	3216/1012
no. of reflns obsd [$I > 2\sigma(I)$]	676
R_1 ($I > 2\sigma(I)$)^a	0.0356
R_1 (all data)	0.1027
wR_2 (all data)^b	0.1361

^{a} $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$, weight scheme $w = [\sigma^2(F_o) + (aP)^2 + bP]^{-1}$, $P = (\max(0,F_o^2) + 2F_c^2)/3$, $a = 0.0447$, $b = 0.0000$.
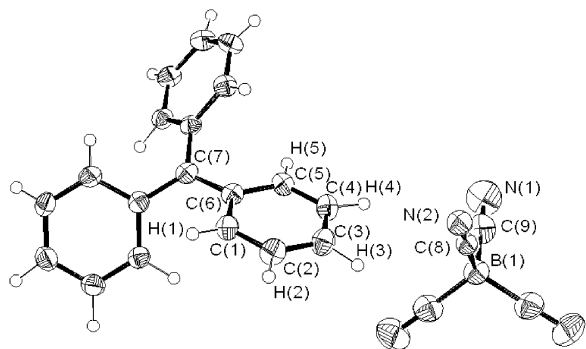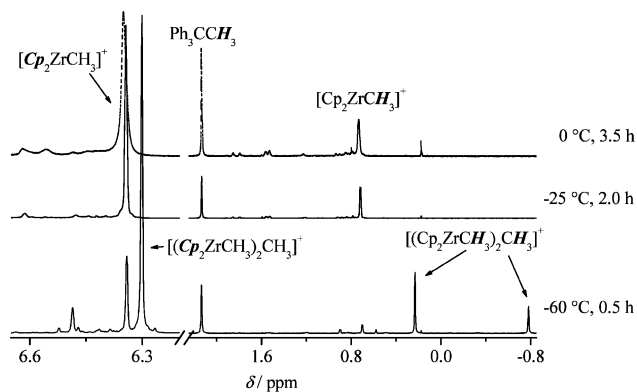

Figure 2. Ion pair of [PPh₃][B(CN)₄] in the solid-state structure (25% probability ellipsoids). Selected bond distances [Å]: C(1)−C(2), 1.371(2); C(2)−C(3), 1.388(2); C(3)−C(4), 1.388(2); C(4)−C(5), 1.380(2); C(5)−C(6), 1.415(2), C(6)−C(7), 1.4463(14); B(1)−C(8), 1.572(4), B(1)−C(9), 1.592(2); N(1)−C(9), 1.152(3); N(2)−C(8), 1.145(3). Selected bond angles [deg]: B(1)−C(8)−N(2), 180; B(1)−C(9)−N(1), 177.6(2); C(8)−B(1)−C(9), 108.51(11).

BNCCPh₃, which is colorless. (CF₃)₃BNCCPh₃ is not a suitable cocatalyst for homogeneous Ziegler−Natta catalysis or a transfer reagent of the [(CF₃)₃BNC]⁻ ion.

Structure of [Ph₃C][B(CN)₄]. [Ph₃C][B(CN)₄] crystallizes in the trigonal space group $R\bar{3}$ with 6 independent formula units in the unit cell. Crystallographic data are collected in Table 1. An ion pair in the crystal structure with selected bond parameters is depicted in Figure 2, and a model of the unit cell is displayed in Figure S3.

The local symmetry of the tetracyanoborate anions in the crystal structure is C_{3v} but with a very small distortion from T_d symmetry. The trityl cations exhibit nearly D_3 symmetry. The shortest contact between the cationic C atom and one N atom of the cyano ligands (3.174(1) Å) is similar to the sum of the van der Waals radii (∼3.3 Å).[19,20] This observation is in agreement with the spectroscopic results and the ionic structure of [Ph₃C][B(CN)₄].
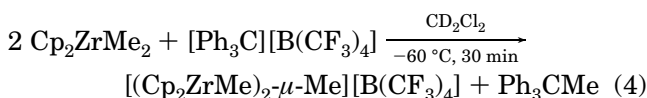
The C−N bond lengths (3 × 1.152(3) Å, 1.145(3) Å) and d(B−C) (3 × 1.572(4) Å, 1.592(2) Å) are comparable to values of other tetracyanoborates.[2,7] For the [Ph₃C]⁺
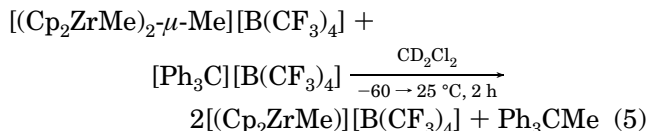
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Figure 3. ¹H NMR spectra of the reaction of Cp₂ZrMe₂ with [Ph₃C][B(CF₃)₄] in CD₂Cl₂.

cation similar bond parameters have been found in other trityl salts.[21]

NMR Spectroscopic Studies on the Reactions of [H(OEt₂)₂][B(CF₃)₄] and [Ph₃C]X (X = [B(CF₃)₄]⁻, [(CF₃)₃BCN]⁻, [B(CN)₄]⁻) with Cp₂ZrMe₂. According to Figure 3 the reaction of [Ph₃C][B(CF₃)₄] with Cp₂ZrMe₂ at −60 °C leads to the formation of the dimeric [(Cp₂ZrMe)₂-μ-Me]⁺ cation (eq 4).

$$2\ Cp_2ZrMe_2 + [Ph_3C][B(CF_3)_4] \xrightarrow[-60\ °C,\ 30\ min]{CD_2Cl_2}$$
$$[(Cp_2ZrMe)_2\text{-}\mu\text{-Me}][B(CF_3)_4] + Ph_3CMe\ \ (4)$$

When the temperature was increased to approximately −25 °C, [(Cp₂ZrMe)₂-μ-Me]⁺ reacted further to form [Cp₂ZrMe]⁺ and Ph₃CMe (eq 5).

$$[(Cp_2ZrMe)_2\text{-}\mu\text{-Me}][B(CF_3)_4] +$$
$$[Ph_3C][B(CF_3)_4] \xrightarrow[-60 \to 25\ °C,\ 2\ h]{CD_2Cl_2}$$
$$2[(Cp_2ZrMe)][B(CF_3)_4] + Ph_3CMe\ \ (5)$$

As the temperature was raised slowly to 0 °C and then to room temperature, the amount of unidentified decomposition products observed in the NMR spectra increased. The NMR spectroscopic data of [(Cp₂ZrMe)₂-μ-Me][B(CF₃)₄] and [Cp₂ZrMe][B(CF₃)₄] are collected in Table 2. The initial formation of the bridged dimeric zirconocene according to eq 4 was previously described for similar systems, for example, [Ph₃C][B(C₆F₅)₄] and Cp₂ZrMe₂.[22] A colorless solid of unknown composition precipitated during the reaction, and its formation rate increased with increasing temperature. After 15 h at room temperature only low-intensity signals remained in the proton spectra, which can be assigned to the cyclopentadienyl ligands. Fast decomposition of the [Cp₂ZrMe]⁺ cation in CD₂Cl₂ solution is known.[22] In the ¹¹B and ¹⁹F NMR spectra neither decomposition products of the counteranion [B(CF₃)₄]⁻ due to F⁻ abstraction[23] nor the possible side products Cp₂ZrMeF[24,25] or Cp₂ZrF₂[25−28] were detected.

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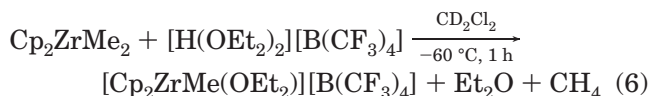(26) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1986**, *26*, 383.

Table 2. NMR Spectroscopic Data of the Products of the Reactions of Cp_2ZrMe_2 with $[Ph_3C][B(CF_3)_4]$, $[Ph_3C][(CF_3)_3BCN]$, $[Ph_3C][B(CN)_4]$, and $[H(OEt_2)_2][B(CF_3)_4]^{a,b}$

$[Cp_2ZrMe][B(CF_3)_4]$	$\delta(^1H) = 0.74$ (CH_3; 3 H), 6.34 (C_5H_5; 10 H);
	$\delta(^{11}B) = -18.9$; $\delta(^{19}F) = -61.6$; $^2J(^{11}B,^{19}F) = 25.9$
$[\{Cp_2ZrMe\}_2\text{-}\mu\text{-}Me][B(CF_3)_4]$	$\delta(^1H) = -0.78$ ($\mu$$-CH_3$; 3 H), 0.23 ($CH_3$; 6 H), 6.30 ($C_5H_5$; 20 H);
	$\delta(^{11}B) = -18.9$; $\delta(^{19}F) = -61.6$; $^2J(^{11}B,^{19}F) = 25.9$
$[Cp_2ZrMe(OEt_2)][B(CF_3)_4]$	$\delta(^1H) = 0.84$ (CH_3; 3 H), 1.24 (CH_2CH_3; 12 H), 3.68 (CH_2; 8 H), 6.46 (C_5H_5; 10 H);
	$\delta(^{11}B) = -18.9$; $\delta(^{19}F) = -61.6$; $^3J(C^1H_2,C^1H_3) = 7.0$; $^2J(^{11}B,^{19}F) = 25.9$
$Cp_2ZrMe\{NCB(CF_3)_3\}$	$\delta(^1H) = 0.64$ (CH_3; 3 H), 6.46 (C_5H_5; 10 H); $\delta(^{11}B) = -21.9$; $\delta(^{19}F) = -61.0$
$Cp_2Zr\{NCB(CF_3)_3\}_2$	$\delta(^1H) = 6.36$ (C_5H_5; 10 H); $\delta(^{11}B) = -21.9$; $\delta(^{19}F) = -60.9$
$Cp_2ZrMe\{NCB(CN)_3\}$	$\delta(^1H) = 0.09$ (CH_3; 3 H), 6.04 (C_5H_5; 10 H); $\delta(^{11}B) = -37.3$
$Cp_2ZrMe\{NCB(CN)_3\}\cdot CD_3CN/$	$\delta(^1H) = 0.08$ (CH_3; 3 H), 6.09 (C_5H_5; 10 H); $\delta(^{11}B) = -38.5$
$[Cp_2ZrMe(NCCD_3)]^+\cdot CD_3CN^c$	
$Cp_2Zr\{NCB(CN)_3\}_2\cdot CD_3CN/$	$\delta(^1H) = 6.55$ (C_5H_5; 10 H); $\delta(^{11}B) = -38.5$
$[Cp_2Zr\{NCB(CN)_3\}(NCCD_3)]^+\cdot CD_3CN/$	
$[Cp_2Zr(NCCD_3)_2]^{2+}\cdot CD_3CN^c$	

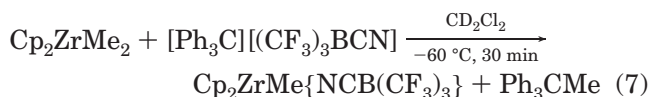^{a} δ in ppm, J in Hz. ^{b} NMR solvent: CD_2Cl_2. ^{c} NMR solvent: CD_3CN.

The reaction of $[Ph_3C][B(CF_3)_4]$ with Cp_2ZrMe_2 was also investigated in d_8-toluene. At 0 °C the main reaction product was the $[Cp_2ZrMe]^+$ cation. Probably due to low solubility of the $[Cp_2ZrMe][B(CF_3)_4]$ salt or a similar species, a brownish precipitate was formed. It easily dissolved in acetonitrile, and in the NMR spectra no evidence was found for a decomposition of the $[B(CF_3)_4]^-$ anion. An assignment of the ^1H NMR signals in the region typical for Cp protons was not possible. Probably zirconocene complexes with one or more CD_3CN ligands are present.[29,30]

Through protonation of Cp_2ZrMe_2 with $[H(OEt_2)_2]$-$[B(CF_3)_4]$, methane is released from the reaction mixture and the vacant coordination site at Zr is saturated by one diethyl ether molecule (eq 6).

$$Cp_2ZrMe_2 + [H(OEt_2)_2][B(CF_3)_4] \xrightarrow[-60\text{ °C, 1 h}]{CD_2Cl_2}$$
$$[Cp_2ZrMe(OEt_2)][B(CF_3)_4] + Et_2O + CH_4 \quad (6)$$

The proton NMR signals of the $[Cp_2ZrMe(OEt_2)]^+$ cation are collected in Table 2 and are assigned by using the relative intensities of the signals and by comparing with data described in the literature.[16] During the reaction a solid was formed that was sparingly soluble in CD_3CN. In the ^{11}B and ^{19}F NMR spectra traces of novel unidentified trifluoromethylborate anions were found that indicate a partial decomposition of the $[B(CF_3)_4]^-$ anion.

In contrast to the reaction of $[Ph_3C][B(CF_3)_4]$ with Cp_2ZrMe_2, in the related reaction of $[Ph_3C][(CF_3)_3BCN]$ with Cp_2ZrMe_2 a bridged dimeric intermediate was not observed and instead only $Cp_2ZrMe\{NCB(CF_3)_3\}$ was formed according to eq 7.

$$Cp_2ZrMe_2 + [Ph_3C][(CF_3)_3BCN] \xrightarrow[-60\text{ °C, 30 min}]{CD_2Cl_2}$$
$$Cp_2ZrMe\{NCB(CF_3)_3\} + Ph_3CMe \quad (7)$$

Since a small excess of the trityl reagent was employed, the formation of a second zirconocene complex was possible: $Cp_2Zr\{NCB(CF_3)_3\}_2$. Similar coordination compounds of the Cp_2Zr^{2+} fragment have been described with acetonitrile as ligand.[29,30] The NMR data of the

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Table 3. Polymerization of Propene with rac-Et(1-Ind)$_2$ZrMe$_2$ and $[Ph_3C][B(CF_3)_4]$, $[Ph_3C][B(CN)_4]$, or $[H(OEt_2)_2][B(CF_3)_4]$

cocatalyst		T [°C]	t [min]	productivity [kg mol(Zr)$^{-1}$ h^{-1}]	mmmm [%]
MAO		20	20	12 000	92
$(C_6F_5)_3B$	$^iBu_3Al$	20	20	360	86
$[Ph_3C][B(C_6F_5)_4]$	$^iBu_3Al$	26	3	153 000	91
$[Ph_3C][B(CF_3)_4]$	$^iBu_3Al$	20	20	5	n.o.^{a}
$[Ph_3C][B(CF_3)_4]$	$^iBu_3Al$	20	120	0.5	84
$[Ph_3C][B(CF_3)_4]$	$^iBu_3Al$	50	20		
$[Ph_3C][B(CN)_4]$	$^iBu_3Al$	20	20		
$[H(OEt_2)_2][B(CF_3)_4]$	$^iBu_3Al$	20	20	1	n.o.

^{a} n.o. = not observed.

neutral complexes are collected in Table 2. The ^{11}B and ^{19}F NMR signals of the $[(CF_3)_3BCN]^-$ ligand are broadened when coordinated to an electrophilic center. As found for the reactions described above, a solid precipitated from solution, and this process also was enhanced with increasing temperature. The precipitate can neither in CD_3CN nor in D_2O completely be dissolved; hence the composition remained unclear. In the NMR spectra no evidence was found for the decomposition of the $[(CF_3)_3BCN]^-$ anion.

The reaction between $[Ph_3C][B(CN)_4]$ and Cp_2ZrMe_2 resulted even at -60 °C in the relatively fast precipitation of $Cp_2ZrMe\{NCB(CN)_3\}$ as main product (eq 8).

$$Cp_2ZrMe_2 + [Ph_3C][B(CN)_4] \xrightarrow[-60\text{ °C, 30 min}]{CD_2Cl_2}$$
$$Cp_2ZrMe\{NCB(CN)_3\} + Ph_3CMe \quad (8)$$
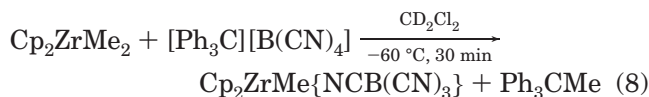
The colorless insoluble reaction product is completely soluble in acetonitrile. The NMR spectroscopic data are summarized in Table 2, and the NMR spectra are presented in Figure S4. The ^1H NMR chemical shifts of the cyclopentadienyl protons in CD_3CN solution are similar to those reported for $[Cp_2ZrMe(NCMe)][BPh_4]$ and $[Cp_2Zr(NCMe)_2][BPh_4]_2$,[29] which indicates a fast ligand exchange between CD_3CN and the $[B(CN)_4]^-$ anion.

Polymerization of Propene. In Table 3 the results of the polymerization reactions of rac-Et(1-Ind)$_2$ZrMe$_2$ and $[H(OEt_2)_2][B(CF_3)_4]$, $[Ph_3C][B(CF_3)_4]$, or $[Ph_3C]$-$[B(CN)_4]$ as cocatalysts in the presence of $^iBu_3Al$ are summarized. For comparison the respective data of the polymerizations with MAO, $(C_6F_5)_3B$, and $[Ph_3C]$-$[B(C_6F_5)_4]$ are listed. The very low to zero productivities with the cocatalysts containing the $[B(CF_3)_4]^-$ anion can be attributed to their obvious low solubility even in d_8-toluene and CD_2Cl_2 as outlined in the NMR experi-

ments. Another reason that cannot be fully excluded is the instability of $[B(CF_3)_4]^-$ under the reaction conditions due to F^- abstraction as found previously under more severe conditions, e.g., in the presence of silyl cations.[23] Especially the polymerization reaction at 50 °C, where no polymer was obtained, supports this hypothesis.

In the case of the activation of the metallocene with $[Ph_3C][B(CN)_4]$ the coordination site at the cationic metallocene complex is occupied by $[B(CN)_4]^-$, and so no reaction with propene can occur.

Summary and Conclusion

Simple reaction routes to salts with the borate anions $[B(CF_3)_4]^-$, $[(CF_3)_3BCN]^-$, and $[B(CN)_4]^-$ are described. The oxonium salt $[H(OEt_2)_2][B(CF_3)_4]$ exhibits an unexpected high thermal stability. The three trityl salts are all ionic in nature, whereas the isocyanoborate anion $[(CF_3)_3BNC]^-$ forms the molecular complex $Ph_3CCNB(CF_3)_3$.

Methyl group abstraction from Cp_2ZrMe_2 using $[H(OEt_2)_2][B(CF_3)_4]$ or $[Ph_3C]X$ (X = $[B(CF_3)_4]^-$, $[(CF_3)_3BCN]^-$, $[B(CN)_4]^-$) generates metallocene cations, with $[B(CF_3)_4]^-$, while $[(CF_3)_3BCN]^-$ and $[B(CN)_4]^-$ coordinate to the metal center. The zirconocene salts with $[B(CF_3)_4]^-$ counteranions are not soluble in common weakly coordinating solvents, e.g., toluene. Hence, they are not suitable for homogeneous Ziegler–Natta catalysis.

Experimental Section

General Considerations. Apparatus. Volatile materials were manipulated in a glass vacuum apparatus equipped with a capacitance pressure gauge (type 280 E Setra Instruments) and fitted with PTFE stem valves (Young, London) and NS 14.5 standard tapers. Air- and moisture-sensitive compounds were handled under an Ar atmosphere in a glovebox (MBraun, Germany). Reactions involving air-sensitive compounds were performed under nitrogen using standard Schlenk techniques.

Solvents were dried and distilled under N_2 and stored over 3 or 4 Å molecular sieves in flasks, equipped with valves with a PTFE stem (Young, London). Ph_3CCl, Ph_3CBr, and MeLi were obtained from Aldrich and Cp_2ZrMe_2 from Strem Chemicals and used as received. $K[B(CF_3)_4]$,[1] $K[(CF_3)_3BCN]$,[8] $K[B(CN)_4]$,[2,4] and *rac*-$(Ind)_2EtZrCl_2$[31] were synthesized according to literature procedures.

NMR Spectroscopy. ^1H, ^{19}F, and ^{11}B NMR spectra were recorded at different temperatures on a Bruker Avance DRX-300 spectrometer operating at 300.13, 282.41, or 96.92 MHz for ^1H, ^{19}F, and ^{11}B nuclei, respectively. ^{13}C NMR spectroscopic studies were performed at room temperature on a Bruker Avance DRX-500 spectrometer, operating at 125.758 MHz. The NMR signals were referenced against TMS and $CFCl_3$ as internal standards and $BF_3 \cdot OEt_2$ as external standard. Samples of moisture-sensitive compounds were prepared in 5 mm o.d. NMR tubes, equipped with special valves with PTFE stems (Young, London).[32]

Vibrational Spectroscopy. IR spectra were recorded at room temperature in the range 4000–400 cm^{-1} on an IFS 66v FTIR instrument (Bruker, Karlsruhe, Germany). A DTGS detector, together with a KBr/Ge beam splitter, was used in the region of 4000–400 cm^{-1}. In this region 128 scans were co-added for each spectrum using an apodized resolution of 2

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cm^{-1}. Solid samples were crushed between AgBr disks. Raman spectra of the solids were recorded at room temperature with a resolution of 2 cm^{-1} on a RFS 100/S FT Raman spectrometer (Bruker, Karlsruhe, Germany) using the 1064 nm excitation (<500 mW) of a Nd:YAG laser.

DSC Measurements. Thermo-analytical measurements were made with a Netzsch DSC204 instrument. Temperature and sensitivity calibrations in the temperature range 20–500 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 5–10 mg of the solid samples was weighed and contained in sealed aluminum crucibles. They were studied in the temperature range 20–600 °C with a heating rate of 5 K min^{-1}; throughout this process the furnace was flushed with dry nitrogen. For the evaluation of the output, Netzsch Protens4.0 software was employed.

$[H(OEt_2)_2][B(CF_3)_4]$. A 250 mL round-bottom flask equipped with a valve with a PTFE stem (Young, London), fitted with a PTFE-coated magnetic stirring bar, was charged with $K[B(CF_3)_4]$ (546 mg, 1.68 mmol) and dried in vacuo. Diethyl ether (80 mL) was vacuum transferred into the flask. The reaction mixture was warmed to −50 °C. Into a second 290 mL round-bottom flask equipped with a valve with a PTFE stem (Young, London) HCl (12 mmol) was added. Both flasks were connected, and the HCl gas was allowed to diffuse into the diethyl ether solution. A colorless solid precipitated. The mixture was warmed to −20 °C for 5 h. All volatiles were removed under reduced pressure, and the colorless residue was extracted two times with CH_2Cl_2 (20 mL, 10 mL). The suspension was filtered through a glass frit with Celite, and the colorless solutions were collected in a 100 mL two-neck round-bottom flask with a standard cone taper and a valve with a PTFE stem (Young, London). After removal of the solvent in vacuo $[H(OEt_2)_2][B(CF_3)_4]$ was obtained as a colorless solid. Yield: 530 mg (1.22 mmol, 73%). ^1H NMR (CD_2Cl_2, RT): δ 16.3 (s, 1H), 4.11 (q, $^3J_{HH}$ = 7.2 Hz, 8H), 1.44 (t, $^3J_{HH}$ = 7.2 Hz, 12H). $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, RT): δ 132.6 (q, $^1J_{BC}$ = 73.4 Hz, 4C, CF_3), 71.1 (tqt, $^1J_{HC}$ = 150.0 Hz, $^2J_{HC}$ = 4.3 Hz, $^3J_{HC}$ = 2.7 Hz, 4C, CH_2), 13.9 (qt, $^1J_{HC}$ = 128.4 Hz, $^2J_{HC}$ = 2.7 Hz, 4C, CH_3). ^{11}B NMR (CD_2Cl_2, RT): δ −18.9 (tridecet, $^2J_{BF}$ = 25.9 Hz). ^{19}F NMR (CD_2Cl_2, RT): δ −61.6 (q, $^2J_{BF}$ = 25.9 Hz). Anal. Calcd for $H_{21}C_{12}BF_{12}O_2$ (436.09): C, 33.05; H, 4.85. Found: C, 32.23; H, 4.84.

$[Ph_3C][B(CF_3)_4]$. $K[B(CF_3)_4]$ (500 mg, 1.53 mmol) and trityl chloride (430 mg, 1.61 mmol) were placed into a 250 mL round-bottom flask equipped with a valve with a PTFE stem (Young, London) and fitted with a PTFE-coated magnetic stirring bar. The solids were carefully dried under reduced pressure. Under a nitrogen atmosphere dichloromethane (100 mL) was added via a PFA cannula. Immediately after addition of the solvent the solution above the suspension turned yellow. The reaction mixture was stirred 4 h at room temperature. The resulting suspension was filtered through a glass frit covered with Celite under an inert atmosphere into a 200 mL Schlenk flask fitted with a PTFE-coated magnetic stirring bar. The reaction flask and the glass frit were washed two times with dichloromethane (20 and 10 mL). The yellow solution was reduced to a volume of 10 mL. Upon addition of hexane (70 mL) a yellow precipitate formed. The yellow solid was separated by filtration through a glass frit, washed with 10 mL of hexane, and dried in a vacuum. Yield: 705 mg (1.33 mmol, 87%). ^1H NMR (CD_2Cl_2, RT): δ 8.31 (m, 1H, *p*-H), 7.93 (m, 2H, *m*-H), 7.73 (m, 2H, *o*-H). $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, RT): δ 211.5 (s, 1C, C^+), 144.1 (dtt, $^1J_{HC}$ = 167.9 Hz, $^2J_{HC}$ = 1.6 Hz, $^3J_{HC}$ = 7.9 Hz, 3C, *p*-C), 143.3 (ddd, $^1J_{HC}$ = 167.9 Hz, $^3J_{HC}$ = 7.5 Hz, $^3J_{HC}$ = 7.6 Hz, 6C, *o*-C), 140.5 (tt, $^2J_{HC}$ = 0.9 Hz, $^3J_{HC}$ = 7.9 Hz, 3C, *i*-C), 132.6 (q, $^1J_{BC}$ = 73.4 Hz, 4C, CF_3), 131.2 (dd, $^1J_{HC}$ = 167.6 Hz, $^3J_{HC}$ = 7.8 Hz, 6C, *m*-C). ^{11}B NMR (CD_2Cl_2, RT): δ −18.9 (tridecet, $^2J_{BF}$ = 25.9 Hz). ^{19}F NMR (CD_2Cl_2, RT): δ −61.6 (q, $^2J_{BF}$ = 25.9 Hz). Anal. Calcd for $H_{15}C_{23}BF_{12}$ (530.16): C, 52.11; H, 2.85. Found: C, 52.06; H, 2.80.

[Ph₃C][(CF₃)₃BCN]. The compound was prepared according to the procedure as described for [Ph₃][B(CF₃)₄]. Substrates: K[(CF₃)₃BCN] (312 mg, 1.10 mmol) and trityl chloride (323 mg, 1.16 mmol). Yield: 445 mg (0.91 mmol, 83%). ^{1}H NMR (CD₂Cl₂, RT): δ 8.31 (m, 1H, *o*-H), 7.93 (m, 2H, *m*-H), 7.73 (m, 2H, *p*-H). ^{13}C{^{19}F} NMR (CD₂Cl₂, RT): δ 211.5 (s, 1C, C⁺), 144.1 (dtt, $^1J_{HC}$ = 167.9 Hz, $^2J_{HC}$ = 1.6 Hz, $^3J_{HC}$ = 7.9 Hz, 3C, *p*-C), 143.3 (ddd, $^1J_{HC}$ = 167.9 Hz, $^3J_{HC}$ = 7.5 Hz, $^3J_{HC}$ = 7.6 Hz, 6C, *o*-C), 140.5 (tt, $^2J_{HC}$ = 0.9 Hz, $^3J_{HC}$ = 7.9 Hz, 3C, *i*-C), 132.4 (q, $^1J_{BC}$ = 76.2 Hz, 3C, CF₃), 131.2 (dd, $^1J_{HC}$ = 167.6 Hz, $^3J_{HC}$ = 7.8 Hz, 6C, *m*-C), 127.5 (q, $^1J_{BC}$ = 64.0 Hz, 1C, CN). ^{11}B NMR (CD₂Cl₂, RT): δ −22.3 (decet, $^2J_{BF}$ = 29.0 Hz). ^{19}F NMR (CD₂Cl₂, RT): δ −62.1 (q, $^2J_{BF}$ = 29.0 Hz). Anal. Calcd for H₁₅C₂₃BF₉N (487.17): C, 56.71; H, 3.10; N, 2.88. Found: C, 55.85; H, 3.15; N, 2.98.

[Ph₃C][B(CN)₄]. The preparation was performed similar to the syntheses of [Ph₃][B(CF₃)₄] and [Ph₃C][(CF₃)₃BCN]. The only difference was the use of acetonitrile as solvent instead of dichloromethane. CH₃CN was removed after the reaction (4 h), and the residue was suspended in CH₂Cl₂ and filtered. Substrates: Ag[B(CN)₄] (500 mg, 2.25 mmol) and trityl bromide (726 mg, 2.25 mmol). Yield: 408 mg (1.14 mmol, 51%). ^{1}H NMR (CD₂Cl₂, RT): δ 8.31 (m, 1H, *p*-H), 7.94 (m, 2H, *m*-H), 7.73 (m, 2H, *o*-H). ^{13}C{^{1}H} NMR (CD₂Cl₂, RT): δ 211.2 (s, 1C, C⁺), 143.8 (s, 3C, *p*-C), 143.0 (s, 6C, *o*-C), 140.2 (s, 3C, *i*-C), 131.0 (s, 6C, *m*-C), 122.7 (q, $^1J_{BC}$ = 71.5 Hz, 4C, CN). ^{11}B NMR (CD₂Cl₂, RT): δ −38.6 (s). Anal. Calcd for H₁₅C₂₃BN₄ (358.21): C, 77.12; H, 4.22; N, 15.64. Found: C, 77.19; H, 4.21; N, 15.50.

(CF₃)₃BNCCPh₃. K[(CF₃)₃BNC] (32 mg, 0.11 mmol) and Ph₃CBr (40 mg, 0.12 mmol) were transferred into a 5 mm o.d. NMR tube, equipped with a valve with a PTFE stem (Young, London) and connected with a glass vacuum apparatus. The mixture was dried in a vacuum, and then CD₂Cl₂ (1.5 mL) was condensed into the NMR tube at −196 °C. The NMR tube was warmed to room temperature and shaken for 3 h. The solution and the precipitate are colorless. ^{1}H NMR (CD₂Cl₂, RT): δ 7.4 (m, 3H), 7.2 (m, 2H). ^{13}C{^{1}H} NMR (CD₂Cl₂, RT): 136.0 (s, 3C), 130.7 (s, 6C), 130.4 (s, 6C), ∼130 (s, 3C, CF₃), 129.0 (s, 3C), 123.1 (s, 1C, CN), δ 60.1 (s, 1C, *C*CN). ^{11}B NMR (CD₂Cl₂, RT): δ −14.4 (s, br). ^{19}F NMR (CD₂Cl₂, RT): δ −66.4 (s, br).

Reactions of Cp₂ZrMe₂ with Cocatalysts Monitored by NMR Spectroscopy. General Procedure. In a glovebox a 5 mm o.d. NMR tube, equipped with a valve with a PTFE stem (Young, London),³² was charged with Cp₂ZrMe₂ and cocatalyst. The NMR tube was connected to a glass vacuum apparatus, and 1 mL of CD₂Cl₂ was added in vacuo. The NMR tube was placed into an ethanol bath at −60 °C, and after 10 min it was transferred into the probe head of a NMR spectrometer (Bruker Avance 300). The first NMR spectra were recorded 30 min after starting the reaction.

Reaction of Cp₂ZrMe₂ with [Ph₃C][B(CF₃)₄] in CD₂Cl₂. [Ph₃C][B(CF₃)₄] (40 mg, 0.08 mmol); Cp₂ZrMe₂ (19 mg, 0.08 mmol). At −60 °C an orange solution was obtained, and slowly a colorless precipitate formed. After 30 min a mixture of [(Cp₂ZrMe)₂-µ-Me][B(CF₃)₄], [Ph₃C][B(CF₃)₄], and Ph₃CMe was observed. The reaction mixture was warmed to −25 °C, and after 1.5 h as sole reaction products [Cp₂ZrMe][B(CF₃)₄] and Ph₃CMe were found. When the reaction mixture was warmed to 0 °C and then to room temperature, other unidentified signals were observed and the precipitation is more rapid. After 15 h only weak, broad signals due to cyclopentadienyl protons were observed in the ^{1}H NMR spectrum.

Reaction of Cp₂ZrMe₂ with [Ph₃C][B(CF₃)₄] in *d₈*-Toluene. [Ph₃C][B(CF₃)₄] (39 mg, 0.07 mmol); Cp₂ZrMe₂ (18 mg, 0.07 mmol). The reaction was started at 0 °C, and a brown precipitate began to form. In the ^{1}H NMR spectrum only the signals of [Cp₂ZrMe]⁺ and Ph₃CMe were observed. After keeping the mixture for 3 h at room temperature no signals were found in the region of the Cp protons anymore. All volatiles were removed at reduced pressure, and the brownish

residue was dissolved in dry CD₃CN. Neither in the ^{11}B nor in the ^{19}F NMR spectrum were decomposition products of [B(CF₃)₄]⁻ identified. In the ^{1}H NMR spectrum signals in the typical range for cyclopentadienyl protons were located, but no assignment was possible.

Reaction of Cp₂ZrMe₂ with [H(OEt₂)₂][B(CF₃)₄]. [H(OEt₂)₂][B(CF₃)₄] (86 mg, 0.20 mmol); Cp₂ZrMe₂ (47 mg, 0.19 mmol). At −60 °C gas evolution and formation of a beige solid was observed. By ^{1}H NMR spectroscopy [Cp₂ZrMe(OEt₂)]⁺, diethyl ether, CH₄, and excess [H(OEt₂)₂]⁺ were identified. The ratio of Et₂O versus [Cp₂ZrMe(OEt₂)]⁺ was 5:1. With increasing temperature and reaction time more solid precipitated and the color changed from orange to brown. After 12 h at room temperature all volatile components were removed in vacuo and dry CD₃CN was condensed into the NMR tube. The resulting brown solution contained a colorless solid and was analyzed by NMR spectroscopy. In the ^{1}H NMR spectra three signals were attributed to Cp protons, but an assignment was impossible. A few other signals of weaker intensity than those of the [B(CF₃)₄]⁻ anion were present in the ^{11}B and ^{19}F NMR spectra.

Reaction of Cp₂ZrMe₂ with [Ph₃C][(CF₃)₃BCN]. [Ph₃C][(CF₃)₃BCN] (53 mg, 0.11 mmol); Cp₂ZrMe₂ (25 mg, 0.10 mmol). At −60 °C a red-brown, clear solution was obtained. According to the NMR spectra Cp₂ZrMe{NCB(CF₃)₃} was the main product and probably Cp₂Zr{NCB(CF₃)₃}₂ was formed as a side product due to the excess of [Ph₃C][(CF₃)₃BCN]. At −30 °C the reaction mixture slowly turned cloudy. At room temperature the rate of precipitation increased. The mixture was kept at room temperature for 1 day before all volatiles were removed under reduced pressure. The residue was not completely soluble in CD₃CN. The ^{11}B and ^{19}F NMR spectra showed only the signals of the [(CF₃)₃BCN]⁻ anion. The signals in the ^{1}H NMR spectrum could not be assigned. Attempts to dissolve the residue in water failed.

Reaction of Cp₂ZrMe₂ with [Ph₃C][B(CN)₄]. [Ph₃C]-[B(CN)₄] (39 mg, 0.11 mmol); Cp₂ZrMe₂ (18 mg, 0.07 mmol). Immediately after warming to −60 °C a white solid precipitated. While at the beginning of the reaction the presence of Cp₂ZrMe{NCB(CN)₃} could be established by NMR spectroscopy, after 15 h at room temperature no boron-, fluorine-, or cyclopentadienyl-containing species were found in solution. The liquid phase and the precipitate were colorless. The solvent was removed in vacuo, and the residue was dissolved in CD₃CN and analyzed by NMR spectroscopy.

X-ray Crystallographic Study of [Ph₃C][B(CN)₄]. Crystals suitable for an X-ray diffraction study were obtained from a saturated solution of [Ph₃C][B(CN)₄] in CD₃CN. The crystals were placed on a copper trough,³³ cooled to −70 °C in a steam of nitrogen. During the preparation the trough was flushed with dry nitrogen. Suitable crystals were selected under a polarizing microscope and fitted into glass capillaries (o.d. 0.1 to 0.3 mm). The capillaries were sealed off at both ends to give glass cylinders of approximately 20 mm length. The glass cylinders, containing the crystals, were attached with wax to the goniometer head. Diffraction data were collected at 173 K on a Nonius diffractometer with a CCD camera using Mo Kα radiation (λ = 0.71069 Å) and a graphite monochromator. At the end of the data collection, the first intensity measurement was repeated, which demonstrated the stability of the crystal during the X-ray diffraction analysis. The intensity data were subsequently corrected with the SCALEPACK program.³⁴ The structure was solved in $R\bar{3}$ (No. 148) by direct methods with SHELXS-97³⁵,³⁶ and refined with anisotropic temperature

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factors.[37] A summary of experimental details and crystal data is presented in Table 1.

Polymerizations. General Considerations for Propylene Polymerization. Methylaluminoxane (MAO) was obtained from Albemarle and dried under vacuum. Triisobutylaluminum (TIBA) was purchased from Aldrich and was used as received. Toluene was passed through two purification columns packed with activated alumina and copper catalyst and collected under nitrogen. Propylene gas was purchased from Matheson, and liquid propylene was purchased from Scott Specialty Gases. Both were passed through two purification columns packed with activated alumina and copper catalyst.

Polymerization Procedure for MAO Activation. In a 300 mL stainless steel Parr reactor, 150 mg of MAO in 8 mL of toluene was equilibrated for 30 min at 20 °C with 90 mL of liquid propylene. Metallocene in toluene (2 mL) was injected into the reactor by argon pressure, and the polymerization was run for 20 min, after which time methanol (10 mL) was injected to quench the reaction. The polypropylene was precipitated from acidified methanol, filtered, washed with methanol, and dried under vacuum at 40 °C.

Liquid Propylene Polymerization (Borate or Borane Activation). In a 300 mL stainless steel Parr reactor, 50 mg of TIBA in 8 mL of toluene was equilibrated for 30 min at 20 °C with 90 mL of liquid propylene. Metallocene and borate/borane (stoichiometric) in toluene (total volume 2 mL) were injected, respectively, into the reactor by argon pressure, and the polymerization was run for 20 min, after which time methanol (10 mL) was injected to quench the reaction. Polypropylene was precipitated from acidified methanol, filtered, washed with methanol, and dried under vacuum at 40 °C.

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(37) Sheldrick, G. M. Universität Göttingen, 1997.

Gaseous Propylene Polymerization at 50 °C (Borate Activation). In a 300 mL stainless steel Parr reactor, 50 mg of TIBA in 95 mL of toluene was equilibrated for 1 h at 50 °C with 75 psig propylene gas. Metallocene and borate (stoichiometric) in toluene (total volume 5 mL) were injected, respectively, into the reactor by propylene pressure, and the polymerization was run for 1 h, after which time methanol (10 mL) was injected to quench the reaction.

Polymer Characterization. Polypropylene pentad distributions were determined by ^{13}C NMR measurements using a Varian Unity Innova 300 MHz instrument. Spectra were acquired with samples (80 mg in 2 mL of *o*-dichlorobenzene/10% vol d_6-benzene with $Cr(acac)_3$ as a relaxation agent) at 100 °C in 10 mm NMR tubes.

Details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the depository number CCDC-273901.

Supporting Information Available: Tables of IR data of $[Ph_3C][B(CN)_4]$ and $[Ph_3C][B(CF_3)_4]$, a view of the unit cell, IR spectra of $[Ph_3C][B(CN)_4]$ and $[Ph_3C][B(CF_3)_4]$, and the ^{1}H NMR spectra of the reaction of Cp_2ZrMe_2 with $[Ph_3C][B(CN)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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