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Synthesis and Characterization of the New Alkyl Borates $[RB(C_6F_5)_3]^-$ (R = CH_2Me, $CHMe_2$, CH_2CMe_3): Utilization of $[Me_3CCH_2B(C_6F_5)_3]^-$ as a Weakly Coordinating Counteranion during Zirconocene-Induced Catalysis of Propylene Polymerization

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Reactions of alkyllithium compounds RLi (R = Me, Et, *i*-Pr, Np) with $B(C_6F_5)_3$ result in the formation of the alkylborate salts $Li[RB(C_6F_5)_3]$. Metathesis reactions of these with Ph_3CCl and chloride salts of $(Ph_3P)_2N^+$, $PMePh_3^+$, and $HNMe_2Ph^+$ proceed with varying degrees of success, as shown by NMR spectroscopy and electrospray mass spectrometry, and the compounds $[PPN][EtB(C_6F_5)_3]$, $[PMePh_3][NpB(C_6F_5)_3]$, and $[HNMe_2Ph][NpB(C_6F_5)_3]$ have been characterized crystallographically. All three anions assume the expected pseudotetrahedral structures with normal B−aryl bond lengths and R−B−aryl and aryl−B−aryl bond angles. The compound $[HNMe_2Ph][NpB(C_6F_5)_3]$ reacts with Cp_2ZrMe_2, $(Indenyl)_2ZrMe_2$, and $SBIZrMe_2$ to give propylene polymerization catalysts that are significantly more active and give higher molecular weight polypropylene than do the catalysts obtained using $B(C_6F_5)_3$. Thus the $[NpB(C_6F_5)_3]^-$ anion is for steric reasons more weakly coordinating than is $[MeB(C_6F_5)_3]^-$.

Recent years have seen huge advances in the development of well-defined, cationic substituted cyclopentadienyl (Cp′) complexes of the group 4 metals as olefin polymerization catalysts.[1] In the most studied catalyst systems, the active species are generated from neutral metallocene precursors as in eqs 1 and 2, reactions that involve the abstraction of methyl carbanions from the metals by $B(C_6F_5)_3$ and trityl ion, respectively.

$$\begin{array}{c} Cp'_2ZrMe_2 + B(C_6F_5)_3 \longrightarrow Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3 \\ \downarrow\!\uparrow \\ \text{"}[Cp'_2ZrMe]\text{"}^+ + [MeB(C_6F_5)_3]^- \qquad (1) \end{array}$$

$$\begin{array}{c} 2Cp'_2ZrMe_2 + [Ph_3C][B(C_6F_5)_4] \longrightarrow [Cp'_2ZrMe(\mu\text{-}Me)ZrMeCp'_2][B(C_6F_5)_4] + Ph_3CMe \\ \Big\downarrow{\scriptstyle [Ph_3C][B(C_6F_5)_4]} \\ 2\text{"}[Cp'_2ZrMe]\text{"}^+ + 2[B(C_6F_5)_4]^- + Ph_3CMe \qquad (2) \end{array}$$

The $[MeB(C_6F_5)_3]^-$ anion of eq 1 coordinates relatively strongly to electron-deficient cations via the hydrogens of the methyl group, and the dissociation postulated is inferred from the chemistry of the complexes formed. In contrast, the $[B(C_6F_5)_4]^-$ anion of eq 2 forms such weakly associated ion pairs that the dizirconium species is formed initially. Again, however, the chemistry of the complexes formed implies the ready availability of $[Cp'_2ZrMe]^+$.[1] Of course, in order for an initiator system to exhibit high activity, the monomer must be able to coordinate readily. Since this generally involves accessing the putative 14-electron intermediate $[Cp'_2ZrMe]^+$ by displacement of the counteranions, considerable attention has been paid to determining the coordinating abilities of anionic species such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ and correlating their ease of dissociation with catalyst activities.[2]

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The development of weakly coordinating anions has thus become an important theme in the context of metallocene-induced Ziegler–Natta polymerizations,[2] and on the premise that delocalization of negative charge over as many atoms as possible in a large anion should be of advantage, there have been reported several very bulky anions in which the perfluorophenyl groups of $[BMe(C_6F_5)_3]^-$ have been substituted by more complex perfluoroaryl groups.[2g–p] Alternative, synthetically less challenging procedures involve interaction of $B(C_6F_5)_3$ with various anions X^- (X^- = e.g., OH^-,[2a,3] CN^-,[2f,4] N_3^-,[4b] OR^-,[3b–d,j] SR^-,[3b–d] imidazolate[4c]) to form the complex anions $[XB(C_6F_5)_3]^-$ and $[(\mu\text{-}X)\{B(C_6F_5)_3\}_2]^-$, and we have recently investigated the synthesis and utilization for olefin polymerization of analogous weakly coordinating anions of the types $[RO\{B(C_6F_5)_3\}_{1,2}]^-$ and $[RCO_2\{B(C_6F_5)_3\}_{1,2}]^-$ (R = alkyl groups), where X = e.g., alkoxide[5] and carboxylate[6] anions, respectively.

Catalytic systems incorporating $[MeB(C_6F_5)_3]^-$ often exhibit relatively low activity because the anion coordinates via the methyl group to the Lewis acidic metal cations too strongly, e.g., with a binding energy of ~30 to 40 kcal/mol, depending on the solvent.[2s,8] It seemed likely, therefore, that catalytic systems involving similar borate anions such as $[EtB(C_6F_5)_3]^-$, $[i\text{-}PrB(C_6F_5)_3]^-$, and $[NpB(C_6F_5)_3]^-$ (Np = Me_3CCH_2), in which binding to the metal would presumably be hindered by the presence of substituents on the α-carbon atom, would be significantly more active. These complex anions are readily prepared via reactions of the corresponding alkyllithium reagent with $B(C_6F_5)_3$, and we now describe the results of our initial foray into this surprisingly little studied area of organoboron chemistry. We have synthesized and characterized structurally a new series of weakly coordinating anions, analogous to the above-mentioned $[MeB(C_6F_5)_3]^-$, in which the methyl group has been replaced by the sterically more demanding ethyl, isopropyl, and neopentyl groups, and we have carried out a series of propylene polymerizations in the presence of the bulky neopentyl anion, $[NpB(C_6F_5)_3]^-$. Aspects of this work have been communicated previously.[7]

Experimental Section

Most synthetic procedures, unless otherwise noted, were carried out under an atmosphere of nitrogen or argon purified by passing through a column of BASF catalyst heated to 140 °C and a column of 5 Å molecular sieves. Manipulation of air-sensitive materials employed standard Schlenk line techniques and an Mbraun Labmaster glovebox. Solvents were dried by passing through activated alumina columns. All chemicals were purchased from Aldrich and were purified as appropriate before use. The compound $B(C_6F_5)_3$ was prepared as described in the literature.[9]

The ^1H NMR and COSY spectra were run on Bruker AC 200, Avance 300, Avance 400, or Avance 600 NMR spectrometers, the residual proton resonances of the deuterated solvents serving as internal references. Mass spectra were obtained on a Quatro Fisons Pro Quadrupole mass spectrometer in either EI+ mode or ES+ mode with CH_2Cl_2 as solvent. Canadian Microanalytical Services of Delta, B.C., performed elemental analyses.

X-ray crystallographic structure determinations were carried out using a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 A) controlled with Crysostream Controller 700. Typically a crystal was mounted on a glass fiber with epoxy glue. No significant decay was observed during data collection, and the data were processed on a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10).[10a] Neutral atom scattering factors were taken from Cromer and Waber.[10b] The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esds using the program SAINT, which corrects for *Lp* and decay. Absorption corrections were applied using the program SADABS. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were calculated, and their contributions were included in the structure factor calculations. Crystallographic data are summarized in Table 1, and selected bond distances and angles of the various borate anions presented in Table 2. Molecular structures are shown in Figures 1–5, and complete crystallographic data are given in the Supporting Information.

Synthesis of $[Ph_3C][MeB(C_6F_5)_3]$ from $Li[MeB(C_6F_5)_3]$. A solution of 0.3 g of $B(C_6F_5)_3$ (0.6 mmol) in 50 mL of ethyl ether at −78° C was treated dropwise with 0.4 mL of a 1.6 M MeLi solution (0.6 mmol) in ethyl ether and was stirred for 2 h. The solvent was then removed under reduced pressure to give 0.2 g of white oily material, $Li[MeB(C_6F_5)_3]\cdot 3Et_2O$. ^1H NMR (C_6D_6): δ 1.0 (br s, BMe); 0.62 (t, 9H, CH_2CH_3); 2.85 (CH_2). ^1H NMR (CD_2Cl_2): δ 0.45 (br s).[11]

A solution of 0.21 g of $Li[MeB(C_6F_5)_3]$ (0.4 mmol) in 50 mL of diethyl ether was treated with 0.11 g of Ph_3CCl (0.4 mmol) in 20 mL of ethyl ether. The orange reaction mixture was stirred for 2 h, becoming deep orange and turning cloudy. The mixture was then filtered through Celite, and the solvent was then removed under reduced pressure to give 0.16 g of an

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Table 1. Summary of Crystallographic Data

	I	II	III	IV	V
formula	$C_{56}H_{35}BF_{15}NP_2$	$C_{37}H_{19}BF_{15}P{\cdot}0.5CH_2Cl_2$	$C_{42}H_{29}BF_{15}P$	$C_{31}H_{23}BF_{15}N$	$C_{36}H_{25}BF_{15}N$
fw	1079.60	832.77	860.43	705.31	767.38
cryst syst	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic
space group	*P*2(1)/*n*	$P\bar{1}$	*Pna*2(1)	*P*2(1)2(1)2(1)	*P*2(1)/*n*
a (Å)	12.854(2)	11.510(3)	16.000(8)	8.340(2)	8.332(6)
b (Å)	18.717(3)	12.420(3)	13.449(7)	15.235(4)	13.691(10)
c (Å)	20.397(4)	13.015(4)	17.474(8)	23.409(6)	28.59(2)
α (deg)	90	70.071(4)	90	90	90
β (deg)	91.713(3)	87.406(4)	90	90	90.570(13)
γ (deg)	90	79.134(6)	90	90	90
V (Å^3)	4905.1(15)	1717.5(8)	3760(3)	2974.5(13)	3261(4)
Z	4	2	4	4	4
density(calcd) (Mg/m^3)	1.462	1.610	1.520	1.575	1.563
abs coeff (mm^{-1})	0.186	0.269	0.180	0.157	0.151
F(000)	2192	834	1744	1424	1552
θ range for data collection (deg)	1.48 to 28.32	1.77 to 28.34	1.91 to 28.30	1.59 to 28.32	1.49 to 28.34
no. of reflns collected	34 522	11 214	25 612	21 031	22 487
no. of indep reflns	11 546	7648	8484	6984	7593
completeness to *θ*	94.5%	88.9%	96.7%	96.6%	93.3%
no. of data/restraints/params	11546/0/796	7648/0/581	8484/1/636	6984/0/525	7593/0/588
goodness-of-fit on F^2	0.799	0.809	0.593	0.818	0.843
final *R* indices [$I > 2.0\sigma(I)$]	R1 = 0.0488, wR2 = 0.0924	R1 = 0.0657, wR2 = 0.1146	R1 = 0.0373, wR2 = 0.0365	R1 = 0.0398, wR2 = 0.0620	R1 = 0.0634, wR2 = 0.1324
R indices (all data)	R1 = 0.1344, wR2 = 0.1082	R1 = 0.2019, wR2 = 0.1433	R1 = 0.1796, wR2 = 0.0494	R1 = 0.0900, wR2 = 0.0698	R1 = 0.1628, wR2 = 0.1571

Table 2. Important Bond Lengths and Angles for the Anions $[RB(C_6F_5)_3]^-$ in $[PPN][EtB(C_6F_5)_3]$ (I), $[PMePh_3][HB(C_6F_5)_3]$ (II), $[PMePh_3][NpB(C_6F_5)_3]$ (III), $[HNMe_2Ph][NpB(C_6F_5)_3]$, and $[HNMePh_2][NpB(C_6F_5)_3]$ (V)

	I	II	III	IV	V
R−B (Å)	1.642(4)	1.27(3)	1.640(6)	1.657(4)	1.664(5)
B−aryl (Å)	1.649(4), 1.662(4), 1.674(4)	1.637(6), 1.638(7), 1.638(6)	1.683(5), 1.667(5), 1.656(5)	1.661(3), 1.671(3), 1.671(3)	1.656(5), 1.669(5), 1.680(5)
R−B−aryl (deg)	106.2(2), 109.2(2), 115.1(2)	109.4(13), 103.1(13), 108.9(12)	106.8(3), 116.6(3), 108.0(3)	105.8(2), 108.11(19), 116.5(2)	106.5(3), 117.6(3), 106.6(3)
aryl−B−aryl (deg)	112.2(2), 111.9(2), 102.3(2)	114.4(4), 112.6(4), 108.2(4)	113.4(3), 111.8(3), 100.0(3)	113.2(18),112.1(18), 101.2(18)	112.1(3), 113.4(3), 106.6(3)

orange, oily material. A ^1H NMR spectrum (CD_2Cl_2) exhibited a broad BMe resonance at δ 0.45 in addition to multiplets at δ 7.67, 7.85, and 8.21, attributable to the trityl ion, and a sharp singlet at δ 5.5 attributable to Ph_3CH. However there were also many other broad resonances in the aromatic and aliphatic regions, and the product was clearly a mixture. Unfortunately, attempted crystallization by layering with methylene chloride−hexanes resulted in further decomposition. Attempted metatheses in methylene chloride and acetonitrile also failed.

Attempted Synthesis of $[Ph_3C][EtB(C_6F_5)_3]$ from $Li[EtB(C_6F_5)_3]$. The compound $Li[CH_3CH_2B(C_6F_5)_3]$ was prepared as above using EtLi and $B(C_6F_5)_3$. ^1H NMR (C_6D_6): δ 0.72 (t, Me), 1.52 (br q, CH_2−B). ^{19}F NMR (C_6D_6): δ −136.74 (d, 6F; *o*-F, J_{FF} 24.85 Hz), −160.26 (t, 3F; *p*-F, J_{FF} 19.95 Hz), −163.58 (t, 6F; *m*-F, J_{FF} 18.45 Hz). ^{11}B NMR (C_6D_6): δ −12.01. ESMS (CH_2Cl_2): *m/z* 541 with appropriate isotope pattern. The metathesis reaction with Ph_3CCl was carried out in chlorobenzene as above to give the orange product. ^1H NMR (CD_2Cl_2): δ 7.67, 7.85, and 8.21 (trityl cation); 0.88 (t, 3H, Me), 2.0 (br q, 2H, CH_2). The presence of $[Ph_3C][EtB(C_6F_5)_3]$ was further confirmed by electrospray mass spectroscopy, run as both positive and negative ion modes. Peaks at *m/z* 243 (positive mode, with appropriate isotope pattern) and *m/z* 541 (negative mode, with appropriate isotope pattern) are attributable to the trityl and ethylborate ions, respectively. Attempted recrystallization resulted in decomposition, Ph_3CH being a major product.

Synthesis of $[(Ph_3P)_2N][EtB(C_6F_5)_3]$. A solution of 0.25 g of $[(Ph_3P)_2N]Cl$ (0.44 mmol) in 50 mL of CH_2Cl_2 was added to 0.24 g of $Li[EtB(C_6F_5)_3]$ (0.44 mmol), and the mixture was stirred for 10 h. Workup as above gave a white, flaky solid in 51% yield. ^1H NMR of $[PPN][EtB(C_6F_5)_3]$ (CD_2Cl_2): δ 0.56 (t, 3H, Me), 1.18 (br q, 2H, CH_2), 7.46−7.66 (m, Ph). ^{19}F NMR (CD_2Cl_2): δ −133.67 (d, 6F; *o*-F, J_{FF} 17.31 Hz), −166.44 (t, 3F; *p*-F, J_{FF} 21.83 Hz), −168.99 (t, 6F; *m*-F, J_{FF} 20.33 Hz). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ −12.58. An attempt to recrystallize this compound by layering a solution in CD_2Cl_2 with

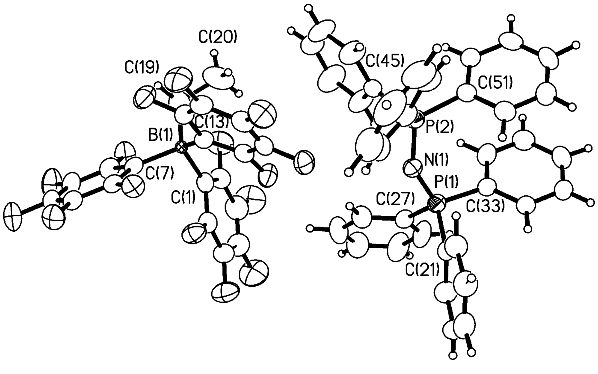

Figure 1. Structure of $[PPN][EtB(C_6F_5)_3]$ (**I**).

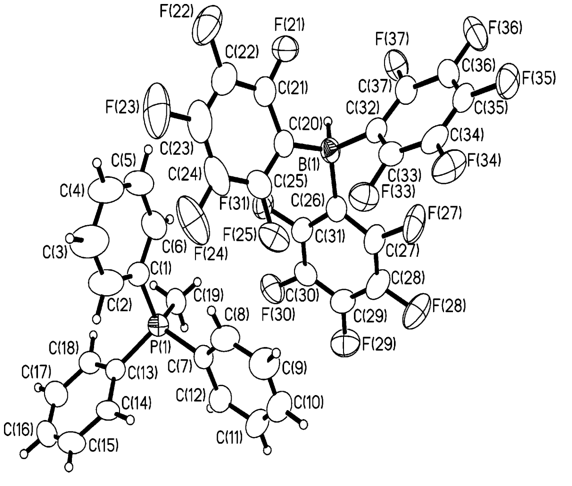

Figure 2. Structure of $[PMePh_3][HB(C_6F_5)_3]$ (**II**).

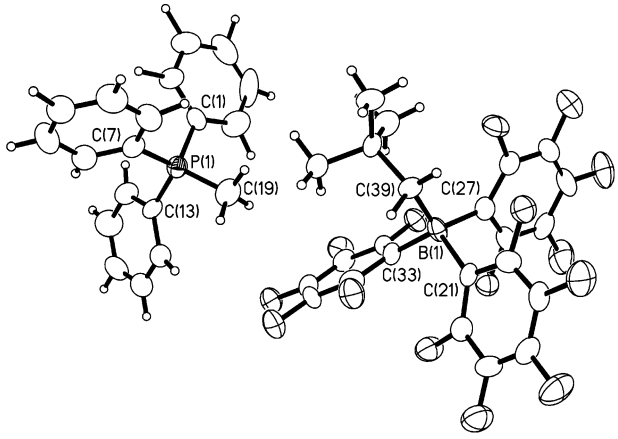

Figure 3. Structure of $[PMePh_3][NpB(C_6F_5)_3]$ (**III**).

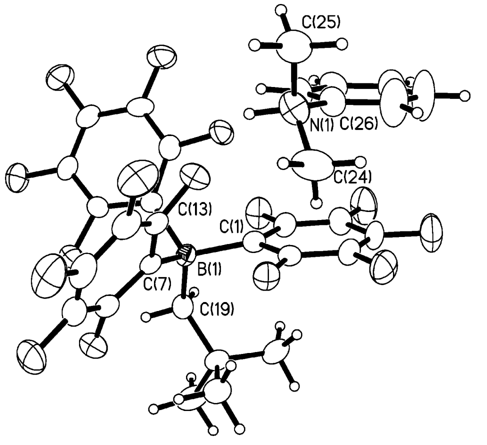

Figure 4. Structure of $[HMe_2NPh][NpB(C_6F_5)_3]$ (**IV**).

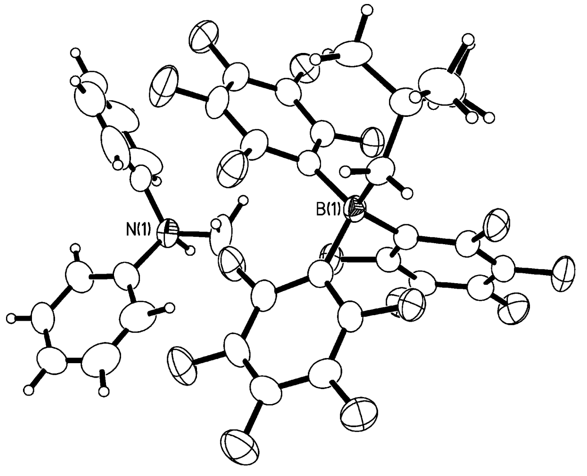

Figure 5. Structure of $[HMeNPh_2][NpB(C_6F_5)_3]$ (**V**).

hexanes resulted in extensive decomposition, but a few crystals suitable for X-ray analysis were obtained.

Synthesis of $[PMePh_3][EtB(C_6F_5)_3]$. A metathesis reaction involving $Li[EtB(C_6F_5)_3]$ and $PMePh_3Br$ was carried out in CH_2Cl_2 as above to give the white product in 40% yield. ^1H NMR (CD_2Cl_2): δ 7.59−7.88 (m, Ph); 2.73 (d, 3H, PMe); 0.55 (t, 3H, Me), 1.15 (br q, 2H, CH_2).

Attempted Synthesis of $[Ph_3C][i\text{-}PrB(C_6F_5)_3]$ from Li[i-PrB$(C_6F_5)_3$]. The compound Li[i-PrB$(C_6F_5)_3$] was prepared as above using i-PrLi and $B(C_6F_5)_3$. ^1H NMR of Li[i-PrB$(C_6F_5)_3$] (C_6D_6): δ 0.94 (d, Me), 3.07 (br m, CH−B). ^{19}F NMR (C_6D_6): δ −138.55 (br s, 6F; o-F), −159.35 (t, 3F; p-F, J_{FF} 19.95 Hz), −163.91 (t, 6F; m-F, J_{FF} 20.70 Hz). ^{11}B NMR (C_6D_6): δ −10.06. ESMS (CH_2Cl_2): m/z 555.1 with appropriate isotope pattern. A metathesis reaction with Ph_3CCl was attempted as above, but yielded very little $[Ph_3C]$[i-PrB$(C_6F_5)_3$]. A major product was Ph_3CH.

Synthesis of $[MePPh_3]$[i-PrB(C_6F_5)]. A solution of 0.19 g of $MePPh_3Br$ (0.53 mmol) in 50 mL of CH_2Cl_2 was added to 0.30 g of Li[^{i}PrB$(C_6F_5)_3$] (0.53 mmol), and the mixture was stirred overnight. The now cloudy mixture was filtered through Celite, and the solvent was removed under reduced pressure to give a white, oily product in 42% yield. ^1H NMR (CD_2Cl_2): δ 0.57 (d, 6H, CHMe_2), 2.46 (m, 1H, CH), 2.73 (d, 3H, PMe), 7.6−7.9 (m, 15H, Ph). Recrystallization for X-ray crystallographic analysis was attempted by layering a solution in CH_2Cl_2 with hexanes, but the structure of the compound obtained was that of $[MePPh_3][HB(C_6F_5)_3]$.[13] ^1H NMR (CD_2Cl_2): δ 3.58 (br q, 1H, BH, J_{BH} 88 Hz), 2.70 (d, 3H, PMe), 7.54−7.87 (m, 15H, Ph). ^{11}B NMR (C_6D_6): δ −25.77 (d, J_{BH} 88 Hz).

Synthesis of $Li[NpB(C_6F_5)_3]$. The compound $Li[NpB(C_6F_5)_3]$ was prepared as above using NpLi and $B(C_6F_5)_3$. ^1H NMR of $Li[NpB(C_6F_5)_3]$ (C_6D_6): δ 0.93 (s, 9H, Me), 1.88 (br s, 2H, CH_2−B). ^{19}F NMR (C_6D_6): δ −135.97 (br s, 6F; o-F), −158.75 (br s, 3F; p-F), −163.95 (br s, 6F; m-F). ^{11}B NMR (C_6D_6): δ −13.05. ESMS (CH_2Cl_2): m/z 583.2 with appropriate isotope pattern.

Attempted Synthesis of $[Ph_3C][NpB(C_6F_5)_3]$. A metathesis reaction with Ph_3CCl was attempted in chlorobenzene, hexanes, and CD_2Cl_2 as above, but yielded only impure $[Ph_3C][NpB(C_6F_5)_3]$. ^1H NMR (CD_2Cl_2): δ 0.63 (s, 9H, Me), 1.48 (br s, 2H, CH_2−B), 7.69, 7.91, and 8.32 (d, t, t, 15H, Ph). ESMS (CD_2Cl_2): 583.2 m/z (negative ion mode, with appropriate isotope pattern), $[NpB(C_6F_5)_3]^-$; 243.1 m/z (positive ion mode, with appropriate isotope pattern), $[Ph_3C]^+$. Attempted purification of this compound resulted in decomposition, in part to triphenylmethane.

Synthesis of $[PMePh_3][NpB(C_6F_5)]$. This compound was prepared as above via the metathesis of $Li[NpB(C_6F_5)_3]$ with $MePPh_3Br$. ^1H NMR (CD_2Cl_2): δ 0.64 (s, 9H, CMe_3), 1.49 (br s, 2H, CH_2B), 2.71 (d, J_{HP} 13.5 Hz, 3H, PMe), 7.5−8.0 (m, Ph). ^{19}F NMR (CD_2Cl_2): δ −131.54 (d, 6F; o-F, J_{FF} 23.71 Hz), −166.51 (t, 3F; p-F, J_{FF} 20.70 Hz), −169.08 (t, 6F; m-F, J_{FF} 21.45 Hz). ^{11}B NMR (CD_2Cl_2): δ −13.63. ESMS: 583.2 m/z (negative ion mode, with appropriate isotope pattern), $[NpB(C_6F_5)_3]^-$; 277.3 m/z (positive ion mode, with appropriate isotope pattern), $[PMePh_3]^+$. Anal. Calc for $C_{42}H_{29}BF_{15}P$: C, 58.6; H, 3.4; P, 3.6. Found: C, 57.8; H, 3.4; P, 2.6. Crystals of $[PMePPh_3][NpB(C_6F_5)_3]$ were grown by layering a solution in CH_2Cl_2 with hexanes.

Synthesis of $[HNMe_3][NpB(C_6F_5)_3]$. A solution of 0.11 g of dried (reduced pressure, 80 °C) $[HNMe_3]Cl$ (1.7 mmol) in 60 mL of CH_2Cl_2 was added to 1 g of $Li[NpB(C_6F_5)_3]$ (1.7 mmol), and the mixture was stirred for 1 h. The resulting cloudy mixture was filtered through Celite to give a light yellow solution. The solvent was removed under reduced pressure, and a white solid was collected in 65% yield. ^1H NMR of $[HNMe_3][NpB(C_6F_5)_3]$ (CD_2Cl_2): δ 0.66 (s, CMe_3), 1.51 (br s, CH_2B), 3.05 (s, NMe_3), 6.52 (br s, H). ^{19}F NMR of $[HNMe_3][NpB(C_6F_5)_3]$ (376.4 MHz, CD_2Cl_2): δ −132.09 (d, 6F; o-F, J_{FF} 22.21 Hz), −165.88 (t, 3F; p-F, J_{FF} 18.82 Hz), −168.76 (t, 6F; m-F, J_{FF} 18.06 Hz). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ −13.59. Recrystallization for analytical and crystallographical purposes was performed by layering a solution in CH_2Cl_2 with hexanes. Anal. Calc for $C_{26}H_{21}BF_{15}N$: C, 48.5; H, 3.3; N, 2.2. Found: C, 47.3; H, 2.9; N, 2.6.

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(12) (a) Walker, D. A.; Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 797. An earlier paper on the anion $[EtB(C_6F_5)_3]^-$ was also found: (b) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772.

(13) (a) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375. (b) Chen, X.; Liu, F.-C.; Ple_nik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Organometallics* **2004**, *23*, 2100. (c) Millot, N.; Santini, C. C.; Fenet, B.; Bassett, J. M. *Eur. J. Inorg. Chem.* **2002**, 3328.

Synthesis of [$HNMe_2Ph$][$NpB(C_6F_5)_3$]. A solution of 0.32 g of [$HNMe_2Ph$]Cl (2 mmol) in 60 mL of CH_2Cl_2 was added to 1.2 g of Li[$NpB(C_6F_5)_3$] (2 mmol), and the mixture was stirred for 30 min to give a cloudy mixture. (It is important not to run the reaction for >1 h, as solutions turn green then blue.) The solution was filtered through Celite to give a light yellow solution. The solvent was removed under reduced pressure, and a creamy solid was collected in 76% yield. ^1H NMR of [$HNMe_2Ph$][$NpB(C_6F_5)_3$] (CD_2Cl_2): δ 0.64 (s, CMe_3), 1.50 (br s, CH_2B), 3.40 (s, NMe_2), 7.4−8.0 (m, Ph). ^{19}F NMR of [$HNMe_2Ph$][$NpB(C_6F_5)_3$] (376.4 MHz, CD_2Cl_2): δ −131.99 (d, 6F; *o*-F, J_{FF} 22.59 Hz), −165.74 (t, 3F; *p*-F, J_{FF} 18.82 Hz), −168.59 (t, 6F; *m*-F, J_{FF} 21.08 Hz). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ −13.53. Recrystallization for analytical and crystallographical purposes was performed by layering a solution in CH_2Cl_2 with hexanes. Anal. Calc for $C_{31}H_{23}BF_{15}N$: C, 52.7; H, 3.3; N, 1.9. Found: C, 51.8; H, 3.3; N, 1.9. Crystals suitable for X-ray crystallographic analysis were also obtained.

Synthesis of [$HNMePh_2$][$NpB(C_6F_5)_3$]. A solution of 0.37 g of [$HNMePh_2$]Cl (1.7 mmol) in 50 mL of CH_2Cl_2 was added to 1 g of Li[$NpB(C_6F_5)_3$] (1.7 mmol), and the mixture was stirred for 30 min to give a cloudy mixture. (It is important not to run the reaction for >1 h, as solutions turn green then blue.) The mixture was filtered through Celite to give a light yellow solution. The solvent was removed under reduced pressure, and a light pink solid was collected in 62% yield. ^1H NMR of [$HNMePh_2$][$NpB(C_6F_5)_3$] (CD_2Cl_2): δ 0.64 (s, CMe_3), 1.51 (br s, CH_2B), 3.74 (s, NMe), 7.4−7.6 (m, 2Ph), 9.81 (br s, H). ^{19}F NMR of [$HNMePh_2$][$NpB(C_6F_5)_3$] (376.4 MHz, CD_2Cl_2): δ −131.72 (d, 6F; *o*-F, J_{FF} 22.58 Hz), −165.96 (t, 3F; *p*-F, J_{FF} 18.82 Hz), −168.69 (t, 6F; *m*-F, J_{FF} 21.58 Hz). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ −13.51. Recrystallization for analytical and crystallographical purposes was performed by layering a solution in CH_2Cl_2 with hexanes and pumping on the crystals so obtained for 3 days to remove occluded solvent. Anal. Calc for $C_{36}H_{25}BF_{15}N$: C, 56.35; H, 3.3; N, 1.8. Found: C, 56.1; H, 3.2; N, 1.8. Crystals suitable for X-ray crystallographic analysis were also obtained.

Polymerization Procedures. In a series of preliminary experiments, 20 mL of toluene in a Schlenk flask was placed in a water bath at 21 °C and saturated with propylene that had been dried by passing through an activated molecular sieves column. At this point 0.08 mmol of the catalyst and 0.12 mmol of the cocatalyst, each dissolved in 3 mL of toluene, were added to the Schlenk and the mixture was stirred as bubbling of propylene through the solution continued. The polymerization reactions were run for 7 min, generally becoming quite warm. The reactions were terminated by the addition of 10 mL of acidified methanol, and the polymers were recovered by the removal of the solvent mixture under reduced pressure. The atactic polymers produced by Cp_2ZrMe_2 and (Indenyl)$_2$$ZrMe_2$ catalysts were viscous, oily materials, which were purified by dissolving in hexanes followed by eluting through a silica column and removal of the solvent under reduced pressure. The isotactic polymers produced by $SBIZrMe_2$ were white, powdery solids and precipitated from the polymerization reaction mixtures on addition of the methanol. These polymer samples were collected by filtration, washed with 20 mL of acetone, and dried under reduced pressure.

In a series of more extensive experiments, typically 50 mL of toluene in a Schlenk flask equipped with a thermocouple was placed in an ice bath at 0 °C and saturated with propylene that had been dried as above. At this point, 0.024 mmol of the catalyst and 0.036 mmol of the cocatalyst, each dissolved in 3 mL of toluene containing 0.048 mmol of Al(^{i}Bu)$_3$, were added to the Schlenk and the mixture was stirred as bubbling of propylene through the solution continued. The polymerization reactions were run for 2 min, the temperatures in all cases remaining at 2 ± 2 °C. The reactions were terminated and the polymers were isolated and purified as above.

NMR studies, molecular weight analyses, and activity calculations were all carried out on purified polymer samples. For isotactic polypropylene samples, samples were prepared for $^{13}C\{^1H\}$ spectra by dissolving the polymer sample in 1,1,2,2-tetrachloroethane-d_2 (25 w/v%) and heating to 120 °C. Spectra (80−120 °C) were acquired with 2600−12 000 scans and a delay of 2 s. Gel permeation chromatography analyses of the atactic polypropylene samples were carried out in toluene at 75 °C using a Waters Model 2690 chromatograph and polystyrene standards. The molecular weights of isotactic polypropylene samples were determined at 145 °C in 1,2,4-trichlorobenzene using a Waters 150-C GPC.

Results and Discussion

Syntheses and Characterization of the Anions [$RB(C_6F_5)_3$]$^-$ (R = Et, *i*-Pr, CH_2CMe_3). Syntheses of the new alkyl borate anions were carried out by reacting $B(C_6F_5)_3$ with the various alkyl lithium compounds (eq 3).

$$LiR + B(C_6F_5)_3 \rightarrow Li[RB(C_6F_5)_3] \qquad (R = Et, i\text{-}Pr, Np) \quad (3)$$

We prepared similarly, to optimize the methodology and for purposes of comparison, the well-known[11] methylborate analogue Li[$MeB(C_6F_5)_3$]. The *i*-Pr and Np compounds seem to be new, as literature searches using STN Easy and Scifinder Scholar resulted in no hits. Indeed, there was only a single mention of the ethylborate anion,[12a] and thus this class of borate anions has been surprisingly little studied. As we show below, the lithium salts of all have now been synthesized and characterized in the usual manner (^1H, ^{19}F, and ^{11}B NMR spectroscopy, electrospray mass spectrometry (ESMS)), although we found it difficult to remove all traces of solvents from the lithium derivatives without inducing significant deterioration. All were therefore used as isolated in a variety of metathesis reactions that were used to obtain salts of PPN^+ ($PPN^+ = [(Ph_3P)_2N]^+$) and $PMePh_3^+$ salts for crystallographic purposes and Ph_3C^+ and trialkylammonium salts for catalytic purposes.

The ethylborate anion, [$EtB(C_6F_5)_3$]$^-$, has been formed previously only via ethyl abstraction from ethylzinc compounds,[12] and no crystallographic data are available. The PPN^+ salt of the ethylborate anion, [PPN][$EtB(C_6F_5)_3$] (**I**), was obtained from Li[$RB(C_6F_5)_3$] through metathesis with [PPN]Cl, and crystals were grown from CH_2Cl_2 by layering with hexanes. The structure of **I** is shown in Figure 1, and important bond length and angle data of the anion are shown in Table 2; more will be said about its structure below.

Similar attempts to obtain useful crystals of [$PMePh_3$][$EtB(C_6F_5)_3$] and [PPN][*i*-$PrB(C_6F_5)_3$] failed, but an attempt to obtain crystals of [$PMePh_3$][*i*-$PrB(C_6F_5)_3$] resulted in the surprising formation of a 1:2 mixture of [$PMePh_3$][*i*-$PrB(C_6F_5)_3$] and [$PMePh_3$][$HB(C_6F_5)_3$] and in the formation of a small number of crystallographic quality crystals of the latter, [$PMePh_3$][$HB(C_6F_5)_3$] (**II**). The borohydride anion, which has previously been formed via hydride abstractions by $B(C_6F_5)_3$ from zirconium hydrides,[13a,b] from the β-carbon of the ethyl ligand of ($C_4H_4NSiMe_2C_5H_4$)ZnEt(TMEDA)[12a] and from the α-carbon of NEt_2Ph,[13c] is probably formed in this case via slow β-hydride elimination from [*i*-$PrB(C_6F_5)_3$]$^-$,

Table 3. ^{1}H NMR Data for the Salts $[HNMe_3][NpB(C_6F_5)_3]$, $[HNMe_2Ph][NpB(C_6F_5)_3]$, $[HNMePh_2][NpB(C_6F_5)_3]$, $[HNMe_3]Cl$, $[HNMe_2Ph]Cl$, and $[HNMePh_2]Cl$ (CD_2Cl_2)

compound	δ (H)	δ (Me)	δ (Ph)	δ (CH_2B)	δ (CMe_3)
$[HNMe_3][NpB(C_6F_5)_3]$	6.52 (v br)	3.05 (s)		1.51 (br)	0.66 (s)
$[HNMe_3]Cl$	12.6 (v br)	2.81 (s)			
NMe_3		2.48 (s)			
$[HNMe_2Ph][NpB(C_6F_5)_3]$	7.20 (br)	3.46 (s)	7.38 (m), 7.69 (m)	1.52 (br)	0.65 (s)
$[HNMe_2Ph]Cl$	14.7 (v br)	3.12 (s)	7.53 (m), 7.77 (m)		
NMe_2Ph		2.96 (s)	6.75 (m), 7.26 (m)		
$[HNMePh_2][NpB(C_6F_5)_3]$	9.82 (br)	3.75 (s)	7.44 (m), 7.60 (m)	1.52 (br)	0.64 (s)
$[HNMePh_2]Cl$	13.4 (v br)	3.47 (s)	7.35−7.58 (m)		
$NMePh_2$		3.32 (s)	7.03 (m), 7.28 (m)		

although this type of reaction appears not to have been previously reported. The ^{1}H NMR spectrum of compound **II** exhibited a broad quartet centered at δ 3.58 ($^1J_{B-H}$ 88 Hz) attributable to the hydrogen of the borohydride anion, while the ^{11}B NMR spectrum exhibited a doublet at δ −25.77 ($^1J_{B-H}$ 88 Hz). These data are consistent with literature data for the borohydride anion reported elsewhere for zirconocenium and $[HNEt_2Ph]^+$ salts.[13b,c] The structure of **II** is shown in Figure 2, and important bond length and angle data of the anion are shown in Table 2; more will be said about its structure below.

The neopentylborate ion, $[NpB(C_6F_5)_3]^-$, has not been reported previously, and its $[PMePh_3]^+$ salt was characterized by NMR spectroscopy and crystallographically. The structure of $[PMePh_3][NpB(C_6F_5)_3]$ (**III**) is shown in Figure 3, and important bond length and angle data of the anion are shown in Table 2; more will be said about its structure below.

Preparation of metallocene-based olefin polymerization catalysts incorporating weakly coordinating anions often utilize trityl salts, and there is a considerable body of relevant literature.[1,2] The normal routes to useful trityl salts involve metathesis reactions of trityl chloride with alkali metal salts of weakly coordinating anions, as in eq 4 (X = weakly coordinating anion).[2f]

$$Ph_3CCl + M^+X^- \rightarrow [Ph_3C][X] + MCl \qquad (4)$$

Interestingly, while attempted metathesis reactions involving $[MeB(C_6F_5)_3]^-$, $[EtB(C_6F_5)_3]^-$, $[i\text{-}PrB(C_6F_5)_3]^-$, and $[NpB(C_6F_5)_3]^-$ all resulted in the formation of the corresponding trityl salts $[Ph_3C][RB(C_6F_5)_3]$, as indicated by NMR spectroscopy and electrospray mass spectrometry, none of the products were sufficiently stable to be isolable in purity sufficient for crystallographic or catalytic studies. Interestingly, Ph_3CH was a ubiquitous product, quite likely formed via β-hydrogen abstraction processes from $[EtB(C_6F_5)_3]^-$ and $[i\text{-}PrB(C_6F_5)_3]^-$. However whether α-hydrogen elimination or electron transfer processes are responsible in the case of $[MeB(C_6F_5)_3]^-$ and $[NpB(C_6F_5)_3]^-$ is not yet known. Absent from all ^{1}H NMR spectra were the olefinic resonances of the head-to-tail dimer of the trityl radical,[14] and thus the latter persistent radical does not seem to play an important role.

Desiring stable catalyst activators that could be satisfactorily purified and stored, we turned our attention to the synthesis of trialkylammonium salts of the anion $[NpB(C_6F_5)_3]^-$, as weakly acidic trialkylammonium salts of weakly coordinating anions are often used to prepare metallocene-based olefin polymerization catalysts.[2e] The catalyst-generating chemistry is generally believed to be as in eq 5 (R = alkyl, aryl; X = weakly coordinating anion).[2e]

$$[HNR_3]X + Cp_2ZrMe_2 \rightarrow [Cp_2ZrMe]X + NR_3 + CH_4 \qquad (5)$$

Accordingly we have synthesized a series of salts of the type $[HNR_3][NpB(C_6F_5)_3]$ involving metathesis reactions of $Li[NpB(C_6F_5)_3]$ with 1 molar equiv each of $[HNMe_3]Cl$, $[HNMe_2Ph]Cl$, and $[HNMePh_2]Cl$ in CH_2Cl_2. In a typical example, a mixture of $[HNMe_3]Cl$ and $Li[NpB(C_6F_5)_3]$ (1:1 molar ratio) in CH_2Cl_2 was stirred for 1 h, and removal of the resulting precipitate of LiCl resulted in a yellow solution. Removal of the solvent under reduced pressure gave pure $[HNMe_3][NpB(C_6F_5)_3]$, which was recrystallized from CH_2Cl_2 and characterized spectroscopically. The salts $[HNMe_2Ph][NpB(C_6F_5)_3]$ (**IV**) and $[HNMePh_2][NpB(C_6F_5)_3]$ (**V**) were prepared and characterized similarly, as well as crystallographically. The crystal structures of **IV** and **V** are shown in Figures 3 and 4, respectively; bond length and angle data, in Table 2.

NMR data for compounds $[HNMe_3][NpB(C_6F_5)_3]$, $[HNMe_2Ph][NpB(C_6F_5)_3]$, and $[HNMePh_2][NpB(C_6F_5)_3]$ are shown in Table 3, where they are compared with the data for the corresponding chlorides and amines. What is most notable is that the NH^+ resonances shift upfield by several ppm on going from the chloride to the $[NpB(C_6F_5)_3]^-$ salts, presumably because of significant differences in the strength of the hydrogen bonding between the NH^+ group and the anion[15] and reinforcing the hypothesis that a bulky anion such as $[NpB(C_6F_5)_3]^-$ does not contain a focal point to which an electrophilic reagent can be readily attracted. Other observations are that the CH_2B and the CMe_3 chemical shifts of the $[NpB(C_6F_5)_3]^-$ ions remain essentially constant for the various trialkylammonium cations, although the chemical shifts are very different from those of $Li[NpB(C_6F_5)_3]$ (δ (CH_2B 1.88, δ (CMe_3) 0.93, in C_6D_6), where presumably strong anion−cation covalent interactions pertain.

Comparing the figures of **I**, **II**, **III**, **IV**, and **V** and the structural data in Table 2, the anions are all seen to assume the pseudotetrahedral structures demonstrated previously for the free methylborate analogue in the presence of a variety of cations.[11] The B−Et and B−Np distances are generally slightly longer than the B−Me distances reported in the literature,[11] and the R−B−aryl and aryl−B−aryl bond angles vary considerably, but this seems to be normal.[11] The B−H bond distance in the anion of **II** is very similar to those reported for

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[14] Lancamp, H.; Nauta, W. T.; Maclean, C. *Tetrahedron Lett.* **1968**, *9*, 249.

[15] Hibbert, F.; Emsley, J. *Adv. Phys. Org. Chem.* **1990**, *26*, 255.

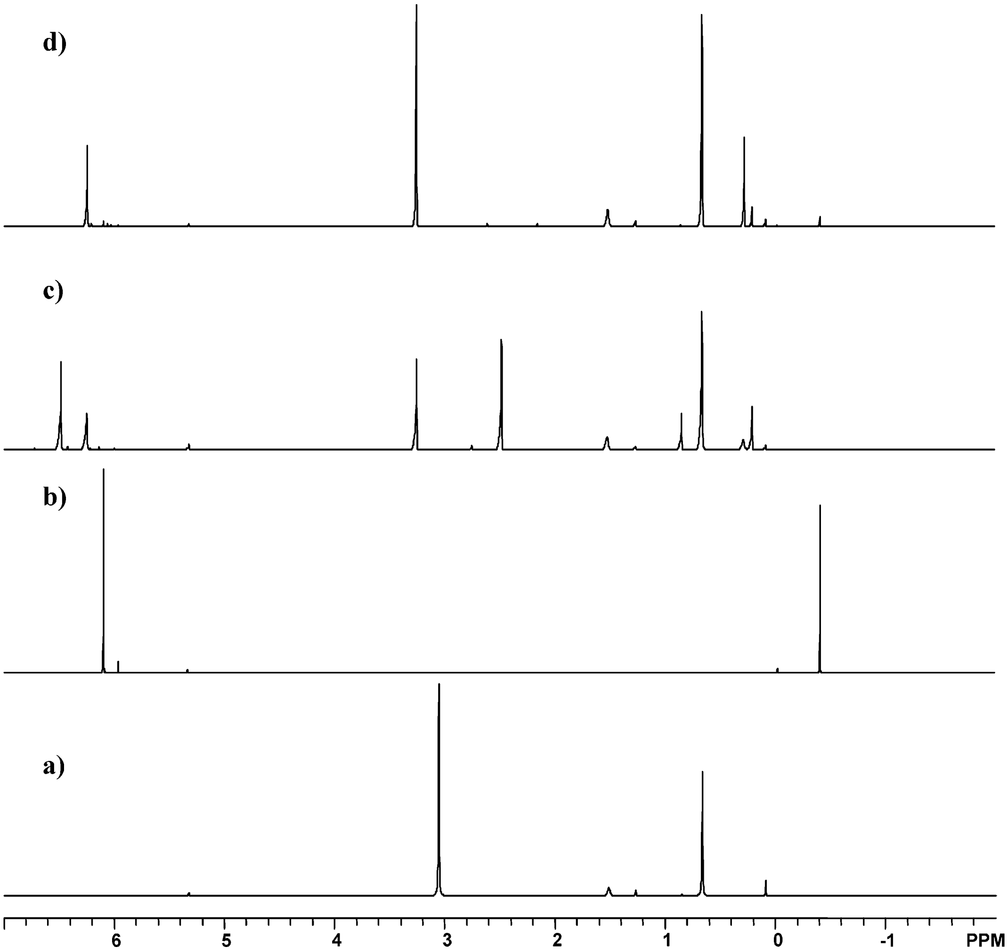

Figure 6. ^1H NMR spectra (CD_2Cl_2) of (a) $[HNMe_3][NpB(C_6F_5)_3]$, (b) Cp_2ZrMe_2, (c) reaction of Cp_2ZrMe_2 and $[HNMe_3][NpB(C_6F_5)_3]$, 1:1, 5 min, and (d) reaction after 45 min.

this species elsewhere,[13b,c] and the anion also exhibits a normal tetrahedral structure.

Activation of Dimethylzirconocenes by Tertiary Ammonium Salts of $[NpB(C_6F_5)_3]^-$. The reaction of Cp_2ZrMe_2 with an equimolar amount of $[HNMe_3][NpB(C_6F_5)_3]$ in CD_2Cl_2 at room temperature was monitored by ^1H NMR spectroscopy, with results as shown in Figure 6. As anticipated, a ^1H NMR spectrum run within a few minutes of mixing (Figure 6c) showed that the resonances of Cp_2ZrMe_2 at δ 6.09 (Cp) and −0.41 (Me) (Figure 6a) and of the $[HNMe_3]^+$ ion (δ 3.05, 6.5) (Figure 6b) had disappeared while the resonance of methane at δ 0.20 and new Cp (δ 6.25, 6.48) and $ZrCH_3$ (δ 0.28, 0.84) resonances appeared. The BCH_2 (δ 1.52) and CMe_3 (δ 0.66) resonances of the neopentyl group shifted slightly. In addition, there appeared also the methyl resonance of free NMe_3 at δ 2.48 *and of coordinated* NMe_3 at δ 3.25, respectively. Over the course of 45 min, the resonance of free NMe_3 and the Cp and Zr−Me resonances at δ 6.48 and 0.84 weakened and disappeared as that of coordinated NMe_3 and the Cp and Zr−Me resonances at δ 6.24 and 0.28 grew in intensity. The latter resonances are clearly to be attributed to the compound $[Cp_2ZrMe(NMe_3)][NpB(C_6F_5)_3]$, and thus the transient resonances at 6.48 and 0.85 are presumably attributable to either the solvate, $[Cp_2ZrMe(CH_2Cl_2)][NpB(C_6F_5)_3]$, or the "base-free" complex $[Cp_2ZrMe][NpB(C_6F_5)_3]$. In an attempt to identify the cationic species in solution, we ran electrospray mass spectra of a similar reaction mixture. As anticipated, the molecular ion of $[Cp_2ZrMe(NMe_3)]^+$ (*m/e* 294 Da with the appropriate isotopic distribution) was a dominant species, but the mass spectrum exhibited a weak peak for $[Cp_2ZrMe]^+$ (*m/e* 235 Da) and no peak for $[Cp_2ZrMe(CH_2Cl_2)]^+$ (*m/e* 321 Da), thus suggesting the former as the species initially formed on the addition of $[HNMe_3][NpB(C_6F_5)_3]$.

We had hoped that the use of NMe_3 would result in the ready formation and isolation of $[Cp_2ZrMe][NpB(C_6F_5)_3]$. Given the volatility of NMe_3 (bp 3−4 °C), it was our hope that the compound $[Cp_2ZrMe(NMe_3)][NpB(C_6F_5)_3]$ would form reversibly (eq 6) and that we might, via removal of the amine, be able to shift the equilibrium sufficiently that we could isolate the "base-free" complex $[Cp_2ZrMe][NpB(C_6F_5)_3]$. It would be of interest to determine crystallographically the mode of interaction, if any, between the $[Cp_2ZrMe]^+$ and the sterically encumbered alkylborate anion.

$$\begin{tikzcd}[HNMe_3][NpB(C_6F_5)_3] + Cp_2ZrMe_2 \arrow[r, "-CH_4"] & {[Cp_2ZrMe][NpB(C_6F_5)_3] + NMe_3} \arrow[d, shift left] \\ & {[Cp_2ZrMe(NMe_3)][NpB(C_6F_5)_3]} \arrow[u, shift left]\end{tikzcd} \qquad (6)$$

However we were unable to persuade the amine to dissociate noticeably, and this aspect of the project was abandoned.

A similar ^1H NMR study of the reaction of equimolar amounts of Cp_2ZrMe_2 and $[HMe_2NPh][NpB(C_6F_5)_3]$ in

Table 4. Propylene Polymerizations Initiated at 21 °C[a]

run	catalyst/cocatalyst	yield (g)	activity[b]	M_w (M_w/M_n)	*mmmm* %
1	$Cp_2ZrMe_2/B(C_6F_5)_3$	0.55	57	480 (1.4)	
2	$Cp_2ZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	1.5	160	5400 (2.3)	
3	$Ind_2ZrMe_2/B(C_6F_5)_3$	1.1	120	880 (2.4)	
4	$Ind_2ZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	1.9	200	9700 (1.6)	
5	$SBIZrMe_2/B(C_6F_5)_3$	3.2	800	7500 (2.1)	80
6	$SBIZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	4.8	1200	10 000 (1.9)	70

[a] Polymerization conditions: 20 mL toluene, 1 atm propylene, 0.08 mmol catalyst, 0.12 mmol cocatalyst, 7 min. [b] kg PP/mol catalyst h atm.

Table 5. Propylene Polymerizations Initiated at 0 °C[a]

expt no.	catalyst/cocatalyst	yield (g)	activity[b]	M_w (M_w/M_n)	*mmmm* %
7	$Cp_2ZrMe_2/B(C_6F_5)_3$	0.3	400	600 (1.3)	
8[3]	$Cp_2ZrMe_2/B(C_6F_5)_3/NMe_2Ph$	0.14	200	800 (1.3)	
9	$Cp_2ZrMe_2/[HNMe_3][NpB(C_6F_5)_3]$	2.3	2900	45 000 (2.1)	
10	$Cp_2ZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	4.4	5600	44 000 (2.1)	
11	$Cp_2ZrMe_2/[HNMePh_2][NpB(C_6F_5)_3]$	2.0	2500	42 000 (2.0)	
12	$Cp_2ZrMe_2/[HNMe_2Ph][B(C_6F_5)_4]$	3.5	4400	74 000 (1.6)	
13	$(Indenyl)_2ZrMe_2/B(C_6F_5)_3$	0.6	800	20 000 (1.4)	
14[c]	$(Indenyl)_2ZrMe_2/B(C_6F_5)_3/NMe_2Ph$	0.3	400	20 000 (1.3)	
15	$(Indenyl)_2ZrMe_2/[HNMe_3][NpB(C_6F_5)_3]$	1.3	1600	74 000(1.5)	
16	$(Indenyl)_2ZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	1.3	1600	89 000 (1.8)	
17	$(Indenyl)_2ZrMe_2/[HNMePh_2][B(C_6F_5)_4]$	1.1	1400	56 000 (1.6)	
18	$(Indenyl)_2ZrMe_2/[HNMe_2Ph][B(C_6F_5)_4]$	1.5	1900	83 000 (1.7)	
19	$SBIZrMe_2/B(C_6F_5)_3$	0.8	1000	41 000 (2.1)	95
20[c]	$SBIZrMe_2/B(C_6F_5)_3/NMe_2Ph$	0.4	500	27 000 (1.7)	94
21	$SBIZrMe_2/[HNMe_3][NpB(C_6F_5)_3]$	4.8	6100	63 000(2.1)	89
22	$SBIZrMe_2/[HNMe_2Ph][NpB(C_6F_5)_3]$	5.2	6500	54 000 (2.7)	90
23	$SBIZrMe_2/[HNMePh_2][NpB(C_6F_5)_3]$	4.5	5700	ND[d]	84
24	$SBIZrMe_2/[HNMe_2Ph][B(C_6F_5)_4]$	6.4	8000	53 000 (2.0)	90

[a] In the presence of Al(*i*-Bu)$_3$. Catalyst:activator:Al(*i*-Bu)$_3$ ratio = 1:1.5:2; 0.024 mmol catalyst and 0.036 mmol cocatalyst in 50 mL toluene at 0 °C initially; 1 atm propylene; 2 min; terminated with methanol. [b] Kg PP/mol catalyst. [c] 1 equiv of Me_2NPh was added following catalyst activation. [d] Not determined.

CD_2Cl_2 was monitored by ^1H NMR spectroscopy. As anticipated, the ^1H NMR spectrum run within a few minutes of mixing again showed that the resonances of Cp_2ZrMe_2 had disappeared while the methane resonance and new Cp (δ 6.27, 6.36), $ZrCH_3$ (δ 0.32, 0.28), BCH_2 (δ 1.51), and CMe_3 (δ 0.65) resonances appeared. In addition, there were also methyl and phenyl resonances of free NMe_2Ph at δ 2.96 and δ 6.75 (m), 7.26 (m), respectively, *and of coordinated* NMe_2Ph at δ 3.67 and δ 7.57 (m), 7.72 (m), respectively. Over 1 h the resonances at δ 0.32, 6.36, 2.96, 6.75, and 7.26 essentially disappeared and the ultimate product appeared to be $[Cp_2ZrMe(NMe_2Ph)][NpB(C_6F_5)_3]$.

A ^1H NMR study of the reaction of a bulkier ammonium salt of the neopentylborate anion, $[HNMePh_2][NpB(C_6F_5)_3]$ (**V**), with an equimolar amount of dimethyl zirconocene gave analogous results. A ^1H NMR spectrum revealed new Cp, $ZrCH_3$, BCH_2, and CMe_3 resonances at δ 6.66, 0.27, 1.53, and 0.66, respectively, as well as the methyl and phenyl resonances of free $NMePh_2$ (with lower intensity) at δ 3.30 and 6.90−7.30, respectively, and of coordinated $NMePh_2$ at δ 4.02 and 7.36−7.67, respectively. The data indicate that the compound $[Cp_2ZrMe(NMePh_2)][NpB(C_6F_5)_3]$ was being formed, but there was considerable overlap of the phenyl and Cp resonances, and the reaction was not studied in detail.

Propylene Polymerization in the Presence of the Weakly Coordinating Anion $[NpB(C_6F_5)_3]^-$. To assess the effectiveness of $[NpB(C_6F_5)_3]^-$ as a weakly coordinating anion, we carried out a series of propylene polymerization reactions utilizing the catalytic precursors Cp_2ZrMe_2,[11a] $(Indenyl)_2ZrMe_2$,[16] and $SBIZrMe_2$ (SBI = *rac*-dimethylsilylbis(1-indenyl)).[2f] The reactions were initiated at room temperature (21 °C) with 1.5 equiv of the protonating agent $[HNMe_2Ph][NpB(C_6F_5)_3]$. Representative results are shown in Table 4, where polymer yields, molecular weights, and tacticities are compared with data for propylene polymerizations carried out under essentially the same conditions but using as a cocatalyst $B(C_6F_5)_3$, i.e., in which the counteranion is $[MeB(C_6F_5)_3]^-$. As can be seen, for all three catalyst systems both the activities and the molecular weights increase significantly on going from the conventional $[MeB(C_6F_5)_3]^-$ (expt 1, 3, 5) to the presumably more weakly coordinating $[NpB(C_6F_5)_3]^-$ (expt 2, 4, 6). Unfortunately, significant warming of several of the reaction mixtures was observed, rendering comparisons inexact, as the increases in temperature varied with the catalyst system but could not be controlled. To extend our study, we therefore modified procedures so that temperature changes would be minimal.

Excellent temperature control (2 ± 2 °C) was achieved by initiating the polymerization reactions at 0 °C (ice bath) and working with catalysts at much lower concentrations, in the presence of 2.0 equiv of Al(*i*-Bu)$_3$ as scavenger. Representative results are shown in Table 5, where polymer yields, molecular weights, and tacticities are shown for polymerizations involving the same three catalysts mentioned above when treated with $B(C_6F_5)_3$ (expt 7, 13, 19), as well as with 1.5 equiv of a more extensive series of protonating agents $[HNMe_3][NpB(C_6F_5)_3]$ (expt 9, 15, 21), $[HNMe_2Ph][NpB(C_6F_5)_3]$ (expt 10, 16, 22), and $[HNMePh_2][NpB(C_6F_5)_3]$ (expt 11,

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17, 23). For purposes of comparison, we also investigated the use of $[HNMe_2Ph][B(C_6F_5)_4]$, where the counteranion is $[B(C_6F_5)_4]^-$ (expt 12, 18, 24), and the use of $B(C_6F_5)_3$ in the presence of free NMe_2Ph (expt 8, 14, 20).

As can be seen from these results, use of the sterically more hindered $[NpB(C_6F_5)_3]^-$ rather than the conventional $[MeB(C_6F_5)_3]^-$ results in quite major increases in both catalyst activities (especially for the Cp system) and molecular weights. Indeed, use of the new anion $[NpB(C_6F_5)_3]^-$ results in activities and molecular weights very similar to those obtained using the bench mark weakly coordinating anion $[B(C_6F_5)_4]^-$ (expt 12, 18, 24). Varying the amine in polymerization systems involving the $[NpB(C_6F_5)_3]^-$ anion (expt 9−11, 15−17, 21−23) seems generally to have little effect on activities and polymer molecular weights, and so the differences do reflect the differences in properties of the borate anions.

The tacticities of the isotactic polypropylene obtained using $SBIZrMe_2$ were obtained using $^{13}C\{^1H\}$ NMR spectroscopy[17] and compare well with literature data for isotactic polypropylene formed by this compound.[2f,i] The tacticities of experiments 19−24 vary somewhat with the counteranions, with the more weakly coordinating anions $[NpB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ resulting in lower tacticities than is found with $[MeB(C_6F_5)_3]^-$. This result is not surprising, as similar results have been observed previously;[2e] it seems that the tighter ion pairing of more strongly coordinating anions results in less freedom for stereoerrors to be introduced. The tacticities of the polymers made at 2 ±2 °C, as well as the molecular weights and the catalyst activities, were all higher than for the corresponding polymers made at higher temperatures. Similar behavior has been reported previously for similar types of metallocene polymerization catalysis and may reflect catalyst degradation at the higher temperatures.[1]

The use of trialkylammonium salts of weakly coordinating anions to activate dimethylmetallocene catalysts has recently been reviewed,[2e] and it seems implicit from much of the literature that the chemistry of eq 5 is generally assumed, i.e., that the free amine is too bulky and/or too weakly basic to coordinate. Furthermore, although examples of coordination complexes of sterically demanding amines are known, little has been done to assess the possibility that amine coordination may affect polymerization.[2e] However, comparisons of experiments 8 with 7, 14 with 13, and 20 with 19 of Table 5, in which the catalyst precursors are activated with $B(C_6F_5)_3$ in the presence and absence of 1 equiv of NMe_2Ph, show clearly that the presence of free amine can have quite deleterious effects on both the conversions and the molecular weights of the polymeric products. Thus the amine byproducts in experiments 9−11, 15−17, and 21−23 probably also result in lowered activities and/or molecular weights.

Summary. Reactions of $B(C_6F_5)_3$ with a series of alkyl lithium reagents result in the formation of the series of borate salts $Li[RB(C_6F_5)_3]$ (R = Me, Et, *i*-Pr, Np). Metathesis reactions with Ph_3CCl, $[(Ph_3P)_2N]Cl$, $[PMePh_3]Cl$, and $[HNMe_2Ph]Cl$ result in the formation of several new derivatives, which have been characterized crystallographically, and in all cases the alkylborate anions assume the expected pseudotetrahedral structures and exhibit normal bond lengths and bond angles. Unfortunately salts of the type $[Ph_3C][RB(C_6F_5)_3]$ cannot be obtained pure, and so compounds of this type do not provide ideal cocatalysts for the activation of dimethylzirconocene derivatives for olefin polymerization. Compounds of the type $[HNR_3][NpB(C_6F_5)_3]$ (R_3 = Me_3, Me_2Ph, $MePh_2$) have therefore been prepared, and these do react with Cp_2ZrMe_2, $(Indenyl)_2ZrMe_2$, and $SBIZrMe_2$ to give propylene polymerization catalysts that are significantly more active and give higher molecular weight polypropylene than do the catalysts obtained using $B(C_6F_5)_3$. Thus the $[NpB(C_6F_5)_3]^-$ anion is for steric reasons more weakly coordinating than is $[MeB(C_6F_5)_3]^-$ and indeed is on par with the much better studied $[B(C_6F_5)_4]^-$ anion. While the amine byproducts do not significantly affect the molecular weights or tacticities of the polymers formed, they do, counter to general perceptions, reduce activities by coordinating to the active sites of the cationic zirconocene catalysts.

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Supporting Information Available: Crystallographic details, including figures of $[PPN][EtB(C_6F_5)_3]$ (**I**), $[PMePh_3][HB(C_6F_5)_3]$ (**II**), $[PMePh_3][NpB(C_6F_5)_3]$ (**III**), $[HNMe_2Ph][NpB(C_6F_5)_3]$ (**IV**), and $[HNMePh_2][NpB(C_6F_5)_3]$ (**V**) showing complete numbering schemes for cations and anions and thermal ellipsoid figures, and tables of positional and thermal parameters and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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