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New Organo-Lewis Acids. Tris(*β*-perfluoronaphthyl)borane (PNB) as a Highly Active Cocatalyst for Metallocene-Mediated Ziegler−Natta α-Olefin Polymerization

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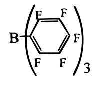
Tris(β-perfluoronaphthyl)borane ($B(C_{10}F_7)_3$, PNB) is synthesized from β-perfluoronaphthyllithium and BCl_3 to serve as a new strong organo-Lewis acid cocatalyst. PNB efficiently activates a variety of group 4 dimethyl complexes to form highly active homogeneous Ziegler−Natta olefin polymerization catalysts. Reaction of PNB with *rac*-$Me_2Si(Ind)_2ZrMe_2$ and $CGCMMe_2$ (M = Zr, Ti; CGC = $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)$) (1:1 molar ratio) rapidly produces the base-free cationic complexes *rac*-$Me_2Si(Ind)_2ZrMe^+MePNB^-$ (**1**) and $CGCMMe^+MePNB^-$ (M = Zr, **2**; Ti, **3**), respectively. The μ-methyl dinuclear cationic complex $[(CGCTiMe)_2(\mu\text{-}Me)]^+MePNB^-$ (**4**) is formed when a 2:1 $CGCTiMe_2$:PNB stoichiometry is employed. In the case of group 4 dimethyl zirconocenes, L_2ZrMe_2 (L = $\eta^5\text{-}C_5H_5$, Cp; η^5-1,2-$Me_2C_5H_3$, Cp″), reaction in a 1:1 metallocene:PNB ratio affords cationic complexes $L_2ZrMe^+MePNB^-$ (L = Cp, **5**; Cp″, **6**), while the reaction with a 1:2 molar ratio affords dinuclear μ-methyl cationic complexes $[(L_2ZrMe)_2(\mu\text{-}Me)]^+MePNB^-$ (L = Cp, **7**; Cp″, **8**). In both reactions, μ-F dinuclear cationic complexes $[(L_2ZrMe)_2(\mu\text{-}F)]^+MePNB^-$ (L = Cp, **9**; Cp″, **10**) are formed as byproducts. $(C_6F_5)_3BNCCH_3$ and $PNBNCCH_3$ were synthesized and characterized. Analysis of the $PNBNCCH_3 + B(C_6F_5)_3 \rightleftharpoons (C_6F_5)_3BNCCH_3 + PNB$ equilibrium yields $\Delta H° = +0.7(2)$ kcal/mol and $\Delta S° = +4.3(5)$ eu, suggesting PNB has somewhat higher Lewis acidity and is sterically more encumbered than $B(C_6F_5)_3$. Solution ν(CN) values for $PNBNCCH_3$ and $(C_6F_5)_3BNCCH_3$ are 2365.3 and 2366.5 cm^{-1}, respectively, which indicate strong Lewis acidity. $PBBNCCH_3$ cannot be detected in the reaction of $(C_6F_5)_3BNCCH_3$ with PBB [PBB = tris(2,2′,2″-perfluorobipheny)lborane] over prolonged periods at 60 °C. In ethylene polymerization, PNB-derived cationic complexes **5**, **6**, **7**, and **8** have catalytic activities similar to the $B(C_6F_5)_3$-derived analogues, while **2** and **3** have substantially higher activities. In propylene polymerization, catalyst **1** has higher activity than the $B(C_6F_5)_3$ analogue. In the case of ethylene and 1-hexene copolymerization, PNB-derived cationic complex **3** exhibits higher polymerization activity with similar 1-hexene incorporation versus the $B(C_6F_5)_3$-derived cationic complex. In large-scale batch copolymerizations of ethylene and 1-octene mediated by $CGCTiMe_2$, the PNB-based catalytic systems exhibit approximately twice the activity of the $B(C_6F_5)_3$-based systems.

Introduction

Cocatalysts for homogeneous metallocene Ziegler−Natta olefin polymerization are of great current interest for both technological and fundamental scientific reasons.[1] Cocatalysts such as methylaluminoxane (MAO)[2] react with metallocenes to generate highly active "cationic" olefin polymerization catalysts. However, large MAO/catalyst precursor ratios, in the range 10^2−10^4:1, are typically necessary for acceptable polymerization activity. In contrast, tris(perfluorophenyl)borane, $B(C_6F_5)_3$ (**I**), undergoes reaction with metallocene dimethyls in 1:1 catalyst:cocatalyst ratios to form highly active, structurally characterizable catalytic species.[3] Recently, a second strong organo-Lewis acid, the sterically encumbered perfluoroarylborane, tris(2,2′,2″-perfluorobi-

I



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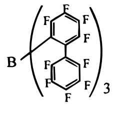

PBB

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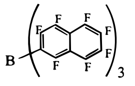

PNB

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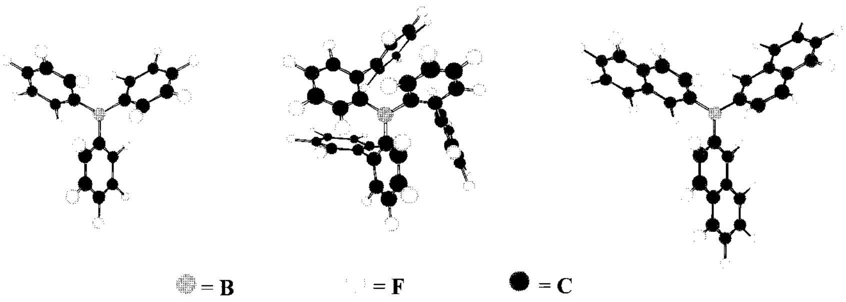

$B(C_6F_5)_3$, **I** PBB, **II** PNB, **III**

Figure 1. Molecular structures of $B(C_6F_5)_3$, PBB, and PNB computed with the AM1 model Hamiltonian.

phenyl)borane (PBB, **II**),[4] was synthesized in our laboratory. PBB generates cationic species with generally higher catalytic activities for olefin polymerizations and copolymerizations than does $B(C_6F_5)_3$. However, in the case of group 4 metallocene dimethyls, PBB preferentially affords cationic dinuclear complexes such as $[Cp_2ZrMe(\mu\text{-}Me)MeZrCp_2]^+$ at room temperature (reflecting the weaker coordinative tendencies of $MePBB^-$ versus $MeB(C_6F_5)_3^-$), even with excess PBB and long reaction times.[4] Monomeric species can only be generated in situ at higher temperatures. The activation of metallocene dimethyls with PBB is also sluggish; for example, 1 h is required to completely activate *rac*-$Me_2Si(Ind)_2ZrMe_2$ in mmol toluene solution. For these reasons, it would be of great interest to investigate the properties of other sterically and electronically modified perfluoroarylboranes. Considering that the perfluoronaphthyl group is bulkier and potentially more strongly electron withdrawing than perfluorophenyl, we undertook a synthetic investigation of the properties of a perfluoronaphthylborane. We report here the synthesis, reactivity, and polymerization catalytic properties of the new strong organo-Lewis acid tris(β-perfluoronaphthyl)borane (PNB, **III**) and demonstrate that it is an excellent cocatalyst for metallocene-mediated ethylene polymerization. The marked dimensional/shape differences between $B(C_6F_5)_3$, PBB, and PNB can be appreciated from the computed geometries shown in Figure 1. These geometries were optimized using the AM1 model Hamiltonian, as incorporated in the Gaussian 94 package, with no symmetry constraints.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10^{-5} Torr), or in a nitrogen-filled vacuum atmospheres glovebox with a high capacity recirculator (<1 ppm O_2). Argon, ethylene, and propylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents were distilled under nitrogen from Na/K alloy. All solvents for high-vacuum line manipulations were stored in vacuo over Na/K alloy in Telflon-valved bulbs. Deuterated solvents obtained from Cambridge Isotope Laboratories (all ≥99 atom % D) were freeze−pump−thaw degassed, dried over Na/K alloy, and stored in resealable flasks. Other nonhalogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from P_2O_5 and stored over activated Davison 4A molecular sieves. The comonomer 1-hexene (Aldrich) was dried over Na/K and vacuum-transferred into a storage tube containing activated 4A molecular sieves. CH_3CN (Aldrich) was dried over CaH_2 and then over activated 4A molecular sieves. $CuBr_2$, BCl_3 (1.0 M in hexane), and ${}^nBuLi$ (1.6 M in hexanes) were purchased from Aldrich and used as received. Octafluoronaphthalene was purchased from Oakwood Products, Inc., and used without further purification. β-Perfluoronaphthylhydrazine,[5] $B(C_6F_5)_3$,[6] $Me_2Si(C_5Me_4)({}^tBuN)TiMe_2$ ($CGCTiMe_2$),[7] $CGCZrMe_2$,[7] *rac*-$Me_2Si(Ind)_2ZrMe_2$,[8] Cp_2ZrMe_2,[9] and Cp''_2ZrMe_2[10] ($Cp'' = 1,2\text{-}Me_2Cp$) were prepared according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either Varian VXR 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C), VXR 400 (FT 400 MHz, ^1H; 100 MHz, ^{13}C; 377 MHz, ^{19}F), or Gemini-300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) instruments. Chemical shifts for ^1H and ^{13}C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, or by

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Midwest Microlab, Indianapolis, IN. ^{13}C NMR assays of polymer microstructure were conducted in $C_2D_2Cl_4$ at 120 °C. Signals were assigned according to the literature for polypropylene[11] and ethylene/1-hexene copolymers,[12] respectively. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 10 °C/min. Solution IR spectra were recorded in toluene solution with a Bio-Rad FTS-60 instrument. Sample solutions were contained in anaerobically capped, single-crystal NaCl cavity cells (Wilmad Glass Company, Inc., Buena, NJ) which were filled in the glovebox and transported to the FT-IR spectrometer in a nitrogen-filled plastic bag.

Synthesis of 2-Bromoheptafluoronaphthalene ($C_{10}F_7Br$). This is a modified version of the literature procedure.[13] *β*-Perfluoronaphthylhydrazine,[5] copper(II) bromide, and hydrobromic acid were heated together under reflux for 1 h. The mixture was then filtered after the solution had cooled to room temperature. The residual solid was washed with water and then extracted with CH_2Cl_2. The CH_2Cl_2 extract was next dried over $MgSO_4$, filtered, and evaporated to leave a brown solid. Sublimation afforded pure 2-bromoheptafluoronaphthalene. Yield: 58%. The ^{19}F NMR spectrum is identical to that in the literature.[14]

Synthesis of Tris(*β*-perfluoronaphthyl)borane ($B(C_{10}F_7)_3$; PNB). In a 250 mL flask, 2-bromoheptafluoronaphthalene (3.0 g, 9.0 mmol) was dissolved in 85 mL dry pentane. The solution was stirred at −30 °C for 10 min, and then 5.63 mL of *n*-butyllithium (1.6 M in hexanes, 9.0 mmol) was added dropwise via syringe over the course of 1 h. A white precipitate formed immediately. The solution was stirred between −40 and −30 °C for 80 min after the addition was complete, and then 3.0 mL of BCl_3 (1.0 M in hexanes, 3.0 mmol) was quickly added at −40 °C. The solution immediately turned yellow and was allowed to warm slowly to room temperature overnight. All the volatiles were then removed in vacuo to afford a yellow solid and LiCl. Repeated sublimation at 150 °C (0.05 Torr) removed yellow, sticky byproducts. Next, sublimation at 220 °C (0.05 Torr) for 3 h gave analytically pure PNB as a pale-yellow solid. Yield: 0.60 g (26%). Sublimation at 150 °C under high vacuum (10^{-5} Torr) gave similar results. Spectroscopic and analytical data for PNB are as follows. ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ −102.97 (dd, 3 F, F-1, $^{4}J_{\mathrm{F1-F8}} = 73$ Hz, $^{5}J_{\mathrm{F1-F4}} = 18$ Hz), −129.66 (d, 3 F, F-3, $^{4}J_{\mathrm{F3-F4}} = 18$ Hz), −142.04 (dt, 3 F, F-8, $^{4}J_{\mathrm{F8-F1}} = 73$ Hz, $^{3}J_{\mathrm{F8-F7}} = {}^{5}J_{\mathrm{F8-F5}} = 17$ Hz), −145.18 (dt, 3 F, F-5, $^{4}J_{\mathrm{F5-F4}} = 58$ Hz, $^{3}J_{\mathrm{F5-F6}} = {}^{5}J_{\mathrm{F8-F5}} = 17$ Hz), −149.33 (dt, 3 F, F-4, $^{4}J_{\mathrm{F4-F5}} = 58$ Hz, $^{3}J_{\mathrm{F4-F3}} = {}^{5}J_{\mathrm{F1-F4}} = 18$ Hz), −149.60 (t, br, 3 F, F-6, $^{3}J_{\mathrm{F6-F7}} = {}^{3}J_{\mathrm{F6-F5}} = 18$ Hz), −155.09 (t, br, 3 F, F-7, $^{3}J_{\mathrm{F7-F8}} = {}^{3}J_{\mathrm{F6-F7}} = 17$ Hz). MS: parent ion at *m*/*e* 770. Anal. Calcd for $C_{30}BF_{21}$: C, 46.79; H, 0.00; N, 0.00. Found: C, 46.91, H, 0.07, N, 0.00.

Synthesis of the Acetonitrile Adduct of PNB ($CH_3CNB(C_{10}F_7)_3$). PNB (50 mg, 0.065 mmol) was loaded into a 25 mL reaction flask in the glovebox. Pentane (5 mL) and CH_3CN (0.3 mL) were then condensed in at −78 °C on the high-vacuum line, and the solution was stirred at room temperature for 3 h. The white precipitate was collected by filtration, washed with pentane, and dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 40 mg (76%). Spectroscopic data for $PNBNCCH_3$ are as follows. ^{1}H NMR (C_7D_8, 23 °C, 399.941 MHz): δ 0.596 (s, 3 H, CH_3CN). ^{13}C NMR (C_7D_8, 23 °C, 100.574 MHz): δ −0.843 (CH_3CN). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ −110.95 (dd, 3 F, F-1, $^{4}J_{\mathrm{F1-F8}} = 76$ Hz, $^{5}J_{\mathrm{F1-F4}} = 18$ Hz), −130.01 (d, 3 F, F-3, $^{3}J_{\mathrm{F3-F4}} = 17$ Hz), −145.15 (dt, 3 F, F-8, $^{4}J_{\mathrm{F1-F8}} = 76$ Hz, $^{5}J_{\mathrm{F8-F5}} = {}^{3}J_{\mathrm{F8-F7}} = 18$ Hz), −146.91 (dt, 3 F, F-5, $^{4}J_{\mathrm{F5-F4}} = 55$ Hz, $^{3}J_{\mathrm{F5-F6}} = {}^{5}J_{\mathrm{F8-F5}} = 17$ Hz), −151.51 (dt, 3 F, F-4, $^{4}J_{\mathrm{F4-F5}} = 58$ Hz, $^{3}J_{\mathrm{F4-F3}} = {}^{5}J_{\mathrm{F1-F4}} = 18$ Hz), −154.79 (t, br, 3 F, F-6, $^{3}J_{\mathrm{F6-F7}} = {}^{3}J_{\mathrm{F6-F5}} = 18$ Hz), −157.05 (t, br, 3 F, F-7, $^{3}J_{\mathrm{F7-F8}} = {}^{3}J_{\mathrm{F6-F7}} = 17$ Hz). ν(CN) = 2365.3 cm^{-1} (41.3 mM toluene solution). Anal. Calcd for $C_{32}H_3BF_{21}N$: C, 47.38; H, 0.37; N, 1.72. Found: C, 47.13; H, 0.33; N, 1.72.

Synthesis of the Acetonitrile Adduct of $B(C_6F_5)_3$ ($CH_3CNB(C_6F_5)_3$). $B(C_6F_5)_3$ (200 mg, 0.391 mmol) was loaded into a 25 mL reaction flask in the glovebox. Toluene (10 mL) and CH_3CN (0.4 mL) were condensed in at −78 °C on the high-vacuum line. The solution was next stirred at room temperature for 1 h, and all the volatiles were removed by vacuum to give white solid. The white solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 190 mg (89%). Spectroscopic data for $(C_6F_5)_3BNCCH_3$ are as follows. ^{1}H NMR (C_6D_6, 23 °C, 399.941 MHz): δ 0.242 (s, 3 H, CH_3CN). ^{13}C NMR (C_6D_6, 23 °C, 100.574 MHz): δ −0.908 (CH_3CN). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ −134.74 (multi, 6 F, *o*-F), −155.21 (t, 3 F, *p*-F, $^{3}J_{\mathrm{F-F}} = 21$ Hz), −163.12 (multi, 6 F, *m*-F). ν(CN) = 2366.5 cm^{-1} (46.9 mM toluene solution). Anal. Calcd for $C_{20}H_3BF_{15}N$: C, 43.44; H, 0.55; N, 2.53. Found: C, 43.55; H, 0.57; N, 2.49.

Variable-Temperature Study of the Equilibrium $PNBNCCH_3 + B(C_6F_5)_3 \rightleftharpoons (C_6F_5)_3BNCCH_3 + PNB$. $PNBNCCH_3$ (8.11 mg, 0.010 mmol) and $B(C_6F_5)_3$ (5.12 mg, 0.010 mmol) were loaded into a J-Young NMR tube in the glovebox, and 0.7 mL C_7H_8 was added to the NMR tube. The solution turned yellow immediately, indicating the formation of free PNB. Variable-temperature NMR studies (−16.3 °C to +41.7 °C) were carried out on the Gemini 300 or VXR 400 NMR instrument with 3 s relaxation delay times. A separate experiment starting with $(C_6F_5)_3BNCCH_3$ (5.53 mg, 0.010 mmol) and PNB (7.70 mg, 0.010 mmol) was also carried out under similar conditions.

In Situ Generation of *rac*-$Me_2Si(Ind)_2ZrMe^+MePNB^-$ (1). *rac*-$Me_2Si(Ind)_2ZrMe_2$ (5.0 mg, 0.013 mmol) and PNB (10.1 mg, 0.0130 mmol) were dissolved in C_6D_6 in a J-Young NMR tube. Reaction occurred immediately to give *rac*-$Me_2Si(Ind)_2ZrMe^+MePNB^-$, which decomposes slowly at room temperature. Spectroscopic data for **1** are as follows. ^{1}H NMR (C_6D_6, 23 °C, 399.941 MHz): δ 7.72−7.76 (1 H, Ind), 7.03−7.18 (3 H, Ind), 6.63−6.75 (3 H, Ind), 6.52 (t, 1 H, $^{3}J_{\mathrm{H-H}} = 4$ Hz, Ind), 6.22−6.28 (m, 1 H, Ind), 6.11−6.16 (m, 1 H, Ind), 5.94−5.96 (m, 1 H, Ind), 5.05 (d, 1 H, $^{3}J_{\mathrm{H-H}} = 4$ Hz, Ind), 0.425 (s, 3 H, *Me*$_2$Si), 0.248 (s, 3 H, *Me*$_2$Si), −0.011 (s, br, 3 H, B-CH_3), −0.355 (s, 3 H, Zr−CH_3). ^{13}C NMR (C_6D_6, 23 °C, 100.577 MHz): δ 132.86 (Ind), 132.38 (Ind), 128.12 (Ind), 127.89 (Ind), 127.34 (Ind), 126.85 (Ind), 126.51 (Ind), 126.47 (Ind), 125.19 (Ind), 125.02 (Ind), 123.68 (Ind), 121.22 (Ind), 117.45 (Ind), 116.44 (Ind), 116.24 (Ind), 111.58 (Ind), 89.81 (Ind), 88.23 (Ind), 49.99 (Zr−Me), 22.51 (B−Me), −2.45 ($SiMe_2$), −3.08 ($SiMe_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ −110.21 (d, 3 F, F-1, $^{4}J_{\mathrm{F1-F8}} = 76$ Hz), −127.24 (br, 3 F, F-3), −145.99 (dt, 3 F, F-8, $^{4}J_{\mathrm{F8-F1}} = 73$ Hz, $^{3}J_{\mathrm{F8-F7}} = {}^{5}J_{\mathrm{F8-F5}} = 17$ Hz), −147.73 (dt, 3 F, F-5, $^{4}J_{\mathrm{F5-F4}} = 55$ Hz, $^{3}J_{\mathrm{F5-F6}} = {}^{5}J_{\mathrm{F5-F8}} = 17$ Hz), −152.93 (dt, 3 F, F-4, $^{4}J_{\mathrm{F4-F5}} = 55$ Hz, $^{3}J_{\mathrm{F4-F3}} = {}^{5}J_{\mathrm{F4-F1}} = 18$ Hz), −156.95 (t, br, 3 F, F-6, $^{3}J_{\mathrm{F6-F7}} = {}^{3}J_{\mathrm{F6-F5}} = 18$ Hz), −158.38 (t, br, 3 F, F-7, $^{3}J_{\mathrm{F7-F8}} = {}^{3}J_{\mathrm{F7-F6}} = 18$ Hz).

Synthesis of $CGCZrMe^+MePNB^-$ (2). $CGCZrMe_2$ (100 mg, 0.270 mmol) and PNB (207.7 mg, 0.270 mmol) were loaded into a 25 mL reaction flask in the glovebox. On the high-vacuum line, C_6H_6 (10 mL) was condensed in at −78 °C. The solution was then stirred at room temperature for 1 h, and all the volatiles were removed under high vacuum to give a yellow solid. Pentane was condensed in to wash the solid twice, and

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the yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 89 mg (61%). The spectroscopic data for **2** are as follows. ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 1.81 (s, 3 H, C_5Me_4), 1.77 (s, 3 H, C_5Me_4), 1.64 (s, 3 H, C_5Me_4), 1.58 (s, 3 H, C_5Me_4), 1.43(s, br, 3 H, B$-$CH$_3$), 1.13 (s, 9 H, NC*Me*$_3$), 0.47 (s, 3 H, Zr$-$Me), 0.28 (s, 3 H, SiMe$_2$), 0.19 (s, 3 H, SiMe$_2$). ^{13}C NMR (C_6D_6, 23 °C, 75.462 MHz): δ 150.38$-$155.63 ($C_{10}F_7$), 136.56$-$142.86 ($C_{10}F_7$), 110.90 (br, $C_{10}F_7$), 108.31 (br, $C_{10}F_7$), 134.40 (*C*$_5$Me$_4$), 133.67 (*C*$_5$Me$_4$), 133.19 (*C*$_5$Me$_4$), 129.46 (*C*$_5$Me$_4$), 102.24 (*C*$_5$Me$_4$), 57.89 (N*C*Me$_3$), 44.21 (Zr$-$*C*H$_3$), 33.07 (NC*Me*$_3$), 15.10 (C$_5$*Me*$_4$), 12.85 (C$_5$*Me*$_4$), 11.42 (C$_5$*Me*$_4$), 10.69 (C$_5$*Me*$_4$), 5.58 (Si*Me*$_2$), 5.12 (Si*Me*$_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$111.05 (br, 3 F, F-1), $-$127.36 (br, 3 F, F-3), $-$146.01 (dt, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz, $^3J_{F8-F7}$ = $^5J_{F8-F5}$ = 17 Hz), $-$147.82 (br, 3 F, F-5), $-$152.51 (br, 3 F, F-4), $-$157.26 (br, 3 F, F-6), $-$158.64 (br, 3 F, F-7). Anal. Calcd for $C_{48}H_{33}BF_{21}NSiZr$: C, 49.48; H, 2.92. Found: C, 49.68, H, 3.23.

Synthesis of CGCTiMe$^+$MePNB$^-$ (3). CGCTiMe$_2$ (40 mg, 0.122 mmol) and PNB (95 mg, 0.122 mmol) were loaded into a 25 mL reaction flask in the glovebox. On the vacuum line, C_6H_6 (10 mL) was condensed in at $-$78 °C, and the solution was stirred at room temperature for 1 h. Next, all the volatiles were removed under high vacuum to give a yellow solid. Pentane was condensed in to wash the solid twice, and the yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 53 mg (40%). The spectroscopic data for **3** are as follows. ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 1.847 (s, 3 H, C$_5$*Me*$_4$), 1.658 (s, 3 H, C$_5$*Me*$_4$), 1.610 (s, 3 H, C$_5$*Me*$_4$), 1.466 (s, 3 H, C$_5$*Me*$_4$), 1.085 (s, 9 H, NC*Me*$_3$), 1.60 (br, 6 H, Ti$-$*Me*, B$-$*Me*), 0.336 (s, 3 H, Si*Me*$_2$), 0.179 (s, 3 H, Si*Me*$_2$). ^{13}C NMR (C_6D_6, 23 °C, 75.462 MHz): δ 141.21 (*C*$_5$Me$_4$), 139.17 (d, C$_5$Me$_4$, J_{C-F} = 2.4 Hz), 138.68 (*C*$_5$Me$_4$), 136.21 (*C*$_5$Me$_4$), 105.54 (*C*$_5$Me$_4$), 66.67 (Ti$-$*C*H$_3$), 63.40 (N*C*Me$_3$), 33.03 (N*C*Me$_3$), 16.07 (C$_5$*Me*$_4$), 13.91 (C$_5$*Me*$_4$), 12.04 (C$_5$*Me*$_4$), 11.58 (C$_5$*Me*$_4$), 5.13 (Si*Me*$_2$), 4.54 (Si*Me*$_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$110.42 (d, br, 3 F, F-1, $^4J_{F1-F8}$ = 76 Hz), $-$127.13 (br, 3 F, F-3), $-$145.94 (multi, 3 F, F-8), $-$148.77 (multi, 3 F, F-5), $-$152.63 (multi, 3 F, F-4), $-$157.14 (t, 3 F, F-6, $^3J_{F6-F7}$ = $^3J_{F6-F5}$ = 18 Hz), $-$158.58 (t, 3 F, F-7, $^3J_{F7-F8}$ = $^3J_{F6-F7}$ = 18 Hz). Anal. Calcd for $C_{48}H_{33}BF_{21}NSiTi$: C, 51.43; H, 3.03. Found: C, 51.48, H, 3.13.

In Situ Generation of [(CGCTiMe)$_2$(μ-Me)]$^+$[MePNB]$^-$ (4). CGCTiMe$_2$ (9.8 mg, 0.030 mmol) and PNB (11.6 mg, 0.015 mmol) were dissolved in the C_6D_6 in a J-Young NMR tube. The reaction occurred immediately to give **4**. No μ-F bridged dimeric cationic species could be detected. Spectroscopic data for **4** are as follows. ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 1.898 (s, 6 H, C$_5$*Me*$_4$), 1.574 (s, 6 H, C$_5$*Me*$_4$), 1.547 (s, 6 H, C$_5$*Me*$_4$), 1.524 (s, 6 H, C$_5$*Me*$_4$), 1.114 (s, 9 H, NC*Me*$_3$), 0.458 (s, 6 H, Ti$-$*Me*), 0.364 (br, 3 H, B$-$*Me*), 0.337 (s, 6 H, Si*Me*$_2$), 0.284 (s, 6 H, Si*Me*$_2$), $-$0.828 (s, 3 H, Ti$-$*Me*$-$Ti). ^{13}C NMR (C_6D_6, 23 °C, 75.462 MHz): δ 142.33 (*C*$_5$Me$_4$), 137.24 (*C*$_5$Me$_4$), 135.81 (*C*$_5$Me$_4$), 134.34 (*C*$_5$Me$_4$), 102.41 (*C*$_5$Me$_4$), 64.82 (Ti$-$*C*H$_3$), 61.59 (N*C*Me$_3$), 44.50 (Ti$-$CH$_3$$-$Ti), 33.70 (N*C*Me$_3$), 15.67 (C$_5$*Me*$_4$), 14.57 (C$_5$*Me*$_4$), 11.90 (C$_5$*Me*$_4$), 11.65 (C$_5$*Me*$_4$), 5.44 (Si*Me*$_2$), 4.26 (Si*Me*$_2$). ^{19}F NMR ($C_6D_6$, 23 °C, 282.330 MHz): δ $-$108.29 (dd, 3 F, F-1, $^4J_{F1-F8}$ = 76 Hz, $^5J_{F1-F4}$ = 16 Hz), $-$123.18 (br, 3 F, F-3), $-$145.94 (dt, 3 F, F-8, $^4J_{F8-F1}$ = 73 Hz, $^3J_{F8-F7}$ = $^5J_{F8-F5}$ = 18 Hz), $-$149.99 (dt, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz, $^3J_{F5-F6}$ = $^5J_{F8-F5}$ = 17 Hz), $-$155.41 (dt, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz, $^3J_{F4-F3}$ = $^5J_{F4-F1}$ = 18 Hz), $-$161.32 (t, 3 F, F-6, $^3J_{F6-F7}$ = $^3J_{F6-F5}$ = 18 Hz), $-$162.19 (t, 3 F, F-7, $^3J_{F7-F8}$ = $^3J_{F6-F7}$ = 18 Hz).

In Situ Generation of Cp$_2$ZrMe$^+$MePNB$^-$ (5). Cp$_2$ZrMe$_2$ (3.8 mg, 0.015 mmol) and PNB (11.6 mg, 0.015 mmol) were dissolved in C_6D_6 in a J-Young NMR tube. Reaction occurred immediately to give Cp$_2$ZrMe$^+$MePNB$^-$ (**5**) and a byproduct, the μ-F bridged dimeric cationic species [Cp$_2$ZrMe(μ-F)-MeZrCp$_2$]$^+$MePNB$^-$ (**9**) in a ratio of 5:1. The spectroscopic data for **5** and **9** are as follows. *Cp$_2$ZrMe$^+$MePNB$^-$ (**5**).* ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.57 (s,10 H, C$_5$*H*$_5$), 0.57 (s, br, 3 H, B$-$*C*H$_3$), 0.43 (s, 3 H, Zr$-$C*H*$_3$).^{13}C NMR (C_6D_6, 23 °C, 75.416 MHz): δ 114.28 (*C*$_5$H$_5$), 40.90 (Zr$-$*C*H$_3$), 27.23 (B$-$*C*H$_3$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$110.71 (d, 3 F, F-1, $^4J_{F1-F8}$ = 76 Hz), $-$127.59 (br, 3 F, F-3), $-$146.30 (d, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz), $-$147.55 (d, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz), $-$152.46 (d, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz), $-$156.90 (br, 3 F, F-6), $-$158.33 (br, 3 F, F-7). *[Cp$_2$ZrMe(μ-F)MeZrCp$_2$]$^+$[MePNB]$^-$ (**9**)*: ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.60 (s, 20 H, C$_5$*H*$_5$), 1.56 (s, br, 3 H, B$-$*C*H$_3$), 0.26 (d, 6 H, Zr$-$C*H*$_3$, $^3J_{H-F}$ = 2.4 Hz).^{13}C NMR (C_6D_6, 23 °C, 75.416 MHz): δ 114.80 (*C*$_5$H$_5$), 39.03 (Zr$-$*C*H$_3$), 26.07 (B$-$*C*H$_3$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$88.32 (s, 1 F, Zr$-$F$-$Zr), $-$108.58 (dd, 3 F, F-1, $^4J_{F1-F8}$ = 73 Hz), $-$124.24 (d, br, 3 F, F-3), $-$146.03 (dt, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz), $-$149.79 (dt, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz), $-$155.23 (dt, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz), $-$160.50 (t, br, 3 F, F-6), $-$161.45 (t, br, 3 F, F-7).

In Situ Generation of Cp$_2$ZrMe(μ-Me)MeZrCp$_2$$^+$MePNB$^-$ (7). Cp$_2$ZrMe$_2$ (7.5 mg, 0.030 mmol) and PNB (11.6 mg, 0.015 mmol) were dissolved in C_6D_6 in a J-Young NMR tube. Reaction occurred immediately to give Cp$_2$ZrMe(μ-Me)MeZrCp$_2$$^+$-MePNB$^-$ (**7**) and a byproduct, the μ-F bridged dimeric cationic species (**9**) in a ratio of 5:1. The spectroscopic data for **7** are as follows. ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.65 (s, 20 H, C$_5$*H*$_5$), 1.56 (s, br, 3 H, B$-$*C*H$_3$), $-$0.07 (s, 6 H, Zr$-$C*H*$_3$), $-$1.15 (s, 3 H, Zr$-$C*H*$_3$$-$Zr).^{13}C NMR ($C_6D_6$, 23 °C, 75.416 MHz): δ 113.26 (*C*$_5$H$_5$), 39.26 (Zr$-$*C*H$_3$), 26.07 (B$-$*C*H$_3$), 22.29-(Zr$-$*C*H$_3$$-$Zr). ^{19}F NMR ($C_6D_6$, 23 °C, 282.330 MHz): δ $-$108.58 (d, 3 F, F-1, $^4J_{F1-F8}$ = 73 Hz), $-$124.24 (br, 3 F, F-3), $-$146.03 (d, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz), $-$149.79 (d, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz), $-$155.23 (d, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz), $-$160.50 (br, 3 F, F-6), $-$161.45 (br, 3 F, F-7).

In Situ Generation of Cp″$_2$ZrMe$^+$MePNB$^-$ (6). Cp″$_2$-ZrMe$_2$ (4.6 mg, 0.015 mmol) and PNB (11.6 mg, 0.015 mmol) were dissolved in C_6D_6 in a J-Young NMR tube. Reaction occurred immediately to give Cp″$_2$ZrMe$^+$MePNB$^-$ (**6**) and a byproduct, the μ-F bridged dimeric cationic species Cp″$_2$ZrMe-(μ-F)MeZrCp″$_2$$^+$MePNB$^-$ (**10**) in a ratio of 7:1. The spectroscopic data for **6** and **10** are as follows. *Cp″$_2$ZrMe$^+$MePNB$^-$ (**6**).* ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.82 (t, 2 H, C$_5$*H*$_3$-Me$_2$, $^3J_{H-H}$ = 2.6 Hz), 5.47 (t, 2 H, C$_5$*H*$_3$Me$_2$, $^3J_{H-H}$ = 3.0 Hz), 4.88 (t, 2 H, C$_5$*H*$_3$Me$_2$, $^3J_{H-H}$ = 2.7 Hz), 1.68 (s, 6 H, C$_5$H$_3$*Me*$_2$), 1.24 (s, 6 H, C$_5$H$_3$*Me*$_2$), 0.44 (s, br, 3 H, B$-$*C*H$_3$), 0.20 (s, 3 H, Zr$-$C*H*$_3$). ^{13}C NMR (C_6D_6, 23 °C, 100.577 MHz): δ 150.67$-$155.07 (*C*$_{10}$F$_7$), 137.16$-$142.55 (*C*$_{10}$F$_7$), 116.37 (*C*$_5$H$_3$Me$_2$), 112.27 (*C*$_5$H$_3$Me$_2$), 110.84 (br, 1C, *C*$_{10}$F$_7$), 108.45 (br, 1C, *C*$_{10}$F$_7$), 106.99 (*C*$_5$H$_3$Me$_2$), 44.82 (Zr$-$*C*H$_3$), 23.03 (B$-$*C*H$_3$), 12.63 (C$_5$H$_3$*Me*$_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$110.40 (dd, 3 F, F-1, $^4J_{F1-F8}$ = 73 Hz, $^5J_{F1-F4}$ = 16 Hz), $-$127.22 (br, 3 F, F-3), $-$146.28 (dt, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz, $^3J_{F8-F7}$ = $^5J_{F8-F5}$ = 17 Hz), $-$146.77 (dt, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz, $^3J_{F5-F6}$ = $^5J_{F8-F5}$ = 17 Hz), $-$152.59 (dt, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz, $^3J_{F4-F3}$ = $^5J_{F1-F4}$ = 18 Hz), $-$157.12 (t, br, 3 F, F-6, $^3J_{F6-F7}$ = $^3J_{F5-F6}$ = 18 Hz), $-$158.53 (t, br, 3 F, F-7, $^3J_{F7-F8}$ = $^3J_{F7-F6}$ = 18 Hz). *Cp″$_2$ZrMe(μ-F)MeZrCp″$_2$$^+$MePNB$^-$ (**10**)*: ^{1}H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.61 (td, 4 H, C$_5$*H*$_3$Me$_2$, $^3J_{H-H}$ = 2.7 Hz, $^3J_{H-F}$ = 1.1 Hz), 5.28 (dd, 4 H, C$_5$*H*$_3$Me$_2$, $^3J_{H-H}$ = 3.3 Hz), 5.16 (t, 4 H, C$_5$*H*$_3$Me$_2$, $^3J_{H-H}$ = 2.7 Hz), 1.66 (s, br, 3 H, B$-$*C*H$_3$), 1.64 (s, 12 H, C$_5$H$_3$*Me*$_2$), 1.36 (s, 12 H, C$_5$H$_3$*Me*$_2$), 0.04 (d, 6 H, Zr$-$C*H*$_3$, $^3J_{H-F}$ = 2.1 Hz). ^{13}C NMR (C_6D_6, 23 °C, 100.577 MHz): δ 126.10 (*C*$_5$H$_3$Me$_2$), 117.38 (*C*$_5$H$_3$Me$_2$), 112.02 (*C*$_5$H$_3$Me$_2$), 107.73 (*C*$_5$H$_3$Me$_2$), 42.28 (Zr$-$*C*H$_3$), 22.58 (B-*C*H$_3$), 12.60 (C$_5$H$_3$*Me*$_2$), 12.42 (C$_5$H$_3$*Me*$_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ $-$91.20 (s, 1 F, Zr$-$F$-$Zr), $-$108.42 (dd, 3 F, F-1, $^4J_{F1-F8}$ = 73 Hz, $^5J_{F1-F4}$ = 16 Hz), $-$123.76 (d, br, 3 F, F-3, $^3J_{F3-F4}$ = 16 Hz), $-$145.95 (dt, 3 F, F-8, $^4J_{F8-F1}$ = 76 Hz, $^3J_{F8-F7}$ = $^5J_{F8-F5}$ = 17 Hz), $-$149.89 (dt, 3 F, F-5, $^4J_{F5-F4}$ = 55 Hz, $^3J_{F5-F6}$ = $^5J_{F8-F5}$ = 17 Hz), $-$155.34 (dt, 3 F, F-4, $^4J_{F4-F5}$ = 55 Hz, $^3J_{F4-F3}$ = $^5J_{F1-F4}$ = 19 Hz), $-$160.96 (t, br, 3 F, F-6, $^3J_{F6-F7}$ = $^5J_{F6-F5}$ = 18 Hz), $-$161.87 (t, br, 3 F, F-7, $^3J_{F7-F8}$ = $^3J_{F7-F6}$ = 18 Hz).

In Situ Generation of $Cp''_2ZrMe(\mu\text{-}Me)MeZrCp''_2{}^+$-$MePNB^-$ (8). Cp''_2ZrMe_2 (9.2 mg, 0.030 mmol) and PNB (11.6 mg, 0.015 mmol) were dissolved in C_6D_6 in a J-Young NMR tube. Reaction occurred immediately to give $[Cp''_2ZrMe(\mu\text{-}Me)MeZrCp''_2]^+MePNB^-$ (**8**) and the byproduct, a μ-F bridged dimeric cationic species (**10**) in a ratio of 5:1. The spectroscopic data for **8** are as follows. ^1H NMR (C_6D_6, 23 °C, 299.910 MHz): δ 5.44 (t, 4 H, $C_5H_3Me_2$, $^3J_{H-H} = 2.7$ Hz), 5.40 (t, 4 H, $C_5H_3Me_2$, $^3J_{H-H} = 3.3$ Hz), 5.11 (t, 4 H, $C_5H_3Me_2$, $^3J_{H-H} = 2.7$ Hz), 1.66 (s, 12 H, $C_5H_3Me_2$), 1.45 (s, 12 H, $C_5H_3Me_2$), 1.65 (s, br, 3 H, $B-CH_3$), -0.32 (s, 6 H, $Zr-CH_3$), -1.59 (s, 3 H, $Zr-CH_3-Zr$). ^{13}C NMR (C_6D_6, 23 °C, 100.577 MHz): δ 126.01 ($C_5H_3Me_2$), 125.63 ($C_5H_3Me_2$), 113.92 ($C_5H_3Me_2$), 111.38 ($C_5H_3Me_2$), 106.46 ($C_5H_3Me_2$), 41.77 ($Zr-CH_3$), 22.58 ($B-CH_3$), 22.34 ($Zr-CH_3-Zr$), 12.93 ($C_5H_3Me_2$), 12.66 ($C_5H_3Me_2$). ^{19}F NMR (C_6D_6, 23 °C, 282.330 MHz): δ -108.42 (dd, 3 F, F-1, $^4J_{F1-F8} = 73$ Hz, $^5J_{F1-F4} = 16$ Hz), -123.76 (d, br, 3 F, F-3, $^3J_{F3-F4} = 16$ Hz), -145.95 (dt, 3 F, F-8, $^4J_{F8-F1} = 76$ Hz, $^3J_{F8-F7} = {}^5J_{F8-F5} = 17$ Hz), -149.89 (dt, 3 F, F-5, $^4J_{F5-F4} = 55$ Hz, $^3J_{F5-F6} = {}^5J_{F5-F8} = 17$ Hz), -155.34 (dt, 3 F, F-4, $^4J_{F4-F5} = 55$ Hz, $^3J_{F4-F3} = {}^5J_{F4-F1} = 18$ Hz), -160.96 (t, br, 3 F, F-6, $^3J_{F6-F7} = {}^3J_{F6-F5} = 18$ Hz), -161.87 (t, br, 3 F, F-7, $^3J_{F7-F8} = {}^5J_{F7-F8} = 18$ Hz).

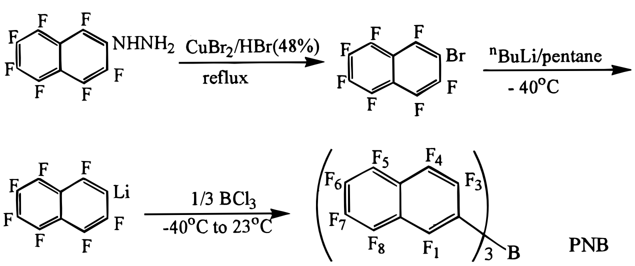
Ethylene, Propylene Polymerization Experiments. This procedure is designed to minimize mass transfer (gas to solution; catalyst entrainment) and exotherm effects while at the same time maintaining strictly anaerobic/anhydrous conditions.[3a,c] On a high-vacuum line (10^{-5} Torr), ethylene and propylene polymerization were carried out in 250 mL round-bottom three-neck flasks equipped with a large magnetic stirring bar and a thermocouple probe. In a typical experiment, a measured quantity of dry toluene (and 1-hexene in the case of ethylene and 1-hexene copolymerization) was vacuum-transferred into the flask, presaturated under 1.0 atm of rigorously purified ethylene or propylene (pressure control using a mercury bubbler), and equilibrated at the desired reaction temperature using an external bath. The catalytically active species was freshly generated (within 1.0 min) using a solution having a 1:1 metallocene/cocatalyst ratio in 1.5 mL of toluene. The solution of catalyst was then quickly injected into the rapidly stirred flask using a gastight syringe equipped with a spraying needle. The temperature of the toluene solution in representative polymerization experiments was monitored using a thermocouple (OMEGA Type K thermocouple with a model HH21 microprocessor thermometer). The reaction exotherm temperature rise was invariably less than 5 °C during these polymerizations. After a measured time interval (short to minimize mass transport and exotherm effects), the polymerization was quenched by the addition of 15 mL of 2% acidified methanol. Another 30 mL of methanol was then added, and the polymer was collected by filtration, washed with methanol, and dried on the high-vacuum line overnight to a constant weight. Uncertainties in activities reported in Table 1 are the average of 3 trials.

Large-Scale Batch Polymerizations. In a typical polymerization, a 2 L stirred Parr reactor was charged with 740 g of Isopar E solvent and 118 g of 1-octene. Hydrogen was added for molecular weight control by differential pressure expansion from a 75 L addition tank at 25 psi. The reactor was heated to 140 °C and saturated with ethylene at 500 psig. Then 2.0 μmol each of catalyst and cocatalyst (0.005 M in toluene) were premixed in the glovebox; the solution was transferred to a catalyst addition tank and injected into the reactor. Polymerization conditions were maintained for 15 min with ethylene on demand. The resulting polymer solutions were removed from the reactor, and a phenol antioxidant (Irganox 1010) was added. Polymers were recovered by removal of solvent in vacuo at 120 °C for 20 h.

Results and Discussion

A. Synthesis of PNB. The starting material, β-bromoheptafluoronaphthalene, was synthesized from β-perfluoronaphthylhydrazine using a modified literature procedure.[13] Low-temperature lithium−halogen exchange using ^nBuLi produced β-perfluoronaphthyllithium, which was then reacted with BCl_3 at low temperature to afford, after solvent removal, yellow tris(β-perfluoronaphthyl)borane (PNB; **1**; Scheme 1). The product was purified by repeated vacuum sublimation. PNB is an air-sensitive yellow solid that is thermally stable at room temperature. It exhibits low solubility in pentane and high solubility in toluene. It was characterized by standard spectroscopic and analytical techniques (see Experimental Section for details). Attempts to grow crystals of PNB from various solvents for X-ray diffraction studies were unsuccessful.

Scheme 1



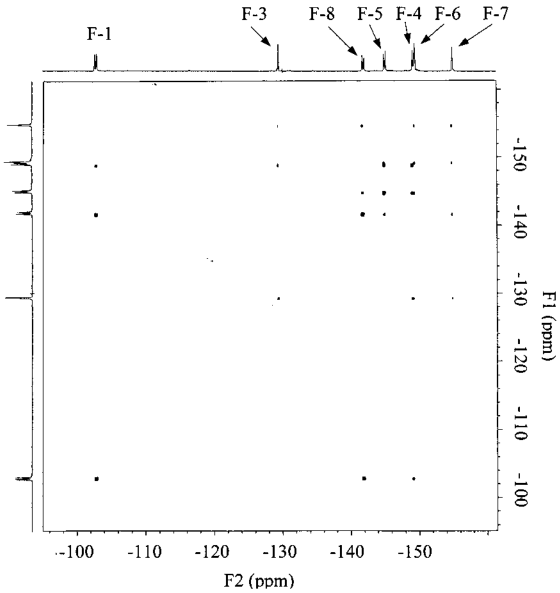
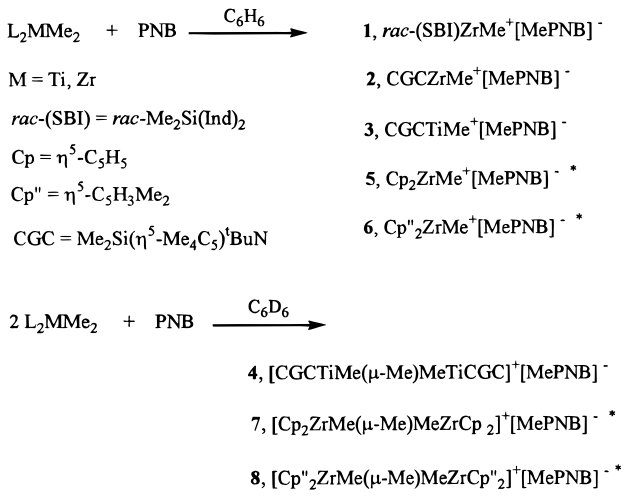


Figure 2. ^{19}F COSY NMR spectrum of PNB in toluene-d_8.

Figure 2 shows the 2D NMR ($^{19}F-^{19}F$) COSY spectrum of PNB. There is a characteristically large coupling between *peri*-fluorines in PNB ($^4J_{F8-F1} = 73$ Hz, $^4J_{F5-F4} = 17$ Hz) as in other polyfluoronaphthalenes.[14] A strong coupling between *para*-fluorines ($^5J_{F8-F5} = 17$ Hz) is also observed in the spectrum. However, the coupling between *meta*-fluorines is too small to resolve. There is also characteristic weak coupling between F_7 and F_3.

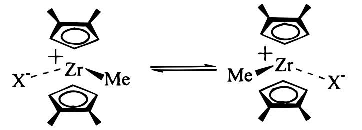
B. Metallocene Cations Generated from PNB. Metallocene cations are rapidly generated by reaction of PNB with metallocene dimethyls in aromatic hydrocarbon solvents (Scheme 2). The reaction of PNB with bis-Cp types of dimethyl zirconocenes forms either monomeric cationic species (with a 1:1 reactant ratio) having the generalized formula $L_2ZrMe^+MePNB^-$ (L = Cp, **5**; Cp″, **6**) or dimeric cationic species (with a 1:2

Scheme 2



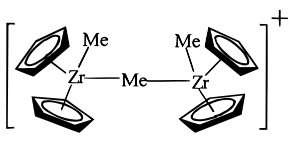
* Small quantities (< 20%) of μ-F bridged cationic complexes form as byproducts: $[Cp_2ZrMe(\mu\text{-}F)MeZrCp_2]^+[MePNB]^-$ (**9**), $[Cp''_2ZrMe(\mu\text{-}F)MeZrCp''_2]^+[MePNB]^-$ (**10**),

reactant ratio) such as $[L_2ZrMe(\mu\text{-}Me)MeZrL_2]^+MePNB^-$ (L = Cp, **7**; Cp″, **8**). These cation–anion complexes were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. The ^1H and ^{13}C NMR spectra of the cationic portions of **5** or **6** are very similar to those of the $B(C_6F_5)_3$-derived complexes,[3c] while the ^1H and ^{13}C NMR spectra of the cationic portions of **7** or **8** are very similar to those of the PBB-derived analogues (that of **8** has been characterized by diffraction[4]). Due to the thermal instability, dynamic NMR studies of ion pair reorganization/symmetrization[3a,c,4,18] (e.g., eq 1) could not be carried out for **2**, **3**, and **6**. Presumably as a consequence of local



(1)

PNB ring current effects, the Me resonance of the $MePNB^-$ anion in the ^1H NMR is generally downfield of that in $MeB(C_6F_5)_3^-$ and $MePBB^-$. The μ-methyl dimeric species react further with PNB to form the corresponding monomeric species. The μ-F bridged dimeric cationic species $[L_2ZrMe(\mu\text{-}F)MeZrL_2]^+MePNB^-$ (L = Cp, **9**; Cp″, **10**) are also detected in these reactions and could not be separated from the desired products.



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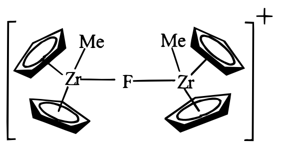
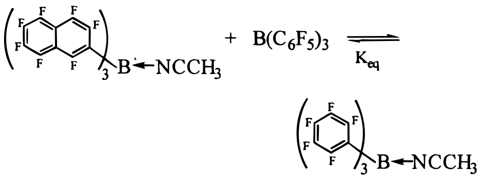


9

A similar μ-F-bridged species, $[Cp''_2ZrMe(\mu\text{-}F)MeZrCp''_2]^+$-$MeB(C_6F_5)_3^-$,[3c] reported to be the thermolysis product of $Cp''_2ZrMe^+MeB(C_6F_5)_3^-$, has been characterized by X-ray diffraction.[3c] There is a distinctive μ-F signal in the ^{19}F NMR spectra of **9** and **10**, while the ^1H NMR spectra show coupling between the μ-F and Zr–Me groups in these complexes. In the case of $CGCTiMe_2$, $CGCZrMe_2$, and *rac*-$SBIZrMe_2$, reactions with PNB lead to clean formation of cationic species, presumably because the relatively open ancillary ligation promotes stronger $MePNB^-$ coordination to the cation, which may stabilize the cation–anion pair. All of these cationic species are somewhat thermally unstable at room temperature and decompose rapidly at higher temperatures. When there is free L_2ZrMe_2 (L = Cp, Cp″) available in solution, $MePNB^-$ and L_2ZrMe_2 compete for the electrophilic L_2ZrMe^+ cations. The formation of dimeric species **7** and **8** argues that $MePNB^-$ is less coordinating than the neutral Cp_2ZrMe_2 and Cp''_2ZrMe_2 dimethyl complexes. As suggested by the upfield ^{19}F NMR spectral shifts versus free PNB, the negative charge of $MePNB^-$ is delocalized over both rings of the perfluoronaphthyl moiety, which is certainly a favorable property to render the $MePNB^-$ anion less coordinating. The ^{19}F NMR data for the $MePNB^-$ anion in both dimeric complexes **7** and **9** or **8** and **10** are identical, which supports the very loose contact between the cation and the anion. In comparing $MePNB^-$ to PNB, position F-6, which is pseudo-*para* relative to the B position, is displaced most upfield in ^{19}F NMR relative to the other fluorine nuclei in $MePNB^-$ (e.g., 7.52 ppm upfield in **6** and 11.36 ppm upfield in **8** versus δ F-6 in neutral PNB). It has been reported in several cases that the "pseudo-*para*" site 6 is the most reactive site in heptafluoro-2-naphthyllithium,[14] 2-methoxyheptafluoronaphthalene,[16] and 2-methylthioheptafluoronaphthalene.[15] This may be a reason PNB-derived cationic metallocene species are less stable than the $B(C_6F_5)_3$-derived and PBB-derived analogues. Thermal decomposition of the monomeric cationic species (**5** or **6**) or dimeric cationic species (**7** or **8**) at room temperature slowly forms the corresponding μ-F bridged dimeric cationic species (**9** or **10**) and other unidentified complexes. Attempts to grow crystals of PNB-derived cationic species have to date been unsuccessful. Solutions of these cationic complexes form oils upon slow cooling or slow diffusion in of a nonsolvent.

C. Quantitative Comparison of PNB and $B(C_6F_5)_3$ Lewis Acidities. Both PNB and $B(C_6F_5)_3$ react with $NCCH_3$ to cleanly afford adducts. The coordination of $NCCH_3$ with PNB or $B(C_6F_5)_3$ is so strong that $NCCH_3$ cannot be removed under high vacuum (10^{-5} Torr). The addition of $B(C_6F_5)_3$ to a solution of $PNBNCCH_3$ in toluene-d_8 yields the equilibrium illustrated in eq 2. No free actonitrile is detected in the solution. At these



(2)

concentrations, the exchange rate of actonitrile between boranes is approximately on the order of the NMR time scale, as indicated by the broadening of NMR peaks as the solution temperature is increased from 19.5 to 55 °C. The process depicted in eq 1 reaches equilibrium within 10 min at 19.5 °C. The ^1H NMR spectra of the

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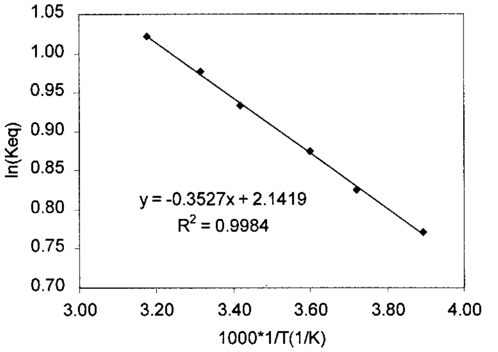

Figure 3. Least-squares van't Hoff plot for the equilibrium PNB($NCCH_3$) + B(C_6F_5)$_3$ $\rightleftharpoons$ (C_6F_5)$_3$B($NCCH_3$) + PNB in toluene-d_8.

mixture shows that the methyl resonance of $NCCH_3$ coordinated to PNB is displaced downfield of that in (C_6F_5)$_3$B$NCCH_3$, the difference in chemical shift being 0.173 ppm. Assuming similar diamagnetic shielding anisotropies, this argues that the Lewis acidity of PNB is higher than that of B(C_6F_5)$_3$.[17] The equilibrium constant K_{eq} was measured over a temperature range of 58 °C in toluene-d_8. $\Delta H°$ and $\Delta S°$ were then calculated from a plot of ln(K_{eq}) versus 1/T (Figure 3), which yields $\Delta H° = +0.7(2)$ kcal/mol and $\Delta S° = +4.3(5)$ eu. The experiment starting with (C_6F_5)$_3$B$NCCH_3$ and PNB affords similar results. The positive reaction enthalpy $\Delta H°$ indicates the coordination of $NCCH_3$ with PNB is stronger than that with B(C_6F_5)$_3$; that is, PNB is a slightly stronger Lewis acid than B(C_6F_5)$_3$. The reaction entropy $\Delta S°$ favors the formation of (C_6F_5)$_3$B$NCCH_3$, possibly reflecting some release of steric crowding effects (constrained degrees of freedom). In identical experiments with more sterically encumbered PBB, no PBB$NCCH_3$ is detected in C_6D_6 over periods as long as 2 days when a PBB and (C_6F_5)$_3$B$NCCH_3$ mixture is stored at 60 °C.

The addition of 1 equiv of PNB to a C_6D_6 solution of [$Cp''_2ZrMe(\mu\text{-}Me)MeZrCp''_2$]$^+$ $MeB(C_6F_5)_3^-$ (**8**) or the addition of an equimolar mixture of PNB and B(C_6F_5)$_3$ to a C_6D_6 solution of Cp''_2ZrMe_2 yields the equilibrium indicated in eq 3, where $K = 0.47$ at 21 °C. The greater

$$Cp''_2ZrMe^+MeB(C_6F_5)_3^- + PNB \underset{K\,=\,0.47}{\rightleftharpoons} Cp''_2ZrMe^+MePNB^- + B(C_6F_5)_3 \quad (3)$$

Lewis acidity and steric bulk of PNB, combined with the greater delocalization of negative charge in $MePNB^-$, renders the coordination between Cp''_2ZrMe^+ and $MePNB^-$ weaker than that between Cp''_2ZrMe^+ and $MeB(C_6F_5)_3^-$. On the other hand, weaker coordination between Cp''_2ZrMe^+ and $MePNB^-$ may also destabilize the cation−anion ion pair with respect to intramolecular C−F or C−H scission.[3a,c,18]

Vibrational spectra have been studied for various Lewis acid-acetonitrile adducts including $MX_5{\cdot}NCCH_3$ (M = As, X = F;[19d] M = Sb, X = Cl,[19d] F[19c]) and $BX_3{\cdot}NCCH_3$ (X = F,[19a] Cl,[19b] Br[19b]). Compared to the free acetonitrile, the most dramatic change in the IR bands is an increase in the ν(CN) frequency. The ν(CN) frequency of free acetonitrile is 2253.3 cm^{-1}, while the reported ν(CN) frequencies of $BX_3{\cdot}NCCH_3$ (X = F, Cl, and Br) are 2376.2, 2369.0, and 2362.0 cm^{-1}, respectively. The measured ν(CN) frequencies of (C_6F_5)$_3$B$NCCH_3$ and PNB$NCCH_3$ in toluene solution are 2366.5 and 2365.3 cm^{-1}, respectively, which suggests that both boranes are very strong Lewis acids and have similar Lewis acidity. Since ν(CN) frequencies have been shown to depend on both electronic and kinematic effects,[19c] these data do not allow rigorous differentiation of the relative PNB and B(C_6F_5)$_3$ acidities.

D. Olefin Polymerization Catalysis. Olefin polymerization experiments were carried out with rigorous exclusion of air and moisture and in a way such as to minimize mass-transfer effects.[3a,c] The results (Table 1) show that both monomeric and dimeric cationic species generated with PNB are highly active catalysts. Cationic complexes **5**, **6**, **7**, and **8** are approximately as active as the B(C_6F_5)$_3$ analogues for ethylene polymerization (entries 5−10).[4] Comparing monomeric cationic species (**5** and **6**) to dimeric cationic species (**7** and **8**), the polyethylenes produced have similar molecular weights and polydispersities. These results may indicate that $MePNB^-$ is only slightly less coordinating toward the cation than the neutral Cp_2ZrMe_2 or Cp''_2ZrMe_2 complexes. In the case of "constrained geometry" catalysts (CGC), complex **3** is ~3× more active than the B(C_6F_5)$_3$ analogue for ethylene polymerization and yields high molecular weight polyethylene with a narrower polydispersity (entries 3, 4). The study of ethylene and 1-hexene copolymerization with catalyst **3** shows that the activity is substantially higher than that of the $CGCTiMe^+MeB(C_6F_5)_3^-$ catalyst (entries 15, 16).[4] In the isospecific polymerization of propylene, catalyst **1** exhibits slightly higher activity than the B(C_6F_5)$_3$-derived analogue (entries 11−14). However, compared to the polymers produced by the analogous B(C_6F_5)$_3$-derived catalysts at various temperatures, the polymer produced by **1** at 23 °C has a similar melting temperature and isotacticity index, while the polymer produced at 60 °C by catalyst **1** exhibits a higher melting temperature and higher molecular weight.[4]

Several large-scale batch polymerizations were carried out in a 2 L Parr reactor. In the copolymerization of ethylene and 1-octene, the activity of catalyst **3** is approximately 60% greater than that of the B(C_6F_5)$_3$-derived $CGCTiMe^+MeB(C_6F_5)_3^-$ catalyst (Table 1, entries 17, 18).

Conclusions

The new organo-Lewis acid, tris(β-perfluoronaphthyl)borane (B($C_{10}F_7$)$_3$, PNB) has been synthesized and characterized. It is a potent cocatalyst which activates a variety of dimethyl group 4 complexes efficiently and rapidly to form highly active cationic olefin polymeri-

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Table 1. Olefin Polymerization Data for Metallocenes Activated by PNB[a]

entry	catalyst	monomer[b]	temp (°C)	cat. (μmol)	cond[c] (mL, min)	polymer yield (g)	activity[d] $\times 10^5$	M_w[e] $\times 10^3$	M_w/M_n	remarks
1	$CGCZrMe^+MePNB^-$ (**2**)	E	23	15	100, 70	0.065	0.037(6)	1480	2.47	
2[h]	$CGCZrMe^+MeB(C_6F_5)_3^-$	E	25	15	100, 20	0				
3	$CGCTiMe^+MePNB^-$ (**3**)	E	23	15	100, 10	0.72	2.9(2)	1330	3.20	
4[h]	$CGCTiMe^+MeB(C_6F_5)_3^-$	E	25	15	100, 10	0.21	0.84	1058	9.54	
5	$Cp_2ZrMe^+MePNB^-$ (**5**)	E	23	15	100, 1.0	0.92	37(5)	97	1.67	
6[h]	$Cp_2ZrMe^+MeB(C_6F_5)_3^-$	E	25	15	100, 1.0	1.00	40.0	124	2.03	
7	$Cp''_2ZrMe^+MePNB^-$ (**6**)	E	23	15	100, 0.5	1.01	81(15)	87	1.88	
8[h]	$Cp''_2ZrMe^+MeB(C_6F_5)_3^-$	E	25	15	100, 1.0	1.50	60.0	321	1.42	
9	$(Cp_2ZrMe)_2(\mu\text{-}Me)^+MePNB^-$ (**7**)	E	23	15	100, 1.0	0.75	34(5)	96	1.54	
10	$(Cp''_2ZrMe)_2(\mu\text{-}Me)^+MePNB^-$ (**8**)	E	23	15	100, 0.5	0.95	76(5)	76	1.61	
11	*rac*-$Me_2Si(Ind)_2ZrMe^+MePNB^-$ (**1**)	P	24	10	50, 2.5	0.88	21(2)	42	2.23	$T_m = 146$ °C % $mmmm = 93$
12[h]	*rac*-$Me_2Si(Ind)_2ZrMe^+MeB(C_6F_5)_3^-$	P	24	10	50, 2.5	0.73	18	33	2.40	$T_m = 146$ °C % $mmmm = 93$
13	*rac*-$Me_2Si(Ind)_2ZrMe^+MePNB^-$ (**1**)	P	60	10	50, 1.5	0.70	32(4)	5.0	1.64	$T_m = 128$ °C % $mmmm = 86$
14[h]	*rac*-$Me_2Si(Ind)_2ZrMe^+MeB(C_6F_5)_3^-$	P	60	10	50, 1.75	0.63	22	2.7	1.39	$T_m = 122$ °C % $mmmm = 86$
15	$CGCTiMe^+MePNB^-$ (**3**)	E/H	23	15	25, 10	2.04	8.1(6)	76	2.20	67% H[f]
16[h]	$CGCTiMe^+MeB(C_6F_5)_3^-$	E/H	25	25	25, 10	0.05	0.12			63.2% H[f]
17	$CGCTiMe^+MeB(C_6F_5)_3^-$	E/O[g]	140	1.0	*g*	28.8	34(1)			
18	$CGCTiMe^+MePNB^-$ (**3**)	E/O[g]	140	1.0	*g*	46.1	54(4)			

[a] All polymerizations carried out on a high-vacuum line (10^{-5} Torr); uncertainties in activities are the average of 3 runs; reproducibility between runs ≈10-15%. [b] Ethylene (E) and propylene (P) 1 atm pressure; 44.0 mmol of 1-hexene (H). [c] Conditions given as milliliters of toluene, reaction time in minutes. [d] Gram of polymer/[(mole of cationic metallocene)·atm·h]. [e] GPC relative to polystyrene standards. [f] 1-Hexene incorporation in E/H copolymer. [g] Ethylene (E), 500 psig; 740 g of Isopar E solvent, and 118 g of 1-octene (O), polymerization time 15 min. [h] Data from ref 4.

zation catalysts. PNB is a stronger Lewis acid than $B(C_6F_5)_3$. Furthermore, the $MePNB^-$ anion exhibits less coordinative tendency than $MeB(C_6F_5)_3^-$ with respect to metallocenium cations. The PNB-generated catalysts have similar or higher olefin polymerization activities than the $B(C_6F_5)_3$-derived analogues.

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