

Bis(pentafluorophenyl)(2-perfluorobiphenyl)borane. A New Perfluoroarylborane Cocatalyst for Single-Site Olefin Polymerization

Liting Li, Charlotte L. Stern, and Tobin J. Marks*

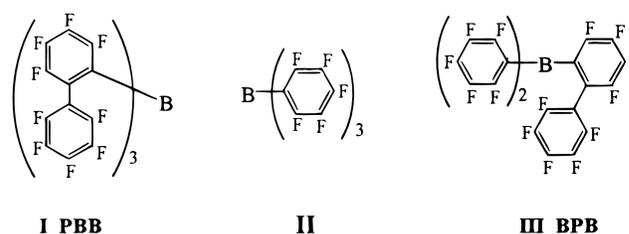
Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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Bis(pentafluorophenyl)(2-perfluorobiphenyl)borane, $(C_6F_5)_2B(C_{12}F_9)$ (BPB), has been synthesized and characterized to serve as a new strong organo-Lewis acid cocatalyst for single-site olefin polymerization. BPB efficiently activates a variety of group 4 dimethyl complexes to form highly active homogeneous Ziegler–Natta olefin polymerization catalysts. Reaction of BPB with Cp_2ZrMe_2 , *rac*- $Me_2Si(Ind)_2ZrMe_2$, and $(CGC)MMe_2$ ($M = Zr, Ti$; $CGC = Me_2Si(\eta^5-Me_4C_5)(tBuN)$) (1:1 molar ratio) rapidly and cleanly produces the base-free cationic complexes $Cp_2ZrMe^+[MeB(C_{12}F_9)(C_6F_5)_2]^-$ (**1**), *rac*- $Me_2Si(Ind)_2ZrMe^+[MeB(C_{12}F_9)(C_6F_5)_2]^-$ (**2**), and $(CGC)MMe^+[MeB(C_{12}F_9)(C_6F_5)_2]^-$ ($M = Zr$, **3**; $M = Ti$, **4**), respectively. These complexes have been characterized by NMR and elemental analysis and are shown to be competent for ethylene and propylene polymerization. In general, BPB-derived catalysts exhibit polymerization activities comparable to or higher than those of the $B(C_6F_5)_3$ -derived analogues, with the products exhibiting higher molecular weights but comparable polydispersities, polypropylene isotacticities, and, for ethylene + 1-hexene, comonomer incorporation.

Introduction

Homogeneous single-site metallocene olefin polymerization catalysts have had a profound impact on contemporary polyolefin science and technology.¹ These catalysts exhibit extremely high intrinsic activities based on transition-metal content, facile control over polymer molecular weight and molecular weight distribution, uniform comonomer incorporation, and precise control of polymer stereoregularity. Cocatalysts are generally used to activate the single-site catalysts by forming ion pairs which are the active agents for olefin polymerization. Organo-Lewis acid cocatalysts such as perfluoroarylboranes are therefore of great current interest for both technological and fundamental scientific reasons.^{1a,2} They undergo reaction with metallocene dimethyls in 1:1 catalyst to cocatalyst ratios to form highly active, structurally characterizable catalytic species. Recently, the sterically encumbered perfluoroarylborane tris(2,2',2''-perfluorobiphenyl)borane (PBB; **I**),^{2c} was reported from our laboratory. PBB generates cationic species with generally higher catalytic activities for olefin polymerization and copolymerization than does $B(C_6F_5)_3$ (**II**). However, in the case of group 4 metallocene dimethyls, PBB preferentially affords cationic dinuclear complexes such as $[Cp_2ZrMe(\mu-Me)MeZrCp_2]^+$



at room temperature (reflecting the weaker coordinative tendencies of $MePBB^-$ versus $MeB(C_6F_5)_3^-$), even with excess PBB and long reaction times.^{2c} Monomeric species can only be generated in situ at higher temperatures. The activation of metallocene dimethyls with PBB is also rather sluggish; for example, 1 h is required to completely activate *rac*- $Me_2Si(Ind)_2ZrMe_2$ in millimolar toluene solution at 25 °C.^{2c} For these reasons, it would be of great interest to investigate the properties of modified perfluoroarylboranes with mixed 2-perfluorobiphenyl ($C_{12}F_9$) and pentafluorophenyl (C_6F_5) substituents which may be sterically and electronically intermediate in properties between PBB and $B(C_6F_5)_3$. We report here the synthesis, molecular structure, reactiv-

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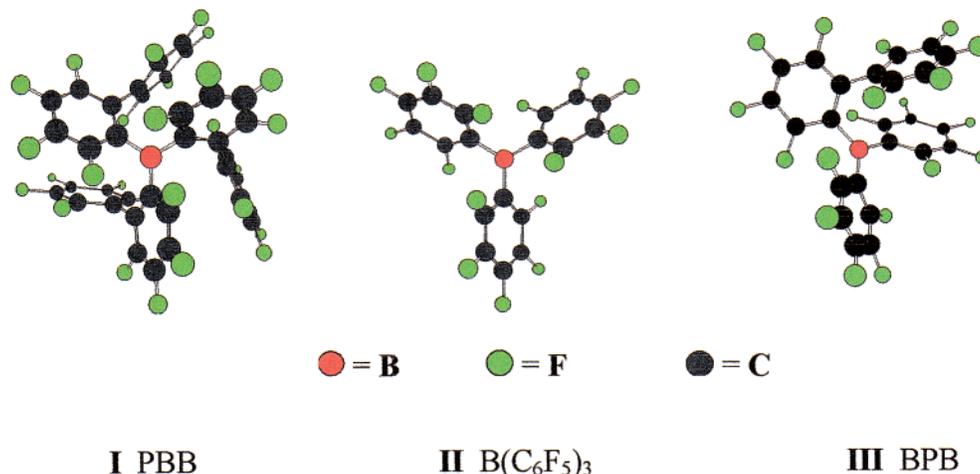


Figure 1. Comparison of the molecular structures of PBB^{2d} and $\text{B}(\text{C}_6\text{F}_5)_3^{2d}$ computed with the AM1 model Hamiltonian and BPB determined by X-ray diffraction in this study.

ity, and polymerization catalytic characteristics of the new strong organo-Lewis acid bis(pentafluorophenyl)-(2-perfluorobiphenyl)borane (BPB, **III**) and demonstrate that it is an excellent cocatalyst for metallocene-mediated ethylene polymerization. The differences in molecular architectures of PBB, $\text{B}(\text{C}_6\text{F}_5)_3$, and BPB can be appreciated from the computed geometries of PBB and $\text{B}(\text{C}_6\text{F}_5)_3^{2d}$ and the molecular structure of BPB from X-ray diffraction shown in Figure 1 and discussed herein.

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 of 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 Teflon-valved bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥ 99 atom %D), were freeze-pump-thaw degassed and dried over Na/K alloy, and were 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. The reagents $\text{Me}_3\text{-SnCl}$, Me_2SnCl_2 , BCl_3 (1.0 M in hexane), and *n*-BuLi (1.6 M in hexanes) were purchased from Aldrich and used as received. $\text{B}(\text{C}_6\text{F}_5)_3$,³ $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})\text{TiMe}_2$ ((CGC)TiMe₂),⁴ (CGC)-ZrMe₂,⁴ *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$,⁵ Cp_2ZrMe_2 ,⁶ $(\text{C}_6\text{F}_5)_2\text{BCl}$,⁷ and

2-perfluorobiphenyl bromide⁸ were prepared according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on 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), and 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 Midwest Microlab, Indianapolis, IN. ^{13}C NMR assays of polypropylene microstructure were conducted in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C . Signals were assigned according to the literature for polypropylene⁹ and ethylene/1-hexene copolymers,¹⁰ respectively. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of $10^\circ\text{C}/\text{min}$.

Synthesis of Bis(pentafluorophenyl)(2-perfluorobiphenyl)borane, $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (BPB; **III).** In a 100 mL flask, 2-perfluorobiphenyl bromide (3.16 g, 8.0 mmol) was dissolved in 20 mL of dry pentane. In another 250 mL flask, 30 mL of pentane and 5.1 mL of *n*-butyllithium (1.6 M in hexanes, 9.0 mmol) was added and the solution was cooled to -50°C . The solution of 2-perfluorobiphenyl bromide was then added dropwise via syringe. A white precipitate formed immediately. The solution was stirred between -40 and -30°C for 90 min after the addition was complete, and then 20 mL of $(\text{C}_6\text{F}_5)_2\text{BCl}$ (3.16 g, 8.0 mmol in pentane) was added at -50°C . The solution was warmed slowly to room temperature overnight. After filtration and removal of all volatiles, a sticky

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oil remained. It was washed with cold pentane ($-78\text{ }^{\circ}\text{C}$) three times to afford a colorless solid product. Yield: 2.0 g (37%). The complex can be further purified by sublimation at $110\text{ }^{\circ}\text{C}$ (0.05 Torr) for 3 h. Spectroscopic and analytical data for BPB (**III**) are as follows. ^{19}F NMR (benzene- d_6 , 282.33 MHz, 23 $^{\circ}\text{C}$): δ -127.48 (d, $^3J_{\text{F-F}} = 21.5$ Hz, 4 F, *o*-F), -128.28 (m, 1 F, 3-F), -135.10 (m, 1 F, 6-F), -139.89 (d, $^3J_{\text{F-F}} = 21.5$ Hz, 2 F, 2', 6'-F), -140.90 (tt, $^3J_{\text{F-F}} = 20.8$ Hz, 2 F, *p*-F), -144.94 (td, $^3J_{\text{F-F}} = 21.0$ Hz, $^5J_{\text{F-F}} = 7.6$ Hz, 1 F, 5-F), -150.07 (t, $^3J_{\text{F-F}} = 21.2$ Hz, 1 F, 4'-F), -151.48 (td, $^3J_{\text{F-F}} = 22.2$ Hz, $^5J_{\text{F-F}} = 6.8$ Hz, 1 F, 4-F), -160.25 (m, 4 F, *m*-F), -160.98 (m, 2 F, 3', 5'-F). Anal. Calcd for $\text{C}_{24}\text{BF}_{19}$: C, 43.67; H, 0.00; N, 0.00. Found: C, 43.65, H, 0.10, N, 0.00.

Synthesis of $\text{Cp}_2\text{ZrMe}^+[\text{MeB}(\text{C}_{12}\text{F}_9)(\text{C}_6\text{F}_5)_2]^-$ (1**).** Cp_2ZrMe_2 (50 mg, 0.21 mmol) and $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (146 mg, 0.22 mmol) were loaded into a 25 mL reaction flask in the glovebox. On the high-vacuum line, C_6H_6 (15 mL) was condensed in at $-78\text{ }^{\circ}\text{C}$. 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 the yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 110 mg (61%). The spectroscopic data for **1** are as follows. ^1H NMR (benzene- d_6 , 299.91 MHz, 23 $^{\circ}\text{C}$): δ 5.47 (s, 10 H, C_5H_5), 0.32 (s, 3 H, ZrCH_3), 0.24 (br, 3 H, BClH_3). ^{13}C NMR (benzene- d_6 , 74.42 MHz, 23 $^{\circ}\text{C}$): δ 114.04 (C_5H_5), 40.92 (ZrCH_3), 26.79 (br, BClH_3). ^{19}F NMR (benzene- d_6 , 282.33 MHz, 23 $^{\circ}\text{C}$): δ -128.75 (s, 1 F, 3-F), -132 (very broad, 4 F, *o*-F), -136.80 (s, 1 F, 6-F), -138.94 (s, 2 F, 2', 6'-F), -153.48 (t, $^3J_{\text{F-F}} = 21.1$ Hz, 1 F, 4'-F), -156.46 (t, $^3J_{\text{F-F}} = 22.2$ Hz, 1 F, 4-F), -158.41 (multi, 3 F, *p*-F, 5-F), -162.91 (s, 2 F, 3', 5'-F), -164.00 (br, 4 F, *m*-F). Anal. Calcd for $\text{C}_{36}\text{H}_{16}\text{BF}_{19}\text{Zr}$: C, 47.44; H, 1.76. Found: C, 47.09, H, 1.67.

Synthesis of $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+[\text{MeB}(\text{C}_{12}\text{F}_9)(\text{C}_6\text{F}_5)_2]^-$ (2**).** $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ (50 mg, 0.13 mmol) and $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (87 mg, 0.13 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 $-78\text{ }^{\circ}\text{C}$. 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 the resulting yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 82 mg (60%). The spectroscopic data for **2** are as follows. ^1H NMR (C_6D_6 , 23 $^{\circ}\text{C}$, 399.941 MHz): δ 7.63 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 1 H, Ind), 7.26 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 1 H, Ind), 7.06 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 1 H, Ind), 6.99 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 1 H, Ind), 6.62–6.72 (m, 2 H, Ind), 6.58 (d, $^3J_{\text{H-H}} = 3.0$ Hz, 1 H, Ind), 6.54 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 1 H, Ind), 6.26 (d, 1 H, $^3J_{\text{H-H}} = 8.1$ Hz, Ind), 6.21 (d, 1 H, $^3J_{\text{H-H}} = 3.0$ Hz, Ind), 5.65 (d, 1 H, $^3J_{\text{H-H}} = 3.3$ Hz, Ind), 4.95 (d, 1 H, $^3J_{\text{H-H}} = 3.3$ Hz, Ind), 0.36 (s, 3 H, Me_2Si), 0.21 (s, 3 H, Me_2Si), -0.32 (s, br, 3 H, *B-CH*), -0.55 (s, 3 H, *Zr-CH*). ^{19}F NMR (benzene- d_6 , 282.33 MHz, 23 $^{\circ}\text{C}$): δ -127.53 (s, 1 F, 3-F), -131 (very broad, 4 F, *o*-F), -137.15 (m, 1 F, 6-F), -137.94 (m, 2 F, 2', 6'-F), -153.74 (t, $^3J_{\text{F-F}} = 21$ Hz, 1 F, 4'-F), -156.65 (t, $^3J_{\text{F-F}} = 22$ Hz, 1 F, 4-F), -158.56 (m, 2 F, *p*-F), -159.26 (t, $^3J_{\text{F-F}} = 21$ Hz, 1 F, 5-F), -162.75 (br, 1 F, 3'/5'-F), -163.33 (br, 1 F, 3'/5'-F), -164.16 (br, 4 F, *m*-F). Anal. Calcd for $\text{C}_{46}\text{H}_{24}\text{BF}_{19}\text{Zr}$: C, 53.14; H, 2.33. Found: C, 52.82, H, 2.37.

Synthesis of $(\text{CGC})\text{ZrMe}^+[\text{MeB}(\text{C}_{12}\text{F}_9)(\text{C}_6\text{F}_5)_2]^-$ (3**).** $(\text{CGC})\text{ZrMe}_2$ (80 mg, 0.22 mmol) and $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (142 mg, 0.22 mmol) were loaded into a 25 mL reaction flask in the glovebox. On the high-vacuum line, C_6H_6 (15 mL) was condensed in at $-78\text{ }^{\circ}\text{C}$. 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 the yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 119 mg (53%). The spectroscopic data for **3** are as follows. ^1H NMR (benzene- d_6 , 299.91 MHz, 23 $^{\circ}\text{C}$): δ 1.73 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.00 (s, 12 H, $\text{CMe}_3 + \text{BClH}_3$), 0.31 (s, 3 H, ZrCH_3), 0.24 (s, 3 H, SiCH_3), 0.17

Table 1. Crystallographic Details for $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (BPB, **III)**

formula	$\text{BC}_{24}\text{F}_{19}$
fw	660.04
cryst dimens	$0.4 \times 0.2 \times 0.1$ mm
cryst color, habit	colorless, columnar
cryst syst	orthorhombic
<i>a</i> , Å	9.663(6)
<i>b</i> , Å	19.673(2)
<i>c</i> , Å	11.826(5)
<i>V</i> , Å ³	2248(1)
space group	$Pna2_1$ (No. 33)
<i>Z</i> value	4
D_{calcd} , g/cm ³	1.950
diffractometer	Enraf-Nonius CAD4
temp, $^{\circ}\text{C}$	-120
transmission factors, range	0.8323–1.000
radiation	Mo K α ($\lambda = 0.710$ 69 Å)
scan type	ω - θ
2θ range, deg	2–48.9
intensities (unique, R_i)	2161, 0.021
intensities > 3.00 $\sigma(I)$	1149
<i>R</i>	0.064
R_w , for $w = 1/\sigma^2(F_o)$	0.047

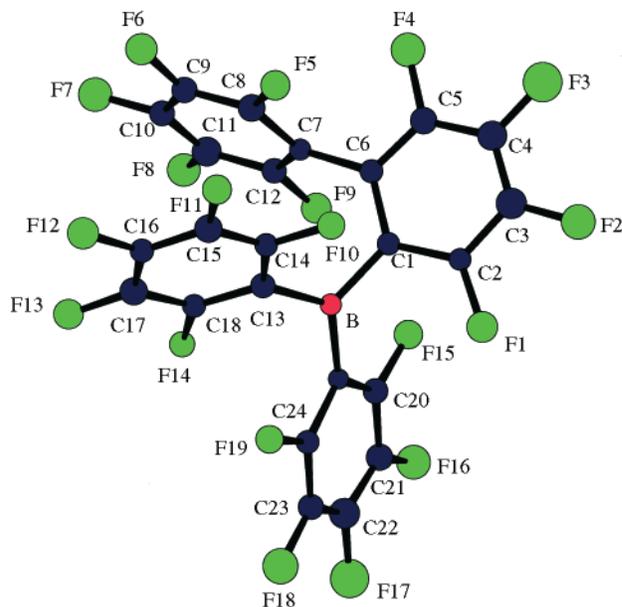
(s, 3 H, SiCH_3). ^{13}C NMR (benzene- d_6 , 74.42 MHz, 23 $^{\circ}\text{C}$): δ 57.74 (ZrCH_3), 44.27 (CMe_3), 33.05 (CMe_3), 15.04 (CH_3), 12.74 (CH_3), 11.37 (CH_3), 10.37 (CH_3), 5.54 (SiCH_3), 5.12 (SiCH_3). The *B-CH*₃ resonance was too broad to be detected with certainty. ^{19}F NMR (benzene- d_6 , 282.33 MHz, 23 $^{\circ}\text{C}$): δ -129.31 (s, 1 F, 3-F), -131.67 (br, 4 F, *o*-F), -136.49 (s, 1 F, 6-F), -138.38 (s, 2 F, 2', 6'-F), -153.48 (t, $^3J_{\text{F-F}} = 21.3$ Hz, 1 F, 4'-F), -156.02 (t, $^3J_{\text{F-F}} = 21.5$ Hz, 1 F, 4-F), -158.42 (s, 3 F, *p*-F, 5-F), -162.99 (s, 2 F, 3', 5'-F), -163.89 (br, 4 F, *m*-F). Anal. Calcd for $\text{C}_{41}\text{H}_{33}\text{BF}_{19}\text{NSiZr}$: C, 47.77; H, 3.22. Found: C, 47.10, H, 3.01.

Synthesis of $\text{CGCTiMe}^+[\text{MeB}(\text{C}_{12}\text{F}_9)(\text{C}_6\text{F}_5)_2]^-$ (4**).** $(\text{CGC})\text{TiMe}_2$ (70 mg, 0.21 mmol) and $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (141 mg, 0.21 mmol) were loaded into a 25 mL reaction flask in the glovebox. On the high-vacuum line, C_6H_6 (15 mL) was condensed in at $-78\text{ }^{\circ}\text{C}$. 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 the yellow solid was dried under vacuum (10^{-5} Torr) for 4 h at room temperature. Yield: 101 mg (48%). The spectroscopic data for **4** are as follows. ^1H NMR (benzene- d_6 , 299.91 MHz, 23 $^{\circ}\text{C}$): δ 1.71 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 0.99 (s, 9 H, CMe_3), 0.95 (s, 3 H, TiCH_3), 0.66 (br, 3 H, BClH_3), 0.29 (s, 3 H, SiCH_3), 0.16 (s, 3 H, SiCH_3). ^{19}F NMR (benzene- d_6 , 282.33 MHz, 23 $^{\circ}\text{C}$): δ -126.96 (s, 1 F, 3-F), -131.04 (br, 4 F, *o*-F), -136.85 (m, 1 F, 6-F), -138.10 (s, 2 F, 2', 6'-F), -153.60 (t, $^3J_{\text{F-F}} = 21$ Hz, 1 F, 4'-F), -156.26 (t, $^3J_{\text{F-F}} = 22$ Hz, 1 F, 4-F), -158.44 to -158.75 (m, 2 F, *p*-F), -158.84 (t, $^3J_{\text{F-F}} = 22$ Hz, 1 F, 5-F), -162.90 (s, 1 F, 3'/5'-F), -163.34 (s, 1 F, 3'/5'-F), -164.12 (br, 4 F, *m*-F). Anal. Calcd for $\text{C}_{41}\text{H}_{33}\text{BF}_{19}\text{NSiTl}$: C, 49.87; H, 3.37. Found: C, 49.89, H, 3.43.

X-ray Crystallographic Study of $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_{12}\text{F}_9)$ (BPB; **III).** Crystals for diffraction analysis were grown by slow cooling of a pentane solution. A colorless, translucent, columnar crystal of **III** having the approximate dimensions $0.4 \times 0.2 \times 0.1$ mm was mounted using oil (Paratone-N, Exxon) on a glass fiber. The crystal was poorly shaped and had been detached from the side of the glass container. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation. The crystal, data collection, and refinement parameters are collected in Table 1. Corrections for Lorentz and polarization effects and anomalous dispersion effects¹¹ were applied to the data, as was an empirical absorption correction (DIFABS).¹²

The structure was solved by direct methods (SHELXS-86)¹³ and expanded using Fourier techniques.¹⁴ Owing to the paucity of data, the non-hydrogen atoms were refined isotro-

a.



b.

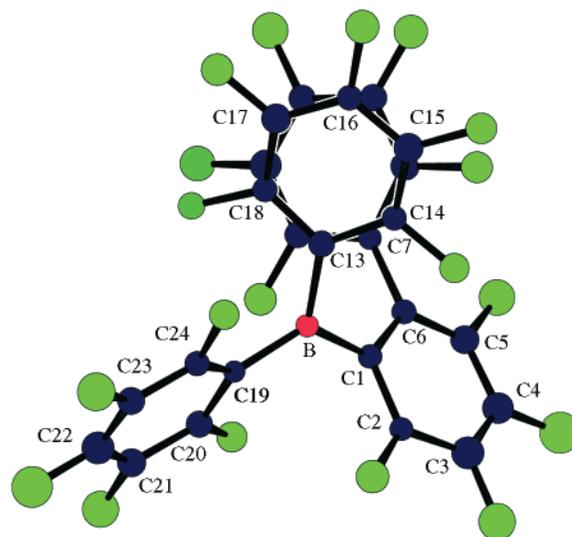


Figure 2. Two views of the molecular structure and atom-numbering scheme for $(C_6F_5)_2B(C_{12}F_9)$ (BPB; **III**).

pically. The enantiomer was refined, giving the same unweighted and weighted agreement factors. Bijvoet reflections were then compared, and this enantiomer was favored slightly. Maximum and minimum peaks on the final difference Fourier map corresponded to 0.45 and $-0.53 \text{ e}^-/\text{\AA}^3$.

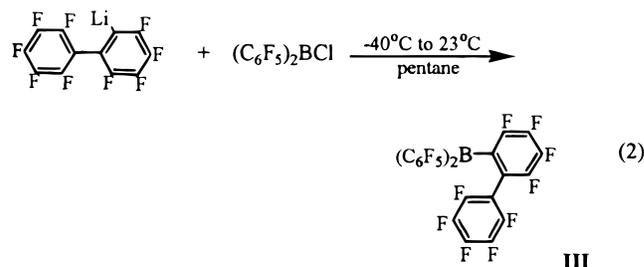
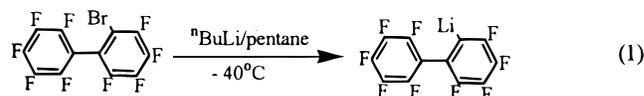
All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

Ethylene and Propylene Polymerization Experiments. On a high-vacuum line (10^{-5} Torr), ethylene and propylene polymerizations were carried out in 250 mL round-bottom three-neck Morton 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 to 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 polymerization 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. Standard deviations in activities reported in Table 3 are the average of three trials.

Results and Discussion

A. Synthesis of BPB, $[(C_6F_5)_2B(C_{12}F_9)]$. The starting materials, $(C_6F_5)_2BCl$ ⁷ and 2-perfluorobiphenyl bromide,⁸ were synthesized using the literature procedure. Low-temperature lithium-halogen exchange using $n\text{BuLi}$ and 2-perfluorobiphenyl bromide produced (2-perfluorobiphenyl)lithium, which was then subjected to reaction with $(C_6F_5)_2BCl$ at low temperature to afford bis(pentafluorophenyl)(2-perfluorobiphenyl)borane ($(C_6F_5)_2B(C_{12}F_9)$; BPB, **III**) (eqs 1 and 2). The product



was purified by washing with pentane at low temperature and vacuum sublimation. BPB is an air-sensitive colorless solid which is thermally stable at room temperature. It was characterized by standard spectroscopic and analytical techniques (see Experimental Section for details). Crystals of BPB were grown from pentane solution for X-ray diffraction studies. Figure 2 shows

(11) (a) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, U.K., 1974; Vol. IV. (b) Creagh, D. C., McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Tables 4.2.6.8 (pp 219–222) and 4.2.4.3 (pp 200–206).

(12) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

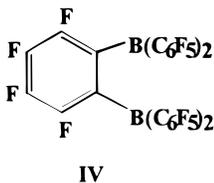
(13) Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189.

(14) Beurskens, P. T.; Admiral, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. M. DIRDIF 94: The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

Table 2. Selected Bond Distances (Å) and Angles (deg) for BPB

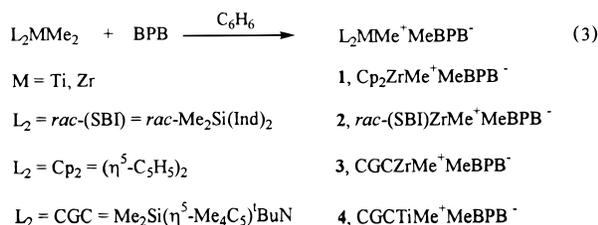
Bond Distances			
B–C19	1.54(2)	B–C1	1.57(2)
B–C13	1.57(2)	C1–C2	1.40(1)
C1–C6	1.40(2)	C6–C7	1.47(2)
C7–C8	1.41(2)	C13–C14	1.40(1)
C14–C15	1.36(2)	C6–C5	1.35(2)
Bond Angles			
C1–B–C19	120(1)	C1–B–C13	116(1)
C13–B–C19	122(1)	B–C1–C6	123(1)
B–C1–C2	119(1)	C1–C6–C7	121(1)
B–C13–C14	123(1)	B–C19–C20	124(1)

two views of the solid-state structure of BPB. Selected bond distances and angles are given in Table 2. The sum of bond angles around the boron atom is 358° , indicating that atoms C1, C19, C13, and B are essentially coplanar. The molecular structure suggests that there is probably a weak π – π interaction between two phenyl rings as shown in Figure 2b. The closest nonbonded intramolecular contact between these two rings is 3.13(2) Å for C7–C13. On the basis of calculated least-squares planes, the dihedral angle between the two phenyl rings is 29.32° . The smaller C13–B–C1 angle (116°) and somewhat larger C19–B–C13 angle (122°) also support the possibility of the weak π stacking interaction. The B–C bond distances in BPB are similar to those recently reported for the *o*-phenylene-bridged diborane 1,2- C_6F_4 -[B(C_6F_5) $_2$] $_2$ (**IV**).^{2b}

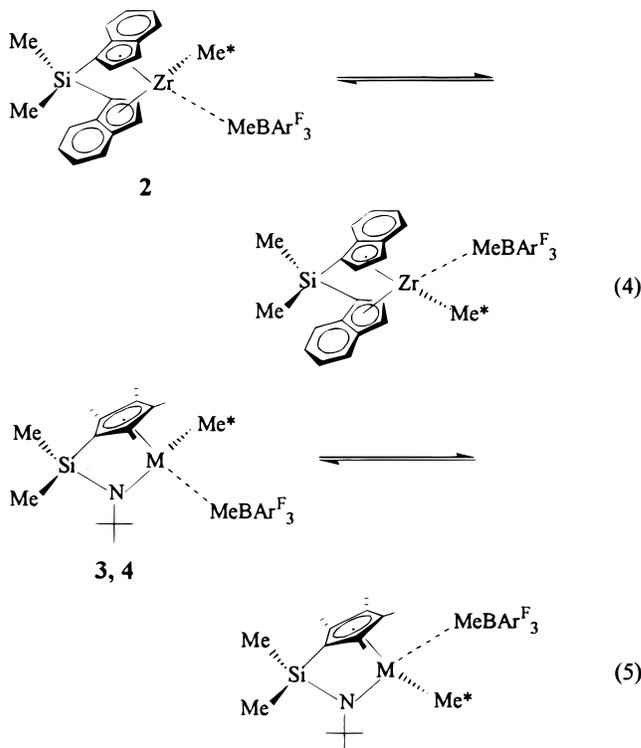


B. Metallocenium Cations Generated from BPB.

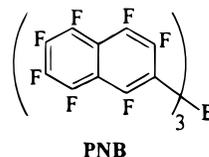
Metallocene cations are rapidly (unlike PBB, **I**) generated by reaction of BPB with metallocene dimethyls in aromatic hydrocarbon solvents (eq 3). The reaction of



BPB with dimethylmetallocenes in benzene cleanly forms monomeric cationic species (using a 1:1 reactant ratio) having the generalized formula $L_2ZrMe^+MeBPB^-$. These cation–anion complexes were isolated and purified by washing with pentane and were characterized by NMR spectroscopy and elemental analysis. The 1H and ^{13}C NMR spectra of the cationic portions of these complexes are very similar to those of the $B(C_6F_5)_3$ -derived complexes,^{2h} with downfield shifted Zr–CH $_3$ resonances and broad, upfield-shifted CH $_3$ –B resonances being particularly distinctive. The diastereotopic ring and MeSi resonances in **2**–**4** indicate that catalyst–cocatalyst ion pairing is relatively “tight” and that symmetrization processes (eqs 4 and 5)^{2a,c,e,h} are slow on the NMR time scale at room temperature.



C. Olefin Polymerization Catalysis. Olefin polymerization experiments were carried out with rigorous exclusion of air and moisture. The results (Table 3) show that cationic species generated with BPB are highly active catalysts. Compared to tris(2-perfluoronaphthyl)borane ($B(C_{10}F_7)_3$; PNB)^{2d} and PBB,^{2c} BPB-derived



catalysts exhibit approximately the same polymerization catalytic characteristics as the PNB-derived analogues^{2d} but exhibit polymerization activities comparable to or lower than those of PBB-derived analogues.^{2c} Cationic complex **1** is approximately as active as the $B(C_6F_5)_3$ analogue for ethylene polymerization (entries 1 and 2). The polyethylenes produced have similar molecular weights and polydispersities. In the case of “constrained geometry” catalysts (CGC), complex **4** is approximately $3\times$ more active than the $B(C_6F_5)_3$ analogue for ethylene polymerization and yields high-molecular-weight polyethylenes with narrower polydispersities. Catalyst **4** is also much more active toward ethylene and 1-hexene copolymerization than the $B(C_6F_5)_3$ analogue and produces a copolymer with comparable levels of comonomer incorporation. In the isospecific polymerization of propylene, catalyst **1** exhibits slightly higher activity than the $B(C_6F_5)_3$ -derived analogue (entries 5–8). Compared to the polymers produced by the analogous $B(C_6F_5)_3$ -derived catalyst at various temperatures, the polymer produced by cocatalyst **III** has higher molecular weight but a similar isotacticity index.

Table 3. Olefin Polymerization Data for Metallocenes Activated by (C₆F₅)₂B(C₁₂F₉) (BPB; III)^a

entry	cat.	mono- mer ^b	temp, °C	amt of cat., μmol	conditions ^c	polym yield, g	activity ^d × 10 ⁵	M _w ^e × 10 ³	M _w / M _n	remarks
1	Cp ₂ ZrMe ⁺ MeBPB ⁻ (1)	E	23	15	100, 1.0	0.85(15)	34(6)	149	1.88	
2	Cp ₂ ZrMe ⁺ MeB(C ₆ F ₅) ₃ ⁻	E	25	15	100, 1.0	1.00 ^g	40 ^g	124	2.03	
3	(CGC)TiMe ⁺ MeBPB ⁻ (4)	E	23	15	100, 10	0.60(8)	2.4(3)	1170	5.90	
4	(CGC)TiMe ⁺ MeB(C ₆ F ₅) ₃ ⁻	E	25	15	100, 10	0.21 ^g	0.84 ^g	1058	9.54	
5	<i>rac</i> -Me ₂ Si(Ind) ₂ ZrMe ⁺ MeBPB ⁻ (2)	P	24	10	50, 2.0	0.67(7)	20(2)	41	2.03	T _m = 146 °C, % <i>mmmm</i> = 93
6	<i>rac</i> -Me ₂ Si(Ind) ₂ ZrMe ⁺ MeB(C ₆ F ₅) ₃ ⁻	P	24	10	50, 2.5	0.73 ^g	18 ^g	33	2.40	T _m = 146 °C, % <i>mmmm</i> = 93
7	<i>rac</i> -Me ₂ Si(Ind) ₂ ZrMe ⁺ MeBPB ⁻ (2)	P	60	10	50, 1.5	0.68(10)	27(4)	3.7	1.51	T _m = 125 °C, % <i>mmmm</i> = 86
8	<i>rac</i> -Me ₂ Si(Ind) ₂ ZrMe ⁺ MeB(C ₆ F ₅) ₃ ⁻	P	60	10	50, 1.75	0.63 ^g	22 ^g	2.7	1.39	T _m = 122 °C, % <i>mmmm</i> = 86
9	(CGC)TiMe ⁺ MeBPB ⁻ (4)	E/H	25	15	25, 10	1.57(15)	6.3(6)	71	2.01	65% H ^f
10	(CGC)TiMe ⁺ MeB(C ₆ F ₅) ₃ ⁻	E/H	25	25	25, 10	0.05 ^g	0.12 ^g			63.2% H ^f

^a All polymerizations carried out on a high-vacuum line (10⁻⁵ Torr); uncertainties in yields and activities are the average of three runs. Standard deviations are given in parentheses. ^b Ethylene (E) and propylene (P) 1 atm pressure; 44.0 mmol of 1-hexene (H). ^c Conditions given as milliliters of toluene, time in minutes. ^d In units of (g of polymer)/(mol of cationic metallocene atm h); quantities in parentheses are estimated standard deviations. ^e GPC relative to polystyrene standards. ^f 1-Hexene incorporation in E/H copolymer. ^g Data from ref 2c (reproducibility between runs 10–15%).

Conclusions

The new organo-Lewis acid bis(pentafluorophenyl)-(2-perfluorobiphenyl)borane ((C₆F₅)₂B(C₁₂F₉); BPB) 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 polymerization catalysts. BPB-derived catalysts are very similar to PNB-derived catalysts in polymerization characteristics and exhibit polymerization activities comparable to or higher than those of B(C₆F₅)₃-derived analogues, with the products exhibiting higher molecular weights but having comparable

polydispersities, polypropylene isotacticities, and, for ethylene + 1-hexene, comonomer incorporation.

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Supporting Information Available: Tables of final positional parameters and isotropic displacement parameters for all atoms and bond lengths and angles in molecule **III**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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