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Synthesis, Structure, and Application of $[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$

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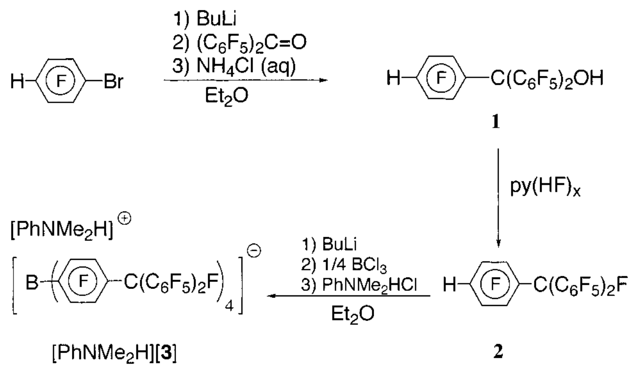
Summary: The new perfluorinated tetraaryl borate $[B\{C_6F_4C(C_6F_5)_2F\}_4]^-$ *(**3**) has been prepared and characterized. The X-ray structural analysis of* $[C_6H_5N(H)(CH_3)_2][$***3***$]$ *confirms the tetrahedral geometry about the boron. The performance of **3** as a weakly coordinating anion in ethylene polymerization was evaluated and compared with that of* $B(C_6F_5)_4^-$ *and* $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$*. The stability of **3** throughout polymerization was evaluated by analyzing anion residues in a polymer sample using mass spectroscopy.*

Introduction

Weakly coordinating anions (WCAs) are used by investigators of the academic and industrial sectors for a wide variety of applications.[1] Of the many WCAs described in the scientific and patent literature, fluorinated tetraaryl borates ($B[Ar_f]_4^-$) are of considerable interest to those working in olefin polymerization. The increasing number of publications in this area is evidence of the growing interest in this type of WCA.[2,3]

Increasing the diversity of WCAs is the first step toward a better understanding of these compounds. More specifically, a large repertoire of structurally and electronically diverse WCAs will provide the information necessary to determine what features need to be manipulated in order to improve polymerization performance.[2] The most common method to prepare fluorinated tetraaryl borates is to react a metalated fluoroaryl (Ar_f−M; M = Li, MgBr, etc.) with a boron trihalide. Therefore, the synthesis of new fluorinated aryls that are easily metalated for subsequent salt metathesis will facilitate the preparation of novel WCAs. The results presented by Marks lend credence to this point of view.[3,4] In this connection, the synthesis of 4-H-$C_6F_4C(C_6F_5)_2F$ is presented along with its use in making $[B\{C_6F_4C(C_6F_5)_2F\}_4]^-$ (**3**) as an *N*,*N*-dimethylanilinium (DMAH) salt. The solid state structure of [DMAH][**3**] is discussed. Additionally, the performance of this new WCA in ethylene polymerization is presented and compared against $B[C_6F_5]_4^-$ and $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$.[5,6]

Scheme 1



Results and Discussion

Synthesis of $[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$. The synthesis of $[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$ (Ph = $-C_6H_5$; Me = $-CH_3$) is depicted in Scheme 1. Decafluorobenzophenone was added to a cold (−78 °C) diethyl ether solution of 4-H-C_6F_4Li.[4] The resulting mixture was quenched with an aqueous solution of NH_4Cl to afford the corresponding alcohol $HC_6F_4C(C_6F_5)_2OH$ (**1**) as a white solid in excellent yield. This procedure is similar to the one used to prepare $(C_6F_5)_3COH$[7] and $HOC(CF_3)_2\text{-}(4\text{-}Si(i\text{-}Pr)_3\text{-}2,6\text{-}C_6H_2(CF_3)_2)$.[8] Replacing the −OH group in **1** with −F was readily accomplished using Olah's reagent[9] and results in $HC_6F_4C(C_6F_5)_2F$ (**2**). After purification via column chromatography, compound **2** was used to prepare [PhNMe$_2$H][**3**] in a one-pot procedure using standard methodology (see Scheme 1 and Experimental Section).[4,5] Compound [PhNMe$_2$H][**3**] was characterized by ^1H, ^{13}C, ^{11}B, and ^{19}F nuclear magnetic resonance (NMR), elemental analysis, and X-ray crystallography.

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(1) (a) Reed, C. A. *Acc. Chem. Res.***1998**, *31*, 133. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (c) Strauss, S. H. *Chemtracts: Inorg. Chem.* **1994**, *6*, 1. (d) Baur, R.; Macholdt, H. DE Patent 4142541. (e) Fisk, T. E.; Tucher, C. J. US Patent 5000873. (f) Waller, F. J.; Barrett, A. G. M.; Braddock, D. C.; Rampasad, D.; McKinnell, R. M.; White, A. J. P.; Williams, D. J.; Ducray, R. *J. Org. Chem.* **1999**, *64*, 2910. (g) Xie. Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403.

(2) An excellent review on the field: Chen, Y.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Bohnen, H.; Achermann, J. W. O. Patent 99/43865. (c) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619. (d) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560. (e) Lanza, G.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764. (f) Zhou, Lancaster, S. J.; Walker, D. A.; Beck, S. Thornton-Pett, M. Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223.

(3) Aluminates are also used in this context: (a) Chen, Y.; Marks, T. J. W. O. Patent 98/07515. (b) Elder, M. J.; Leyder, F. European Patent 0 573 403 A2. (c) Sun, Y.; Metz, M. V.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 1625 (and references therein). (d) Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541.

(4) Chen, Y.-X.; Metz, M. V.; Stern C. L.; Marks *J. Am. Chem. Soc.* **1998**, *120*, 6287.

(5) (a) Turner, H. W. European Patent No. 277,0041998. (b) Hlatky, G. G.; Upton, D. J.; Turner, H. W. U.S. Patent Appl. P 459921, 1990.

(6) (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(7) Filler, R.; Wang, C.-S.; McKinney, M. A.; Miller, F. N. *J. Am. Chem. Soc.* **1967**, *89*, 1026.

(8) Barbarich, T. J.; Runthner, C. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 4280.

(9) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872.

10.1021/om001080i CCC: $20.00

Table 1. Results of Ethylene Polymerization Reactions[a]

run	anion[b]	catalyst (mg)	time (min)	yield (g)	activity (g/mmol min)	M_n[d] (10^{-3})	M_w[d] (10^{-3})	M_w/M_n[d]
1	**3**	33.6	20	9.0	6.6	74	131	1.77
2	**3**	32.0	20	7.4	5.7	51	104	2.06
3	**3**	31.9	30	12.1	6.2	49	94	1.92
4	**3**	31.4	40	17.6	6.9	110	197	1.80
5	$B(Ar_f)_4^-$ [c]	48.2	20	27.6	20	114	228	1.99
6	$B(Ar_f)_4^-$ [c]	45.8	20	34.6	15	109	234	2.14
7	$B(C_6F_5)_4^-$	30.7	30	22.4	12	103	227	2.20
8	$B(C_6F_5)_4^-$	38.7	20	15.8	10	111	247	2.22

[a] Catalyst activations and polymerizations were performed in toluene. [b] Cationic activator for all runs was *N,N'*-dimethylanilinium. [c] $Ar_f = -(3,5\text{-}(CF_3)_2C_6H_3)_4$. [d] Determined by GPC.

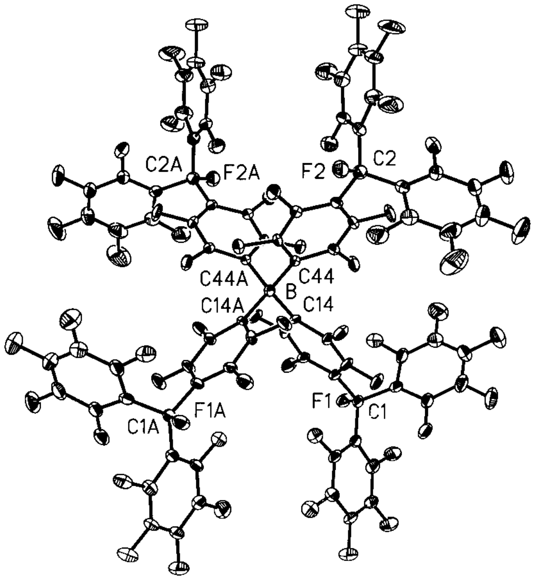

Figure 1. ORTEP diagram of **3**. Thermal ellipsoids are shown at the 50% level.

The one-pot approach used here is noteworthy since it is atypical in this context.[2] The lithium salts of tetraaryl borates are typically isolated prior to the reaction with the desired ammonium chloride (e.g., $PhNMe_2HCl$). However, attempts to isolate the lithium salt of **3** resulted in a dark green material. No characterization of this green material was attempted. When $PhNMe_2HCl$ is added to the lithium salt prepared in situ, the product was isolated using standard workup procedures.

Structure of $[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$. The solid state structure of $[PhNMe_2H][\mathbf{3}]$ was determined by single-crystal X-ray crystallography (Figure 1). Compound $[PhNMe_2H][\mathbf{3}]$ crystallizes in the *Pbcn* space group with boron lying on a special position. The $PhNMe_2H$ cation was disordered over two sites. Despite the cation disorder, the anion refined well enough to discuss connectivity and ligand orientation. The boron atom adopts a tetrahedral geometry. The B−C distances (1.640(10) Å, 1.651(10) Å) and C−B−C angles (102.0°, 114.3°) are similar to those found in $B(C_6F_5)_4^-$ and $B(C_6F_4{-}SiR_3)^-$.[4] The similarities between these metric parameters vis-à-vis those of $B(C_6F_5)_4^-$ and $B(C_6F_4{-}SiR_3)^-$ allow us to conclude that the molecular structures of tetraaryl borates are not affected by large substituents on the para positions. All of the C−F distances and angles are unexceptional.

The ^{19}F NMR spectrum of $[PhNMe_2H][\mathbf{3}]$ in CH_2Cl_2 at room temperature is consistent with a fluxional structure.[10] Within the ^{19}F NMR time scale, rapid rotation about the $BC_6F_5{-}C(F)C_6F_5$ bond is indicated by the equivalent ortho fluorines on the tetrafluorophenyl rings. The corresponding meta fluorines are equivalent as well. Similarly, rapid rotation about the $BC_6F_5C(F){-}C_6F_5$ bonds readily explains the three signals attributed to the fluorines on the pentafluorophenyl rings.

Application of $[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$. Combining $L\text{-}NiMe_2$ (L = $(2,6\text{-}C_6H_3(i\text{-}Pr)_2)N{=}C(Me)C(Me){=}N(2,6\text{-}C_6H_3(i\text{-}Pr)_2)$, Me = CH_3) with $[PhNMe_2H][\mathbf{3}]$ in toluene resulted in a deep purple solution. This is the same color observed when $L\text{-}NiMe_2$ is activated with either $[PhNMe_2H][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$. On the basis of the ^{19}F NMR spectrum of this solution, it is clear that **3** remains intact after activation. Table 1 shows the results of ethylene polymerization reactions using $[L\text{-}NiMe][\mathbf{3}]$. Comparative polymerization reactions using $[PhNMe_2H][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$[11] and $[PhNMe_2H][B(C_6F_5)_4]$[2,5,11] as cocatalysts are shown in Table 1 as well. On the basis of these results it may be concluded that the molecular weights of the polymers prepared with $[L\text{-}NiMe][B(C_6F_5)_4]$ and $[L\text{-}NiMe][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ are higher than those made with $[L\text{-}NiMe][\mathbf{3}]$. Additionally, the activities of the latter system were lower than those obtained with the first two combinations. The reason the first two catalyst systems and $[L\text{-}NiMe][\mathbf{3}]$ behave so differently with respect to molecular weight capability and activity is unclear at this point.

Attempts to obtain a group 4 metallocene cation stabilized with **3** were unsuccessful. Combining a variety of dimethyl zirconocenes or hafnocenes with $[PhNMe_2H][\mathbf{3}]$ in toluene resulted in black solutions and precipitates. The ^1H and ^{19}F NMR spectra of these mixtures indicated the presence of numerous indiscernible byproducts. Similar results were observed when the activation reactions were done in the presence of olefin (octene or ethylene). When the activation step was performed in THF-d_8, stable complexes were obtained. These complexes are most likely the metallocenium-THF adducts.[12] These metallocene adducts did not polymerized α olefins. In this context, it is worth noting that activation of most dimethyl zirconocenes or hafno-

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(10) For ^{19}F NMR discussion see: Hudlicky, M.; Pavlath, A. E. *Chemistry of Organic Fluorine Compounds II, A Critical Review*; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; pp 1037−1088.

(11) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Stefan, M.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(12) Polymerization with THF adduct: Jordan, R. F. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

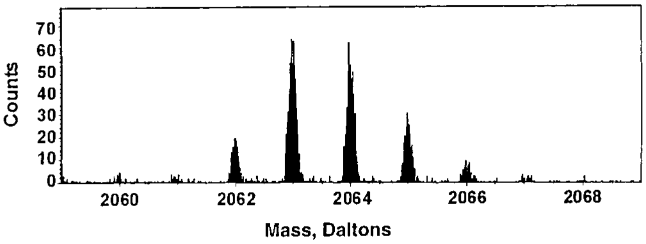

Figure 2. Mass spectra of **3**.

cenes in toluene with $[PhNMe_2H][B(C_6F_5)_4]$ typically results in clear, colored solution (see Experimental Section).

Stability of 3. The narrow polydispersities obtained for runs 1−4 indicate that **3** remains intact throughout polymerization. In this connection a polymer sample from run 4 was analyzed using time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The use of mass spectroscopy in this context has been reported separately by Erker[13] and Brant et al.[14]

The result of this experiment is depicted in Figure 2. The parent peak is clearly seen at 2063 atomic mass units. Due to the severe conditions the anion is subjected to during the experiment (see Experimental Section), the two smaller features at higher atomic mass units are likely products generated at this stage. For example, the cluster at 2083 amu is consistent with the addition of HF (20 amu) to one of the aromatic rings. One possible hydrogen source is the countercation. Another possibility is the toluene used to prepare the sample (see Experimental Section).

In summary, the new anion $B[C_6F_4C(C_6F_5)_2F]_4^-$ (**3**) is readily accessible by the application of a straightforward synthetic methodology. The tetrahedral geometry about the boron has been corroborated by single-crystal X-ray crystallography. Although $[L\text{-}NiMe][B(C_6F_5)_4]$ and $[L\text{-}NiMe][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ exhibit higher molecular weight capabilities and catalyst activities than [L-NiMe]-[**3**], it has been demonstrated that **3** is an effective weakly coordinating anion in ethylene polymerization reactions.

Experimental Section

General Considerations. All manipulations were carried out using either high-vacuum or glovebox techniques as described previously.[15] All solvents were dried with anhydrous alumina. Elemental analyses were carried out by Galbraith Laboratory. $CFCl_3$ (0 ppm) was used as internal reference in the ^{19}F NMR experiments.

$HC_6F_4C(C_6F_5)_2OH$ (1). HC_6F_4Br (5.496 g, 24 mmol) was dissolved in 100 mL of diethyl ether. The solution was chilled to −78 °C and treated with BuLi (15.0 mL, 24 mmol, 1.6 M). The reaction was allowed to stir for 2 h. To the resulting solution was added a solution of decafluorobenzophenone (8.691 g, 24 mmol). The reaction was allowed to stir for an additional 0.5 h, then quenched with 4 M NH_4Cl(aq). The mixture was allowed to reach room temperature. The organic layer was separated, washed with brine, and dried over $MgSO_4$. The $MgSO_4$ was removed by filtration, and the solvent was evaporated. The product solidifies after several hours to afford the product as a white crystalline solid: yield 11.60 g (94%). ^1H NMR ($CDCl_3$, 25°): δ 7.08 (m, 1H), 3.72 (t, 1H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 146.5 (dm, $J_{C-F} = 250$ Hz), 145.3 (dm, $J_{C-F} = 250$ Hz), 144.4 (dm, $J_{C-F} = 250$ Hz), 139.8 (dm, $J_{C-F} = 250$ Hz), 138.5 (dm, $J_{C-F} = 250$ Hz), 121.5 (t, $J_{C-F} = 10$ Hz), 116.5 (bs), 106.9 (t, $J_{C-F} = 22$ Hz), 74.0 (s). ^{19}F NMR ($CDCl_3$, 25 °C): δ 137.9 (m, 2F), 140.0 (d, 4F), 141.2 (m, 2F), 152.3 (t, 2F), 161.4 (m, 4F).

$HC_6F_4C(C_6F_5)_2F$ (2). In a polyethylene bottle, $HC_6F_4C(C_6F_5)_2OH$ (0.650 g, 1.3 mmol) was suspended in 7.0 g of pyridinium polyhydrogenfluoride (Olah's reagent). The suspension was stirred for 14 h. The product was extracted with pentane. Evaporation of the pentane afforded the product as a pale yellow crystalline solid: yield 0.490 g (75%). Analytically pure crystals were obtained by recrystallization from diethyl ether. ^{13}C NMR ($CDCl_3$, 25 °C): δ 146.4 (dm, J_{C-F} 264 Hz), 145.0 (dm, J_{C-F} 257 Hz), 144.4 (dm, J_{C-F} 254 Hz), 142.3 (dm, J_{C-F} 264 Hz), 137.0 (dm, J_{C-F} 247 Hz), 117.8 (m), 112.9 (m), 108.3 (t, J_{C-F} 22 Hz), 89.0 (J_{C-F} 191 Hz). ^{19}F NMR ($CDCl_3$, 25 C): δ −127.9 (m, 1F), −137.4 (m, 2F), −139.6 (m, 4F), −140.2 (m, 2F), −149.9 (m, 2F), −160.7 (m, 4F). Anal. Calcd for $C_{19}HF_{19}$: C, 44.38; H, 0.19. Found: C, 43.74; H, <0.5.

$[PhNMe_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$. $HC_6F_4C(C_6F_5)_2F$ (2.058 g, 4.0 mmol) was dissolved in 100 mL of diethyl ether, chilled to −78 °C, and treated with a BuLi solution in hexane (2.5 mL, 4.0 mmol). The reaction was allowed to stir for 45 min at −78 °C. BCl_3 in hexane (1.0 mL, 1.0 mmol, 1.6 M) was added and stirred for 20 min. The cold bath was removed, and the reaction was stirred for 1 h. At this point there was a white precipitate suspended in a pale pink solution. A methylenechloride solution of $C_6H_5N(CH_3)_2HCl$ (0.158 g, 1.0 mmol) was added, and the reaction stirred for 1 h. The white LiCl precipitate was removed by filtration, and the solvent evaporated. This afforded a pale pink semisolid. Triturating the pink material with pentane afforded a light blue solid: yield 2.001 g (91%). Analytically pure crystals were obtained by permitting pentane to slowly diffuse into a glyme (DME) solution. This afforded clear, colorless crystals which, by ^1H NMR and elemental analysis, were found to contain two molecules of DME. ^{13}C NMR (THF-d_8, 25 °C): δ 149.6 (dm, $J_{C-F} = 245$ Hz), 145.9 (dm, $J_{C-F} = 258$ Hz), 144.5 (dm, $J_{C-F} = 251$ Hz), 145.2 (s), 138.9 (dm, $J_{C-F} = 253$ Hz), 134.1 (b), 130.7 (s), 129.4 (s), 121.7 (s), 114.8 (m), 113.4 (m), 109.9 (t, J_{C-F} 25 Hz), 90.1 (t, $J_{C-F} = 188$ Hz), 46.4 (s). ^{19}F NMR ($CDCl_3$, 25 C): δ −126.2 (m, 1F), −131.8 (m, 2F), −139.8 (m, 4F), −145.1 (m, 2F), −151.7 (m, 2F), −161.8 (m, 4F). ^{11}B NMR (THF-d_8, 25 °C): δ −16.2. Anal. Calcd for $C_{92}H_{28}BF_{60}NO_4$: C, 46.75; H, 1.20. Found: C, 46.19, 46.34; H, 1.22, 1.18.

Activation Experiments. (a) Tetrahydrofuran: To a THF-d_8 solution of bis(pentamethylcyclopentadienyl)hafniumdimethyl (22 mg, 0.05 mmol) was added a THF-d_8 solution of $[PhNMe_2H][B(C_6F_5)_4]$ (40 mg, 0.05 mmol). A pale yellow solution resulted. The ^1H NMR spectrum is consistent with the presence of the metallocenium-THF adduct.[12] A similar result was obtained when the activation was performed with $[C_6H_5N(CH_3)_2H]B[C_6F_4C(C_6F_5)_2F]_4$ (same molar scale). The ^{19}F NMR spectrum of this last combination is identical to that of the starting material (i.e., $[C_6H_5N(CH_3)_2H]B[C_6F_4C(C_6F_5)_2F]_4$ in THF-d_8, see previous paragraph). Analogous results were obtained with bis(cyclopentadienyl)zirconiumdimethyl. (b) Toluene: To a toluene-d_8 solution of bis(pentamethylcyclopentadienyl)hafniumdimethyl (23 mg, 0.05 mmol) was added a toluene-d_8 solution of $[C_6H_5N(CH_3)_2H][B\{C_6F_4C(C_6F_5)_2F\}_4]$ (112 mg, 0.05 mmol). This combination resulted in a black solution and black precipitate. The ^1H NMR spectrum of this combination consisted of numerous broad peaks.

Batch Polymerization Reactions. Ethylene polymerization reactions were carried out in a well-stirred batch reactor equipped to perform coordination polymerization in the presence of an inert hydrocarbon (toluene) solvent at pressures up to 500 psi and temperatures up to 150 °C. Ethylene was

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[13] Erker, T. G.; Luftman, K. H.; Frohlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 1755.

[14] Brant, P.; Wu, K.-J. *J. Matt. Sci. Lett.* **2000**, 189.

[15] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry;* Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symp. Ser. 353; American Chemical Society: Washington, D.C., 1987.

continuously fed into the reactor to keep the vapor pressure constant at 80 psi during the polymerization reactions. In all experiments, the reactor temperature was kept constant at 80 °C by electronically controlling the flow of steam through the reactor jacket. Typically, the catalyst solution (catalyst and activator dissolved in 40 mL of toluene) was first prepared inside a nitrogen purge box, transferred to a glass vial, capped, sealed, and brought out of the box. Toluene (400 mL) was then fed into the dry reactor from a 20 L toluene tank. The catalyst solution was transferred into the reactor via a cannula. The reactor was closed and heated to 80 °C. The reactor was pressurized with ethylene and maintained at constant pressure throughout the polymerization. Polymerization began immediately upon addition of ethylene and was allowed to continue under controlled temperature and pressure. After the indicated times (Table 1), the reactor was allowed to reach room temperature and depressurized by venting. The polymerization solution was poured into methanol to induce precipitation. The amorphous polymer was collected and allowed to dry over 16 h. The polymer was dried further under vacuum.

Polymer Molecular Weight Determination. GPC measurements were carried out using a Waters 150C GPC equipped with a differential refractive index detector, a Precision Detector light scattering (LS) detector, and a Viscotek high temperature differential viscometer for accurate molecular weight measurement. Three Polymer Laboratory Mixed B (10 μm spheres) type columns are used. Polymer samples were dissolved in 1,2,4-trichlorobenzene (TCB) at 135 °C and run at a flow rate of 0.5 mL/min. In all cases the injected volume was 300 μL.

The GPC is routinely calibrated with a series of polymers of known molecular weights and intrinsic viscosities (a combination of National Bureau of Standards polyethylenes and narrow polystyrene standards).

X-ray Structure Determination. Crystallographic data for $[C_6H_5N(CH_3)_2H]B[C_6F_4C(C_6F_5)_2F]_4$ were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structure was solved using direct methods and standard difference map techniques and was refined by full-matrix least-squares procedures using SHELXTL.[16] Systematic absences were consistent uniquely with *Pbcn* (No. 60). The dimethylanilinium counterion was disordered about an inversion center, and the disorder was modeled accordingly. Hydrogen atoms on carbon were included in calculated positions. Crystal data, data collection, and refinement parameters are summarized in Table 2.

Table 2. Crystal Data and Structure Refinement for $[PhN(CH_3)_2H][3]$

empirical formula	$C_{84}H_{12}BF_{60}N$
temperature	228(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	*Pbcn*
unit cell dimens	$a = 16.612(7)$ Å, $\alpha = 90°$ $b = 18.808(7)$ Å, $\beta = 90°$ $c = 26.104(10)$ Å, $\gamma = 90°$
volume, Z	8156(5) Å^3, 4
density (calcd)	1.780 Mg/m^3
abs coeff	0.201 mm^{-1}
$F(000)$	4272
cryst size	0.20 × 0.20 × 0.10
θ range for data collected	1.56−28.46°
limiting indices	$-21 \le h \le 21$, $-10 \le k \le 24$, $-30 \le l \le 33$
no. of reflns	45 142
no. of ind reflns	9466 ($R_{int} = 0.2088$)
completeness to $\theta = 28.46°$	91.9%
max. and min. transmn	0.9802 and 0.9610
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9466/0/643
final R indices $[I>2\sigma(I)]$	R1 = 0.0878, wR2 = 0.2180
extinction coeff	0.0014(2)
largest diff peak and hole	1.781 and −0.350 e Å^{-3}

Procedure for Mass Spectroscopy. The mass spectrum was recorded using a PHI-Evans triple sector electrostatic analyzer time-of-flight mass spectrometer equipped with a pulsed liquid metal ion source (^{115}In) for time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis and a nitrogen laser ($\lambda = 337$ nm) for laser desorption mass spectrometry (LDMS) analysis. The ToF-SIMS spectrum was obtained operating the ion gun at 15 keV and 600 pA. Mass calibration was carried out using a variety of known standards.

The resin sample was prepared using the following protocols: polymer resin (~30 mg) was placed in a glass vial containing 10 mL of toluene and the mixture heated to 90 °C. After extraction for 3 min, approximately 1 μL of the solution is deposited on a sample substrate (clean Si wafer). The solvent was evaporated in air, and the wafer with extracted material was then inserted into the instrument for mass spectral analysis.

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Supporting Information Available: Complete numbering scheme for the ORTEP including the *N,N′*-dimethylanilinium cation. Tables of crystallographic data including atomic coordinates, thermal parameters, and bond distances and angles. This material is also available free of charge via the Internet at http://pubs.acs.org.

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(16) Sheldrick, G. M. *SHELXTL*, An Intergrated System for Solving, Refining and Displaying Crystal Structures form Diffraction Data; University of Gröttingen: Federal Republic of Germany, 1981.