Synthesis and Reactivity of a Sterically Crowded Tris(pyrazolyl)borate Hafnium Benzyl Complex

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Received June 23, 2008

The reaction of $Hf(CH_2Ph)_4$ and $Tl[Tp^{Ms*}]$ (Tp^{Ms*} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$) yields $Tp^{Ms*}Hf(CH_2Ph)_3$ (**1**), bibenzyl, and Tl^0 via ligand exchange followed by thermal decomposition of $Tl[CH_2Ph]$. Compound **1** reacts with $[H(OEt_2)_2][B(C_6F_5)_4]$ to form $Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)^+$ (**2**, 100%) and with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ to form an unstable species characterized by NMR as Tp^{Ms*}-$Hf(CH_2Ph)_2^+$. **1**/$[Ph_3C][B(C_6F_5)_4]$ behaves similarly to $Tp^{Ms*}HfCl_3$/MAO in olefin polymerization, producing high molecular weight, linear PE, and ethylene/1-hexene copolymer with good hexene incorporation. These results are consistent with the proposal that similar cationic $Tp^{Ms*}Hf(X)R^+$ species (X = Cl or R) are active species in these catalysts. Ethylene polymerization by **1**/$[Ph_3C][B(C_6F_5)_4]$ at low temperature proceeds without significant chain transfer, enabling the synthesis of bromo benzyl double-end-capped linear PE ($PhCH_2(CH_2CH_2)_nBr$).

Introduction

Group 4 metal $Tp'MCl_3$ tris(pyrazolyl)borate complexes (Tp′ = generic tris(pyrazolyl)borate) react with methylalumoxane (MAO) to produce active olefin polymerization catalysts.[1−4] In particular, sterically crowded $Tp'MCl_3$ complexes that contain mesityl-substituted Tp′ ligands, such as HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$ (Tp^{Ms*}), exhibit very high productivities in MAO-activated ethylene polymerization, which are comparable to those of zirconocene catalysts.[1c,d] The dominant chain-transfer mechanism in ethylene polymerization by many $Tp'MCl_3$/MAO catalysts is chain transfer to MAO and the $AlMe_3$ contained therein. β-H transfer is usually insignificant in these systems.

Cationic $Tp'M(X)R^+$ species (X = alkyl or Cl) are reasonable candidates for the active species in $Tp'MCl_3$/MAO catalysts. Investigation of discrete $Tp'MR_2^+$ complexes may provide insight to how $Tp'MCl_3$/MAO catalysts function and may enable Al-free versions of these catalysts to be developed for living polymerization applications.[5] However, group 4 metal Tp′M alkyl complexes are difficult to prepare by alkylation of $Tp'MX_3$ halide complexes and their chemistry is virtually unexplored.[6−9] Recently, we reported the synthesis of discrete Tp*Zr benzyl complexes (Tp* = HB(3,5-Me$_2$-pyrazolyl)$_3$).[10] The neutral complex $Tp^*Zr(CH_2Ph)_3$ can be prepared by the reaction of K[Tp*] with $Zr(CH_2Ph)_4$.[11] The reaction of $Tp^*Zr(CH_2Ph)_3$ with $[Ph_3C][B(C_6F_5)_4]$ at −60 °C yields the $Tp^*Zr(CH_2Ph)_2^+$ cation, which rearranges to $\{(PhCH_2)(H)B(\mu\text{-}Me_2pz)_2\}Zr(\eta^2\text{-}Me_2pz)(CH_2Ph)^+$ at 0 °C by net exchange of a Zr-*CH_2Ph* group and a B-*pz** group (pz* = 3,5-Me$_2$-pyrazolyl).[12] Both of these

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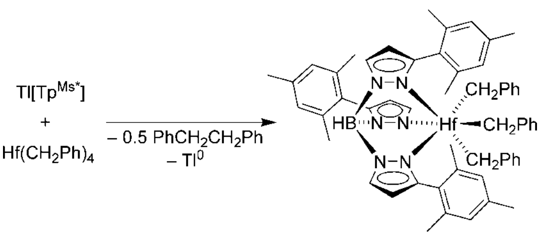
10.1021/om8005799 CCC: $40.75

Scheme 1



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cationic Zr benzyl species polymerize ethylene at low temperature to linear polyethylene (PE) without significant chain transfer and both undergo multiple alkyne insertions. Building on these results, we describe here the synthesis of $Tp^{Ms*}Hf(CH_2Ph)_3$ (**1**), initial studies of the generation and reactivity of $Tp^{Ms*}Hf(CH_2Ph)_2^+$ species, and the use of **1**/$[Ph_3C][B(C_6F_5)_4]$ to prepare end-functionalized polyethylene.

Results and Discussion

Synthesis and Structure of $Tp^{Ms*}Hf(CH_2Ph)_3$ (1). The reaction of $Hf(CH_2Ph)_4$ with $Tl[Tp^{Ms*}]$ in benzene at 23 °C affords $Tp^{Ms*}Hf(CH_2Ph)_3$ (**1**) in 65% isolated yield (Scheme 1). NMR analysis of this reaction in CD_2Cl_2 shows that **1** and 0.5 equiv of bibenzyl form quantitatively within 10 min at 23 °C. A Tl^0 mirror is also formed. These results are consistent with initial ligand exchange to form **1** and $Tl(CH_2Ph)$, followed by rapid decomposition of the thermally unstable $Tl(CH_2Ph)$ to Tl^0 and bibenzyl.[13] Complex **1** is stable in CD_2Cl_2 solution for at least 3 h at room temperature and as a solid for at least 3 months at −35 °C under nitrogen.

The molecular structure of **1** was determined by X-ray diffraction and is shown in Figure 1. Key metrical parameters are listed in Table 1. Complex **1** has distorted octahedral geometry at hafnium with *cis*-L−Hf−L angles in the range of 75.7(1)−101.0(2)°. The Hf and B substituents on a given pyrazole ring are slightly staggered, such that the Hf−N−N−B dihedral angles are in the range of −0.7 to −15.6° (average −8.3°). The core structure of **1** is similar to that of $Tp^{Ms*}HfCl_3$,[1c] but the Hf−N bond distances in **1** (ave 2.385 Å) are slightly longer than those in $Tp^{Ms*}HfCl_3$ (avg 2.295 Å), and the N−Hf−N angles in **1** (avg 78.0°) are correspondingly smaller than those in $Tp^{Ms*}HfCl_3$ (avg 80.2°). All three benzyl groups of **1** are coordinated to Hf in an η^1 mode (all $Hf-C_{ipso}$ distances >3.2 Å, all Hf−C−C angles >116°).

The NMR spectra of **1** are consistent with the solid-state structure with facile rotation around the Hf−benzyl bonds and restricted rotation around the pz-mesityl bonds. The ^1H NMR spectrum of **1** in CD_2Cl_2 contains two sets of $-CH_2\mathit{Ph}$ phenyl resonances in a 2/1 integral ratio, two sets of pyrazolyl resonances in a 2/1 integral ratio, and five mesityl-*methyl* resonances in a 1/2/2/2/2 intensity pattern. The ^1H spectrum also contains two doublets and one singlet in a 2/2/2 intensity pattern for the $-C\mathit{H_2}Ph$ hydrogens, as expected for a C_s-symmetric structure in which the $-C\mathit{H_2}Ph$ hydrogens of the benzyl ligand that is trans to the 5-mesityl-pz unit are equivalent, while those for other benzyl ligands are inequivalent. The $^1J_{CH}$ values for the $-\mathit{CH_2}Ph$ groups (113 and 115 Hz) show that the η^1-benzyl coordination mode is retained in CD_2Cl_2 solution.

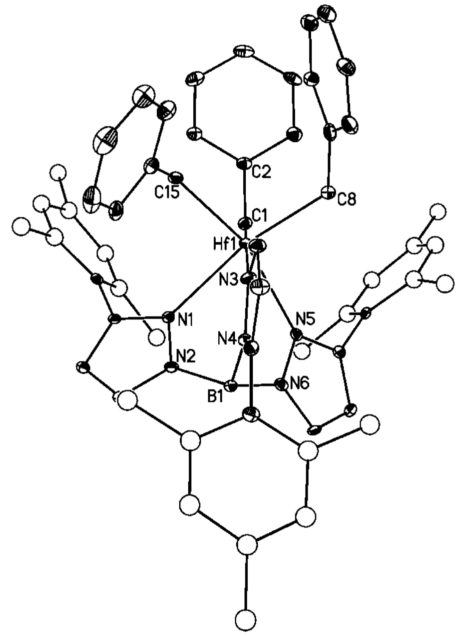
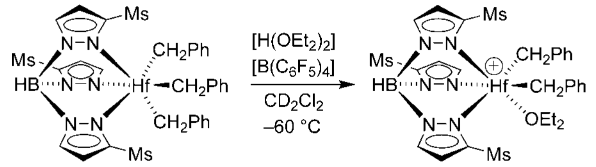


Figure 1. Molecular structure of $Tp^{Ms*}Hf(CH_2Ph)_3$ (**1**) showing 15% probability ellipsoids. For clarity, most carbon atoms of the mesityl rings are shown as open spheres and all H atoms are omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Tp^{Ms*}Hf(CH_2Ph)_3$ (1)

Hf(1)−C(1)	2.249(4)	Hf(1)−C(8)	2.229(5)
Hf(1)−C(15)	2.225(4)	Hf(1)−N(1)	2.431(3)
Hf(1)−N(3)	2.336(4)	Hf(1)−N(5)	2.388(4)
B(1)−N(2)	1.548(6)	B(1)−N(4)	1.517(6)
B(1)−N(6)	1.548(6)		
C(15)−Hf(1)−C(8)	101.0(2)	C(15)−Hf(1)−C(1)	96.1(2)
C(8)−Hf(1)−C(1)	97.8(2)	C(15)−Hf(1)−N(3)	89.0(1)
C(8)−Hf(1)−N(3)	85.3(2)	C(8)−Hf(1)−N(5)	94.1(1)
C(1)−Hf(1)−N(5)	94.5(1)	N(3)−Hf(1)−N(5)	79.6(1)
C(15)−Hf(1)−N(1)	86.4(1)	C(1)−Hf(1)−N(1)	97.5(1)
N(3)−Hf(1)−N(1)	78.6(1)	N(5)−Hf(1)−N(1)	75.7(1)

Scheme 2



1, Ms = mesityl **2**

$Tp^{Ms*}Zr(CH_2Ph)_3$. The reaction of $Zr(CH_2Ph)_4$ with $Tl[Tp^{Ms*}]$ in CD_2Cl_2 at 23 °C yields bibenzyl, Tl^0, and several Tp^{Ms*} products. The major Tp^{Ms*} product (61%) exhibits a ^1H NMR spectrum that is very similar to that of **1** and therefore is assigned as $Tp^{Ms*}Zr(CH_2Ph)_3$. However, this species decomposes completely to a mixture of unidentified products within 3 h at ambient temperature.

Generation of $Tp^{Ms*}Hf(CH_2Ph)_2^+$ species. The reaction of **1** with $[H(OEt_2)_2][B(C_6F_5)_4]$ in CD_2Cl_2 at −40 °C generates $[Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)][B(C_6F_5)_4]$ (**2**) quantitatively, along with 1 equiv of toluene and 1 equiv of free Et_2O (Scheme 2). Assuming octahedral geometry at Hf, two isomers are possible for **2**: a C_1-symmetric isomer in which the bound Et_2O is trans to a 3-mesityl-pz unit and a C_s-symmetric isomer in which the Et_2O ligand is trans to the 5-mesityl-pz unit. The ^1H NMR spectrum of **2** at −60 °C contains two doublets of quartets (J = 12.3, 6.7 Hz) for the Et_2O methylene hydrogens, indicating

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Table 2. Ethylene Polymerization by $Tp^{Ms*}Hf$ Catalysts[a] (Activation Method: A = 1/$[Ph_3C][B(C_6F_5)_4]$; B = 1/$B(C_6F_5)_3$)

entry	activation method	**1** (μmol)	cocatalyst (μmol)	MAD (μmol)	T (°C)	yield (g)	P[b]	M_w[c] ($\times 10^6$)	M_w/M_n[c]	chains/Hf	T_m[d] (°C)
1	B	1.0	1.2	20	23	0.47	3.5	1.9	2.2	0.6	134
2	B	1.0	1.2	20	0	0.51	3.8	1.4	2.9	1.1	135
3	B	1.0	1.2	100	23	0.61	4.5	0.9	2.6	1.1	138
4	B	1.0	1.2	100	0	0.69	5.1	1.6	1.7	0.8	134
5	B	25	30	0	23	0.56	0.16	1.1	3.0	1.5	135
6	A	1.0	1.2	100	23	0.73	56[e]	0.71	1.9	3.2	134

[a] Polymerization conditions: glass Fischer−Porter bottle, 6 min, 80 mL of toluene, $P_{C2H4} = 1.4$ atm. [b] = productivity in units of (kg polymer) (mmol **1**)$^{-1}$ (atm ethylene)$^{-1}$ h^{-1}. [c] Determined by GPC. [d] Determined by DSC. [e] Reaction stopped at 0.6 min due to aggregation of polymer to the stirrer.

Table 3. Ethylene/1-Hexene Copolymerization by $Tp^{Ms*}Hf$ Catalysts[a] (Activation Method: A = 1/$[Ph_3C][B(C_6F_5)_4]$; B = 1/$B(C_6F_5)_3$; C = $Tp^{Ms*}HfCl_3$/MAO)

entry	activation method	**1** (μmol)	cocatalyst (μmol)	hexene (M)	yield (g)	P[b]	M_w[c] ($\times 10^6$)	M_w/M_n[c]	T_m[d] (°C)	hexene[e] (mol %)
1	A	1.0	1.2	2	1.2	8.6	0.43	2.6	117.4	
2	A	1.0	1.2	5	0.94	6.9	1.0	4.7	109.9	7.5
3	B	1.0	1.2	2	0.18	1.4	0.72	3.3	127.1	
4	B	1.0	1.2	5	0.085	0.63	0.80	4.1	125.5	0.6
5	C	1.0	1000	2	1.4	41[f]	0.34	3.8	115.0	
6	C	1.0	1000	5	1.2	36[f]	0.53	4.1	104.9	9.9

[a] Polymerization conditions: glass Fischer−Porter bottle, 6 min, 80 mL of toluene, $P_{C2H4} = 1.4$ atm, 100 μmol of MAD added to entries 1−4. [b] P = productivity in units of (kg polymer) (mmol of precatalyst)$^{-1}$ (atm ethylene)$^{-1}$ h^{-1}. [c] Determined by GPC. [d] Determined by DSC. [e] Hexene incorporation determined by ^{13}C NMR. [f] Reaction stopped at 1.5 min due to aggregation of polymer to the stirrer.

that the two hydrogens in each O*CH*$_2$Me unit are diastereotopic, and nine singlets for the mesityl-*methyl* groups integrating for 3H each. Two doublets (1H each) and a singlet (2H) are observed for the benzyl methylene hydrogens. These results show that **2** adopts the C_1-symmetric structure shown in Scheme 2. The two hydrogens in each Hf*CH*$_2$Ph unit are diastereotopic; however, for one of the benzyls, the two hydrogens are coincidentally isochronous and give rise to a singlet.[14] The ^{13}C NMR spectrum of **2** is also consistent with a C_1-symmetric structure. Complex **2** is stable at 0 °C in CD_2Cl_2 but decomposes to a mixture of unidentified products at 20 °C.

The reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ at −40 °C in CD_2Cl_2 produces a mixture of products. However, the ^{1}H NMR spectrum of the reaction mixture contains a major set of resonances that is consistent with $Tp^{Ms*}Hf(CH_2Ph)_2^+$ (52% NMR yield). The ^{1}H spectrum of this species contains two sets of pyrazolyl resonances in a 2/1 integral ratio, one set of −CH$_2$*Ph* phenyl resonances, and five mesityl-*methyl* resonances in a 1/2/2/2/2 intensity pattern, consistent with a C_s-symmetric structure. When the reaction mixture is warmed to room temperature, the proposed $Tp^{Ms*}Hf(CH_2Ph)_2^+$ decomposes to unidentified products. Similarly, the reaction of **1** with $B(C_6F_5)_3$ at −60 °C gives a mixture of products. The ^{1}H NMR spectrum of the reaction mixture contains a major set of resonances for the proposed $Tp^{Ms*}Hf(CH_2Ph)_2^+$ cation (70% NMR yield), resonances for the free $(PhCH_2)B(C_6F_5)_3^-$ anion, and resonances for other unidentified species. In this case, when the reaction mixture is warmed to ambient temperature, $Tp^{Ms*}HfCl_3$ is formed.[1c] These results show that base-free $Tp^{Ms*}Hf(CH_2Ph)_2^+$ is thermally unstable in CD_2Cl_2 and that net chloride abstraction from the solvent is a significant decomposition mode. However, $Tp^{Ms*}Hf(CH_2Ph)_2^+$ can be stabilized by coordination of Et_2O.

Olefin polymerization by $Tp^{Ms*}Hf(CH_2Ph)_2^+$. The olefin polymerization behavior of $Tp^{Ms*}Hf(CH_2Ph)_2^+$ generated in situ in toluene by the reaction of **1** with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ was investigated for comparison to earlier results for $Tp^{Ms*}HfCl_3$/MAO.[1c,d] Representative ethylene homopolymerization results are summarized in Table 2. At 60 °C and 1.4 atm ethylene pressure in the presence of MAD (MeAl{O-(2,6-di-^{t}Bu-4-Me-phenyl)}$_2$) as a scavenger,[15] **1**/$B(C_6F_5)_3$ produces high molecular weight, linear PE (T_m = 134−138 °C) with good activity (entries 1−4). In the absence of MAD, **1**/$B(C_6F_5)_3$ produces similar PE (entry 5); however, activities are lower and higher catalyst concentrations are required for reproducible results. The ethylene polymerization activity of **1**/$[Ph_3C][B(C_6F_5)_4]$ (entry 6) is much higher than that of **1**/$B(C_6F_5)_3$. These results show that **1**/$B(C_6F_5)_3$ and **1**/$[Ph_3C][B(C_6F_5)_4]$ behave similarly to $Tp^{Ms*}HfCl_3$/MAO in that all three catalysts produce high molecular weight, linear PE.

Ethylene/1-hexene copolymerizations by **1**/$B(C_6F_5)_3$ and **1**/$[Ph_3C][B(C_6F_5)_4]$ were studied to provide a more informative comparison of these catalysts with $Tp^{Ms*}HfCl_3$/MAO. Representative results are summarized in Table 3. **1**/$[Ph_3C][B(C_6F_5)_4]$ exhibits high activity and good comonomer incorporation in ethylene/hexene copolymerization. The levels of hexene incorporation by **1**/$[Ph_3C][B(C_6F_5)_4]$ and $Tp^{Ms*}HfCl_3$/MAO are very similar. In contrast, **1**/$B(C_6F_5)_3$ is much less active than **1**/$[Ph_3C][B(C_6F_5)_4]$ and incorporates only a minimal amount of hexene.

These results suggest that active species formed in **1**/$[Ph_3C][B(C_6F_5)_4]$ and $Tp^{Ms*}HfCl_3$/MAO are similar but are different from that formed in **1**/$B(C_6F_5)_3$. One possibility is that a tight $[Tp^{Ms*}HfR_2][(PhCH_2)B(C_6F_5)_3]$ ion pair is formed in the latter case, and is less reactive with ethylene and much less reactive with hexene than the presumed $Tp^{Ms*}Hf(X)R^+A^-$ species formed in **1**/$[Ph_3C][B(C_6F_5)_4]$ and $Tp^{Ms*}HfCl_3$/MAO.[16] While the NMR data for $[Tp^{Ms*}Hf(CH_2Ph)_2][B(C_6F_5)_4]$ and $[Tp^{Ms*}Hf(CH_2Ph)_2][(PhCH_2)B(C_6F_5)_3]$ suggest that these species are not strongly ion-paired in CD_2Cl_2, strong ion-pairing may occur in toluene, the solvent used in the polymerization reactions. Additionally, the productivity of **1**/$B(C_6F_5)_3$ may be

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(14) The observed J_{HH} value for the Hf-*CH*$_2$Ph group of **2** (12.5 Hz) is similar to that for **1** (11.4 Hz) and is consistent with η^1-coordination: Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282, and references therein.

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reduced by decomposition of the active species via reaction with $\mathrm{PhCH_2B(C_6F_5)_3^-}$, which is much more reactive than $\mathrm{B(C_6F_5)_4^-}$.[17,18]

Chain Capping Experiments. An interesting issue in ethylene polymerization by **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ or **1**/$\mathrm{B(C_6F_5)_3}$ is the question of whether chain transfer occurs. The molecular weight distributions (M_w/M_n) of the PEs produced by these systems (Table 2) are in the range of 1.7−3.0, which is consistent with the occurrence of chain transfer. However, the number of polymer chains produced per Hf center (assuming 100% activation efficiency) is very low (0.6−3.2), which suggests that chain transfer is not very efficient. Several factors complicate interpretation of these observations. First, the activation efficiency is unknown. While **1** is converted to **2** cleanly in the presence of $\mathrm{Et_2O}$, the efficiency of trapping of $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$ by ethylene to form $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2(CH_2{=}CH_2)^+}$ in polymerization experiments is unknown. Furthermore, the formation of a mixture of species during the generation of $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$ in the absence of trapping ligands and the facile rearrangement of $\mathrm{Tp^*Zr(CH_2Ph)_2^+}$ observed earlier[10] suggest that multiple species may form in **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ and **1**/$\mathrm{B(C_6F_5)_3}$ in polymerization experiments. Also, mass transport limitations resulting from precipitation of PE and the active Hf−polymeryl species,[19] and the fact that ethylene insertion into the Hf−$\mathrm{CH_2Ph}$ bond (initiation) is probably slower than insertion of ethylene into Hf−$\mathrm{CH_2(CH_2CH_2)_{\mathit{n}}Ph}$ bonds (chain growth), may broaden the molecular weight distribution.

To disfavor chain transfer in ethylene polymerization by $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$, we investigated low temperature batch ethylene polymerizations with **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$. $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$ was generated from **1** and $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ at −78 °C, reacted with ethylene (38 equiv) at −78 °C, and quenched with $\mathrm{H_2O}$ at −78 °C. NMR analysis of the resulting polymer established that it is a benzyl-terminated, linear PE that does not contain olefin units. The ^{1}H NMR spectrum of the PE (Figure 2) contains resonances for −C*H*$_2$Ph (δ 2.65, t) and −C*H*$_3$ (δ 0.94, t) chain ends in a 2/3 integral ratio.[20] In addition, the spectrum contains a resonance for the penultimate −*CH*$_2$CH$_2$Ph unit (δ 1.69, virtual pentet).[21]

Similarly, $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$ was generated from **1** and $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ and reacted with ethylene (38 equiv) at −78 °C, and the reaction was quenched with excess $\mathrm{Br_2}$ to produce bromo benzyl double-end-capped PE (Scheme 3). The ^{1}H NMR spectrum of this polymer (Figure 3) contains resonances for the −C*H*$_2$Br (δ 3.34, t) and −C*H*$_2$Ph (δ 2.65, t) end groups in a 1/1 integral ratio.[20,22] The spectrum also contains signals for the penultimate −C*H*$_2$CH$_2$Br (δ 1.83, pentet) and −C*H*$_2$CH$_2$Ph (δ 1.69, pentet) methylene units in a 1/1 integral ratio. Similar results were obtained in larger scale reactions. These results show that ethylene polymerization by **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ proceeds without significant chain transfer at −78 °C.[21]

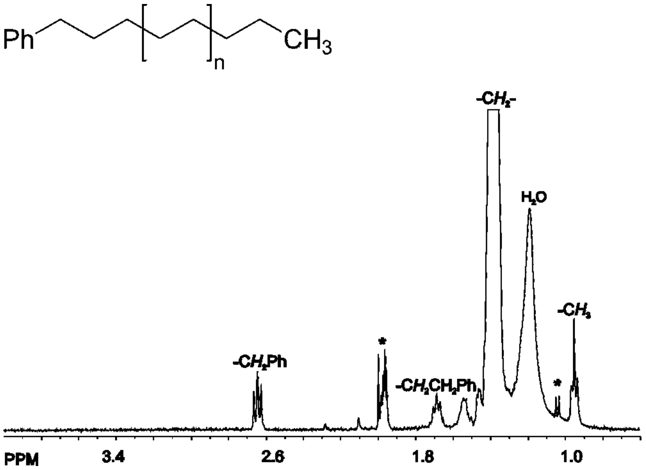
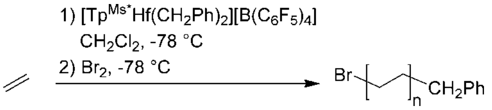


Figure 2. ^{1}H NMR spectrum (*o*-dichlorobenzene-d_4, 120 °C) of a benzyl-capped polyethylene produced by **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ at −78 °C in $\mathrm{CD_2Cl_2}$ followed by $\mathrm{H_2O}$ quenching. Peaks marked with "*" are due to solvent impurities. The resonance at δ 1.55 is a ^{13}C satellite of the main chain −CH$_2$− resonance.

Scheme 3



Conclusions

The reaction of $\mathrm{Hf(CH_2Ph)_4}$ and $\mathrm{Tl[Tp^{Ms*}]}$ yields $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_3}$ (**1**), bibenzyl, and $\mathrm{Tl^0}$ via ligand exchange followed by thermal decomposition of $\mathrm{Tl[CH_2Ph]}$. Compound **1** reacts with $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ and $\mathrm{B(C_6F_5)_3}$ in $\mathrm{CD_2Cl_2}$ to form an unstable species characterized by NMR as $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2^+}$. Compound **1** also reacts with $\mathrm{[H(OEt_2)_2][B(C_6F_5)_4]}$ to form the ether adduct $\mathrm{Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)^+}$ (**2**) quantitatively. Compound **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ behaves similarly to $\mathrm{Tp^{Ms*}HfCl_3}$/MAO in olefin polymerization, producing high molecular weight, linear PE, and ethylene/1-hexene copolymer with good hexene incorporation. These results are consistent with the proposal that similar cationic $\mathrm{Tp^{Ms*}Hf(X)R^+}$ species (X = Cl or R) are active species in these systems. In contrast, **1**/$\mathrm{B(C_6F_5)_3}$ is less active than **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ in ethylene homopolymerization and displays minimal hexene incorporation in ethylene/1-hexene copolymerization, showing that counterion effects may be significant in $\mathrm{Tp^{Ms*}Hf}$ catalysts. Ethylene polymerization by **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ at low temperature proceeds without significant chain transfer, enabling the synthesis of bromo benzyl double-end-capped linear PE ($\mathrm{PhCH_2(CH_2CH_2)_{\mathit{n}}Br}$).

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(17) (a) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 829. (b) Bavarian, N.; Baird, M. C. *Organometallics* **2005**, *24*, 2889.

(18) Polymerizations with **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ were run for shorter times than polymerizations with **1**/$\mathrm{B(C_6F_5)_3}$ due to stirring problems caused by aggregation of polymer to the stirring shaft in the former case. Therefore, the difference in activity between **1**/$\mathrm{[Ph_3C][B(C_6F_5)_4]}$ and **1**/$\mathrm{B(C_6F_5)_3}$ may be less than suggested by the data in Table 2.

(19) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223.

(20) (a) The assignment of the−*CH*$_2$*CH*$_2$Ph resonances is based on data for $\mathrm{CH_3(CH_2)_{10}CH_2CH_2Ph}$. ^{1}H NMR (CDCl$_3$): δ 2.59 (t, J = 8 Hz, 2H,−CH$_2$C*H*$_2$Ph), 1.60 (m, 2H,−C*H*$_2$CH$_2$Ph), 1.25 (m, 20H,−(CH$_2$)$_{10}$−),−0.88 (t, J = 7 Hz,−CH$_2$C*H*$_3$). (b) Pilcher, A. S.; DeShong, P. *J. Org. Chem.* **1996**, *61*, 6901. (c) The assignment of the−*CH*$_2$*CH*$_2$Br resonances is based on data for $\mathrm{CH_3(CH_2)_9CH_2CH_2Br}$. ^{1}H NMR (*o*-dichlorobenzene-d_4): δ 3.31 (t, J = 7 Hz, 2H,−CH$_2$C*H*$_2$Br), 1.82 (quint, J = 7 Hz, 2H,−C*H*$_2$CH$_2$Br), 1.31 (s, 18H,−(C*H*$_2$)$_9$−), 0.92 (t, J = 7 Hz, 3H,−C*H*$_3$).

(21) If these polymerizations proceed in a living fashion with growth at one Hf−CH$_2$Ph group, it is expected that X_n = 38 and M_n = 1156 (for MeOH quench) or 1235 (for Br$_2$ quench). The observed M_n values determined by ^{1}H NMR (2800−3800) are higher than these values. This difference is ascribed to incomplete activation and to the fact that the initial insertion into a Hf−CH$_2$Ph bond is probably slower than subsequent insertions into Hf-(CH$_2$CH$_2$)$_n$CH$_2$Ph bonds. In ethylene polymerization by $\mathrm{Tp^*Zr(CH_2Ph)_2^+}$, growth occurs at only one Zr−CH$_2$Ph group.

(22) In some cases, the integral ratio $I_{\mathrm{CH_2Ph}}/I_{\mathrm{CH_2Br}} > 1$ due to adventitious hydrolysis prior to quenching; in these cases $I_{\mathrm{CH_3}} + I_{\mathrm{CH_2Br}} = I_{\mathrm{CH_2Ph}}$. Some NMR spectra show a broad signal at δ 0.9 in the expected range for methyl end groups. Control experiments conclusively established that this signal is due to external impurities.

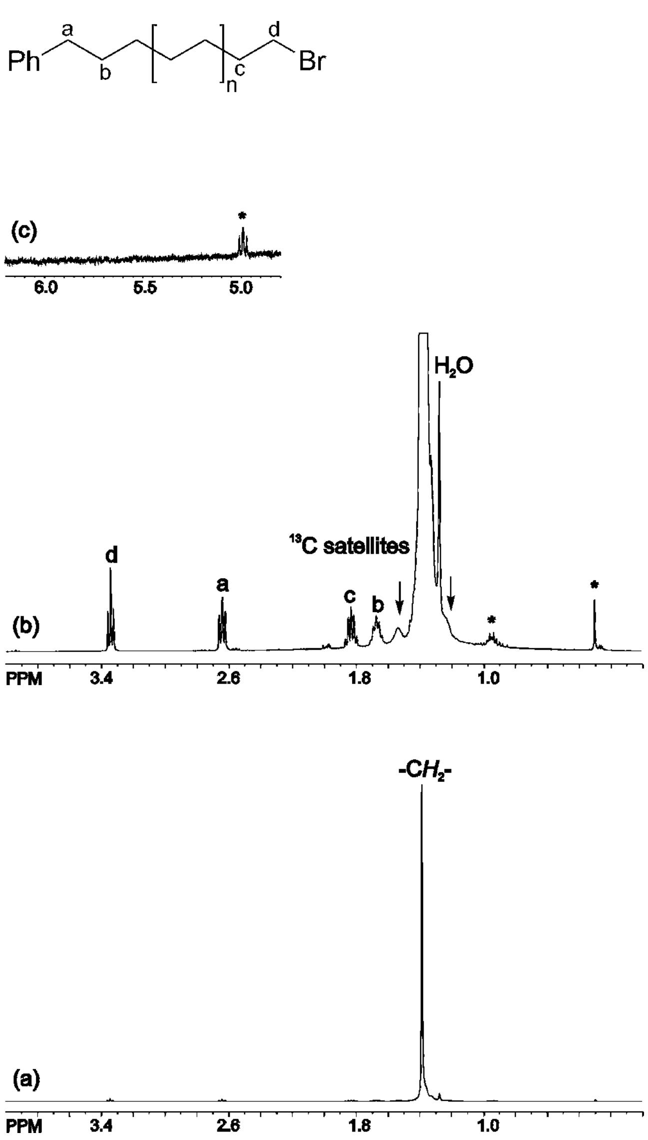

Figure 3. ^{1}H NMR spectrum (*o*-dichlorobenzene-d_4, 120 °C) of a bromo benzyl double-end-capped polyethylene prepared with **1**/[Ph_3C][$B(C_6F_5)_4$] in CD_2Cl_2 at −78 °C followed by Br_2 quenching. (a) High-field region showing the polymer main chain $-CH_2-$ resonance; (b) expansion of high-field region showing the $-CH_2CH_2Br$ and $-CH_2CH_2Ph$ end group resonances; (c) expansion of olefin region. Peaks marked with "*" are due to solvent impurities.

Experimental Section

General Procedures. All reactions were performed under purified N_2 or vacuum using vacuum line techniques or in an N_2-filled drybox. Nitrogen was purified by passage through activated molecular sieves and Q-5 oxygen scavenger. Benzene and toluene were purified by passage through activated alumina and BASF R3-11 oxygen scavenger. Dichloromethane was degassed by three freeze/pump/thaw cycles and dried over CaH_2 and/or P_2O_5. Ethylene (Matheson, research grade), *o*-dichlorobenzene-d_4 (Sigma-Aldrich), and [Ph_3C][$B(C_6F_5)_4$] (Boulder) were used as received. CD_2Cl_2 was dried over CaH_2 and distilled. $B(C_6F_5)_3$ was sublimed prior to use. $Hf(CH_2Ph)_4$, Tl[Tp^{Ms*}] and [$H(OEt_2)_2$][$B(C_6F_5)_4$] were prepared by literature procedures.[23−25] Elemental analyses were performed by Midwest Microlabs.

NMR spectra of the organometallic compounds were recorded at ambient temperature unless specified otherwise. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent resonances. ^{11}B chemical shifts are reported relative to external $BF_3 \cdot Et_2O$, and ^{19}F chemical shifts are reported relative to external $CFCl_3$. Coupling constants are given in Hz. $^1J_{CH}$ values were obtained from gated-{^{1}H} ^{13}C NMR spectra. NMR samples of polymers were prepared by addition of ca. 10 mg of the polymer to 0.7 g of *o*-dichlorobenzene-d_4 and were preheated at 100 °C to ensure complete dissolution. NMR spectra of polymers were recorded in *o*-dichlorobenzene-d_4 at 120 °C (^{1}H: pulse width 90°, relaxation delay 30 s; ^{13}C: pulse width 90°, relaxation delay 0.1 s). ^{13}C chemical shifts of polyethylenes were determined by reference to the main chain methylene peak (δ 30.0) and are reported relative to $SiMe_4$.[26] The hexene incorporation levels in ethylene/hexene copolymers were determined by Randall's method.[27]

Gel permeation chromatography (GPC) was performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 160 °C. A set of three PLgel 10 μm Mixed-B or Mixed-B LS columns was used. Samples were prepared at 160 °C and filtered through 2 or 5 μm stainless steel frits prior to injection. Molecular weights were determined by GPC using narrow polystyrene standards and are corrected for linear polyethylene by universal calibration using the Mark−Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and $\alpha = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for polyethylene.[28,29]

$Tp^{Ms*}Hf(CH_2Ph)_3$ (1). A solution of Tl[Tp^{Ms*}] (0.41 g, 0.53 mmol) in benzene (15 mL) was added dropwise to a solution of $Hf(CH_2Ph)_4$ (0.29 g, 0.53 mmol) in benzene (10 mL). The mixture was stirred at room temperature in the dark for 1 h. The mixture was filtered through Celite, and the filtrate was dried under vacuum to yield a yellow solid. The solid was dissolved in toluene (5 mL), and pentane (25 mL) was layered on top of the toluene solution. The mixture was kept at −35 °C for 3 days. A yellow crystalline solid formed and was collected by filtration and dried under vacuum to yield a yellow solid (0.35 g, 65%). Anal. Calcd for $C_{57}H_{61}BHfN_6$: C, 67.16; H, 6.03; N, 8.24. Found: C, 67.28; H, 6.21; N, 8.24. ^{1}H NMR (CD_2Cl_2): δ 7.80 (d, J = 2.2, 2H, 5-pz), 7.03 (t, J = 7.6, 2H, *p*- or *m*-Ph), 7.02 (s, 2H, Ms), 7.02 (s, 2H, Ms), 6.95 (s, 2H, Ms), 6.72 (t, J = 7.3, 1H, *p*-Ph), 6.67 (t, J = 7.7, 4H, *m*-Ph), 6.61 (d, J = 2.1, 1H, 3-pz), 6.48 (t, J = 7.3, 2H, *m*- or *p*-Ph), 6.23 (d, J = 2.1, 2H, 4-pz), 5.82 (d, J = 7.2, 2H, *o*-Ph), 5.60 (d, J = 2.1, 1H, 4-pz), 5.55 (d, J = 7.3, 4H, *o*-Ph), 4.16 (br, 1H, BH), 2.40 (s, 3H, Me), 2.35 (s, 6H, Me), 2.09 (d, J = 11.4, 2H, CH_2), 2.05 (d, J = 11.4, 2H, CH_2), 2.04 (s, 6H, Me), 1.96 (s, 6H, Me), 1.90 (s, 6H, Me), 1.73 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.9, 150.2, 150.2, 147.0, 144.1, 139.6, 138.8, 138.8, 138.7, 138.6, 137.9, 130.0, 128.8, 128.8, 128.7, 128.2, 128.0, 127.4, 127.2, 126.6, 120.8, 120.7, 108.3, 106.3, 94.4 ($^1J_{CH}$ = 113, CH_2), 89.5 ($^1J_{CH}$ = 115, CH_2), 21.4, 21.3, 21.2, 21.2, 20.1. ^{11}B{^{1}H} NMR (CD_2Cl_2): δ −4.3.

Reaction of $Zr(CH_2Ph)_4$ and Tl[Tp^{Ms*}]. A valved NMR tube was charged with Tl[Tp^{Ms*}] (8.8 mg, 11 μmol) and $Zr(CH_2Ph)_4$

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(5.2 mg, 11 μmol), and $\mathrm{CD_2Cl_2}$ (0.6 mL) was added by vacuum transfer at −196 °C. The tube was warmed to ambient temperature. A $\mathrm{Tl^0}$ mirror formed immediately. A ^{1}H NMR spectrum obtained after 20 min contained a set of resonances consistent with $\mathrm{Tp^{Ms*}Zr(CH_2Ph)_3}$, corresponding to a 61% yield based on the integration of all of the resonances in the aliphatic region. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.80 (d, $J = 2.0$, 2H, 5-pz), 7.05 (t, $J = 7.6$, 2H, *m*- or *p*-Ph), 7.03 (s, 2H, Ms), 7.02 (s, 2H, Ms), 6.96 (s, 2H, Ms), 6.80 (t, $J = 7.3$, 1H, *p*-Ph), 6.67 (t, $J = 7.6$, 4H, *m*-Ph), 6.62 (d, $J = 2.2$, 1H, 3-pz), 6.55 (t, $J = 7.3$, 2H, *m*- or *p*-Ph), 6.21 (d, $J = 2.2$, 2H, 4-pz), 5.95 (d, $J = 7.3$, 2H, *o*-Ph), 5.60 (d, $J = 7.8$, 4H, *o*-Ph), 5.59 (d, $J = 2.1$, 1H, 4-pz), 4.18 (br, 1H, BH), 2.66 (d, $J = 10.4$, 2H, $\mathrm{CH_2}$), 2.45 (d, $J = 10.4$, 2H, $\mathrm{CH_2}$), 2.40 (s, 3H, Me), 2.36 (s, 6H, Me), 2.15 (s, 2H, $\mathrm{CH_2}$), 2.03 (s, 6H, Me), 1.96 (s, 6H, Me), 1.91 (s, 6H, Me). This compound decomposes completely to a mixture of unidentified products within 3 h at ambient temperature.

Generation of $\mathbf{[Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)][B(C_6F_5)_4]}$ (2). A valved NMR tube was charged with **1** (6.4 mg, 6.2 μmol) and $\mathrm{[H(OEt_2)_2][B(C_6F_5)_4]}$ (5.2 mg, 6.2 μmol), and $\mathrm{CD_2Cl_2}$ (0.6 mL) was added by vacuum transfer at −78 °C. The tube was shaken at this temperature to give a yellow solution and was placed in an NMR probe that had been precooled to −40 °C. The tube was kept at −40 °C for 10 min and cooled to −60 °C. A ^{1}H NMR spectrum was obtained and showed that $\mathrm{[Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)][B(C_6F_5)_4]}$ had formed quantitatively. The ^{19}F NMR spectrum contains resonances at the free $\mathrm{B(C_6F_5)_4^-}$ anion positions. Free $\mathrm{Et_2O}$ and toluene are also formed. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 8.00 (d, $J = 2.1$, 1H, pz), 7.89 (d, $J = 2.0$, 1H, pz), 7.15 (s, 1H, Ms), 7.06 (s, 1H, Ms), 7.04 (s, 1H, Ms), 7.02 (s, 1H, Ms), 6.99 (t, $J = 7.7$, 2H, *m*-Ph), 6.97 (s, 1H, Ms), 6.89 (t, $J = 7.7$, 2H, *m*-Ph), 6.88 (s, 1H, Ms), 6.74 (t, $J = 7.4$, 1H, *p*-Ph), 6.66 (t, $J = 7.4$, 1H, *p*-Ph), 6.61 (d, $J = 2.1$, 1H, pz), 6.52 (d, $J = 2.1$, 1H, pz), 6.33 (d, $J = 2.1$, 1H, pz), 5.98 (d, $J = 7.6$, 2H, *o*-Ph), 5.93 (d, $J = 2.1$, 1H, pz), 5.61 (br d, $J = 7.1$, 2H, *o*-Ph), 4.13 (br, 1H, BH), 4.03 (dq, $J = 12.3, 6.7$, 2H, coordinated O(CH_2CH$_3$)$_2$), 3.89 (dq, $J = 12.3, 6.7$, 2H, coordinated O(CH_2CH$_3$)$_2$), 2.59 (d, $J = 12.5$, 1H, $\mathrm{CH_2}$), 2.37 (s, 3H, Me), 2.34 (s, 5H, Me and $\mathrm{CH_2}$), 2.34 (d, $J = 12.5$, 1H, $\mathrm{CH_2}$), 2.27 (s, 3H, Me), 2.18 (s, 3H, Me), 2.05 (s, 3H, Me), 1.97 (s, 3H, Me), 1.94 (s, 3H, Me), 1.85 (s, 3H, Me), 1.68 (s, 3H, Me), 0.84 (t, $J = 6.8$, 6H, coordinated O(CH$_2$CH_3)$_2$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ −133.7 (br s, 2F, *o*-F), −163.0 (t, $J = 23$, 1F, *p*-F), −167.0 (t, $J = 19$, 2F, *m*-F). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 157.8, 156.8, 149.5, 148.3, 147.3, 143.6, 141.3, 141.0, 140.8, 140.4, 139.2, 137.8, 137.6, 137.2, 136.8, 136.7, 128.9, 128.8, 128.6, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 126.9, 126.5, 125.5, 125.0, 123.2, 122.4, 109.6, 109.5, 107.5, 106.5, 95.2 (HfCH_2), 93.5 (HfCH$_2$), 68.5 ($\mathrm{Et_2O}$), 22.0, 21.2, 21.1, 20.9 (2C), 20.8 (2C), 19.9, 19.3, 11.9 ($\mathrm{Et_2O}$).

Reaction of 1 with $\mathbf{[Ph_3C][[B(C_6F_5)_4]}$. A valved NMR tube was charged with **1** (7.0 mg, 6.9 μmol) and $\mathrm{[Ph_3C][[B(C_6F_5)_4]}$ (6.3 mg, 6.9 μmol), and $\mathrm{CD_2Cl_2}$ (0.6 mL) was added by vacuum transfer at −78 °C. The tube was shaken at this temperature to give a yellow mixture. The tube was warmed to −40 °C for 1 h. A ^{1}H NMR spectrum was obtained at −60 °C and showed a set of resonances that are consistent with $\mathrm{[Tp^{Ms*}Hf(CH_2Ph)_2][B(C_6F_5)_4]}$, corresponding to a 52% yield based on the integration of all of the resonances in the aliphatic region. The ^{19}F NMR spectrum contains resonances at the free $\mathrm{B(C_6F_5)_4^-}$ anion positions. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 7.85 (br, 2H, 5-pz), 7.15 (t, $J = 7.4$, 4H, *m*-Ph), 7.04 (s, 2H, Ms), 7.01 (t, $J = 7.3$, 2H, *p*-Ph), 7.00 (s, 2H, Ms), 7.00 (s, 2H, Ms), 6.83 (br, 1H, 3-pz), 6.48 (br, 2H, 4-pz), 6.04 (br, 1H, 4-pz), 5.92 (d, $J = 7.6$, 4H, *o*-Ph), 4.03 (br, 1H, BH), 2.33 (s, 3H, Me), 2.26 (s, 6H, Me), 2.17 (br, 6H, Me), 1.91 (br, 6H, Me), 1.79 (s, 6H, Me). The resonances for the benzyl methylene were not identified. ^{19}F NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ −133.7 (br s, 2F, *o*-F), −163.0 (t, $J = 23$, 1F, *p*-F), −167.0 (t, $J = 19$, 2F, *m*-F).

Table 4. Summary of X-ray Diffraction Data for 1

compd	1
formula	$\mathrm{C_{57}H_{59}BHfN_6}$
formula wt	1019.42
cryst syst	trigonal
space group	$P3_121$
a (Å)	20.872(3)
b (Å)	20.872(3)
c (Å)	21.022(4)
α (°)	90.0
β (°)	90.0
γ (°)	120.0
V (Å^3)	7931(2)
Z	6
T (K)	100
crystal color, habit	yellow, prism
GOF on F^2	1.092
R indices [$I > 2\sigma(I)$][a]	R1 = 0.0314, wR2 = 0.0808
R indices (all data)[a]	R1 = 0.0330, wR2 = 0.0816

[a] $\mathrm{R1} = \Sigma||F_c|/\ \Sigma||$; $\mathrm{wR2} = [\Sigma[\mathrm{w}(F_o{}^2 - F_c{}^2)^2]/\Sigma[\mathrm{w}(F_o{}^2)^2]]^{1/2}$, where $w = q[\sigma^2/(F_o{}^2) + (aP)^2 + bP]^{-1}$.

Reaction of 1 with $\mathbf{B(C_6F_5)_3}$. A valved NMR tube was charged with **1** (10 mg, 9.8 μmol) and $\mathrm{B(C_6F_5)_3}$ (5.0 mg, 9.8 μmol), and $\mathrm{CD_2Cl_2}$ (0.6 mL) was added by vacuum transfer at −78 °C. The tube was shaken at this temperature to give a yellow mixture and was placed in an NMR probe that had been precooled to −60 °C. A ^{1}H NMR spectrum was obtained and showed a set of resonances that are consistent with $\mathrm{[Tp^{Ms*}Hf(CH_2Ph)_2][PhCH_2B(C_6F_5)_3]}$, corresponding to a 70% yield. The ^{19}F and ^{1}H NMR spectra contain resonances at the free $\mathrm{PhCH_2B(C_6F_5)_3^-}$ anion positions. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 7.85 (br, 2H, 5-pz), 7.15 (t, $J = 7.4$, 4H, *m*-Ph), 7.04 (s, 2H, Ms), 7.01 (t, $J = 7.3$, 2H, *p*-Ph), 7.00 (s, 2H, Ms), 7.00 (s, 2H, Ms), 6.86 (t, $J = 7.8$, 2H, *m*-$\mathrm{PhCH_2B}$), 6.83 (br, 1H, 3-pz), 6.79 (t, $J = 7.4$, 1H, *p*-$\mathrm{PhCH_2B}$), 6.63 (d, $J = 7.5$, 2H, *o*-$\mathrm{PhCH_2B}$), 6.48 (br, 2H, 4-pz), 6.04 (br, 1H, 4-pz), 5.92 (d, $J = 7.6$, 4H, *o*-Ph), 4.02 (br, 1H, BH), 2.70 (s, 2H, PhCH_2B), 2.33 (s, 3H, Me), 2.26 (s, 6H, Me), 2.17 (br, 6H, Me), 1.91 (br, 6H, Me), 1.79 (s, 6H, Me). The HfCH_2 resonance is obscured by the δ 1.91 resonance. ^{19}F NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ −127.1 (d, $J = 38$, 2F, *o*-F), −147.0 (t, $J = 21$, 1F, *p*-F), −160.2 (t, $J = 22$, 2F, *m*-F).

Ethylene Polymerization. Ethylene polymerization reactions were performed in a 200 mL glass Fischer−Porter bottle equipped with a magnetic stir bar and a stainless steel pressure head equipped with inlet and outlet needle valves, a septum-capped ball valve for injections, a pressure release valve for safety, and a pressure gauge. In a glovebox, the bottle was charged with MAD, $\mathrm{B(C_6F_5)_3}$ or $\mathrm{[Ph_3C][B(C_6F_5)_3]}$, and dry toluene (70 mL), and then sealed. The bottle was removed from the glovebox and attached to a stainless steel double manifold (vacuum/ethylene) line. The nitrogen atmosphere was removed by vacuum, and the bottle was pressurized with 1.4 atm ethylene and thermally equilibrated at the specified temperature for 10 min. The polymerization was started by injection of a solution of **1** in dry toluene (10 mL). The total volume of the reaction mixture was 80 mL for all polymerization reactions. The pressure was kept constant at 1.4 atm by feeding ethylene on demand. After the specified reaction time, the reaction vessel was vented, and methanol (10 mL) and acidic methanol (1 N HCl in methanol, 100 mL) were added. The mixture was stirred for several hours, and the white polymer was collected by filtration. The polymer was washed with methanol and dried at 70 °C under vacuum for 12 h.

Ethylene/1-Hexene Copolymerization. The procedure was identical with that for the ethylene homopolymerizations, except that 1-hexene was added to the Fischer−Porter bottle along with MAD, $\mathrm{B(C_6F_5)_3}$, or $\mathrm{[Ph_3C][B(C_6F_5)_3]}$ and dry toluene. The total volume was 80 mL for all copolymerization reactions.

Low-Temperature Batch Ethylene Polymerization. A solution of $\mathrm{[Tp^{Ms*}HfBn_2][B(C_6F_5)_4]}$ in $\mathrm{CH_2Cl_2}$ (10 mL) was prepared from $\mathrm{Tp^{Ms*}HfBn_3}$ (21.2 μmol) and $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ (21.2 μmol) at −78

°C. The solution was frozen at −196 °C, and ethylene (38 equiv) was added by vacuum transfer from a calibrated gas bulb. The mixture was warmed to −78 °C and mixed vigorously at this temperature for ca. 10 min. The mixture was quenched by addition of excess H_2O or Br_2 at −78 °C. The polymer was collected by filtration, washed with methanol and chloroform, and dried under vacuum.

X-ray Crystallographic Analysis of Tp^{Ms*}Hf(CH_2Ph)$_3$ (1). Crystallographic data are summarized in Table 4. Single crystals of **1** were obtained by recrystallization from CH_2Cl_2 and hexanes at −35 °C. Data were collected on a Bruker Smart Apex diffractometer using Mo Kα radiation (0.71073 Å). The space group was determined as $P3_121$ based on systematic absences and intensity statistics. Direct methods were used to locate the Hf as well as many C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, B, and N atoms. Following anisotropic refinement of all non-H atoms, ideal H-atom positions were calculated. The H on B was located from the difference map. Final refinement was anisotropic for all non-H atoms and isotropic-riding for H atoms. A disordered CH_2Cl_2 solvent was noted but could not be refined reliably. Therefore, the program SQUEEZE was used to remove its contribution to the intensity data. No anomalous bond lengths or thermal parameters were noted in the main molecule.

Acknowledgment. This work was supported by the Department of Energy (DE-FG-02-00ER15036) and the National Science Foundation (CHE-0516950).

Supporting Information Available: Crystallographic data for **1** including CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8005799