Organoborane-Modified Silica Supports for Olefin Polymerization: Soluble Models for Metallocene Catalyst Deactivation

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Treatment of silsesquioxane **1** with 3.3 equiv of the reactive organoboranes **2** [$(C_6F_5)_2BX$; X = H or Cl] provides the novel, trifunctional organoborane **3**, which was characterized by spectroscopic means and single-crystal X-ray crystallography. Compound **3** is an effective cocatalyst for ethylene polymerization in combination with Cp_2ZrMe_2 but only when these two compounds are combined in situ, in the presence of monomer, suggesting limited stability of the putative ion-pair derived from these compounds. Reaction of **3** with Cp_2ZrMe_2 in toluene solution leads to formation of $MeB(C_6F_5)_2$- and Cp_2Zr-functionalized silsesquioxane **5** at room temperature. Monitoring of this reaction by NMR spectroscopy at low temperatures indicates that the only ion-pair present is $[Cp_2ZrMe][Me_2B(C_6F_5)_2]$ (**4**), which results from reaction of Cp_2ZrMe_2 with the byproduct $MeB(C_6F_5)_2$. Formation of **4** is reversible under these conditions, while production of **5** (from **3** and Cp_2ZrMe_2) is not; the latter process occurs at a rate that exceeds that observed for independent decomposition of **4** to form $Me_2B(C_6F_5)$ and $Cp_2Zr(C_6F_5)Me$. These studies suggest that the active polymerization catalyst generated in situ from **3** and Cp_2ZrMe_2 is probably ion-pair **4**.

Introduction

There is considerable interest in the development of suitable supports for metallocene-based olefin polymerization catalysts.[1] One productive approach involves treatment of hydroxylated silica with a cocatalyst such as MAO,[2] while more recent work has focused on silica-supported, trityl-borate cocatalysts.[3] We recently reported a complementary approach where hydroxylated silica was treated with a reactive and Lewis acidic organoborane (R'_2BX: X = H, Cl, R′ = C_6F_5).[4] Treatment of these borane-modified supports with Cp_2ZrMe_2 led to supported catalysts that were marginally active in olefin polymerization, while in the presence of small quantities of methyl aluminoxane (≥10:1 Al:Zr), these Cp_2ZrMe_2-treated supports displayed markedly enhanced polymerization activity for reasons that were not readily apparent.

Part of the difficulty in optimizing the performance of supported metallocene catalysts, or discerning why particular approaches are less than successful, is that the determination of the nature of the active species present on the support can be quite challenging.[5] On the basis of the work of Feher and co-workers,[6] silsesquioxanes appear to be excellent soluble models for silanol sites on the surface of silica, and we elected to explore their reactions with organoboranes R'_2BX in the hopes of addressing these issues in an indirect manner.

We report here the synthesis and characterization of a novel, trifunctional, organoborane (**3**), the behavior of compound **3** as a cocatalyst in ethylene polymerization, and its reaction with a simple, dialkylmetallocene complex. While this work was in progress, complementary studies of organoborate-functionalized (i.e., R'_3BO) silsesquioxanes[7] and the use of silsesquioxanes as ligands for group 4 organometallic complexes[8] have

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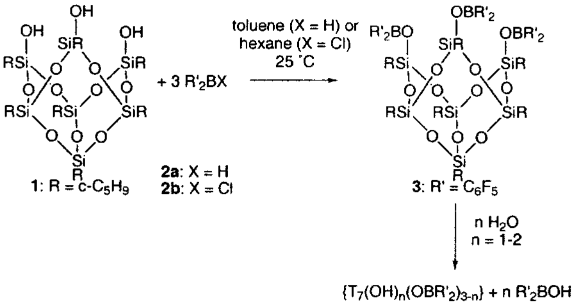
appeared. These studies have indicated that, in general, silsesquioxanes do serve as relevant models for silica-supported polymerization catalysts or cocatalysts.

Results and Discussion

Treatment of the commercially available silsesquioxane **1** with 3.3 equiv of either $(C_6F_5)_2BH$ (**2a**)[9] in toluene or $(C_6F_5)_2BCl$ (**2b**)[10] in hexane or toluene solution, respectively, provides compound **3** as a white, crystalline solid in high yield (eq 1). The latter conditions are particularly suited to the preparation of **3** on a gram scale due to the better solubility properties of **2b** compared with dimeric borane **2a**.[9] Compound **3** is a moisture sensitive solid; in solution, the presence of adventitious water in inadequately dried NMR solvents[11] leads to partial hydrolysis, affording $(C_6F_5)_2BOH$[4] and a mixture of partially borylated species derived from **3** (eq 1). The latter compounds were also detected on reaction of **1** with <3 equiv of **2a** or **2b**. It was not possible to control conditions so as to selectively produce one of these partially functionalized compounds as a predominant product.



(1)

Compound **3** was readily identified from its spectroscopic properties; the ^{13}C, ^{19}F, and ^{29}Si NMR spectra are consistent with compound **3** having time-averaged, 3-fold symmetry in solution. The DEPT-135 $^{13}C\{^1H\}$ NMR spectrum of **3** exhibited three different signals due to the C−H carbon atoms of the cyclopentane rings at δ 24.3, 23.9, and 22.9 in a ratio of 3:3:1, respectively, while the $^{29}Si\{^1H\}$ spectrum also had three resonances at −66.95, −66.26, and −65.50 ppm present in the same ratio. A single set of signals due to the *o*-, *p*-, and *m*-F atoms on the $B(C_6F_5)_2$ groups of compound **3** were observed at δ −131.88 (m), −148.5 (tt, J = 20, 5.6 Hz), and −161.32 (m), respectively, in the $^{19}F\{^1H\}$ NMR spectrum.

Single crystals of this compound could be obtained by slow cooling of a concentrated hexane solution and the molecular structure appears in Figure 1a, while selected crystallographic and refinement data, and bond lengths and angles appear in Tables 1 and 2, respectively. In the solid state two of the terminal $B(C_6F_5)_2$ groups are tangentially oriented with respect to the periphery of the silsesquioxane cage, while the third adopts a conformation in which one of the C_6F_5 substituents is directed over the missing vertex of the silsesquioxane framework, "sandwiched" between the other two $B(C_6F_5)_2$ moieties (Figure 1b).

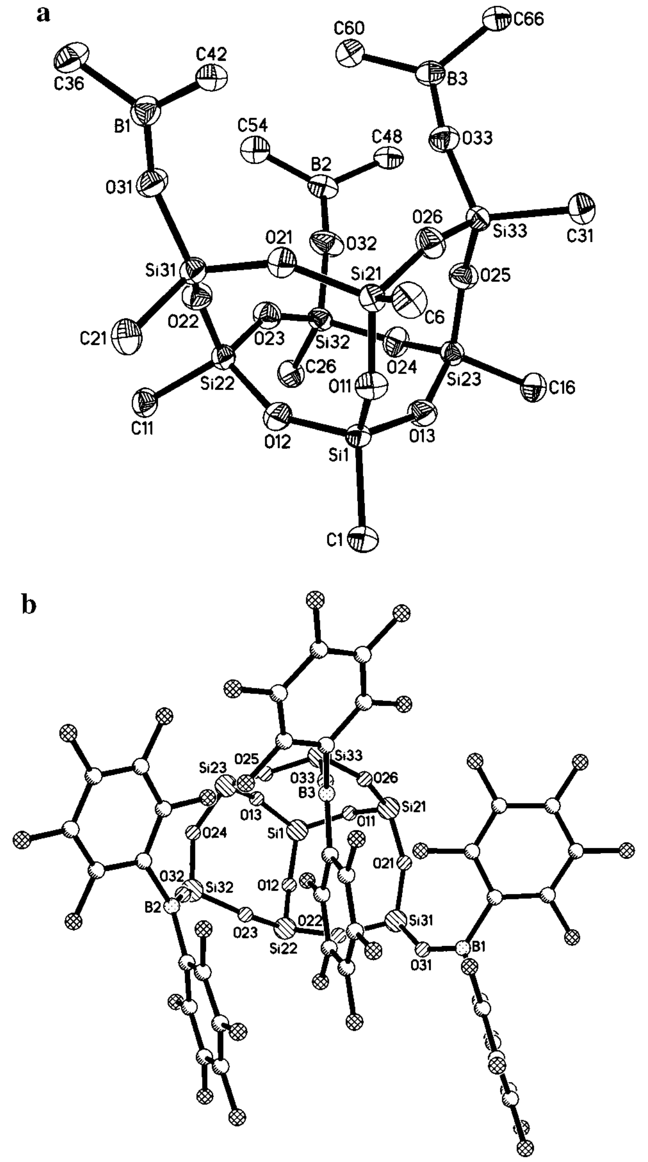


Figure 1. Molecular structure of compound **3**: (a) 50% thermal ellipsoid plot depicted with only the ipso C atom of the C_6F_5 groups on B and the methine C atom of the cyclopentane rings on Si shown for reasons of clarity; (b) ball-and-stick plot showing the orientation of the $B(C_6F_5)_2$ groups with respect to the silsesquioxane cage (cyclopentane rings omitted for clarity).

In comparison to other silsesquioxane structures,[6−8,12] the SiO framework of compound **3** appears slightly splayed open as a result of the three $-OB(C_6F_5)_2$ substituents. This distortion is evident from a number of obtuse Si−O−Si angles [e.g., Si(33)−O(25)−Si(23) = 156.1(1) and Si(33)−O(26)−Si(21) = 157.5(1)°] compared to the average value observed here [148.2(7)°]. The Si−O−B angles for two of the terminal $Si-O-B(C_6F_5)_2$ groups are considerably obtuse [169.0(1)° and 170.7(1)° for Si(33)−O(33)−B(3) and Si(32)−O(32)−B(2), respectively], while the remaining angle is acute in comparison

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[9] Parks, D. J.; von H. Spence, R. E.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809.

[10] Chambers, R. D.; Chivers, T. J. *J. Chem. Soc.* **1965**, 3933.

[11] The MW of compound **3** is in excess of 1900 g mol^{-1}; it is obvious that this property allows for a sensitive test for the presence of trace water in NMR solvents.

[12] (a) Feher, F. J.; Blanski, R. L. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 95. (b) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526. (c) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.*, **1989**, *111*, 1741.

Table 1. Selected Crystallographic and Refinement Data for Compound 3

empirical formula	$C_{71}H_{63}B_3F_{30}O_{12}Si_7$
fw	1907.27
temperature	200(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 13.6019(1)$ Å, $\alpha = 81.448(1)°$ $b = 14.3838(2)$ Å, $\beta = 75.656(1)°$ $c = 22.8040(3)$ Å, $\gamma = 67.699(1)°$
volume	3991.69(8) Å^3
Z	2
density (calc)	1.587 mg/m^3
abs coeff	0.250 mm^{-1}
$F(000)$	1936
cryst size	0.4 × 0.3 × 0.25 mm
θ range for data collection	1.65−27.12°
limiting indices	$0 \leq h \leq 17, -16 \leq k \leq 18,$ $-28 \leq l \leq 29$
no. of reflns collected	22 594
no. of ind reflns	17 266 ($R_{int} = 0.025$)
completeness to $\theta = 27.12°$	97.8%
abs corr	Scalepack
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	17266/0/1121
goodness-of-fit on F^2	2.096
final R indices [$I > 2\sigma(I)$]	$R = 0.0418$, $R_w = 0.0975$
R indices (all data)	$R = 0.0549$, $R_w = 0.1000$
largest diff peak and hole	0.512 and −0.500 e Å^{-3}

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3 with esds in Parentheses

Bond Lengths	
Si(1)−O(13) 1.615 (1)	Si(31)−C(21) 1.836(1)
Si(1)−O(12) 1.616 (1)	Si(32)−O(24) 1.609(1)
Si(1)−O(11) 1.623(1)	Si(32)−O(23) 1.609(1)
Si(1)−C(1) 1.828(1)	Si(32)−O(32) 1.627(1)
Si(21)−O(11) 1.613(1)	Si(32)−C(26) 1.836(1)
Si(21)−O(26) 1.617(1)	Si(33)−O(26) 1.607(1)
Si(21)−O(21) 1.621(1)	Si(33)−O(25) 1.608(1)
Si(21)−C(6) 1.847(1)	Si(33)−O(33) 1.625(1)
Si(22)−O(23) 1.615(1)	Si(33)−C(31) 1.837(1)
Si(22)−O(12) 1.616(1)	O(31)−B(1) 1.334(1)
Si(22)−O(22) 1.621(1)	O(32)−B(2) 1.326(1)
Si(22)−C(11) 1.835 (1)	O(33)−B(3) 1.331(1)
Si(23)−O(25) 1.616 (1)	C(36)−B(1) 1.578(1)
Si(23)−O(13) 1.617(1)	C(42)−B(1) 1.579(1)
Si(23)−O(24) 1.620(1)	C(48)−B(2) 1.584(1)
Si(23)−C(16) 1.835 (1)	C(54)−B(2) 1.575(1)
Si(31)−O(22) 1.610(1)	C(60)−B(3) 1.571(1)
Si(31)−O(21) 1.614(1)	C(66)−B(3) 1.584(1)
Si(31)−O(31) 1.650(1)	
Bond Angles	
O(13)−Si(1)−O(12) 109.24(1)	O(23)−Si(32)−O(32) 107.25(1)
O(13)−Si(1)−O(11) 108.17(1)	O(24)−Si(32)−C(26) 110.63(1)
O(12)−Si(1)−O(11) 109.82(1)	O(23)−Si(32)−C(26) 113.46(1)
O(13)−Si(1)−C(1) 110.74(1)	O(32)−Si(32)−C(26) 108.27(1)
O(12)−Si(1)−C(1) 109.47(1)	O(26)−Si(33)−O(25) 110.50(1)
O(11)−Si(1)−C(1) 109.39(1)	O(26)−Si(33)−O(33) 106.49(1)
O(11)−Si(21)−O(26) 109.61(1)	O(25)−Si(33)−O(33) 107.12(1)
O(11)−Si(21)−O(21) 108.14(1)	O(26)−Si(33)−C(31) 112.79(1)
O(26)−Si(21)−O(21) 109.43(1)	O(25)−Si(33)−C(31) 109.96(1)
O(11)−Si(21)−C(6) 110.73(1)	O(33)−Si(33)−C(31) 109.76(1)
O(26)−Si(21)−C(9) 108.72(1)	Si(21)−O(11)−Si(1) 147.99(1)
O(21)−Si(21)−C(6) 110.20(1)	Si(22)−O(12)−Si(1) 149.52(1)
O(23)−Si(22)−O(12) 109.41(1)	Si(1)−O(13)−Si(23) 147.38(1)
O(23)−Si(22)−O(22) 107.78(1)	Si(31)−O(21)−Si(21) 149.55(1)
O(12)−Si(22)−O(22) 107.94(1)	Si(31)−O(22)−Si(22) 146.26(1)
O(23)−Si(22)−C(11) 110.12(1)	Si(32)−O(23)−Si(22) 148.59(1)
O(12)−Si(22)−C(11) 110.61(1)	Si(32)−O(24)−Si(23) 147.07(1)
O(22)−Si(22)−C(11) 110.91(1)	Si(33)−O(25)−Si(23) 156.08(1)
O(25)−Si(23)−O(13) 108.83(1)	Si(33)−O(26)−Si(21) 157.54(1)
O(25)−Si(23)−O(24) 107.90(1)	B(1)−O(31)−Si(31) 143.8(1)
O(13)−Si(23)−O(24) 109.97(1)	B(2)−O(32)−Si(32) 170.7(1)
O(25)−Si(23)−C(16) 113.25(1)	B(3)−O(33)−Si(33) 169.0(1)
O(13)−Si(23)−C(16) 108.53(1)	O(31)−B(1)−C(36) 117.5(1)
O(24)−Si(23)−C(16) 108.34(1)	O(31)−B(1)−C(42) 122.2(1)
O(22)−Si(31)−O(21) 111.88(1)	C(36)−B(1)−C(42) 120.2(1)
O(22)−Si(31)−O(31) 104.54(1)	O(32)−B(2)−C(54) 120.7(1)
O(21)−Si(31)−O(31) 108.22(1)	O(32)−B(2)−C(48) 118.0(1)
O(22)−Si(31)−C(21) 112.75(1)	C(54)−B(2)−C(48) 121.3(1)
O(21)−Si(31)−C(21) 111.58(1)	O(33)−B(3)−C(60) 119.5(1)
O(31)−Si(31)−C(21) 107.42(1)	O(33)−B(3)−C(66) 118.5(1)
O(24)−Si(32)−O(23) 109.71(1)	C(60)−B(3)−C(66) 122.0(1)
O(24)−Si(32)−O(32) 107.26(1)	

[143.8(1)°]. Despite these angular variations, all three B−O bonds are short and not significantly different in length [B(1)−O(31) 1.334(2), B(2)−O(32) 1.326(2), and B(3)−O(33) 1.331(2) Å]. Interestingly, the corresponding Si−O bond lengths are all appreciably longer [Si(31)−O(31) 1.650(1), Si(32)−O(32) 1.626(1), and Si(33)−O(33) 1.625(1) Å] than the average observed for the other Si−O bonds [1.615(5) Å], which might be reflective of a reduced Si−O bond order due to an increased π-bonding interaction between B and O.

It is difficult to gauge the extent of B−O π-bonding in compound **3**. Certainly, the observed B−O bond lengths are significantly shorter than the sum of the single-bond covalent radii of B and O (∼1.45 Å) and are shorter than those observed for trigonal boron in boric acid or borates [typically 1.36−1.37 Å]. On the other hand, the average B−O bond length [1.340(4) Å] in $(C_6F_5)_2BOB(C_6F_5)_2$, a compound closely related to **3** which has been structurally characterized,[13] is insignificantly different from that observed here [1.330(6) Å].[14] It could be argued that in $(C_6F_5)_2BOB(C_6F_5)_2$ both $B(C_6F_5)_2$ groups compete for lone pair electron density on O, and thus neither B−O bond can attain a B−O bond order approaching 2. We suspect, on the basis of the chemistry observed for compound **3** (vide infra), that the B−O π bonding in this compound is not so pronounced so as to eliminate Lewis acidity of the B atoms.

Compound **3** is an *ineffective* cocatalyst for ethylene polymerization if this compound and Cp_2ZrMe_2 are combined in toluene at 25 °C *prior* to delivery to a polymerization reactor containing toluene presaturated with monomer in the presence of $MeAl(BHT)_2$ (MAD; BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) as an inert scrubbing agent.[15] However, in situ reaction of Cp_2ZrMe_2 and **3**, in the presence of monomer, under the same conditions (see Experimental Section for details) leads to modest production of PE $\{A = 7.9 \times 10^5$ g PE/mol Zr × h at 75 psi C_2H_4 and 30 °C with $[Zr] = 50\ \mu M$, $[\mathbf{3}] = 60\ \mu M$, and $[MAD] = 1.25$ mM$\}$ of high MW with a narrow MWD ($M_w = 255$ K, $M_w/M_n = 2.1$).

We have observed this type of behavior previously;[15,16] in particular, the ion-pair **4** formed from reaction of Cp_2-

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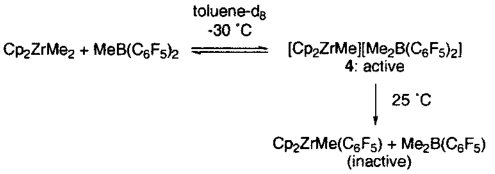
[13] Taylor, N. J.; Tian, J.; Kreller, D. J.; Collins, S. Manuscript in preparation.

[14] We have also characterized the corresponding borinic acid $(C_6F_5)_2BOH$, which adopts an unusual trimeric structure in the solid state; here the B−OH distances average 1.526(6) Å, considerably elongated from the sum of the B−O single bond covalent radii presumably due to a tetrahedral and trigonal pyramidal geometry at B and O, respectively.

[15] Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695.

[16] Kohler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Bravakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557.

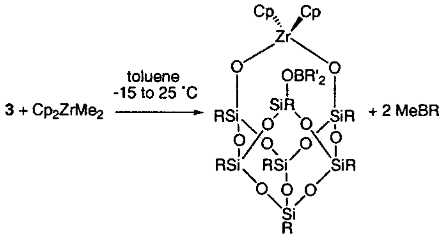
$ZrMe_2$ with $MeB(C_6F_5)_2$ (eq 2) is a viable polymerization catalyst when generated in situ in the presence of monomer, while prior combination of catalyst and cocatalyst leads to irreversible formation of $Cp_2ZrMe(C_6F_5)$ and $Me_2B(C_6F_5)$ and loss of activity.[16]



(2)

Although the polymerization behavior exhibited by compound **3** and Cp_2ZrMe_2 is consistent with the same interpretation, it is not clear from the experiments outlined above if the ion-pair responsible for polymerization is the one expected from ionization of Cp_2ZrMe_2 by **3** and/or whether this ion-pair is thermally unstable. To further study this issue from a fundamental perspective, we examined the reaction of compound **3** with Cp_2ZrMe_2.

Reaction of **3** with 1.2 equiv of Cp_2ZrMe_2, initially at −15 °C in toluene solution, leads to the formation of 2 equiv of $MeB(C_6F_5)_2$ and 1 equiv of the Cp_2Zr-functionalized silsesquioxane **5** on warming to room temperature (eq 3). Compound **5** is unstable in the presence of $MeB(C_6F_5)_2$ in concentrated solution at room temperature[17] and must thus be separated from this compound by size-exclusion chromatography of the crude, *dilute* reaction mixture on Bio-Beads SX-2 eluting with toluene.



5

(3)

Compound **5** can be isolated as a microcrystalline solid following freeze-drying of a benzene solution in spectroscopically pure form and about 50−60% of theoretical yield. This material appears to be thermally unstable in the solid state or in concentrated solution at room temperature and has not yet been obtained in analytically pure form. It is best stored refrigerated at −30 °C under N_2.

The $^{29}Si\{^1H\}$ NMR spectrum of **5** shows five signals in a ratio of 1:2:1:1:2 at δ −64.39, −64.87, −65.21, −65.56, −66.62, while the ^1H NMR spectrum in $C_6D_5Br/C_6D_5CD_3$ solution at low temperatures exhibits two singlets arising from inequivalent Cp rings at 6.05 and 6.08 ppm in addition to resonances associated with the cyclopentyl groups. The $^{19}F\{^1H\}$ spectrum [δ −131.71 (m, *o*-F), −149.27 (tt, *p*-F), −161.86 (m, *m*-F)] is consistent with a single type of $B(C_6F_5)_2$ moiety analogous to those present in **3**.

Although we have been unable to obtain single crystals of this compound, the spectroscopic data are consistent with the C_s-symmetric structure shown in eq 3. The proposed structure for compound **5** is analogous to that of $\{T_7(O_2ZrCp_2)(OSiMePh_2)\}$ recently reported and structurally characterized by Duchateau and coworkers;[18] the similarity of the ^{29}Si and ^1H NMR spectroscopic data for these two compounds is striking and lends support to the structural assignment given here. The observed reactivity of compound **3** toward Cp_2ZrMe_2 to form **5** certainly accounts for the lack of polymerization activity observed when these two compounds are premixed prior to polymerization, but the identity of the ion-pair that is responsible for polymerization, when generated in situ in the presence of monomer, is not evident from this experiment.

The reaction between **3** and Cp_2ZrMe_2 (1.0 equiv) was monitored by ^1H and ^{19}F NMR spectroscopy in mixed $C_6D_5Br/C_6D_5CD_3$ solution (1:1 v/v) over the temperature range −80 to 25 °C. At −80 °C all of the signals in both the ^1H and ^{19}F NMR spectra are exchange-broadened, precluding identification of any intermediates/products present. On warming, initial formation of **5** and $MeB(C_6F_5)_2$[19] was clearly evident at −55 °C, and an ion-pair was also present (as revealed by ^{19}F NMR signals at δ −134.2, −160.95, and −164.55 characteristic of a tetrahedral perfluorophenylborate moiety[20]) and whose concentration was maximal at −30 °C (Figure 2a).

On the basis of both the ^1H and ^{19}F NMR spectra, this ion-pair is $[Cp_2ZrMe][Me_2B(C_6F_5)_2]$ (**4**),[4,16] derived from independent reaction of Cp_2ZrMe_2 with $MeB(C_6F_5)_2$ (eq 2, see Experimental Section for details) and not that expected from ionization of Cp_2ZrMe_2 by **3**. There are some additional, weak and broadened signals present at −133.6, −160.7, and −166.2 ppm (Figure 2a,b) which might be due to the latter species, but this hypothesis must be viewed as speculative, at best, given the low concentration of this material.

Importantly, at a 1:1 stoichiometry, a ^1H NMR spectrum revealed that all of the added Cp_2ZrMe_2 had been consumed, the only predominant Zr-containing products were **4** and **5**, and yet a significant quantity of compound **3** remained at −30 °C (Figure 2a). In fact, on the basis of the observed integration, compound **3**, ion-pair **4**, $MeB(C_6F_5)_2$, and the ultimate product **5** are present in about a 1:1:1:1 ratio at this temperature.

On warming this mixture above −30 °C, ion-pair **4** decomposed, and compound **5** (ca. 1.0 equiv) and $MeB(C_6F_5)_2$ (ca. 2.0 equiv) were produced at the expense of compounds **3** and **4** (~87% conversion of **3** at 298 K using 1.0 equiv of Cp_2ZrMe_2, Figure 2b,c). Further addition of excess Cp_2ZrMe_2 (0.4 equiv) to the solution at room temperature led to complete consumption of **3**

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[17] The principle Zr-containing product of this reaction is $Cp_2Zr(C_6F_5)_2$. We presume this forms via repetitive slow/reversible ionization of **5** by $MeB(C_6F_5)_2$ followed by irreversible perfluorophenyl transfer to Zr.

[18] Skowronska-Ptasinska, M. D.; Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2001**, *20*, 3519.

[19] The ^{19}F NMR signals due to this compound appear line-broadened over the entire temperature range studied. The nature of this dynamic process is not clear, as none of the other ^{19}F resonances are broadened. Addition of excess **3** at room temperature to the mixture leads to sharpening of the resonances due to $MeB(C_6F_5)_2$, suggesting reversible binding of this compound to **3** and/or competition between **3** and $MeB(C_6F_5)_2$ for some unidentified component (Metcalfe, R. Unpublished observations).

[20] Chen, X.-Y.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391, and references therein.

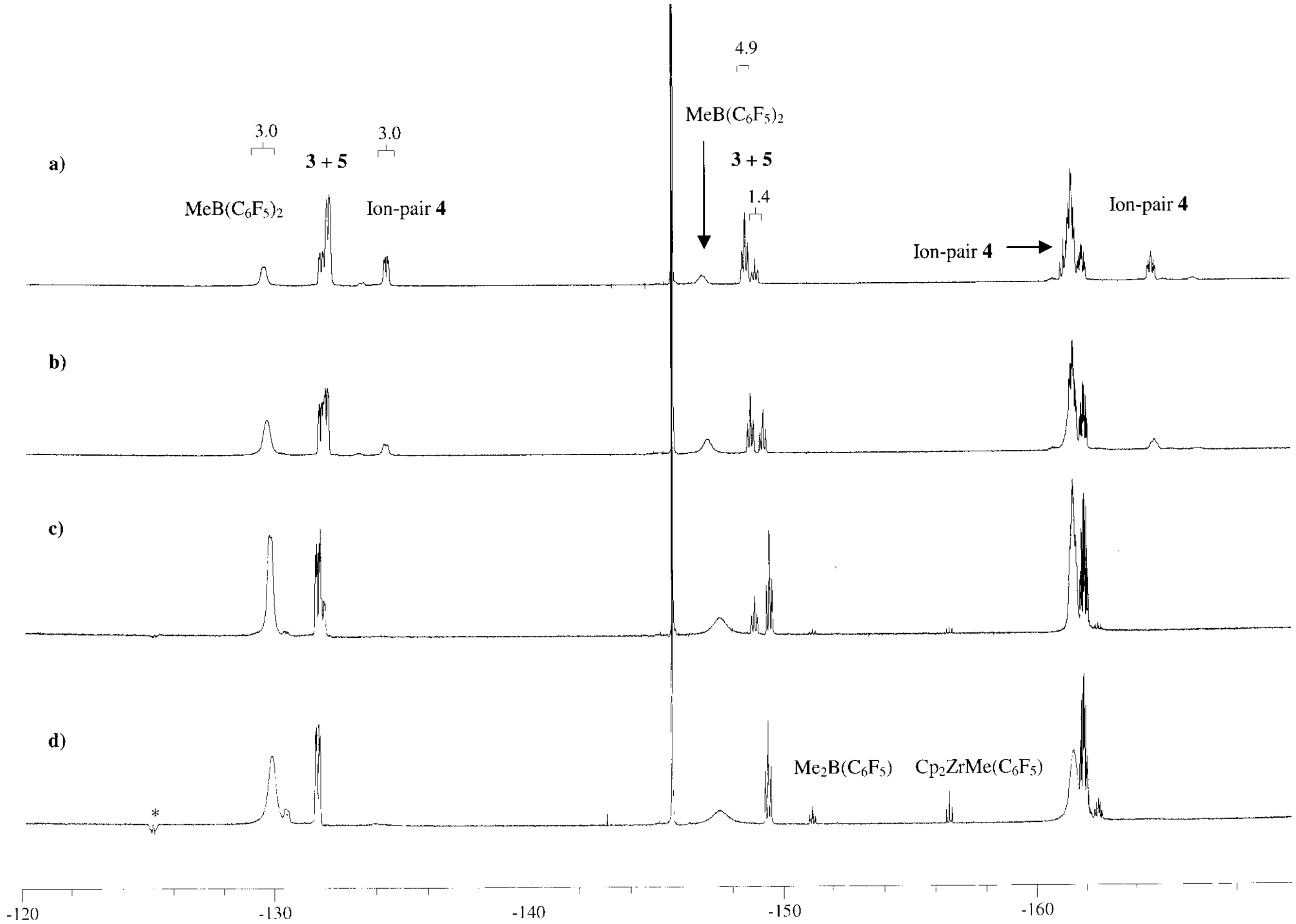
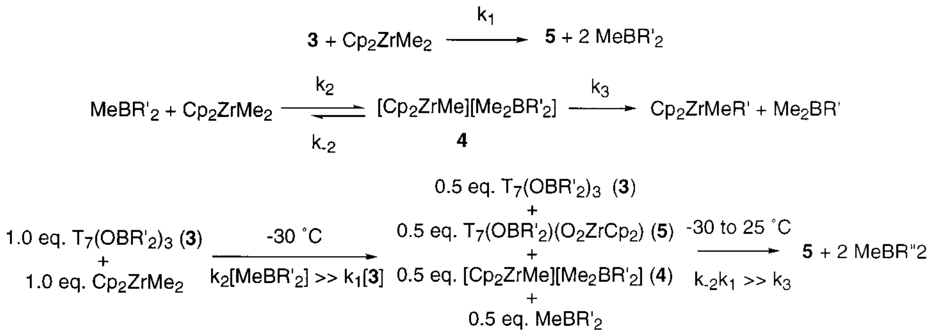


Figure 2. Variable-temperature ^{19}F NMR spectra of a 1:1 mixture of compound **3** and Cp_2ZrMe_2 at (a) 243 K, (b) 268 K, (c) 298 K, and (d) 298 K after the addition of 0.4 equiv of Cp_2ZrMe_2. Tetrafluoro-*p*-xylene added as an internal standard. Integrals are denoted by brackets in part a. The peak in part d marked with an asterisk is the inverted *o*-F signal due to $Cp_2ZrMe(C_6F_5)$ (δ −115 ppm).

Scheme 1



$$\mathbf{3} + Cp_2ZrMe_2 \xrightarrow{k_1} \mathbf{5} + 2\ MeBR'_2$$

$$MeBR'_2 + Cp_2ZrMe_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{4}}{[Cp_2ZrMe][Me_2BR'_2]} \xrightarrow{k_3} Cp_2ZrMeR' + Me_2BR'$$

$$\begin{array}{c}1.0\ eq.\ T_7(OBR'_2)_3\ (\mathbf{3})\\ +\\ 1.0\ eq.\ Cp_2ZrMe_2\end{array} \xrightarrow[k_2[MeBR'_2] \gg k_1[\mathbf{3}]]{-30\ ^\circ C} \begin{array}{c}0.5\ eq.\ T_7(OBR'_2)_3\ (\mathbf{3})\\ +\\ 0.5\ eq.\ T_7(OBR'_2)(O_2ZrCp_2)\ (\mathbf{5})\\ +\\ 0.5\ eq.\ [Cp_2ZrMe][Me_2BR'_2]\ (\mathbf{4})\\ +\\ 0.5\ eq.\ MeBR'_2\end{array} \xrightarrow[k_{-2}k_1 \gg k_3]{-30\ to\ 25\ ^\circ C} \mathbf{5} + 2\ MeBR''2$$

(to form **5**), while detectable amounts of $Cp_2Zr(C_6F_5)Me$ and $Me_2BC_6F_5$ were also formed at the expense of $MeB(C_6F_5)_2$ (Figure 2d).

These observations can be explained with reference to Scheme 1. The competitive formation of ion-pair **4** and compound **5** from **3** and Cp_2ZrMe_2 indicates that reaction of Cp_2ZrMe_2 with **3** (to form **5**) is slow compared to its ionization by the byproduct $MeB(C_6F_5)_2$ to form **4**. Thus, at a 1:1 stoichiometry of **3** and Cp_2ZrMe_2, all of the Cp_2ZrMe_2 is consumed at low temperature and roughly equal amounts of **4** and **5** [and $MeB(C_6F_5)_2$] are formed along with unreacted compound **3** (Figure 2a).

On warming to room temperature, ion-pair **4** is consumed, but the net effect of this process is to convert unreacted compound **3** to **5**. While it is possible that ion-pair **4** might directly react with **3** to form **5** and $MeB(C_6F_5)_2$, a more likely explanation is that formation of **4** from $MeB(C_6F_5)_2$ and Cp_2ZrMe_2 is reversible (eq 2),[21] and the rate at which **3** reacts with Cp_2ZrMe_2 (reversibly generated from **4**) to form **5** must exceed that for independent decomposition of **4** (Scheme 1). Only when consumption of **3** is essentially complete and excess Cp_2ZrMe_2 has been added are significant quantities of the

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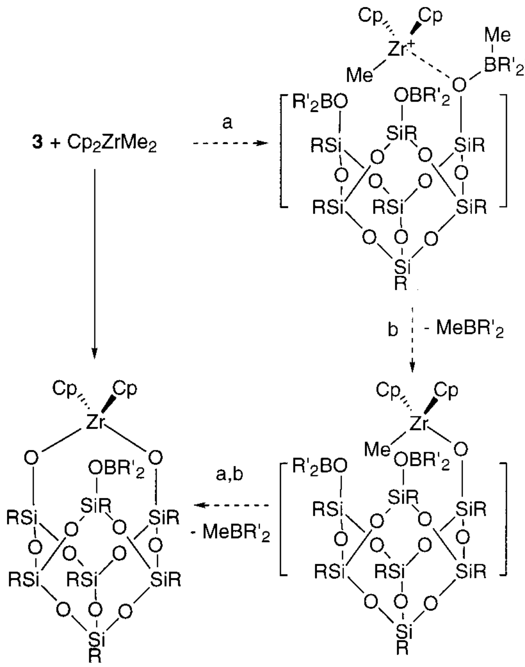
[21] The ^1H NMR spectrum of ion-pair **4** at −30 °C exhibits a reasonably sharp signal for the Zr-Me group superimposed on a very broad signal due to the B-Me groups. At higher temperatures, the former signal is exchange-broadened, and a single broad signal for both Zr-Me and B-Me groups is seen at ≤25 °C, suggesting reversible ionization.

Scheme 2



expected byproducts arising from decomposition of ion-pair **4** formed (eq 2, Figure 2d).

Although it might be tempting to attribute the polymerization results (vide supra) to, for example, enhanced stability of the putative ion-pair derived from **3** and Cp_2ZrMe_2 in the presence of monomer, it is much more likely that the observed polymerization activity results from in-situ formation of ion-pair **4** on the basis of the chemistry observed (Scheme 1). We have previously shown that this ion-pair is a viable ethylene polymerization catalyst when generated in situ from Cp_2ZrMe_2 and $MeB(C_6F_5)_2$,[16] and the polymerization activity and MWD observed under these conditions are comparable to that observed here (given that the amount of **4** formed in situ from **3** and Cp_2ZrMe_2 during polymerization is unknown).

The ultimate formation of compound **5** and $MeB(C_6F_5)_2$ from **3** and Cp_2ZrMe_2 can be viewed as arising from methide abstraction to form an (unstable) ion-pair, with subsequent back-transfer of the silsesquioxane cage to Zr [and elimination of $MeB(C_6F_5)_2$], followed by an intramolecular version of this same process (Scheme 2). The overall chemistry is consistent with that observed for reactions of Cp_2ZrMe_2 with hydroxylated silica modified by $(C_6F_5)_2BX$ (X = Cl or H), where formation of $MeB(C_6F_5)_2$ as a soluble byproduct was also inferred (but not directly observed),[4] and readily explains the low polymerization activity observed for the resulting supported catalysts, i.e., predominant formation of inactive, surface-bound $Cp_2Zr(OSi)_n$ species.

On the basis of work with silsesquioxane-ligated metallocenes,[8,18] it is now appreciated that such moieties may be reactivated by MAO, thus highlighting the unique utility of silsesquioxanes as models for silica-supported catalysts.[1-4] Future work along these lines will focus on the use of silsesquioxanes as models for tethered ansa-metallocene complexes[22] given the striking similarities in the chemistry of soluble versus supported cocatalysts seen here.

Experimental Section

General Procedures. All solvents and chemicals were reagent grade and purified as required. All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted. Tetrahydrofuran, diethyl ether, hexane, toluene, and dichloromethane were dried and deoxygenated by passage through columns of A2 alumina and Q5 deoxo catalyst as described in the literature.[23] $(c\text{-}C_5H_9)_7T_7(OH)_3$ (**1**) was obtained from Aldrich Chemical Co., while Bio-Beads SX-2 were purchased from BioRad Laboratories. The latter material had to be dried by refluxing with Me_3SiCl followed by filtration and drying in vacuo; it was further deactivated by passage of solution of either $MeB(C_6F_5)_2$ or **2b** in toluene down a column followed by rinsing with dry toluene. Compounds **2a**[9] and **2b**[10] and Cp_2ZrMe_2[24] were synthesized using literature methods, while $MeB(C_6F_5)_2$ was synthesized from reaction of Cp_2ZrMe_2 with 2 equiv of **2b**.[4]

Routine ^1H and ^{13}C NMR spectra were recorded in benzene-d_6 or $CDCl_3$ solution on either a Bruker AM-250, AC-200, or AC-300 or Varian Mercury 300 spectrometer. Low-temperature ^1H and ^{19}F NMR spectra were recorded using a Bruker AC-200 spectrometer in toluene-d_8/bromobenzene-d_5 solution using a solution of methanol in CD_3OD for temperature calibration purposes and tetrafluoro-para-xylene as an internal reference (−145.69 ppm relative to $CFCl_3$). ^{11}B and ^{29}Si NMR spectra were recorded on a Bruker AC-200 spectrometer and are referenced to external $BF_3{\cdot}OEt_2$ and Me_4Si, respectively; baseline subtraction was used in the former case to minimize the intensity of signals arising from borosilicate glass in the tube and probehead. Elemental analyses were determined by Oneida Research Services, Inc. New York.

***endo*-3,7,14-Tris{[bis(pentafluorophenyl)boryl]oxy}-1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1^{5,11}]heptasiloxane, 3.** *endo*-Trisilanol **1** (500 mg, 0.57 mmol) was suspended in 10 mL of hexane at room temperature. Then $(C_6F_5)_2BCl$ (650 mg, 1.71 mmol, 3.0 equiv), dissolved in hexane (5 mL), was added dropwise, via cannula, to the stirred suspension of compound **1**. The suspension became clear as compound **1** dissolved within minutes upon addition of the $(C_6F_5)_2BCl$. The solution was stirred at room temperature for 30 min, and the solvent was removed under vacuum. The crude product (980 mg, 90% yield), which was substantially pure by ^{19}F NMR spectroscopy, could be further purified by low-temperature recrystallization (−32 °C) from hexane. Compound **3**: ^1H NMR (200 MHz, C_6D_6) δ 1.11−1.15 (br m, 7H), 1.61−1.66 (br, m 28 H) 1.86 (br m, 28 H); ^{19}F NMR (188 MHz, C_6D_6) δ −131.88 (m, *o*-F), −148.46 (tt, J = 20.0, 5.6 Hz, *p*-F), −161.32 (m, *m*-F); ^{11}B NMR (64.2 MHz, C_6D_6) δ 38.1 (br); $^{13}C\{^1H\}$ NMR (50.3 MHz, DEPT-135, C_6D_6) δ 27.74 (CH_2), 27.69 (CH_2), 27.62 (CH_2), 27.34 (CH_2), 27.15 (CH_2), 24.3 (CH, 3), 23.9 (CH, 3) 22.9 (CH, 1); $^{29}Si\{^1H\}$ NMR (39.7 MHz, 0.02 M $Cr(acac)_3$ toluene-d_8) δ −66.95 (3), −66.26 (3), 65.5 (1). Anal. Calcd for $C_{71}H_{63}B_3F_{30}O_{12}Si_7$: C, 44.71; H, 3.33; F, 29.88. Found: C, 44.34; H, 3.22; F, 29.85.

Crystals for X-ray analysis were obtained by dissolving 125 mg of compound **3** in a minimum amount of hot hexane (~0.5 mL) and then allowing the solution to slowly cool to room temperature. This produced large, colorless prisms. A crystal of dimensions 0.40 × 0.30 × 0.25 mm was mounted on the goniometer head of a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream at 200 K, and data were

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(22) Tian, J.; Ko, Y.-S.; Metcalfe, R. A.; Feng, Y.; Collins, S. *Macromolecules* **2001**, *34*, 3120.

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *13*, 1518.

(24) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 162.

collected using ϕ frames. From a total of 22 592 absorption-corrected reflections measured [$2\theta(\max) = 54.2°$], 17 266 were unique ($R_{\mathrm{int}} = 0.025$) with 14 106 considered observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix, least-squares methods based on F^2 (SHELXTL-IRIX). Two cyclopentane rings were found to be conformationally disordered, which could be modeled by including atoms C4A/C4B and C13A/C13B in the refinement with 50:50 and 80:20 site occupancies, respectively. Final $R(F)$ and $wR(F^2)$ were 0.0418 and 0.0975 with maximum residuals of 0.51 and −0.50 e Å^3. Selected crystallographic and refinement data appear in Table 1, and selected bond lengths and angles in Table 2. Full details of the structure are included in the Supporting Information.

Synthesis of Compound 5. Compound **3** (342 mg, 0.179 mmol) was dissolved in 3 mL of toluene, and the solution cooled to −15 °C. Then, Cp_2ZrMe_2 (90.0 mg, 0.356 mmol) was dissolved in 1 mL of toluene, and this solution was also cooled to −15 °C. The latter solution (500 μL, 1.0 equiv) was slowly added to the solution of compound **3** via syringe. The yellow solution was stirred for 20 min at −15 °C, the cooling bath was removed, and on warming to room temperature the solution was stirred for an additional 20 min. The solution decolorized upon warming. An additional 100 μL (0.2 equiv) of the Cp_2ZrMe_2 solution was added at room temperature, and stirring was continued for 30 min.

The volume was reduced by half under vacuum, and the solution was transferred into a glovebox. The solution was chromatographed on purified Bio Beads SX-2 (10.525 g of dry beads swollen in dry toluene, column bed volume ~40 mL) eluting with toluene. Five fractions were collected in the following amounts: 10, 5, 10, 10, and 50 mL, and ^{19}F NMR spectra were recorded of each fraction. The third fraction contained the desired compound, while the fourth contained a mixture of this compound and $MeB(C_6F_5)_2$. The latter fraction was concentrated and then rechromatographed to provide additional material. Fractions containing only compound **5** were combined and concentrated in vacuo to provide an oil. A white solid was obtained after freeze-drying a benzene solution of this oil (140 mg, 54% yield). Compound **5**: ^{1}H NMR (200 MHz, toluene-d_8) δ 1.19 (br m, 7H), 1.67 (br, m 28 H) 1.91 (br m, 28 H), 6.02 (s, 10 H); the latter signal appears as two closely spaced singlets (5 H each) in mixed toluene-d_8/bromobenze-d_5 solution at lower temperatures; ^{19}F NMR (188 MHz, toluene-d_8) δ −131.71 (m, *o*-F), −149.27 (tt, J = 20.8, 5.3 Hz *p*-F), −161.86 (m, *m*-F); ^{11}B NMR (64.2 MHz, toluene-d_8) δ 32.9 (br); ^{29}Si{^{1}H} NMR (39.7 MHz, 0.02 M Cr(acac)$_3$ toluene-d_8) δ −64.39 (1 Si), −64.87 (2 Si), −65.21(1 Si), −65.56 (1 Si), −66.62 (2 Si). Anal. Calcd for $C_{57}H_{73}BF_{10}O_{12}Si_7Zr$: C, 47.59; H 5.11; F, 13.21. Found: C, 51.15; H, 5.24; F, 14.58.

Subsequent work has revealed that this compound is unstable in solid form and in concentrated solution. The nature of the decomposition process is as yet unclear but may be responsible for the unsatisfactory analysis obtained. A solid sample stored in a glovebox for a period exceeding 6 months at room temperature was found not to contain detectable C_6F_5 groups (!), while oily samples noticeably decompose after several days at room temperature to form a complex mixture. This compound is reasonably stable (~1 week) when stored at −30 °C under N_2 or in dilute solution at room temperature.

^{19}F and ^{1}H NMR Reaction between Compound 3 and Cp_2ZrMe_2. A stock solution containing 47.7 mg of 2,3,5,6-tetrafluoro-*p*-xylene dissolved in 1500 μL of solvent (55:45 v/v of toluene-d_8/bromobenzene-d_5) was prepared. Using this solution, a 600 μL solution containing 134.6 mg (0.070 mmol) of compound **3** and a 500 μL solution containing 80.1 mg (0.317 mmol) of Cp_2ZrMe_2 were prepared. Small aliquots were removed, and the ^{19}F NMR spectrum of the first solution and the ^{1}H NMR spectrum of the second solution were recorded. On the basis of integration of signals due to compound **3** and Cp_2ZrMe_2 with respect to the tetrafluoro-*p*-xylene standard, the volume of each required to give a 1:1 stoichiometry was calculated.

To 350 μL of a solution of compound **3** in an NMR tube was added ~64 μL of the solution of Cp_2ZrMe_2 at −80 °C. The tube was quickly shaken to mix the contents and then transferred to a probe maintained at −80 °C. ^{19}F and ^{1}H NMR spectra were recorded while the temperature was increased in ca. 10° increments. Representative ^{19}F NMR spectra are shown in Figure 2.

^{19}F and ^{1}H NMR Reaction between Cp_2ZrMe_2 and $MeB(C_6F_5)_2$. A similar procedure was employed as that described above using about 0.1 mmol of each compound, and the ion-pair **4** was generated at ca. −40 °C before being transferred into the NMR probe maintained at −30 °C. Variable-temperature ^{19}F and ^{1}H NMR spectroscopic data are provided in the Supporting Information. Ion-pair **4**: ^{1}H NMR (200 MHz, 55:45 v/v of toluene-d_8/bromobenzene-d_5, −30 °C) δ 5.78 (s, 10 H, Cp) 0.35 (s, 3H, ZrMe) superimposed on 0.30 (v br s, 6H BMe_2); at higher T (e.g., 0 °C) the signals due to both Zr-Me and B-Me groups are coincident and exchange-broadened; ^{19}F NMR (188 MHz, 55:45 v/v of toluene-d_8/bromobenzene-d_5, −30 °C) δ −134.2 (dd, *o*-F), −160.95 (t, *p*-F) −164.55 (m, *m*-F). On warming the solution to room temperature, decomposition of **4** occurred to provide $Me_2B(C_6F_5)$ and $Cp_2ZrMe(C_6F_5)$. For spectroscopic data see ref 4 and Supporting Information.

^{19}F and ^{1}H NMR Reaction between Compound 3 and MeAl(BHT)$_2$. A solution of MeAl(BHT)$_2$ in benzene-d_6 (27 mg. 0.062 mmol in 1.0 mL) was prepared at room temperature, and about 0.5 mL of this solution was used to dissolve compound **3** (20 mg, 0.010 mmol). ^{19}F and ^{1}H NMR spectra were recorded periodically every few minutes, but no reaction was evident after = 1 h and 24 h at 25 °C. The concentrations of MAD and **3** employed here are about 50× and 167× higher, respectively, than those employed in the following polymerization experiments.

Polymerization Experiments. Detailed polymerization procedures and methods for polymer characterization are described in the literature.[25] In the first experiment summarized in the text, 10.0 mL of a solution of Cp_2ZrMe_2 (2.5 mM in toluene) was added to a solution of compound **3** (3.0 mM) in 10.0 mL of toluene in a glovebox, and the resulting solution was transferred to a sample bomb, which was then attached to a polymerization reactor containg 480 mL of toluene, presaturated with ethylene at 75 psi at 30 °C, 1000 rpm, and containing 272 mg (0.625 mmol) of MeAl(BHT)$_2$ as a scrubbing agent. The contents of the sample vessel were introduced into the reactor (after a total period of about 15 min at room temperature) by slightly overpressurizing the vessel with dry nitrogen while stirring at 1000 rpm. In this case, ethylene uptake was minimal (as measured by a calibrated mass flow meter), and only trace quantities of PE were obtained (i.e., <100 mg) after 60 min.

The second experiment involved prior addition of a solution of compound **3** to the reactor in the same manner, followed by the addition of a solution of Cp_2ZrMe_2 shortly thereafter. In this case, after a brief induction period of <5 min duration, rapid uptake of ethylene was observed and steady consumption of ethylene at a rate of 0.21 ± 0.02 mmol s^{-1} was observed for a total period of 35 min. The reactor was quenched by the addition of a small quantity of MeOH and then vented. A total of 10.5 g of PE was recovered by filtration, washing with MeOH, and then drying in vacuo.

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(25) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000, and references therein.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H atom coordinates, and isotropic thermal parameters for compound **3**. Variable-temperature ^1H and ^{19}F NMR spectra of the reaction of $MeB(C_6F_5)_2$ and **3** with Cp_2ZrMe_2 in toluene-d_6/bromobenzene-d_5 solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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