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Silica-Grafted Borato Cocatalysts for Olefin Polymerization Modeled by Silsesquioxane−Borato Complexes

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The syntheses and reactivity studies of silsesquioxane−borato complexes are described. Treatment of $B(C_6F_5)_3$ with $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ in the presence of a Brønsted base yields the silsesquioxane−borates $X^+\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-$ (**1a**, $X^+ = PhN(H)Me_2^+$; **1b**, $X^+ = Et_3NH^+$) and $X^+\{[(c\text{-}C_5H_9)_7Si_7(OH)_2O_{10}]B(C_6F_5)_3\}^-$ (**1b**, $X^+ = PhN(H)Me_2^+$; **2b**, $X^+ = Et_3NH^+$), respectively. When the more nucleophilic base pyridine is used, $(C_6F_5)_3B{\cdot}NC_5H_5$ (**3**) is formed instead, demonstrating the competition between $B(C_6F_5)_3$ and H^+ to react with the amine. The dimethylaniline in **1a** and **2a** is readily exchanged by NEt_3 to form **1b** and **2b**. With the nucleophilic Lewis base NC_5H_5, the B−O bond in **1a** and **2a** is split, yielding $(C_6F_5)_3B{\cdot}NC_5H_5$ (**3**) and the free silsesquioxanes. Complexes **1** and **2** rapidly undergo hydrolysis under formation of the hydroxyl complexes $X^+\{(C_6F_5)_3BOH\}^-$ (**4a**, $X^+ = PhN(H)Me_2^+$; **4b**, $X^+ = Et_3NH^+$). Likewise, alcoholysis of **1a** and **2a** with *i*-PrOH yields the alkoxide $\{PhN(H)Me_2\}^+\{i\text{-}PrOB(C_6F_5)_3\}^-$ (**5**). The B−O bond is only moderately stable toward early-transition-metal alkyls. Nevertheless, $Cp_2Zr(CH_2Ph)_2$ + **1a** and $Zr(CH_2Ph)_4$ + **2a** form single-site ethylene polymerization catalysts. Detailed reactivity studies demonstrated that both B−O and B−C bond splitting plays a crucial role, as not **1a** and **2a**, but their decomposition product $B(C_6F_5)_3$ is the actual cocatalyst. The solid-state structures of **1a** and **4b** were determined by single-crystal X-ray analysis.

Introduction

For the industrial production of polyolefins heterogeneous catalysts are generally preferred over homogeneous ones. For example, the polymers formed in gasphase, slurry, or bulk-monomer processes are usually of high density and are insoluble in most solvents. For these processes only heterogeneous catalysts allow polymer morphology control and narrow particle size distribution and avoid reactor fouling.[1] Besides traditional heterogeneous olefin polymerization catalysts (Ziegler−Natta, Phillips),[1] immobilization of well-defined homogeneous metallocene catalysts is receiving increasing interest.[2,3] The most common immobilization technique consists of adsorption of a combination of methylalumoxane (MAO) and the metallocene precursor onto a silica support.[2]

In search of alternatives for MAO, weakly coordinating boron-based cocatalysts such as $X^+\{B(C_6F_5)_4\}^-$ ($X^+ = PhN(H)Me_2^+$, Ph_3C^+) and $B(C_6F_5)_3$ have been found to effectively activate metallocenes.[4] Hence, immobilized borato cocatalysts might also afford well-defined heterogeneous olefin polymerization catalysts. Reports on immobilization of boron-based cocatalysts have appeared nearly exclusively in patent literature.[5,6] Most commonly the borates are physisorbed or tethered to

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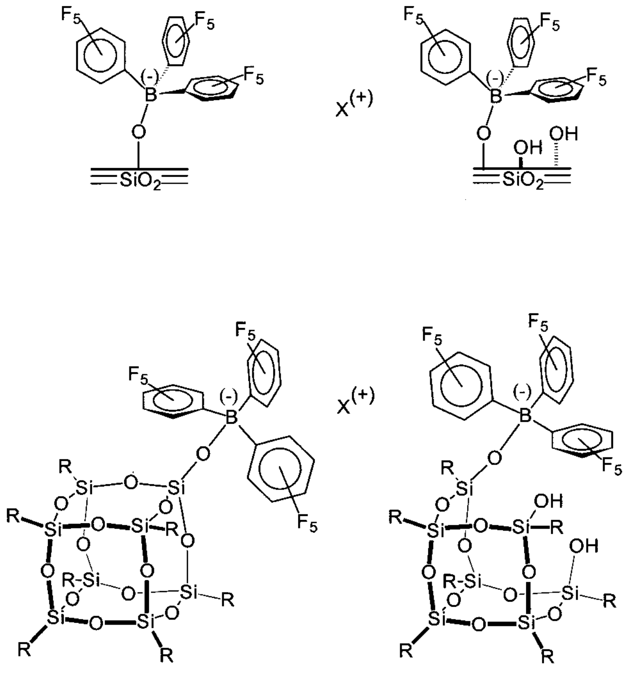
Chart 1. Silica-Supported Borate Cocatalysts and Their Silsesquioxane Based Analogues



1a-b **2a-b**

R = c-C_5H_9; X^+ = $PhN(H)Me_2^+$ (**1a**, **2a**), Et_3NH^+ (**1b**, **2b**).

the support. Interestingly, effective olefin polymerization cocatalysts formed by simply grafting $B(C_6F_5)_3$ onto silica in the presence of an amine have been claimed (Chart 1).[5d,7] Comparable $X^+\{(C_6F_5)_3BOR\}^-$ (R = alkyl; X = H, Et_3NH) complexes have been used as cocatalysts in olefin polymerization as well.[8] To our knowledge, however, no serious investigations on the stability and reactivity of the B–O bond of siloxy–borato species formed upon grafting onto silica[5d,7] have been reported.

As part of our interest in developing useful immobilization strategies,[9] we tried to get an insight into the stability of the B–O bond and the suitability of silica-grafted borato species as olefin polymerization cocatalysts. As homogeneous model systems are much easier to characterize than those of amorphous silica, they provide a powerful tool to study the interaction of substrates, such as boranes, with silanol sites. We used silsesquioxanes, soluble auxiliaries that have proven to be realistic models for a variety of silica surface silanol sites.[9,10]

Here we describe the synthesis of several silsesquioxane–borato complexes. The stability of the B–O bond in these complexes is studied in detail, as well as the applicability of the siloxy–borato systems as cocatalysts in olefin polymerization reactions.

Results and Discussion

Chart 1 shows two possible silica surface sites containing a grafted boron cocatalyst and their homogeneous analogues that have been mimicked using the silsesquioxanes $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ ($c\text{-}C_5H_9$ = cyclopentyl), respectively.

As is indicated by the broad signals in the ^{19}F NMR (toluene-d_8), in the absence of a proton acceptor, the silsesquioxanes $[(c\text{-}C_5H_9)_7Si_8O_{12}(OH)]$ and $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ form fluxional, weakly bonded adducts with the borane $B(C_6F_5)_3$ (Scheme 1). In the presence of proton acceptors such as the strong Brønsted basic amines $PhNMe_2$ and NEt_3,[11] equimolar amounts of the silsesquioxanes and $B(C_6F_5)_3$ react to yield the stable silsesquioxane–borato ammonium salts **1** and **2** (Chart 1 and Scheme 1). Interestingly, the more nucleophilic Lewis base pyridine yield the borane base adduct $(C_6F_5)_3B{\cdot}Py$ (**3**) instead (Scheme 1). This clearly indicates that high Brønsted basicity and low nucleophilicity of the amine are required to form the desired silsesquioxane–borato complexes (Scheme 1).

Ammonium silsesquioxane borates $X^+\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-$ (**1a**, $X^+ = PhN(H)Me_2^+$; **1b**, $X^+ = Et_3NH^+$) are very soluble in toluene and even slightly soluble in hexane. In contrast, the silsesquioxane bis(silanol) borato complexes $X^+\{[(c\text{-}C_5H_9)_7Si_7(OH)_2O_{10}]B(C_6F_5)_3\}^-$ (**2a**, $X^+ = PhN(H)Me_2^+$; **2b**, $X^+ = Et_3NH^+$) are only moderately soluble in toluene and insoluble in hexane. The ^{13}C and ^{29}Si NMR spectra of **1a** and **1b** are in agreement with a C_3-symmetric structure in solution. With five methine and silicon resonances in a 1:1:1:2:2 ratio, the ^{13}C and ^{29}Si spectra of **2a** and **2b** support the expected C_{2v} symmetric structure. The ^{13}C, ^{19}F, and ^{29}Si NMR resonances for the silsesquioxane–borato anion of **1a** are significantly shifted with respect to those of **1b**. The NH resonance in the ^1H NMR of **1a** is found at 9.40 ppm, which is typical for a hydrogen-bonded NH group. The high-field shift of the NH resonance of **1b** to 4.25 ppm suggests an even stronger

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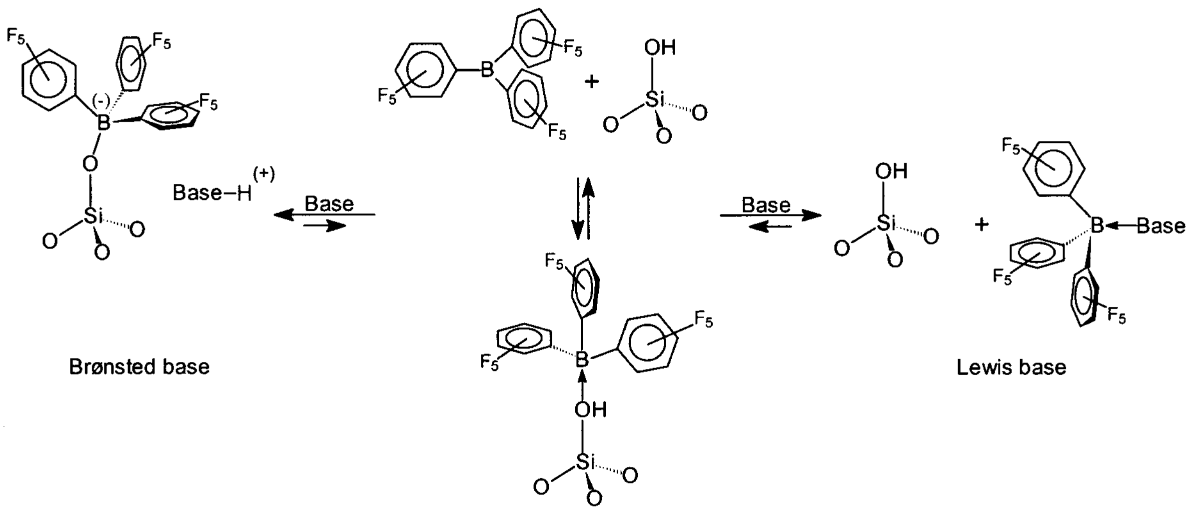
Scheme 1. Deprotonation versus Adduct Formation Depending on the Proton-Accepting Capability of the Base



interaction of the ammonium cation with the silsesquioxane−borato anion of **1b** than in **1a**.[12] For **2a** and **2b**, the differences in the ^{13}C, ^{19}F, and ^{29}Si NMR are much smaller, indicating that in the latter type of silsesquioxane−borates strong cation−anion interaction is less apparent.[13] Possible intramolecular hydrogen bonding in the anions of **2a** and **2b** may also explain the smaller shift differences observed as compared to those in the anions of **1a** and **1b**.[14]

Definite proof for an interaction between the ammonium cation and the silsesquioxane−borato anion in **1a** was provided by a single-crystal X-ray analysis (Figure 1). The ammonium cation is clearly hydrogen-bonded to the silsesquioxane−borato anion (N−O1 = 2.874(6) Å). As a result of the hydrogen bridge, the oxygen (O1) adopts a trigonal-planar rather than a linear geometry.[15] Due to the anionic charge at boron in **1a**, the B−O1 bond distance of 1.505(5) Å in **1a** is significantly longer than the B−O distances in the neutral boron-containing silsesquioxane $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]B\}_2$, ranging from 1.325(23) to 1.406(18) Å.[16] The B−O bond distance in **1a** is within the wide range found for transition-metal borato complexes $L_nM{-}O{-}B(C_6F_5)_3$ (L_nM = Ti[η^2-(OCMe)$_2$CH]$_2$, 1.496(3) Å;[15a] L_nM = V[η^2-(OCMe)$_2$CH]$_2$, 1.527(2) Å;[15a] L_nM = Mo(=O)[η^2-(OCMe)$_2$CH]$_2$, 1.521(3) Å;[15a] L_nM = $(C_5H_4Me)_2$Mo, 1.484(2) Å;[15b] L_nM = $(C_5Me_5)_2$Zr, 1.460(6) Å[8b]) and $[L_nM][(C_6F_5)_3BOH]$ (L_nM = $(C_5Me_5)_2$Ta(OH)Me, 1.490(10) Å;[15c] L_nM = (4,4′-di-*tert*-butyl-2,2′-bipyridine)PtMe, 1.526(3) Å[15d]). The B−C bonds in **1a** are normal for borates[15,17] and are significantly elongated (by approximately 0.1 Å) compared to the corresponding B−C bonds in base-free boranes.[18]

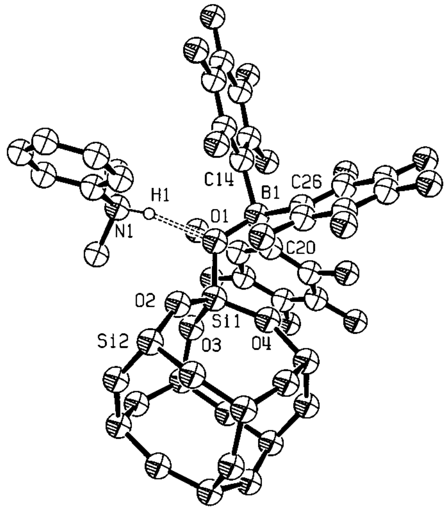


Figure 1. ORTEP drawing of $\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-\{PhN(H)Me_2\}^+$ (**1a**). Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms and cyclopentyl groups are omitted for clarity. Selected bond distances (Å): Si1−O1, 1.615(2); Si1−O2, 1.614(2); Si1−O3, 1.619(2); Si1−O4, 1.604(2); O1−B, 1.505(5); O1−N, 2.874(6); B−C14, 1.669(5); B−C20, 1.657(5); B−C26, 1.656(5). Angles (deg): B−O1−Si1, 125.0(2); B−O1−N, 126.1(2); Si1−O1−N, 107.2(2); O1−Si1−O2, 106.03(13); O1−Si1−O3, 109.44(13); O1−Si1−O4, 112.59(13); O1−B−C14, 110.4(3); O1−B−C20, 105.6(3); O1−B−C26, 111.4(3); C6−N−C7, 113.0(3); C6−N−C8, 110.9(3); C7−N−C8, 110.3(3).

The presence of the hydrogen bridge in **1a** might suggest that the B−O bond is quite labile and that formation of the silsesquioxane−borate is reversible. To verify this possibility, the stability of the B−O bond in silsesquioxane−borato complexes **1** and **2** was determined.

The Lewis acidic $B(C_6F_5)_3$ is known to form stable nitrile and amine adducts $(C_6F_5)_3B{\cdot}L$ (L = MeC≡N,

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[12] The concentrations of NMR tube solutions of **1a**,**b** and **2a**,**b** were comparable, 65(±10) mM.

[13] IR spectra of **1a**,**b** and **2a**,**b** did not provide additional information about possible hydrogen bonding in these complexes.

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Py).[19] Hence, when **1** and **2** are in equilibrium with free silsesquioxane and $B(C_6F_5)_3$, in the presence of excess of Lewis base, the equilibrium is expected to be pushed to the formation of the borane Lewis base adduct. None of the silsesquioxane–borates (**1** and **2**) react with $MeC{\equiv}N$. However, treating a benzene-d_6 solution of **1a** with pyridine gave a significant amount (~30%) of the borane–pyridine adduct $(C_6F_5)_3B{\cdot}NC_5H_5$ (**3**).[20] Benzene-d_6 solutions of **2a** treated with pyridine quantitatively afforded **3**, as the poorly soluble silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ precipitated from the benzene solution, pushing the equilibrium to the formation of the borane–Lewis base adducts **3**. The triethylammonium salts **1b** and **2b** clearly show less tendency to react with Lewis bases, as only a small amount (~7%) of the pyridine adduct **3** was detected by ^1H and ^{19}F NMR spectroscopy (benzene-d_6).[20] The difference in reactivity toward pyridine of **1a**, **2a** compared to that of **1b**, **2b** can be explained on the basis of the different pK_a values of the ammonium ions ($C_5H_5NH^+$, pK_a = 3.5; $PhN(H)Me_2^+$, pK_a = 2.5; Et_3NH^+, pK_a = 9.0).[11] This also agrees with the observation that treating the dimethylanilinium salts **1a** and **2a** with the stronger Brønsted base NEt_3 quantitatively afforded the corresponding triethylammonium salts **1b** and **2b**.

Because of the hydrolyzable nature of the B–O bond, siloxy–borato complexes **1** and **2** are moisture sensitive. Treatment of **1** and **2** with equimolar amounts of water quantitatively yielded the corresponding hydroxyl complexes $\{R_3NH\}^+\{(C_6F_5)_3BOH\}^-$ ($R_3N = PhNMe_2$ (**4a**), NEt_3 (**4b**)). Similarly, alcoholysis of **1a** and **2a** with *i*-PrOH quantitatively affords the corresponding alkoxyborate $\{PhN(H)Me_2\}^+\{i\text{-}PrOB(C_6F_5)_3\}^-$ (**5**), which fits in with the higher acidity of silsesquioxane silanols compared to alcohols.[21]

Figure 2 shows the X-ray structure of **4b**. With an O–N distance of 2.734(6) Å the ammonium cation in **4b** is clearly hydrogen-bonded to the borato oxygen, which corresponds well with the hydrogen bridge found in **1a**. The B–O and B–C bond distances and O–B–C angles in **4b** are virtually identical with those in **1a** and compare well with those of other oxoborates.[15,22] Due to differences in steric bulk compared to that of **1a**, the B–O–N bond angle in **4b** (134.6(3)°) is widened compared to the B–O–N angle in **1a** (126.1(2)°).

From the results above it is clear that substitution of the amine in ammonium siloxyborates **1** and **2** can be accomplished by a stronger Brønsted base. On the other hand, when these compounds are treated with a strong nucleophile, formation of the borane–Lewis base adduct is likely to occur. Depending on its Brønsted/Lewis base character, the base shows a clear preference for either the Brønsted acid H^+ or the Lewis acid $B(C_6F_5)_3$ (Scheme 1). The alkyl substituent in early-transition-metal complexes such as Cp_2MR_2 (M = Ti, Zr, Hf; R = alkyl) can react either as a Brønsted base or a nucleophile. Furthermore, tetravalent group 4 metal ions are strongly oxophilic. Therefore, the question arises whether the B–O bond of siloxyborates is stable in the presence of group 4 metal alkyl complexes. Comparable $X^+\{(C_6F_5)_3BOR\}^-$ (R = alkyl; X = H, Et_3NH) complexes were reported to be stable toward such exchange and have been used as cocatalysts in olefin polymerization.[8a,b,15c] In preliminary polymerization experiments, $Cp_2Zr(CH_2Ph)_2$ activated by **1a** (M_w = 566 000, M_w/M_n = 2.3) and $Zr(CH_2Ph)_4$ activated by **2a** (M_w = 17 000, M_w/M_n = 2.4) did indeed give single-site ethylene polymerization catalysts.

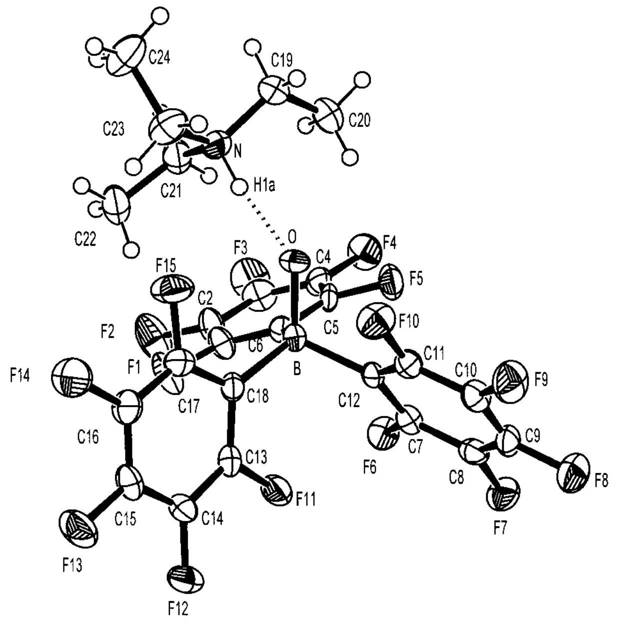

Figure 2. ORTEP drawing of $\{(C_6F_5)_3BOH\}^-\{Et_3NH\}^+$ (**4b**). Ellipsoids are scaled to enclose 50% of the electron density. Selected bond distances (Å): B–O, 1.495(5); B–C6, 1.652(6); B–C12, 1.662(6); B–C18, 1.665(6); O–N, 2.734(6). Angles (deg): O–B–C6, 102.3(3); O–B–C12, 109.3(3); O–B–C18, 112.3(3); B–O–N, 134.6(3).

NMR studies on a toluene-d_8 solution of equimolar amounts of $Cp_2Zr(CH_2Ph)_2$ and **1a** showed that at −25 °C a rapid reaction occurs, yielding the cationic $\{[(c\text{-}C_5H_9)_7Si_8O_{13}]ZrCp_2\}^+\{PhCH_2B(C_6F_5)_3\}^-$ (**6**) as the main product (>90%) (Scheme 2). Hence, the initially formed cationic alkyl complex is rapidly transformed into the inactive cationic silsesquioxane complex **6**. The reaction of $Cp_2Zr(CH_2Ph)_2$ with **1b** is considerably slower. Warming to room temperature is required for the reaction to proceed. This strongly suggests that the first step of the reaction is protonolysis of one of the benzyl groups by the ammonium cation, as protonolysis is more facile for $PhN(H)Me_2^+$ than for the less acidic Et_3NH^+. The concurrent formation of $\{(C_6F_5)_3BCH_2Ph\}^-\{Et_3NH\}^+$ and $[(c\text{-}C_5H_9)_7Si_8O_{13}]Zr(CH_2Ph)Cp_2$ (**7**) indicates that direct exchange between $Cp_2Zr(CH_2Ph)_2$ and **1b** is also possible when protolysis is hampered.[23]

The ^1H NMR spectrum of **6** shows the characteristic broad B*CH*$_2$Ph resonance at 3.60 ppm. With a $\Delta\delta(F_m - F_p)$ value of 2.89 for the $[PhCH_2B(C_6F_5)_3]^-$ group, limited

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[19] (a) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245. (c) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, *521*, 212.

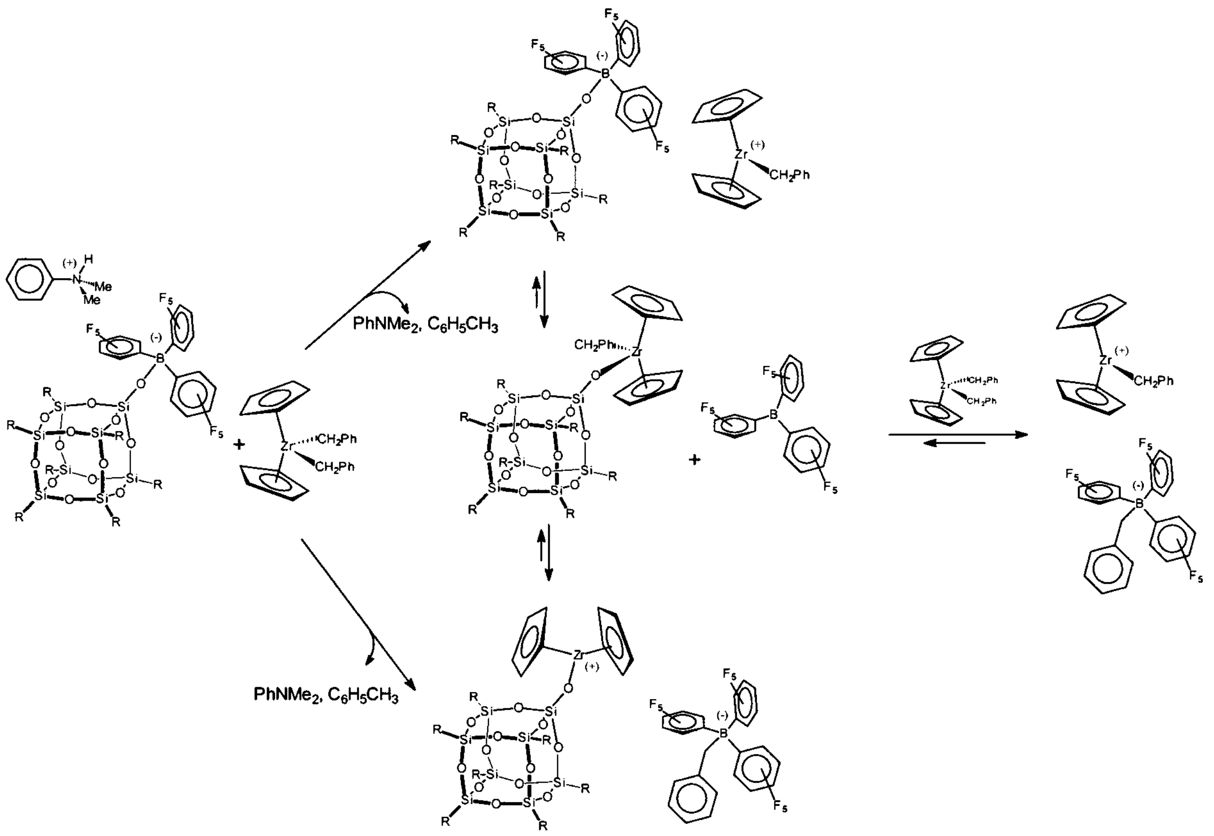
[20] Long reaction time (1 week) did not lead to an increase in the concentration of **3**, indicating that the equilibrium is rapidly established.

[21] pK_a values determined in THF: $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, p$K_a$ = 7.6; $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$, p$K_a$ = 8.9; PhOH, pK_a = 10.0.[9b]

[22] Without referring to an X-ray structure analysis, Siedle et al. reported a B–O bond distance of 1.487(3) Å for $\{(C_6H_5)_3BOH\}^-\{N(H)Et_3\}^+$.[8c]

[23] $\{Et_3NH\}^+\{(C_6F_5)_3BCH_2Ph\}^-$ crystallized from the toluene-d_8 solution: $C_{31}H_{23}BF_{15}N$, monoclinic, $P2_1/n$, a = 13.119(1) Å, b = 14.090(1) Å, c = 17.099(2) Å, β = 109.645(2)°, V = 2976.8(5) Å^3, Z = 4, R = 0.0482, R_w = 0.1167.

Scheme 2. Activation and Poisoning of $Cp_2Zr(CH_2Ph)_2$ by 1a



anion−cation interaction is present in **6**.[24] Complex **6** is stable at −25 °C, but around room temperature it is clearly in equilibrium with the neutral **7** and $B(C_6F_5)$. Since both **6** and **7** are inactive species, only unreacted $Cp_2Zr(CH_2Ph)_2$ activated by the released $B(C_6F_5)_3$ can be held responsible for the observed catalytic activity in ethylene polymerization (Scheme 2). Indeed, when a polymerization experiment was carried out with $Cp_2Zr(CH_2Ph)_2$ plus a slight excess of **1a**, no polyethylene was formed. However, as soon as additional $Cp_2Zr(CH_2Ph)_2$ was added, rapid polymerization occurred. As a control experiment, ethylene polymerization was carried out with $Cp_2Zr(CH_2Ph)_2$ as catalyst precursor activated with $B(C_6F_5)_3$ in the presence of $PhNMe_2$. As expected, a considerably larger exotherm was observed than when **1a** was used, since only a fraction of **1a** is transformed into the actual cocatalyst $B(C_6F_5)_3$. This is in agreement with the difference in observed activity between $Cp_2Zr(CH_2Ph)_2$ + **1a** (0.4×10^6 g of PE ((mol of [Zr]) h)$^{-1}$) and $Cp_2Zr(CH_2Ph)_2 + B(C_6F_5)_3/PhNMe_2$ (1.6×10^6 g of PE ((mol of [Zr]) h)$^{-1}$) and may explain the lower molecular weight and broader molecular weight distribution of the polymer of the latter system (M_w = 177 500, $M_w/M_n = 4.5$).

Not surprisingly, the B−O bond in the silsesquioxane−borate **2a** is also unstable to zirconium alkyls. A variable-temperature (−30 to 40 °C) ^1H and ^{19}F NMR study on a toluene-d_8 solution containing equimolar amounts of $Zr(CH_2Ph)_4$ and **2a** showed the formation of $B(C_6F_5)_3$ and $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2Zr_2CH_2Ph\}^+\{PhCH_2B(C_6F_5)_3\}^-$ in a 1:1 ratio.[9a] The latter complex has been reported to be the active ethylene polymerization catalyst formed upon treatment of $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]ZrCH_2Ph\}_2$ with $B(C_6F_5)_3$.[9a] Indeed, the low-molecular-weight polyethylene formed by the $Zr(CH_2Ph)_4$ + **2a** system (25 °C, M_w = 17 000) resembles that of $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2Zr_2CH_2Ph\}^+\{PhCH_2B(C_6F_5)_3\}^-$ (80 °C, M_w = 7000)[9a] (cf. $\{Zr(CH_2Ph)_3\}^+\{PhCH_2B(C_6F_5)_3\}^-$, M_w = 500 000).[25]

Variable-temperature NMR studies on toluene-d_8 solutions of equimolar amounts of $Cp_2Zr(CH_2Ph)_2$ and $\{PhN(H)Me_2\}^+\{(C_6F_5)_3BOR\}^-$ (R = H (**4a**), *i*-Pr (**5**)) also showed the formation of considerable amounts of $B(C_6F_5)_3$ as one of the side products. Like the silsesquioxane−borates, these alkoxy- and hydroxyborates only show catalytic activity in the presence of an excess of $Cp_2Zr(CH_2Ph)_2$.

Conclusions

The silsesquioxane−borates are useful soluble models that can provide significant information about reactions taking place at silica surfaces. Although stable in apolar solvents, the silsesquioxane−borato species reported in this study show a limited stability toward both Brønsted and Lewis bases. Ammonium ions can easily be exchanged, and with strong nucleophiles, splitting of the B−O bond is likely to occur. B−O bond breaking by hydrolysis or alcoholysis is also facile, emphasizing that the silsesquioxane is more acidic than alcohols and water and therefore less able to stabilize the high Lewis acidity of $B(C_6F_5)_3$. The silsesquioxane−borates are also unstable toward zirconium alkyl species. Although protonolysis of the benzyl group by the ammonium

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(24) (a) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (b) Horton, A. D.; de With, J.; van der Linden, A. J.; van der Weg, H. *Organometallics* **1996**, *15*, 2672.

(25) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633.

cation seems to be the first step for the reaction, the thus formed cationic alkyl complex is rapidly transformed into the inactive cationic silsesquioxane complex **6**. Whereas the facile B−O bond splitting makes the silsesquioxane−borato systems unsuitable as cocatalysts, subsequent B−C bond breaking and formation of $B(C_6F_5)_3$ explains the fact that ethylene polymerization activity is still observed. On the basis of these results it is likely that the B−O bond in silica-grafted borates is also labile. Hence, under influence of transition-metal alkyls, silica-grafted borates are assumed to be transformed into physisorbed borane, which can be considered as being the actual cocatalyst.

Experimental Section

General Comments. All manipulations were performed under an argon atmosphere using glovebox (Braun MB-150 GI) and Schlenk techniques. Solvents were distilled from Na (toluene), K (THF), Na/K alloy (ether, hexanes), or CaH_2 (CH_2Cl_2) and stored under argon. NMR solvents were dried over Na/K alloy (benzene-d_6) or 4 Å molecular sieves (toluene-d_8, $CDCl_3$, CD_2Cl_2, C_6D_5Br). NMR spectra were recorded on Varian GEMINI 300 and Varian 400 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C NMR) or external standards (^{29}Si, $SiMe_4$ at 0 ppm; ^{19}F, CF_3CO_2H at 0 ppm). Elemental analyses were carried out at the Analytical Department of the University of Groningen (Groningen, The Netherlands). The molecular weights and molecular-weight distributions were measured at 135 °C by gel-permeation chromatography (GPC; GPC210, Polymer Labs) at the University of Groningen, using 1,2,4-trichlorobenzene as solvent. Silsesquioxanes $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$[9] and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$[10] were prepared by following literature procedures.

$\{PhN(H)Me_2\}^+\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-$ (1a). Solid $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ (2.42 g, 2.64 mmol) was added to a solution of $B(C_6F_5)_3$ (1.35 g, 2.64 mmol) in toluene (25 mL). The mixture was stirred and warmed until a clear solution was obtained. $PhNMe_2$ (0.35 mL, 2.76 mmol) was then added and the resultant solution warmed to reflux. The volatiles were evaporated, leaving crude **1a** as a white foam. Crystallization from a 1:5 toluene−hexane mixture (30 mL) yielded **1** as colorless crystals (1.80 g, 1.16 mmol, 44%). After the mother liquor was evaporated to dryness, the remaining solid was dissolved in hot hexane (20 mL). Crystallization at −30 °C gave a second crop of colorless crystals of **1a** (0.8 g, 0.52 mmol, 19%). ^{1}H NMR (benzene-d_6, δ): 9.40 (s-br, 1H, $PhN(H)Me_2$), 6.75 (m, 5 H, $C_6H_5N(H)Me_2$), 2.36 (s, 6H, $PhN(H)(CH_3)_2$), 1.80 (m, 14H, CH_2 C_5H_9), 1.59 (m, 28H, CH_2 C_5H_9), 1.46 (m, 14H, CH_2 C_5H_9), 1.08 (m, 4H, CH C_5H_9), 0.94 (m, 3H, CH C_5H_9). $^{13}C\{^1H\}$ NMR (benzene-d_6, δ): 148.61 (d, C_6F_5, $^1J_{C-F} = 231$ Hz), 141.15 (s, *ipso*-$C_6H_5N(H)Me_2$), 139.49 (d, C_6F_5, $^1J_{C-F} = 237$ Hz), 137.00 (d, C_6F_5, $^1J_{C-F} = 235$ Hz), 130.31 (s, *p*-$C_6H_5N(H)Me_2$), 130.12 (s, *m*-$C_6H_5N(H)Me_2$), 119.53 (s, *o*-$C_6H_5N(H)Me_2$), 46.93 (s, $PhN(H)(CH_3)_2$), 28.03, 27.87, 27.80, 27.62, 27.53 (s, CH_2 C_5H_9), 22.68, 22.60, 22.54 (s, CH C_5H_9, 1:3:3 ratio). ^{19}F NMR (benzene-d_6, δ): −56.14 (d, *o*-C_6F_5, $^3J_{F-F} = 23$ Hz), −83.53 (t, *p*-C_6F_5, $^3J_{F-F} = 21$ Hz), −88.28 (t, *m*-C_6F_5, $^3J_{F-F} = 19$ Hz). ^{29}Si NMR (benzene-d_6, δ): −65.92, −65.98, −66.03, −104.30 (1:3:3:1 ratio). Anal. Calcd for $C_{61}H_{75}BF_{15}NO_{13}Si_8$: C, 47.25; H, 4.88; N, 0.90. Found: C, 46.95; H, 4.75; N, 1.01.

$\{N(H)Et_3\}^+\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-$ (1b). Solid $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ (2.24 g, 2.44 mmol) was added to a toluene (25 mL) solution of $B(C_6F_5)_3$ (1.25 g, 2.44 mmol). The mixture was stirred and warmed until a clear solution was obtained. NEt_3 (0.40 mL, 2.88 mmol) was then added. The resultant solution was warmed to reflux and evaporated to dryness. The crude product was dissolved in hot hexane (30 mL) and filtered. Slow cooling to room temperature yielded colorless crystals of **1b** (0.75 g, 0.49 mmol, 20%). Cooling of the mother liquor to −30 °C yielded a second crop of **1b** (0.69 g, 0.45 mmol, 18%). ^{1}H NMR (benzene-d_6, δ): 4.25 (s-br, 1H, $HNEt_3$), 1.86 (q, 6H, $HN(CH_2CH_3)_3$, $^3J_{H-H} = 4$ Hz), 1.82 (m, 14H, CH_2 C_5H_9), 1.70 (m, 28H, CH_2 C_5H_9), 1.48 (m, 14H, CH_2 C_5H_9), 1.29 (t, 9H, $HN(CH_2CH_3)_3$, $^3J_{H-H} = 4$ Hz), 1.00 (m, 6H, CH C_5H_9), 0.72 (m, 1H, CH C_5H_9). $^{13}C\{^1H\}$ NMR (benzene-d_6, δ): 148.67 (d, C_6F_5, $^1J_{C-F} = 230$ Hz), 138.77 (d, C_6F_5, $^1J_{C-F} = 246$ Hz), 137.06 (d, C_6F_5, $^1J_{C-F} = 233$ Hz), 47.24 (s, $HN(CH_2CH_3)_3$), 28.00, 27.64, 27.52 (s, CH_2 C_5H_9), 23.40, 22.99 (s, CH C_5H_9, 3:4 ratio), 8.35 (s, $HN(CH_2CH_3)_3$). ^{19}F NMR (benzene-d_6, δ): −56.55 (d, *o*-C_6F_5, $^3J_{F-F} = 20$ Hz), −86.30 (t, *p*-C_6F_5, $^3J_{F-F} = 10$ Hz), −89.83 (s, *m*-C_6F_5). ^{29}Si NMR (benzene-d_6, δ): −66.16, −66.39, −110.15 (4:3:1 ratio). Anal. Calcd for $C_{59}H_{79}BF_{15}NO_{13}Si_8$: C, 46.29; H, 5.20; N, 0.92. found: C, 45.88; H, 5.32; N, 0.92.

$\{PhN(H)Me_2\}^+\{[(c\text{-}C_5H_9)_7Si_7(OH)_2O_{10}]B(C_6F_5)_3\}^-$ (2a). A mixture of $B(C_6F_5)_3$ (1.42 g, 2.77 mmol) and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (2.43 g, 2.78 mmol) in toluene (25 mL) was treated with $PhNMe_2$ (0.36 mL, 2.84 mmol) at room temperature. The mixture was heated to reflux until a clear solution was formed. The volatiles were evaporated, and the crude product was thoroughly dried. Crystallization of the product from a hot toluene−hexane (1:1, 40 mL) mixture yielded **2a** as colorless crystals (2.48 g, 1.64 mmol, 59%). The crystals gradually lost hexane from the lattice. ^{1}H NMR (toluene-d_8, δ): 8.75 (s-br, 1H, $PhN(H)Me_2$), 6.91 (m, 3H, $C_6H_5N(H)Me_2$), 6.77 (m, 2H, $C_6H_5N(H)Me_2$), 2.42 (s, 6H, $PhN(H)(CH_3)_2$), 1.81 (m, 14H, CH_2 C_5H_9), 1.67 (m, 28H, CH_2 C_5H_9), 1.54 (m, 14H, CH_2 C_5H_9), 1.09 (m, 4H, CH C_5H_9), 0.94 (m, 3H, CH C_5H_9). $^{13}C\{^1H\}$ NMR (toluene-d_8, δ): 149.2 (d, C_6F_5, $^1J_{C-F} = 237$), 142.2 (s, *ipso*-$C_6H_5N(H)Me_2$), 139.9 (d, *p*-C_6F_5, $^1J_{C-F} = 224$ Hz), 137.69 (d, C_6F_5, $^1J_{C-F} = 236$ Hz), 131.48 (s, *m*-$C_6H_5N(H)Me_2$), 131.35 (s, *p*-$C_6H_5N(H)Me_2$), 120.01 (s, *o*-$C_6H_5N(H)Me_2$), 46.59 (s, $PhN(H)(CH_3)_2$), 29.82, 28.96, 28.80, 28.69, 28.53, 28.44, 28.35, 28.32, 28.28, 28.21, 28.16 (s, CH_2 C_5H_9), 25.27, 24.08, 23.63, 23.58, 23.49 (s, CH C_5H_9, 1:2:1:1:2 ratio). ^{19}F NMR (toluene-d_8, δ): −55.30 (d, *o*-C_6F_5, $^3J_{F-F} = 21$ Hz), −84.79 (t, *p*-C_6F_5, $^3J_{F-F} = 21$ Hz), −88.90 (t, *m*-C_6F_5, $^3J_{F-F} = 20$ Hz). ^{29}Si NMR (toluene-d_8, δ): −56.07, −62.02, −64.28, −65.07, −67.25 (2:1:1:1:2 ratio). Anal. Calcd for $C_{61}H_{77}BF_{15}NO_{12}Si_7(C_6H_{14})_{0.5}$: C, 49.54; H, 5.46; N, 0.90. Found: C, 49.53; H, 5.49; N, 0.95.

$\{N(H)Et_3\}^+\{[(c\text{-}C_5H_9)_7Si_7(OH)_2O_{10}]B(C_6F_5)_3\}^-$ (2b). NEt_3 (0.45 mL, 3.25 mmol) was added to a suspension of $B(C_6F_5)_3$ (1.42 g, 2.77 mmol) and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (2.43 g, 2.65 mmol) in toluene (25 mL). The mixture was warmed until a clear solution was formed. Then the solvent was evaporated and the crude product suspended in hot hexane (30 mL). Toluene (20 mL) was added until a clear solution was obtained. Slow cooling of the hot solution to room temperature afforded **2b** as a colorless microcrystalline material (2.55 g, 1.71 mmol, 65%). ^{1}H NMR (toluene-d_8, δ): 8.26 (s-br, 1H, $N(H)Et_3$), 6.85 (s-br, 2H, OH), 2.40 (q, 6H, $HN(CH_2CH_3)_3$, $^2J_{H-H} = 7$ Hz), 1.92 (m, 56 H, CH_2 C_5H_9), 1.38 (m, 4H, CH C_5H_9), 1.24 (m, 3H, CH C_5H_9), 0.89 (t, 9H, $HN(CH_2CH_3)_3$, $^2J_{H-H} = 7$ Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, δ): 149.32 (d, C_6F_5, $^1J_{C-F} = 231$ Hz), 139.74 (d, C_6F_5, $^1J_{C-F} = 247$ Hz), 137.77 (d, C_6F_5, $^1J_{C-F} = 244$ Hz), 46.85 (s, $HN(CH_2CH_3)_3$), 29.79, 29.00, 28.82, 28.69, 28.54, 28.44, 28.41, 28.33, 28.18 (s, CH_2 C_5H_9), 25.44, 24.17, 23.72, 23.67, 23.61 (s, CH C_5H_9, 1:2:2:1:1 ratio), 8.76 (s, $HN(CH_2CH_3)_3$). ^{19}F NMR (toluene-d_8, δ): −55.30 (d, *o*-C_6F_5, $^3J_{F-F} = 21$ Hz), −85.19 (t, *p*-C_6F_5, $^3J_{F-F} = 21$ Hz), −89.07 (t, *m*-C_6F_5, $^3J_{F-F} = 20$ Hz). ^{29}Si NMR (toluene-d_8, δ): −56.40, −61.80, −64.49, −65.08, −67.33 (2:1:1:1:2 ratio). Anal. Calcd for $C_{59}H_{81}BF_{15}NO_{12}Si_7$: C, 47.60; H, 5.48; N, 0.94. Found: C, 47.55; H, 5.54; N, 0.98.

$(C_6F_5)_3B\cdot NC_5H_5$ (3). (a) Pyridine (0.3 mL, 3.7 mmol) was added to a toluene solution (10 mL) of $B(C_6F_5)_3$ (0.95 g, 1.86 mmol) at room temperature. The solution was stirred for 1 h, after which time the volatiles were evaporated, affording a white solid. The crude product was washed with hexane (2 × 5 mL) and recrystallized from CH_2Cl_2. Cooling to −30 °C yielded **3** as large colorless crystals (0.45 g, 0.76 mmol, 41%).

Concentration and cooling to −30 °C of the mother liquor yielded a second crop of **3** (0.28 g, 0.47 mmol, 25%). ^{1}H NMR (benzene-d_6, δ): 7.99 (d, 2H, pyridine *o*-C*H*, $^3J_{\mathrm{H-H}} = 5$ Hz), 6.67 (t, 1H, pyridine *p*-C*H*, $^3J_{\mathrm{H-H}} = 8$ Hz), 6.32 (t, 2H, pyridine *m*-C*H*, $^3J_{\mathrm{H-H}} = 7$ Hz). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 148.09 (d, C_6F_5, $^1J_{\mathrm{C-F}} = 239$ Hz), 146.18 (s, pyridine *m*-*C*H), 141.59 (s, pyridine *p*-*C*H), 140.49 (d, C_6F_5, $^1J_{\mathrm{C-F}} = 240$ Hz), 137.56 (d, C_6F_5, $^1J_{\mathrm{C-F}} = 247$ Hz), 124.87 (s, pyridine *o*-*C*H). ^{19}F NMR (benzene-d_6, δ): −54.81 (d, *o*-C_6F_5, $^3J_{\mathrm{F-F}} = 21$ Hz), −79.01 (t, *p*-C_6F_5, $^3J_{\mathrm{F-F}} = 22$ Hz), −86.12 (t, *m*-C_6F_5, $^3J_{\mathrm{F-F}} = 19$ Hz). Anal. Calcd for $C_{23}H_5BF_{15}N$: C, 46.74; H, 0.85; N, 2.37. Found: C, 46.29; H, 0.96; N, 2.14.

(b) NMR tubes containing benzene-d_6 solutions of **1a** and **2a** were treated with pyridine (4 equiv). On the basis of ^{19}F NMR, at room temperature approximately 30% of **1a** was converted into **3**. For the reaction of **2a** with pyridine, **3** was the only fluorine-containing product, as the silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ quantitatively precipitated from solution.

$\{PhN(H)Me_2\}^+\{(C_6F_5)_3BOH\}^-$ (4a). H_2O (0.10 mL, 5.6 mmol) and $PhNMe_2$ (0.3 mL, 2.4 mmol) were added to a toluene (15 mL) solution of $B(C_6F_5)_3$ (1.20 g, 2.34 mmol), and the resulting mixture was stirred for 2 h at room temperature. The volatiles were removed under vacuum, leaving a white microcrystalline solid. Recrystallization from $CHCl_3$ (10 mL) at −30 °C yielded **4a** (0.83 g, 1.28 mmol, 55%) as colorless crystals. ^{1}H NMR (benzene-d_6, δ): 7.42 (s-br, 1H, PhN(*H*)Me$_2$), 6.81 (m, 3H, *Ph*N(H)Me$_2$), 6.51 (d, 2H, *Ph*N(H)Me$_2$, $^3J_{\mathrm{H-H}} = 8$ Hz), 1.70 (s, 6H, PhN(H)*Me*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 148.35 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 234$ Hz), 141.45 (s, *ipso*-*C*$_6$F$_5$), 139.49 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 238$ Hz), 137.29 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 246$ Hz), 130.08 (s, *C*$_6$F$_5$), 129.93 (s, *C*$_6$F$_5$), 119.42 (s, *C*$_6$F$_5$), 44.68 (s, *C*H$_3$). ^{19}F NMR (benzene-d_6, δ): −58.88 (d, *o*-C_6F_5, $^3J_{\mathrm{F-F}} = 17$ Hz), −82.87 (t, *p*-C_6F_5, $^3J_{\mathrm{F-F}} = 20$ Hz), 87.77 (t, *m*-C_6F_5, $^3J_{\mathrm{F-F}} = 22$ Hz). Anal. Calcd for $C_{26}H_{13}BF_{15}NO$: C, 47.96; H, 2.01; N, 2.15. Found: C, 47.60; H, 2.04; N, 1.95.

$\{Et_3NH\}^+\{(C_6F_5)_3BOH\}^-$ (4b). NEt_3 (1 mL, 7.2 mmol) and H_2O (0.12 mL, 6.7 mmol) were added to a toluene solution (15 mL) of $B(C_6F_5)_3$ (1.81 g, 3.53 mmol). The mixture was stirred at room temperature for 3 h, upon which a white precipitate was formed. After evaporation of the volatiles the crude white product was recrystallized from CH_2Cl_2 (10 mL). Cooling to −30 °C afforded **4b** as colorless crystals (1.61 g, 2.55 mmol, 72%). ^{1}H NMR ($CDCl_3$, δ): 11.04 (s-br, 1H, Et$_3$N*H*), 2.91 (q, 6H, HN(C*H*$_2$CH$_3$)$_3$, $^3J_{\mathrm{H-H}} = 7$ Hz), 2.47 (s-br, 1H, (C$_6$F$_5$)$_3$BO*H*), 1.21 (t, 9H, HN(CH$_2$C*H*$_3$)$_3$, $^3J_{\mathrm{H-H}} = 8$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 147.71 (d, C_6F_5, $^1J_{\mathrm{C-F}} = 243$ Hz), 138.82 (d, C_6F_5, $^1J_{\mathrm{C-F}} = 236$ Hz), 136.60 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 209$ Hz), 45.95 (s, HN(*C*H$_2$CH$_3$)$_3$), 8.20 (s, HN(CH$_2$*C*H$_3$)$_3$). ^{19}F NMR ($CDCl_3$, δ): −59.24 (d, *m*-C_6F_5, $^3J_{\mathrm{F-F}} = 21$ Hz), −83.30 (t, *p*-C_6F_5, $^3J_{\mathrm{F-F}} = 21$ Hz), −88.12 (t, *o*-C_6F_5, $^3J_{\mathrm{F-F}} = 20$ Hz). Anal. Calcd for $C_{24}H_{17}BF_{15}NO$: C, 45.67; H, 2.71; N, 2.22. Found: C, 45.43; H, 2.79; N, 2.20.

$\{PhN(H)Me_2\}^+\{i\text{-}PrOB(C_6F_5)_3\}^-\cdot 0.5C_6H_5CH_3$ (5). At room temperature, a toluene (20 mL) solution of $B(C_6F_5)_3$ (1.66 g, 3.22 mmol) was treated with *i*-PrOH (0.4 mL) and $PhNMe_2$ (0.5 mL). After 15 min at room temperature, hexane (20 mL) was added. Crystallization at −30 °C yielded **5** as colorless needles (1.90 g, 2.57 mmol, 80%). Complex **5** contains 0.5 equiv of toluene in the lattice. ^{1}H NMR (benzene-d_6, δ): 9.23 (s-br, 1H, N*H*), 6.96 (m, 2H, *m*-C$_6$*H*$_5$), 6.82 (t, 1H, *p*-C$_6$*H*$_5$, $^3J_{\mathrm{H-H}} = 8$ Hz), 6.69 (d, 2H, *i*-C$_6$*H*$_5$, $^3J_{\mathrm{H-H}} = 8$ Hz), 3.982 (h, 1H, C*H*Me$_2$, $^3J_{\mathrm{H-H}} = 6$ Hz), 2.14 (s, 6H, PhN(H)(C*H*$_3$)$_2$), 0.65 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{\mathrm{H-H}} = 6$ Hz). ^{13}C NMR (benzene-d_6, δ): 148.50 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 246$ Hz), 139.74 (d, *C*$_6$F$_5$, $^1J_{\mathrm{C-F}} = 246$ Hz), 137.26 (d, *C*$_6$F$_5$, $^3J_{\mathrm{C-F}} = 250$ Hz), 129.83 (s, *C*$_6$H$_5$N(H)Me$_2$), 129.19 (s, *C*$_6$H$_5$N(H)Me$_2$), 117.83 (s, *C*$_6$H$_5$N(H)Me$_2$), 70.60 (s, *C*HMe$_2$), 44.08 (s, PhN(H)(*C*H$_3$)$_2$), 24.73 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR (benzene-d_6, δ): −55.59 (d, *o*-C$_6$*F*$_5$, $^3J_{\mathrm{F-F}} = 21$ Hz), −82.30 (d, *p*-C$_6$*F*$_5$, $^3J_{\mathrm{F-F}} = 21$ Hz), −87.83 (m, *m*-C$_6$*F*$_5$). Anal. Calcd for $C_{29}H_{19}BF_{15}NO\cdot 0.5C_7H_8$: C, 52.80; H, 3.14; N, 1.89. Found: C, 52.61; H, 3.27; N, 1.66.

Table 1. Crystallographic Data for the X-ray Structure Determination of $\{[(c\text{-}C_5H_9)_7Si_8O_{13}]B(C_6F_5)_3\}^-\{PhN(H)Me_2\}^+$ (1a) and $\{(C_6F_5)_3BOH\}^-\{Et_3NH\}^+$ (4b)

	1a	**4b**
formula	$C_{61}H_{75}BF_{15}NO_{13}Si_8$	$C_{24}H_{16}BF_{15}NO$
fw	1550.75	631.19
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	17.050(3)	11.891(2)
b (Å)	20.919(4)	15.397(2)
c (Å)	20.046(4)	14.230(2)
β (deg)	90.975(4)	107.098(3)
V (Å^3)	7149(2)	2490.1(7)
Z	4	4
D_{calcd} (g cm^{-3})	1.441	1.681
λ(Mo Kα) (Å)	0.710 73	0.710 73
F(000)	3216	1260
μ (mm^{-1})	0.249	0.179
cryst size (mm)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2
T (K)	238(2)	213(2)
θ range (deg)	$1.83 < \theta < 21.97$	$1.97 < \theta < 28.64$
scan type	$\omega/2\theta$	$\omega/2\theta$
hkl	*h*, −17 to +17; *k*, 0−22; *l*, 0−21	*h*, −15 to +14; *k*, 0−18; *l*, 0−18
no. of rflns total	56141	5659
no. of data ($I > 2\sigma(I)$)	8714	4300
no. of params refined	892	379
R1 ($I > 2\sigma(I)$)[a]	0.0426	0.0547
wR2 ($I > 2\sigma(I)$)[b]	0.1052	0.1186
GOF ($I > 2\sigma(I)$)	1.014	1.031
diff peak and hole (e Å^{-3})	0.438, −0.440	0.476, −0.367

[a] The structure was refined in F_o^2 using all data; the value of R1 is given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$. $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\mathrm{wR2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (nP)^2]$, $P = (F_o^2 + 2F_c^2)/3$, and $n = 0.06$ for **1a** and 0.03 for **4b**.

NMR Tube Reaction of $Cp_2Zr(CH_2Ph)_2$ with 1a: Formation of $\{[(c\text{-}C_5H_9)_7Si_8O_{13}]ZrCp_2\}^+\{PhCH_2B(C_6F_5)_3\}^-$ (6) and $[(c\text{-}C_5H_9)_7Si_8O_{13}]Zr(CH_2Ph)Cp_2$ (7). A toluene-d_8 solution (0.5 mL) of $Cp_2Zr(CH_2Ph)_2$ (26 mg, 64 μmol) was added to an NMR tube containing a frozen toluene-d_8 solution (0.5 mL) of **1a** (100 mg, 64 μmol). The solution was defrosted at −40 °C. ^{1}H and ^{19}F NMR measured at −25 °C (after 10 min) showed the formation of $\{[(c\text{-}C_5H_9)_7Si_8O_{13}]ZrCp_2\}^+\{PhCH_2B(C_6F_5)_3\}^-$ (**6**) in approximately 90% yield. ^{1}H NMR (toluene-d_8, 25 °C, δ): 7.48−7.16 (m, 5H, C$_6$*H*$_5$), 5.98 (s, 10H, C$_5$*H*$_5$), 3.60 (s-br, 2H, BC*H*$_2$), 2.10 (m, 14H, C*H*$_2$ C$_5$H$_9$), 1.90 (m, 28H, C*H*$_2$ C$_5$H$_9$), 1.74 (m, 14H, C*H*$_2$ C$_5$H$_9$), 1.39 (m, 7H, C*H* C$_5$H$_9$). ^{19}F NMR (toluene-d_8, 25 °C, δ): −53.91 (d, *o*-C_6F_5, $^3J_{\mathrm{F-F}} = 23$ Hz), −86.90 (t, *p*-C_6F_5, $^3J_{\mathrm{F-F}} = 21$ Hz), −89.87 (m, *m*-C_6F_5). Warming of the solution to room temperature showed the formation of significant amounts of $[(c\text{-}C_5H_9)_7Si_8O_{13}]Zr(CH_2Ph)Cp_2$ (**7**) and $B(C_6F_5)_3$. On the basis of ^{19}F NMR at room temperature, the ratio $\{PhCH_2B(C_6F_5)_3\}^-$:$B(C_6F_5)_3$ was found to be 9:1. To prove the presence of **7**, this complex was also prepared independently.

$[(c\text{-}C_5H_9)_7Si_8O_{13}]Zr(CH_2Ph)Cp_2$ (7). A toluene (50 mL) solution of $Cp_2Zr(CH_2Ph)_2$ (0.40 g, 0.98 mmol) was cooled to −80 °C, and $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ (0.90 g, 0.98 mmol) was added. The mixture was warmed to room temperature. At room temperature, the solution slowly decolorized. The solvent was evaporated, and the crude product was washed and suspended in hexane (10 mL). The pale yellow solution was decanted, leaving **7** as an off-white powder (0.85 g, 0.69 mmol, 70%). ^{1}H NMR (benzene-d_6, δ): 7.37 (t, 2H, *m*-C$_6$*H*$_5$, $^3J_{\mathrm{H-H}} = 8$ Hz), 7.19 (d, 2H, *o*-C$_6$*H*$_5$, $^3J_{\mathrm{H-H}} = 7$ Hz), 6.98 (t, *p*-C$_6$*H*$_5$, $^3J_{\mathrm{H-H}} = 7$ Hz), 5.78 (s, 10H, C$_5$*H*$_5$), 2.44 (s, 2H, C*H*$_2$Ph), 1.75 (m, 42H, C*H*$_2$ C$_5$H$_9$), 1.50 (m, 14H, C*H*$_2$ C$_5$H$_9$), 1.20 (m, 7H, C*H* C$_5$H$_9$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 152.86 (*ipso*-*C*$_6$H$_5$), 128.21, 127.26, 121.20 (s, *C*$_6$H$_5$), 112.33 (s, *C*$_5$H$_5$), 51.81 (s, *C*H$_2$Ph), 27.85, 27.77, 27.41, 27.37 (s, *C*H$_2$ C$_5$H$_9$), 22.71, 22.66 (s, *C*H C$_5$H$_9$, 3:4 ratio). Anal. Calcd for $C_{52}H_{80}O_{13}Si_8Zr$: C, 50.82; H, 6.56. Found: C, 50.59; H, 6.60.

Ethylene Polymerization Experiments. Ethylene polymerization reactions were carried out in a 200 mL glass Büchi autoclave equipped with a mechanical stirrer at room temperature. In a typical experiment, 5 min before the cocatalyst was added, a toluene (5 mL) solution of the catalyst precursor ($Cp_2Zr(CH_2Ph)_2$ or $Zr(CH_2Ph)_4$; 50 μmol) was injected into the ethylene-presaturated autoclave charged with toluene (100 mL). After the addition of the cocatalyst (30 μmol) solution, the ethylene pressure was increased to 5 atm. After 5 min, the polymerization was quenched by the addition of methanol. The polymer was then collected by filtration, washed with methanol, and dried overnight under vacuum. The polymers were characterized by GPC analysis.

X-ray Structural Determination of 1a and 4b. Suitable crystals were selected, mounted on a thin, glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1K CCD diffractometer using 0.3° ω scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[26] Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scatering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library.[27] The detailed data are listed in Table 1.

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Supporting Information Available: Tables of atomic coordinates, thermal displacement parameters, bond lengths, and bond angles, in CIF format, for **1a** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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