Catalytic System for Homogeneous Ethylene Polymerization Based on Aluminohydride−Zirconocene Complexes

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Ethylene polymerization using catalysts derived from activation of zirconocene aluminohydride complexes with either methyl aluminoxane or $B(C_6F_5)_3$ is reported. Variable-temperature NMR spectra of mixtures of $Cp^*_2ZrH_3AlH_2$ or $Cp'_2ZrH_3AlH_2$ and excess $B(C_6F_5)_3$ reveal the formation of di- or polynuclear metallocenium ion-pairs featuring terminal or both terminal and bridging borohydride counteranions $HB(C_6F_5)_3$ arising from hydride abstraction. At higher *T*, ion-pairs featuring the terminal $HB(C_6F_5)_3$ counterion decompose, and the AlH_3 that is liberated degrades $B(C_6F_5)_3$ to furnish mixtures of $(C_6F_5)_nAlH_{3-n}$ and, in the case of $Cp^*_2ZrH_3AlH_2$, a new ion-pair partnered with the diborohydride counteranion $[Cp^*_2ZrH][(\mu\text{-}H)_2B(C_6F_5)_2]$. The latter compound was independently prepared from $Cp^*_2ZrH_2$ and $HB(C_6F_5)_2$ and is active in ethylene polymerization; however it is 1000 times less active than the catalyst formed from $Cp^*_2ZrH_3AlH_2$ and $B(C_6F_5)_3$ and so cannot account for the multisite behavior of the latter combination. There is evidence of chemical exchange between “free” or terminal $HB(C_6F_5)_3$ and excess $B(C_6F_5)_3$ in these mixtures, and on the basis of model studies with $[^nBu_4N][HB(C_6F_5)_3]$ and $B(C_6F_5)_3$, this involves reversible formation of $[^nBu_4N][(C_6F_5)_3B)(\mu\text{-}H)B(C_6F_5)_3]$, which can be detected by ^{19}F NMR spectroscopy in solution at low *T*.

Introduction

There is considerable interest in the use of single-component cocatalysts for the activation of metallocene complexes toward olefin polymerization, as these activators obviate the need for the use of a large excess of methylaluminoxane as cocatalyst.[1] A particularly attractive approach involves in situ alkylation and ionization using metallocene dichlorides, tri-isobutylaluminum, and, for example, $[Ph_3C][B(C_6F_5)_4]$,[2] while preformed dialkyls are necessary in the case of Lewis acidic organoboranes.[1]

Surprisingly, there has been comparatively little study of the activation and utility of other types of potential catalyst precursors that might be derived from prior, or ideally in situ, derivatization of metallocene dichlorides. In particular, the use of metallocene dihydride complexes as precursors to cationic hydride complexes has been practically restricted to the study of sterically hindered, mono- or dinuclear and thus soluble complexes of this type.[3] Cationic hydride complexes can be generated in situ via hydrogenolysis of the corresponding alkylmetallocenium ions[4] and are thus involved in polymerizations conducted in the presence of dihydrogen. Also, there have been several reports on the reactions of borohydride and related metallocene complexes of group 4 with $B(C_6F_5)_3$,[5] but no systematic studies of the use of these complexes in olefin polymerization to our knowledge.[6]

It had occurred to us that the use of aluminohydride complexes of zirconocenes (generically $Cp_2ZrH_3AlH_2$)[7] might be convenient for in situ activation, as they can be readily prepared from metallocene dichloride complexes and $LiAlH_4$. The coordinated alane in these complexes might help to stabilize the resulting cationic hydrides generated in situ. A complicating feature of this class of compounds, compared with, for example, borohydride complexes, is their limited thermal stability and variable state of aggregation both within the solid state[8] and in solution,[7,8] and this was anticipated to affect their activation chemistry.

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Table 1. Polymerization of Ethylene Using Metallocene Complexes[a]

entry	catalyst (C) (μM)	activator (A) (mM)	A:C	T (°C)	activity[b]	M_w (K)	M_w/M_n
1	$(^nBuCp)_2ZrCl_2$ (4.2)	MAO (33.8)	8000	50	11.8	275	3.4
2	$(^nBuCp)_2ZrCl_2$ (4.2)	MAO (33.8)	8000	75	14.4	43.0	1.9
3	$(^nBuCp)_2ZrH_3AlH_2$ (3.0)	MAO (33.8)	11500	50	16.5	511	3.6
4	$(^nBuCp)_2ZrH_3AlH_2$ (3.0)	MAO (33.8)	11500	75	24.0	91.1	2.3
5	$(TMSCp)_2ZrCl_2$ (1.1)	MAO (44.2)	40000	50	43.6	56.8	3.7
6	$(TMSCp)_2ZrCl_2$ (1.1)	MAO (44.2)	40000	70	48.0	65.1	3.3
7	$(TMSCp)_2ZrH_3AlH_2$(1.1)	MAO (44.2)	40000	50	58.1	81.4	3.2
8	$(TMSCp)_2ZrH_3AlH_2$(1.1)	MAO (44.2)	40000	70	56.3	51.5	3.1
9	$(TMSCp)_2ZrH_3AlH_2$ (510)	$B(C_6F_5)_3$[c]	1.0	25	0.16	172	2.4
10	$(TMSCp)_2ZrH_3AlH_2$ (260)	$B(C_6F_5)_3$[c]	3.0	25	0.65	137	2.6
11	$(TMSCp)_2ZrH_3AlH_2$ (5.4)	$B(C_6F_5)_3$[c]	3.0	50	1.8	199	2.4
12	$(TMSCp)_2ZrH_3AlH_2$ (5.4)	$B(C_6F_5)_3$[c]	10.0	50	3.4	180	2.3
13	$(TMSCp)_2ZrH_3AlH_2$ (2.7)	$B(C_6F_5)_3$[c]	10.0	50	4.9	247	3.3
14	$(TMSCp)_2ZrH_3AlH_2$ (2.7)	$B(C_6F_5)_3$[c]	10.0	50	5.5	378	2.4
15	$(TMSCp)_2ZrH_3AlH_2$ (1.6)	$B(C_6F_5)_3$[c]	10.0	50	6.6	410	2.4
16	$Cp^*_2ZrH_3AlH_2$ (3.2)	$B(C_6F_5)_3$[d]	1.0	0	1.3		
17	$Cp^*_2ZrH_3AlH_2$ (6.4)	$B(C_6F_5)_3$[d]	1.0	0	1.8	124	6.8
18	$Cp^*_2ZrH_3AlH_2$ (6.4)	$B(C_6F_5)_3$[d]	3.0	0	1.5	80	4.6
19	$Cp^*_2ZrH_3AlH_2$ (6.4)	$B(C_6F_5)_3$[d]	1.0	25	3.7		
20	$Cp^*_2ZrH_3AlH_2$ (6.4)	$B(C_6F_5)_3$[d]	1.0	50	1.3	89	4.0
21	$Cp^*_2ZrH(\mu\text{-}H)_2B(C_6F_5)_2$ (100)			25	4.3×10^{-3}	219	2.2

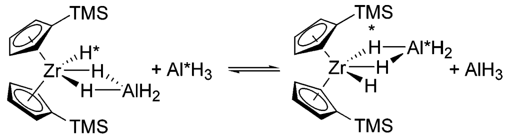
[a] Conditions: iso-octane (200 mL), 2.7 atm C_2H_4, 30 min. [b] Activity = 10^6 g PE/mol Zr × h. [c] The ion-pair was preformed in toluene solution at 25 °C and then injected into iso-octane with TIBAL (0.5 mL) added as scavenger ([Al] = 9.9 mM) in the presence of ethylene. [d] The ion-pair was preformed in a mixture of bromobenzene and toluene at −50 °C and then injected into a solution of iso-octane, ethylene, and TIBAL at the indicated *T*.

In this paper we report that a number of $Cp_2ZrH_3AlH_2$ complexes [Cp = Me_5C_5 = Cp*, TMSCp = Cp′, ^nBuCp] can be activated using methylaluminoxane for ethylene polymerization where polymerization activity is superior to conventional activation involving the corresponding dichlorides and methylaluminoxane. In addition, we have investigated the activation chemistry of two of these complexes with $B(C_6F_5)_3$, which highlights the complexity of this process.

Results and Discussion

In most cases, the $Cp_2ZrH_3AlH_2$ complexes were prepared from the metallocene dichloride and $LiAlH_4$ in Et_2O; crude material was then extracted into benzene and the extracts were concentrated in vacuo to provide stock solutions that were used directly for polymerization experiments. Spectroscopic analyses of these stock solutions indicated little to no contamination with Et_2O, although variable amounts of $(AlH_3)_n$ were present and in dynamic exchange with the $Cp_2ZrH_3AlH_2$ complexes. This was particularly evident in the case of $(TMSCp)_2ZrH_3AlH_2$, which when free of alane shows a characteristic four-signal pattern in the Cp region of the ^1H NMR spectrum, consistent with the unsymmetrical nature of the aggregated species present.[8b] In contrast, even small amounts of $(AlH_3)_n$ result in fluxional behavior, where at room temperature, the Cp region consists of two line-broadened signals whose appearance was concentration and temperature dependent. On cooling to lower temperature, these signals decoalesce and the low-temperature spectrum is consistent with that of pure $(TMSCp)_2ZrH_3AlH_2$.[8b]

We attribute the observed behavior to $(AlH_3)_n$-mediated exchange of terminal and bridging Zr-hydrides as suggested in eq 1. The mechanism of this process is undoubtedly more complicated due to the polynuclear nature of both $(TMSCp)_2ZrH_3AlH_2$ and $(AlH_3)_n$.



(1)

Ethylene polymerization experiments using these stock solutions were conducted in iso-octane solution at various *T* and *P* using MAO or $B(C_6F_5)_3$ as activator, and the results are summarized in Table 1. The activity of $(^nBuCp)_2ZrH_3AlH_2$ is about 40% higher than that of its dichloride analogue at 50 °C when activated by MAO (entries 1−4). Also, the MW of the PE formed is significantly higher (i.e., double) despite the use of larger amounts of MAO to activate the catalyst. This result is intriguing, as it suggests that the tendency toward chain transfer is reduced using these catalyst precursors.

Similar results were observed using the more hindered $(TMSCp)_2ZrH_3AlH_2$ catalyst (entries 5−8). At 50 °C, the activity of the aluminohydride complex is nearly 50% greater than that of the corresponding dichloride complex, while the MW of the polymer formed was increased by a similar amount. From a practical perspective, the increased activity and MW are attractive and justify the prior derivatization of these metallocene complexes.

The $(TMSCp)_2ZrH_3AlH_2$ complex was also activated using various amounts of $B(C_6F_5)_3$ in toluene solution at 25 °C and then added to an iso-octane solution of ethylene containing triisobutylaluminum (TIBAL) as a scavenger at the indicated *T*. The activity of the $B(C_6F_5)_3$-activated catalyst is much lower than that of the MAO-activated complex (entries 11−15 vs 7, 8) at 50 °C. Although $B(C_6F_5)_3$-activated catalysts are frequently less active than MAO-activated catalysts,[1] the difference here (ca. 15−50 times less active depending on conditions) is quite pronounced.

It is tempting to attribute this lowered activity to degradation of added $B(C_6F_5)_3$ by excess TIBAL present as scavenger.[9] However, these experiments involved the use of a preformed ion-pair (vide infra), and generally speaking metallocenium ion-pairs are less susceptible to degradation by alkylaluminum compounds than $B(C_6F_5)_3$.[10] Further, as shown in Table 1, experiments at lower [Zr] but constant TIBAL resulted in significantly higher activities and MW (entries 11−15). These

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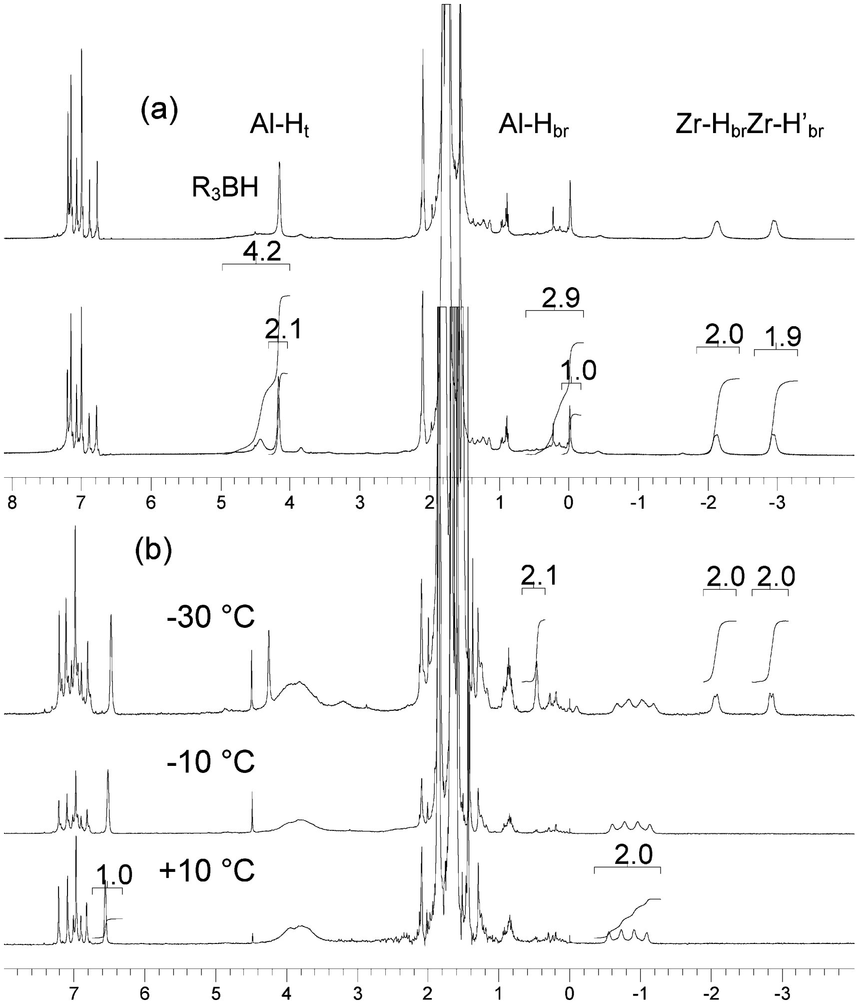

Figure 1. (a) ^{1}H (top) and ^{1}H{^{11}B} (bottom) NMR spectra (C_7D_8/C_6D_5Br, 1:1; −50 °C) of a mixture of $Cp^*_2ZrH_3AlH_2$ and $B(C_6F_5)_3$. (b) ^{1}H NMR spectra (C_7D_8/C_6D_5Br, 1:1) of a mixture of $Cp^*_2ZrH_3AlH_2$ and $B(C_6F_5)_3$ as a function of temperature.

findings are inconsistent with TIBAL degrading either $B(C_6F_5)_3$ or the ion-pair. Thus, the lower activities must be viewed as intrinsic and may reflect either inefficient ionization or thermal instability of the ion-pairs.

It can be seen that there is a 2−4-fold increase in activity when using higher amounts of $B(C_6F_5)_3$ with respect to Zr at 25 and 50 °C (entries 9−12). This effect has been noted elsewhere in propene polymerization experiments involving preformed metallocenium ion-pairs such as [$Me_2C(Cp)IndZrMe$][$MeB(C_6F_5)_3$].[11] In that case, excess $B(C_6F_5)_3$ activates these ion-pairs toward initial insertion[11a,b] and also activates [$Me_2C(Cp)IndZrMe$][(μ-H)$B(C_6F_5)_3$], the principle product of chain transfer, for further insertion.[11c] Since an ion-pair featuring the μ-$HB(C_6F_5)_3$ anion is also generated from $(TMSCp)_2ZrH_3AlH_2$ and $B(C_6F_5)_3$ (vide infra), it is probable that the effect of excess $B(C_6F_5)_3$ is similar here.

The sterically hindered, dinuclear aluminohydride complex [$Cp^*_2ZrH_3AlH_2$]$_2$, which was obtained and used in pure form, showed different behavior on activation with $B(C_6F_5)_3$. These experiments were conducted by mixing this complex and $B(C_6F_5)_3$ together at −50 °C in a mixture of bromobenzene and toluene and then injecting the solution of the resulting thermally unstable ion-pair (vide infra) into iso-octane and ethylene at the indicated *T*. The activity of this catalyst was largely unaffected in the presence of excess $B(C_6F_5)_3$, although the stability and thus activity of the catalyst are lower at higher *T*. Also, a polymer with a broad and bimodal MWD was obtained, suggesting the formation of more than one type of active species. Alternately, time-dependent chain transfer to Al,[12] a process that is expected to be important at lower temperatures,[13] could be invoked.

To gain insight into the nature of the active species produced on activation with $B(C_6F_5)_3$, the reactions of $(TMSCp)_2ZrH_3AlH_2$ and $Cp^*_2ZrH_3AlH_2$ with $B(C_6F_5)_3$ were studied by variable-*T*, multinuclear NMR spectroscopy.

The reaction of $Cp^*_2ZrH_3AlH_2$ with excess $B(C_6F_5)_3$ was initially studied in toluene-d_8. Unfortunately, the ion-pair formed (vide infra) has limited solubility in this solvent at low *T* and is unstable in solution above −20 °C. The major Zr product formed from these two compounds at room temperature is the novel complex $Cp^*_2ZrH(\mu\text{-}H_2)B(C_6F_5)_2$ (eq 2). Although this compound could not be isolated in pure form from these mixtures,

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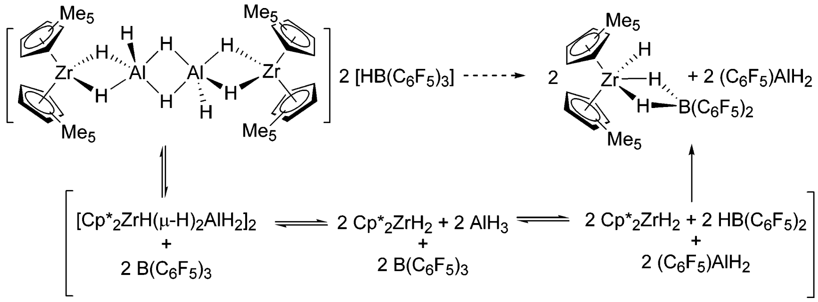
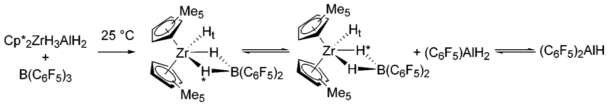
Scheme 1



it was independently generated from the reaction of Cp*$_2$ZrH$_2$[14] and HB(C$_6$F$_5$)$_2$,[15] so its identity is not in doubt.

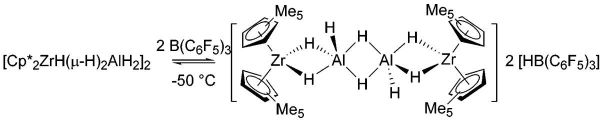


(2)

In particular, a characteristic, line-broadened 1:1:1:1 quartet ($J_{HB} = 75$ Hz) at δ −0.84 appears in the ^{1}H NMR spectrum (Figure 1b), along with a broadened singlet at δ 6.57. These signals are present in an integral ratio of 2:1 along with a Cp* resonance integrating to 30 protons. Evidently, this compound must be fluxional such that the two bridging B-H undergo rapid exchange, between central and lateral positions (eq 2), but neither exchange with the terminal Zr-H. A mechanism that is consistent with this finding involves a zwitterionic [Cp*$_2$ZrH]-[(μ-H)BH(C$_6$F$_5$)$_2$] intermediate. In the corresponding ^{19}F NMR spectrum, a set of signals at δ −130.0, −157.8, and −163.8 are characteristic of a tetrahedral H$_2$B(C$_6$F$_5$)$_2^-$ moiety that is coordinated to Zr ($\Delta\delta = 6.0$ ppm).[16]

The other products formed are a mixture of perfluorophenylalanes [Al(C$_6$F$_5$)$_n$H$_{3-n}$]$_m$ ($n = 1$ and possibly 2) and their adducts with Cp*$_2$ZrH$_2$ analogous to that shown in eq 2. Mixed perfluorophenylalanes of this type have not been reported in the literature, except as ether or amine complexes;[17] a mixture consisting primarily of [Al(C$_6$F$_5$)$_2$H]$_m$ was independently generated in situ from the reaction of ClAl(C$_6$F$_5$)$_2$[18] and Cp$_2$ZrHCl. This compound exhibits reasonably sharp, but multiple resonances, in the region δ −122, −152, and −161 ppm, presumably due to compounds of differing nuclearity. In addition, the adducts formed from this alane and Cp*$_2$ZrH$_2$ exhibit multiple signals in the same regions (see the Supporting Information). These signals do not exactly coincide with those present in a mixture of Cp*$_2$ZrH$_3$AlH$_2$ and B(C$_6$F$_5$)$_3$, but then the principal alane byproduct [(C$_6$F$_5$)AlH$_2$]$_n$ is different. Thus, although the spectra of these mixtures are complicated, the actual net reaction chemistry is simple, as shown in eq 2.

At low *T* and in more polar 1:1 bromobenzene-d_5/toluene-d_8 (B/T) solution, predominantly one ion-pair is formed in a reversible process (eq 3). The structure of this ion-pair was deduced from its ^{1}H and ^{19}F NMR spectra at −50 °C. In particular, the dication is dinuclear, based on Zr, as revealed by the presence of two different C$_5$Me$_5$ signals in a 1:1 ratio (total 60 H), two different signals due to bridging hydrides at δ −2.94 (2 H) and −2.13 (2 H), which are mutually coupled, but line-broadened doublets ($J = 14$ Hz), and a signal due to a terminal hydride at δ 4.16 (2 H) in the ^{1}H NMR spectrum at −50 °C (Figure 1a). There is a broad feature at δ 0.4 integrating to a total of two protons, which represents the remaining bridging Al-H required for the structure shown in eq 3 (or its C_2-symmetric isomer). The appearance of this signal is *T* dependent: it sharpens at higher *T* as the ion-pair also decomposes (see Figure 1a vs b). The B-H of the HB(C$_6$F$_5$)$_3$ counteranion resonates at 4.4 ppm in the ^{1}H{^{11}B} NMR spectrum (Figure 1a), in agreement with data reported for this anion in the literature[5] and also by comparison to an authentic sample of [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$][19] in the same solvent mixture at this *T*.



(3)

The ^{19}F NMR signals of this counterion are sensitive to whether it is bridging[11c] or terminal,[5] and only one principal species is seen with chemical shifts characteristic of a terminal HB(C$_6$F$_5$)$_3$ anion at δ −133.0, −163.2, and −166.3. It should be mentioned that the appearance of these ^{19}F NMR spectra at low *T* was dependent on the presence of excess B(C$_6$F$_5$)$_3$; signals due to the HB(C$_6$F$_5$)$_3$ anion were exchange broadened along with those due to excess B(C$_6$F$_5$)$_3$. This exchange process will be commented upon later.

The ^{11}B NMR spectrum of this ion-pair was somewhat uninformative. A single line-broadened singlet at δ −24.3 was observed in either the ^{11}B or ^{11}B{^{1}H} spectra of these mixtures at low *T*, which is at the correct shift for this anion.[5] The lack of B-H coupling is partly due to quadrupole relaxation induced B-H decoupling as the temperature is decreased. The ^{11}B NMR spectrum of [Bu$_4$N][HB(C$_6$F$_5$)$_3$] shows similar behavior. At 25 °C a doublet is observed with $J_{BH} = 95$ Hz[5] versus a line-broadened doublet where coupling is barely detectable at −50 °C.

As indicated in Figure 1, on warming these solutions, decomposition of the ion-pair occurs, forming the same products that are generated in toluene solution. In essence, as ionization is reversible, then at higher *T*, alane that is reversibly liberated from the neutral precursor can degrade B(C$_6$F$_5$)$_3$ to form (C$_6$F$_5$)$_2$-

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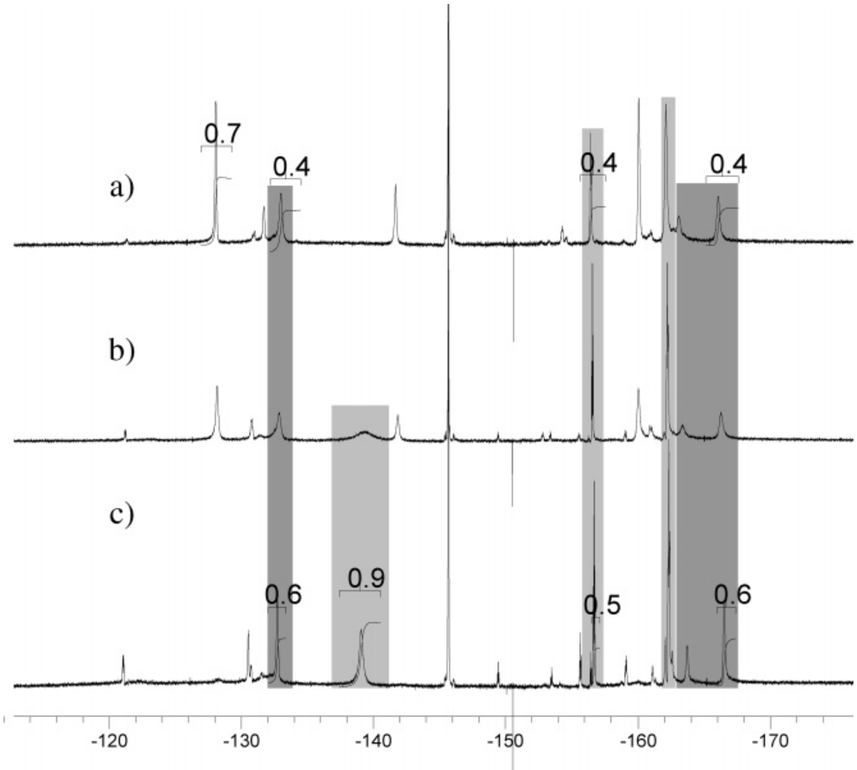

Figure 2. ^{19}F NMR spectra (384 MHz) of a mixture of $Cp'_2ZrH_3AlH_2$ and ca. 1.0 equiv of $B(C_6F_5)_3$ in 1:1 bromobenzene-d_5/toluene-d_8 at (a) −50, (b) −25, and (c) 0 °C. The signals due to the terminal and bridging borohydride anions are highlighted in dark and light gray, respectively.

BH and $(C_6F_5)AlH_2$. The latter material can further disproportionate to form different species at elevated *T*. This reaction is thus analogous to that documented for $AlMe_3$ and $B(C_6F_5)_3$,[9] although in that case the ultimate B-containing product is BMe_3. Here the $(C_6F_5)_2BH$ initially formed is sequestered by $Cp^*_2ZrH_2$ to form the observed product (Scheme 1). Neither the latter dihydride complex nor $(C_6F_5)_2BH$ was detected in these reactions, suggesting that binding of this borane to $Cp^*_2ZrH_2$ occurs irreversibly, as verified by independent synthesis from these two compounds.

As mentioned previously, activation of this aluminohydride complex with $B(C_6F_5)_3$ produces PE with a bimodal MWD, implying inter alia the existence of two different active species. Since we could independently prepare the principle decomposition product of the initially formed ion-pair (Scheme 1), we evaluated this complex in ethylene polymerization. As might be expected from the strongly coordinating nature of the $(\mu\text{-}H)_2B(C_6F_5)_2$ "anion", $Cp^*_2ZrH(\mu\text{-}H_2)B(C_6F_5)_2$ was not very active in ethylene polymerization (entry 21, Table 1). Thus, polymerization activity was modest at ca. 4×10^3 g PE/mol Zr h at 25 °C and 2.7 atm, but this catalyst did exhibit single-site behavior ($M_w = 218$ K with PDI = 2.1). It can be concluded that the multisite behavior of the $B(C_6F_5)_3$-activated $Cp^*_2ZrH_3AlH_2$ catalyst, which is roughly 1000 times more active under similar conditions, does not arise from competing polymerization by this species.

In the case of the less hindered $(TMSCp)_2ZrH_3AlH_2$ precursor similar, though more complex, behavior was observed (Figure 2). At low temperatures in 1:1 B/T solution, ionization proceeds and at least two different ion-pairs are formed, one of which, on the basis of the ^{19}F NMR spectra, features a terminal $HB(C_6F_5)_3$ anion and the other has a bridging $HB(C_6F_5)_3$ anion in a ratio of 1:1.9 at −50 °C. The species with the bridging anion is fluxional in solution at low *T*, and in particular the signal due to the *o*-F atoms of this anion is at coalescence at −50 °C and sharpens at higher *T*. In contrast the *p*-F and *m*-F signals are largely unaffected over the entire *T* range; we attribute this behavior to interaction of the *o*-F with the metal center in this ion-pair, as has been observed with other complexes that feature this type of interaction.[4a−e,20] We were unable to access the slow exchange limit in this mixed solvent system due to the freezing point of this mixture (ca. −60 °C).

At higher *T* it is evident that the species with a terminal $HB(C_6F_5)_3$ anion is in chemical exchange with excess $B(C_6F_5)_3$ (compare the top two spectra where excess borane is still present), while the complex with the bridging borohydride anion is not or to a lesser extent. Interestingly, the thermal stability of the two anions (and by extension the corresponding cations) appears different; the ion-pair with a bridging $HB(C_6F_5)_3$ anion is thermally stable at room temperature, while that with the terminal borohydride anion decomposes between 0 and 25 °C.

Unfortunately the ^{1}H NMR spectra were uninformative over the entire *T* range studied; multiple $SiMe_3$ and hydride signals were present, while the Cp-H region consisted of a set of overlapping multiplets (see Supporting Information). However, in the $^1H\{^{11}B\}$ NMR spectrum at low temperature signals due to a terminal and bridging B-H were observed at δ 4.27 and −1.39, in an approximate 1:2 ratio, respectively, thus corroborating the analysis of the ^{19}F NMR spectra.

Thus, the structure of the countercations can only be speculated upon. It is known that the neutral precursor is present as two, isomeric dinuclear complexes $[(TMSCp)_2ZrH_3]_2AlH$ and one trinuclear complex $[(TMSCp)_2ZrH_3]_3Al$ in the solid state in a 1:1:1 ratio.[8] Presumably these species are also present in

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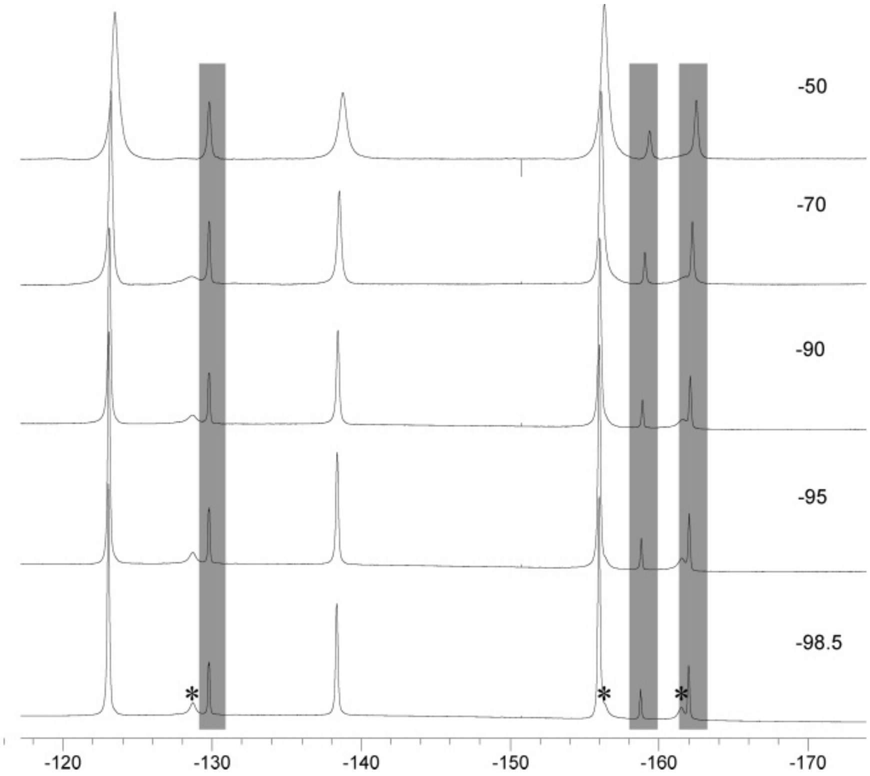

Figure 3. ^{19}F NMR spectra (388 MHz, CD_2Cl_2) of a 4:1 mixture of $B(C_6F_5)_3$ and $[Bu_4N][HB(C_6F_5)_3]$. Signals due to the latter compound are highlighted in gray, while signals attributed to $[Bu_4N][(C_6F_5)_3B(\mu\text{-}H)B(C_6F_5)_3]$ are indicated with an asterisk at low *T*. The signal due to the *p*-F nuclei of this species is barely resolved from that due to the *m*-F nuclei of $B(C_6F_5)_3$.

solution [along with coordinated AlH_3 since their stoichiometry does not correspond to $(TMSCp)_2ZrH_3AlH_2$]. Since the former dinuclear complexes are less hindered than the trinuclear complex, it is possible they could form dinuclear ion-pairs with bridging borohydride anions, while the latter gives a trinuclear ion-pair with terminal borohydride anions. This leads to the prediction that these anions would form in a ratio of 1.33:1 (as opposed to 1.9:1 that is observed) if the solid-state stoichiometry corresponds to that in solution.

It has been noted that the appearance of the ^{19}F NMR spectra of the ion-pairs formed at low *T* with a terminal $HB(C_6F_5)_3$ anion in both the Cp* and Cp′ system was dependent on the presence of excess $B(C_6F_5)_3$. Signals due to $B(C_6F_5)_3$ and $HB(C_6F_5)_3$ were exchange broadened, where the rate of the exchange process was sensitive to concentration (both relative and absolute) and *T*. Control experiments using $[Bu_4N][HB(C_6F_5)_3]$ and $B(C_6F_5)_3$ in mixed $CD_2Cl_2/CFCl_3$ solution revealed identical behavior, and the slow exchange limit was accessible at *T* below −80 °C in this solvent.

At this low *T* (Figure 3), the principal components are the two starting materials. A third set of weak signals is evident (indicated by an asterisk), which are still line-broadened, perhaps due to hindered rotation of the C_6F_5 groups. The intensity of these signals, relative to $[Bu_4N][HB(C_6F_5)_3]$, was sensitive both to the ratio of $B(C_6F_5)_3$ to $HB(C_6F_5)_3^-$ and the absolute concentration, becoming less intense on dilution.

We attribute the behavior seen to reversible formation of the unknown diborohydride anion $[(C_6F_5)_3B(\mu\text{-}H)B(C_6F_5)_3]$ from the two mononuclear components (eq 3). The ^{19}F chemical shifts of this species are very similar to analogous dinuclear anions $[(C_6F_5)_3B(\mu\text{-}X)B(C_6F_5)_3]$ (X = NH_2, CN) reported by the Bochmann group.[21] There is literature precedent for the formation of such dinuclear μ-H species,[22] and the equilibrium appears favorable here ($K \approx 9.3\ M^{-1}$ at −90 °C).

$$(C_6F_5)_3B + HB(C_6F_5)_3 \rightleftharpoons (C_6F_5)_3B{-}H{-}B(C_6F_5)_3 \quad (4)$$

We have been unable to detect this μ-H species in the ^{11}B NMR spectrum at low *T*. The only signal detected at low *T* is that due to the terminal $HB(C_6F_5)_3$ anion;[5] it is present as a line-broadened singlet at all *T* studied [$B(C_6F_5)_3$ is not detectable at low *T* due to efficient quadrupolar relaxation]. While *T*-induced decoupling of ^{11}B and ^1H is responsible for part of this behavior (vide supra), the additional line-broadening seen in the presence of excess $B(C_6F_5)_3$ is likely due to chemical exchange between this anion and the unobserved μ-H species that is still fast on the ^{11}B NMR time scale.

The corresponding ^1H or $^1H\{^{11}B\}$ NMR spectrum was also not informative since the region where a bridging hydride might appear was obscured by the intense ^nBu resonances of the countercation. We thus prepared the analogous $[PPN][HB(C_6F_5)_3]$ salt. At the lowest *T* investigated, only a single line-broadened resonance was observed for the ^1H signal of this compound in the presence of $B(C_6F_5)_3$; the identification of the species detected by ^{19}F NMR spectroscopy as the $(C_6F_5)_3B(\mu\text{-}H)B(C_6F_5)_3$ anion must therefore be viewed as tentative.

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Conclusions

Zirconocene aluminohydride complexes are useful catalyst precursors, which when activated by MAO offer advantages with respect to both polymerization activity and polymer MW. On the other hand activation with discrete Lewis acids such as $B(C_6F_5)_3$ is, unsurprisingly, complicated by the presence of alane in these formulations. Thus, there is limited utility for these catalyst precursors when compared with the corresponding metallocene dialkyls and this discrete Lewis acid.

The multisite behavior exhibited by the $B(C_6F_5)_3$-activated Cp* catalyst at lower *T* can be viewed as arising from two different catalysts. The model studies indicate that the initially formed dinuclear ion-pair is thermally unstable, consistent with multisite behavior. The ultimate decomposition product $[Cp^*_2ZrH][\mu\text{-}H_2B(C_6F_5)_2]$ formed in the absence of monomer is much less active and thus cannot account for the multisite behavior. Given the propensity of zirconocene hydride complexes to engage in reversible C−H activation of the Cp* groups,[23] it is possible that the multisite behavior results from formation of “tuck-in” complexes during propagation.

The $(TMSCp)_2ZrH_3AlH_2$ complex gives rise to a more active (and single-site) catalyst at elevated *T* when activated with $B(C_6F_5)_3$. It is reasonable to attribute this to the higher thermal stability of the species partnered with the bridging $HB(C_6F_5)_3$ anion. Certainly, discrete mononuclear complexes with this bridging counterion are quite robust.[11c] Further, the increased activity seen in the presence of excess $B(C_6F_5)_3$ may be related to activation of this otherwise dormant species, as seen with other structurally characterized ion-pairs that feature a bridging borohydride anion.[11c]

Given the tentative detection of a $[(C_6F_5)_3B(\mu\text{-}H)B(C_6F_5)_3]$ anion in solution at low *T* in the present study, it is plausible to invoke reversible, though transient, formation of an ion-pair partnered with this counteranion as a possible mechanism for this activation, and this will be the subject of future work.

Experimental Section

General Data. All operations were carried out on a standard high-vacuum line or in a drybox under inert atmosphere. Toluene, diethyl ether, benzene, and bromobenzene were reagent grade, distilled from the appropriate drying agents under Ar atmosphere. Deuterated solvents were dried over P_2O_5 and distilled from potassium and benzophenone. The $B(C_6F_5)_3$ obtained from Aldrich Co. was recrystallized from pentane or hexane solution at low *T*, after being treated with a solution of BCl_3 in heptane to remove traces of water. Tri-isobutylaluminum (Aldrich), MAO (10% toluene, Aldrich), and $LiAlH_4$ (1M, Et_2O, Aldrich) were used as purchased. The compounds $HB(C_6F_5)_2$,[15] $Cp^*_2ZrH_2$,[14] $ClAl(C_6F_5)_2$,[18] $(n\text{-}BuCp)_2ZrCl_2$,[24] and $(TMSCp)_2ZrCl_2$[25] were prepared by literature methods.

The ^1H and ^{11}B NMR spectra were recorded on a Varian Inova 400 MHz instrument and were referenced to residual deuterated solvent and external $BF_3\cdot Et_2O$, respectively. The ^{19}F NMR spectra were obtained on a Varian Inova 400 or Mercury 300 MHz instrument using 2,3,5,6-tetrafluoroxylene (TFX) as an internal reference at δ −145.69 relative to $CFCl_3$. Polymer molecular weights were determined by gel permeation chromatography using a Waters 150-C chromatograph eluting with 1,2,4-tricholorobenzene at 135 °C. Narrow MWD polystyrene standards were used for GPC calibration.

Synthesis of $Cp_2ZrH_3AlH_2$ Complexes [Cp = Cp*, TMSCp, ^nBuCp]. Complexes $(TMSCp)_2ZrH_3AlH_2$ and $(^nBuCp)_2ZrH_3AlH_2$ were synthesized using the methods reported by Stephan and coworkers,[8b,c] varying the solvent and temperature of reaction. A solution of the corresponding metallocene dichloride $(TMSCp)_2ZrCl_2$ or $(^nBuCp)_2ZrCl_2$ (4.57 mmol) in diethyl ether (25 mL) was stirred at 0 °C, and 2.2 equiv of $LiAlH_4$ (10.05 mmol) in diethyl ether was added. The formation of a fine white powder was observed when the mixture was allowed to warm to room temperature (30 min), and the solution was filtered through Celite. The diethyl ether was evaporated to provide the aluminohydride complexes in quantitative yield, which were dissolved in benzene, to obtain a known concentration solution for each complex, which were stored frozen at −30 °C.

The preparation of the $Cp^*_2ZrH_3AlH_2$ aluminohydride was similar to the procedure described by Stephan in THF.[8b,c] $Cp^*_2ZrCl_2$ (1.02 mmol) was dissolved in THF (6 mL), $LiAlH_4$ (2.2 mmol, 2.0 M in THF) was added at room temperature, and the solution was stirred for 1.5 h. The solvent was partially evaporated, and the residue was extracted with hexane and filtered through Celite. A white powder was obtained on concentrating the extracts to dryness (98% crude yield) and was recrystallized from a mixture of benzene and hexane at low temperature.

Synthesis of $Cp^*_2ZrH(\mu\text{-}H)_2B(C_6F_5)_2$. $Cp^*_2ZrH_2$ (0.18 g, 0.49 mmol) was added to a suspension of $HB(C_6F_5)_2$ (0.17 g, 0.49 mmol) in 5 mL of toluene a room temperature. After all the solids dissolved, volatiles were removed in vacuo. A yellow solid was obtained. Yield: 0.33 g, 95%. ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 6.64 (s, 1H), 1.63 (s, 30 H), −0.73 (1:1:1:1 quartet, J_{BH} = 75 Hz, 2H). ^{19}F NMR (288 MHz, 25 °C, C_6D_6): δ −130.3 (br d, *o*-F), −157.6 (t, *p*-F), −163.6 (m, *m*-F). IR (Nujol, NaCl): 2139m, 2091m and 2018m (μ-H-B), 1639m, 1510s (Zr-H), 1377s, 1325s, 1096s, 1024m, 960s, 882m, 802m, 725m, 631m cm^{-1}. Anal. Calcd for $C_{32}H_{33}F_{10}BZr$: C, 54.15; H, 4.65. Found: C, 54.01; H 4.48.

Formation of $HAl(C_6F_5)_2$. R_2AlCl (0.4 g, 0.1 mmol) and Cp_2ZrHCl (0.26 g, 1 mmol) were mixed at room temperature in 20 mL of toluene. The mixture was stirred for 4 h, and all volatiles were removed in a vacuum. Benzene (10 mL) was added and the suspension filtered to remove Cp_2ZrCl_2. An oil was obtained after the solvent was removed. ^1H and ^{19}F NMR spectra show a mixture of $HAl(C_6F_5)_2$ with residual zirconium impurities. By comparing the intensity of ^1H and ^{19}F signals of a weighed amount of this oil to those of a weighed amount of TFX in C_6D_6 the estimated purity of this compound is about 95 mol %. ^1H NMR (toluene-d_8:/bromobenzene-d_5, 1:1, 300 MHz): δ 6.11 (br, Al-H). ^{19}F NMR (toluene-d_8:/bromobenzene-d_5, 1:1, 300 MHz): δ −122.3, −122.6, −152.1, −152.4, −161.3, −161.8.

The ^{19}F NMR spectra and those obtained on the addition of a small amount of $Cp^*_2ZrH_2$ to this material are included as Supporting Information.

Activation of $Cp_2ZrH_3AlH_2$ Complexes [Cp = Cp*, TMSCp, ^nBuCp]. The activations with MAO were carried out dissolving the aluminohydride in toluene, adding the prescribed amount of MAO, and then the activated complexes were transferred to the polymerization reactor by syringe. The activation of the aluminohydride complexes with $B(C_6F_5)_3$ was carried out in toluene solution at −30 °C or in bromobenzene/toluene (B/T) (1:1) mixtures at −50 °C. As for activations in toluene, the Cp'_2ZrAlH_5 complex was sealed in a vial. The corresponding equivalents of the $B(C_6F_5)_3$ dissolved in toluene were added at −30 °C. The reaction mixture was allowed to warm at room temperature and added by syringe to the polymerization reactor. In B/T mixtures, the $Cp^*_2ZrAlH_5$, dissolved in 1:1 bromobenzene/toluene, was added at −50 °C to the corresponding equivalents of $B(C_6F_5)_3$ in bromobenzene/toluene

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solution previously cooled to −50 °C. The solution was then added to the polymerization reactor using a precooled syringe. The same procedure in bromobenzene-d_5/toluene-d_8 at −50 °C was also carried out in NMR tubes for the characterization of the species present.

Polymerization Procedure. The aluminohydride complexes were activated with $B(C_6F_5)_3$ or MAO in toluene or bromobenzene/toluene (1:1) mixtures, as described above, and in all the cases the solutions were transferred by syringe to the reactor. Polymerizations were carried out in a 600 mL Parr reactor equipped with mass flow meter and temperature control. Before each reaction, the reactor was heated for 1 h to 90 °C with $AlMe_3$/toluene to remove all moisture traces.

Polymerization conditions for all the runs were as follows: ethylene pressure of 40 psig, 200 mL of iso-octane, polymerization temperature at 25, 50, or 75 °C. The monomer flow rate was continually monitored through the mass flow meter, and polymerizations were carried out for 30 min. For ethylene polymerizations using catalytic systems activated with $B(C_6F_5)_3$, 0.5 mL of TIBAL was added previously to the iso-octane as scavenger before saturating with monomer.

The polymerization was stopped by rapid depressurization of the reactor and quenching with methanol for $Cp_2ZrH_3AlH_2/B(C_6F_5)_3$ systems and acidified methanol (10 wt % HCl) for $Cp_2ZrH_3AlH_2$/MAO. Then the polymers were washed several times with methanol, filtered, and dried in a vacuum oven for 4 h.

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Supporting Information Available: Variable-temperature ^1H, ^{11}B, and ^{19}F NMR spectra of mixtures of aluminohydride complexes and $B(C_6F_5)_3$. This information is available free of charge via the Internet at http://pubs.acs.org.

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