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Sterically Hindered Aluminum Alkyls: Weakly Interacting Scavenging Agents of Use in Olefin Polymerization

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Sterically hindered aluminum methyl compounds derived from reaction of hindered phenols with $AlMe_3$ (i.e., $MeAl(BHT)_2$ and $MeAl(BHT^*)_2$; BHT = 2,6-di-*tert*-butyl-4-methylphenoxide; BHT* = 2,4,6-tri-*tert*-butylphenoxide) are useful scavenging agents in olefin polymerization using metallocene catalysts. They do not, or only slowly, react with activators such as $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ at 25 °C, nor do they coordinate to or react with metallocenium ion-pairs derived from metallocene dialkyls and these activators. A mixture of $AlMe_3$ and a large excess of $MeAl(BHT)_2$ proves advantageous for catalysts that are susceptible to reaction with BHT-H, the hydrolysis product of $MeAl(BHT)_2$. Ethylene polymerization experiments establish that the activity of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ is only slightly inhibited by $AlMe_3$ in the presence of a significant excess of $MeAl(BHT)_2$. Spectroscopic studies have revealed that $AlMe_3$ is in equilibrium with $MeAl(BHT)_2$, forming $Me_2Al(BHT)$. At low temperature using ^{13}C NMR spectroscopy, a 1:1 mixture of $AlMe_3$ and $MeAl(BHT)_2$ is shown to consist of Al_2Me_6, $MeAl(BHT)_2$, and primarily $Me_2Al(\mu\text{-}BHT)_2AlMe_2$. A higher temperature, both intra- and intermolecular exchange of both Al-Me and Al-BHT groups, coupled with the temperature dependence of the various equilibria involved, lead to ^1H and ^{13}C NMR spectra that are consistent with monomeric $Me_2Al(BHT)$. ^1H and ^{19}F NMR spectroscopic studies of mixtures of the ion-pairs $[Me_2C(Cp)IndMMe][MeB(C_6F_5)_3]$ (M = Zr, Hf) or $[Me_2SiCp_2ZrMe][MeB(C_6F_5)_3]$ with various quantities of $AlMe_3$ in the presence of $MeAl(BHT)_2$ were conducted. The $AlMe_3$-mediated degradation of ion-pairs that are susceptible to $B(C_6F_5)_3$ dissociation is largely absent in the presence of excess $MeAl(BHT)_2$, although reversible formation of $[Me_2SiCp_2Zr(\mu\text{-}Me)_2AlMe_2][MeB(C_6F_5)_3]$ and related adducts is observed at low ratios of $MeAl(BHT)_2$ to $AlMe_3$.

Introduction

The mechanistic study of metallocene-catalyzed olefin polymerization has been considerably simplified through the development of discrete activators such as $B(C_6F_5)_3$, which give rise to thermally stable and isolable ion-pairs.[1] The ion-pairs can be characterized in both the solid state and solution, and a wealth of information is now available on their intrinsic behavior. Because of the extreme air- and moisture-sensitivity of these compounds, polymerization studies may require the use of high-vacuum techniques and/or relatively high concentrations of these compounds (ca. 0.1 mM). In contrast, MAO-activated metallocene catalysts are typically generated using micromolar concentrations of metallocene complexes in efficiently stirred autoclave reactors, where a large excess of MAO serves as both scavenger and activator.[2]

Although trialkylaluminum compounds are used as scavengers (and alkylating agents) in polymerization studies involving $[Ph_3C][B(C_6F_5)_4]$ and metallocene dichlorides,[3] the activation process is complicated and leads to the formation of different catalyst precursors as recent mechanistic studies have shown.[3a−c] Further, a specific order of catalyst/cocatalyst introduction is required due to the incompatibility of $[Ph_3C][B(C_6F_5)_4]$ with higher AlR_3 (due to facile β-H abstraction; even with $AlMe_3$ slower Me abstraction and activator degradation is observed).[3b] In the case of metallocene dialkyls activated by $B(C_6F_5)$ or related compounds, the use of preformed ion-pairs is preferable. In situ generation of these ion-pairs in the presence of AlR_3 can be complicated by competing AlR_3-mediated degradation of $B(C_6F_5)_3$.[4] Even when preformed ion-pairs are employed, the amount of AlR_3 must be controlled to avoid reversible catalyst inhibition, which results from formation of thermally stable, but unreactive adducts of the type $[Cp_2Zr(\mu\text{-}R)_2AlR_2][MeB(C_6F_5)_3]$.[5] Finally, some ion-pairs that are prone to dissociation of $B(C_6F_5)_3$ (e.g., hafnocene complexes[6]) can be readily degraded in the presence of AlR_3 compounds (vide infra).[7]

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[1] (a) Bochmann, M.; Lancaster, S. J.; Hannant, M. D.; Rodriguez, A.; Schormann, M.; Walker, D. A.; Woodman, T. J. *Pure Appl. Chem.* **2003**, *75*, 1183−1195. (b) Chen, E. X.-Y.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

[2] (a) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911−3921. (b) Zurek, E.; Ziegler, T. *Prog. Polym. Sci.* **2004**, *29*, 107−148. (c) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Zakharov, V. A.; Brintzinger, H. H.; Ystenes, M.; Rytter, E.; Talsi, E. P. *J. Organomet. Chem.* **2003**, *683*, 92−102. (d) Babushkin, D. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2002**, *124*, 12869−12873.

[3] (a) Gotz, C.; Rau, A.; Luft, J. *J. Mol. Catal. A: Chem.* **2002**, *184*, 95. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (c) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. (d) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D *J. Am. Chem. Soc.* **1991**, *113*, 8570.

[4] (a) Klosin, J.; Roof, G. R.; Chen, E. X.-Y.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686. (b) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912.

[5] Bochmann, M.; Lancaster, S. J. *Angew. Chem.* **1994**, *106*, 1715−18.

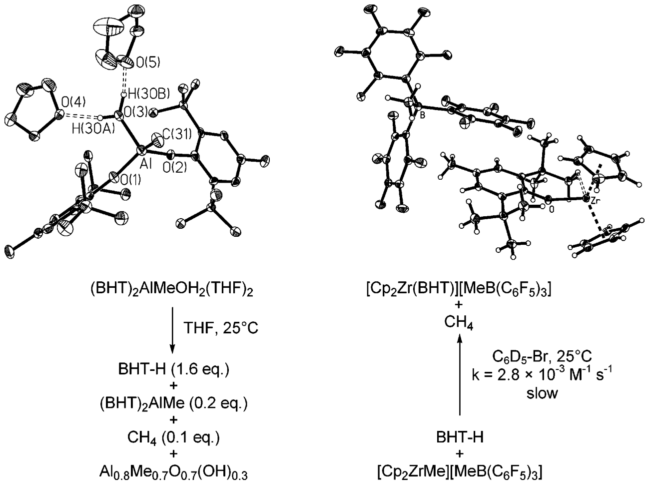
10.1021/om060474s CCC: \$33.50

Several years ago, it occurred to us that if one could use *monomeric* alkylaluminums[8] as scavenging agents, both inhibition of catalysts and degradation of organoborane or even borate activators might be mitigated, thus simplifying the conduct of olefin polymerization using discrete, metallocenium ion-pairs at least in autoclave reactors. As the key step in both processes involves formation of hetero-dinuclear species with μ-R bridges, by definition, a monomeric alkylaluminum should not as readily participate in such processes. Finally, we anticipated that the use of a discrete and "weakly interacting" alkylaluminum scavenger of this type would lead to chemically cleaner systems useful in mechanistic study of metallocene catalysts and catalyst precursors under conditions that are relevant to an industrial setting (i.e., efficiently stirred autoclave reactors).

We were attracted to the use of $MeAl(BHT)_2$ for this purpose due to its crystallinity and ready availability from inexpensive starting materials.[9] Also, since this compound lacks β-H atoms, it should be more compatible with activators such as $[Ph_3C][B(C_6F_5)_4]$. This compound proved to be an effective scavenger of use in ethylene or propene polymerization using either preformed or in situ generated ion-pairs derived from a variety of metallocene and even some nonmetallocene catalysts.[10] It could be used in large excess without inhibiting catalyst activity and is not pyrophoric and thus easily handled.[11] Activities in ethylene polymerization using, for example, $[Cp_2ZrMe][MeB(C_6F_5)_3]$ were ca. 10 times higher than could be achieved in the presence of conventional AlR_3 scavengers (R = Me, Et, ^{i}Bu etc.).[10e,f]

On the other hand, it became apparent that with less hindered (and generally much less active) catalysts, the use of $MeAl(BHT)_2$ as scavenger inhibited polymerization for reasons that were not apparent. NMR spectroscopic studies indicated no reaction nor even evidence for coordination to the ion-pairs.[12] It is during these studies that we became aware that the hydrolysis product of $MeAl(BHT)_2$ is in fact the corresponding phenol (BHT-H) rather than CH_4.[13] Preliminary work established that this reaction proceeds through formation of a tetrahedral adduct $(BHT)_2AlMe{\cdot}OH_2$, which was structurally characterized[14] and which decomposed in THF solution to form 1.6 equiv of BHT-H, 0.2 equiv of $MeAl(BHT)_2$, and only 0.1 equiv of CH_4 (Scheme 1). Material balance required the formation of a species with the empirical formula $Al_{0.8}Me_{0.7}O_{0.7}(OH)_{0.3}$, and though formation of a methylaluminoxane species was evident in the NMR spectra of these mixtures, it has resisted purification and characterization.

Scheme 1



In a preliminary communication we showed that although BHT-H does react with $[Cp_2ZrMe][MeB(C_6F_5)_3]$ to form $[Cp_2ZrBHT][MeB(C_6F_5)_3]$ and CH_4 (Scheme 1), the rate of that reaction is about *7 orders of* magnitude slower than the apparent rate of ethylene insertion at 25 °C.[14] Consequently, the presence of BHT-H during catalysis using many catalysts is innocuous and one can even deliberately add significant amounts of (dry) BHT-H to a polymerizing system without ill effect.[14]

However, for other less hindered and less active catalysts, where the rate of reaction of BHT-H with the ion-pair is essentially instantaneous on mixing at typical NMR concentrations (1−10 mM),[12] it was evident that a scavenger that only forms alkane on initial hydrolysis was required. Motivated by reports in the patent literature on the utility of R_2AlBHT (R = ^{i}Bu, etc.) and related compounds,[15] we investigated the utility of mixtures of $MeAl(BHT)_2$ and $AlMe_3$[16] and have discovered that this combination is very effective for use in ethylene

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(6) (a) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358−10370. (b) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772−1784.

(7) Collins, S.; Dai, C.; Li, Z.; Mohammed, M.; Tian, J.; Tomazsewski, R.; Vollermhaus, R. *Polym. Mater. Sci. Eng.* **2001**, *84*, 921−22.

(8) (a) Roesky, H. W.; Walawalkar, M. G.; Murugavel, R. *Acc. Chem. Res.* **2001**, *34*, 201−211. (b) Wehmschulte, R. J.; Power, P. P. *Polyhedron* **2000**, *19*, 1649−1661. (c) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63−135.

(9) (a) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543−2548. (b) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409−416. (c) Skowronska-Ptasinska, M.; Staowieyski, K. B.; Pasynkiewicz, S.; Carewska, M. *J. Organomet. Chem.* **1978**, *160*, 403−409. (d) Skowronska-Ptasinska, M.; Starowieyski, K. B.; Pasynkiewicz, S. *J. Organomet. Chem.* **1977**, *141*, 149−156. (e) Skowronska-Ptasinska, M.; Starowieyski, K. B.; Pasynkiewicz, S. *J. Organomet. Chem.* **1975**, *90*, C43−C44.

(10) (a) Al-Humydi, A.; Garrison, J. C.; Youngs, W. J.; Collins, S. *Organometallics* **2005**, *24*, 193−196. (b) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapleton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 7930−7941. (c) Metcalfe, R. A.; Kreller, D. I.; Tian, J.; Kim, H.; Taylor, N. J.; Corrigan, J. F.; Collins, S. *Organometallics* **2002**, *21*, 1719−1726. (d) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161−2169. (e) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619−1621. (f) 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*, 3695−3698.

(11) For other studies involving the use of $MeAl(OAr)_2$ or methylaluminoxane modified by hindered phenols see: (a) Busico, V.; Cipullo, R.; Cutillo, F.; Friedrichs, N.; Ronca, S.; Wang, B. *J. Am. Chem. Soc.* **2003**, *125*, 12402−12403. (b) Kissin, Y. V. *Macromolecules* **2003**, *36*, 7413−7421. (c) Rösch, J. Eur. Pat. Appl. EP 0781783, 1997, 14 pp. (d) Tran, N. H.; Davenport, D. L.; Malpass, D. B.; Rabbit, C. S. Eur. Pat. Appl. EP 0561476, 1993, 20 pp. (e) Marks, T. J.; Yang, X.; Mirviss, S. B. PCT Int. Appl. WO 9410180, 1994, 18 pp.

(12) Tomaszewski, R.; Vollmerhaus, R.; Al-Humydi, A.; Wang, Q.; Taylor, N. J.; Collins, S. *Can. J. Chem.* **2006**, *84*, 214−224.

(13) Related chemoselective protonolyses of aluminum phenoxides or their donor adducts are known. (a) VanPoppel, L. G.; Bott, S. G.; Barron, A. R. *J. Chem. Crystallogr.* **2001**, *31*, 417−420. (b) Taden, I.; Kang, H. C.; Massa, W.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2000**, 441−445. (c) McMahon, C. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3703−3704. (d) Healy, M. D.; Leman, J. T.; A, R., Barron *J. Am. Chem. Soc.* **1991**, *113*, 2776−2777. (e) Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 597−608. (f) Healy, M. D.; Mason, M. R.; Gravelle, P. W.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441−454.

(14) Stapleton, R. A.; Galan, B. R.; Collins, S.; Simons, R. S.; Garrison, J. C.; Youngs, W. J. *J. Am. Chem. Soc.* **2003**, *125*, 9246−9247.

(15) (a) Chen, E. Y.; Kruper, W. J., Jr.; Roof, G. R.; Schwartz, D. J.; Storer, J. W. PCT Int. Appl. WO 2000,009514, 2000, 32 pp. (b) Chen, E. Y.; Kruper, W. J., Jr.; Roof, G. R.; Schwartz, D. J.; Storer, J. W. PCT Int. Appl. WO 2000,009513, 2000, 32 pp. (c) Rosen, R. K.; Vanderlende, D. D. PCT Int. Appl. WO 9735893, 1997, 27 pp. (d) Rosen, R. K.; Stevens, J. C.; Tracy, J. C. PCT Int. Appl. WO 9727228, 1997, 23 pp.

(16) For an early report on the use of this mixture to activate Cp_2ZrCl_2 for ethylene polymerization see: Reddy, S. S.; Shashidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180−1182. This mixture was no more effective than $AlMe_3$ at the same concentrations, etc.

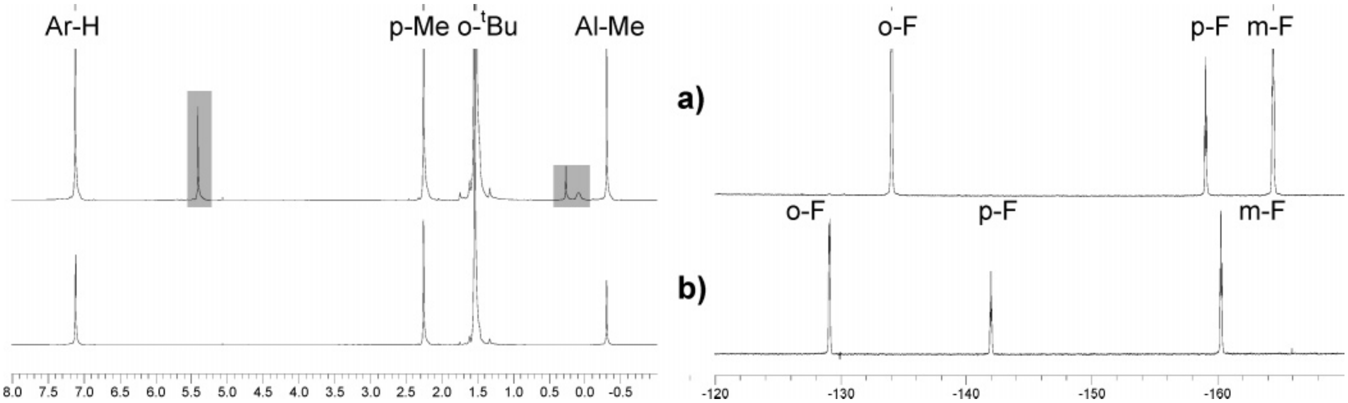

Figure 1. ^1H (300 MHz, C_6D_6, left) and ^{19}F NMR (282 MHz, C_6D_6, right) spectra of (a) a 5:1 mixture of $MeAl(BHT)_2$ and $[Cp_2ZrMe][MeB(C_6F_5)_3]$ and (b) a 5:1 mixture of $MeAl(BHT)_2$ and $B(C_6F_5)_3$. Signals due to $[Cp_2ZrMe][MeB(C_6F_5)_3]$ are highlighted in gray.

polymerization. In this paper we provide details of this work and the mechanistic reasons underlying the efficacy of these hindered scavengers in olefin polymerization using metallocene catalysts.

Results and Discussion

Compatibility of $MeAl(BHT)_2$ with Metallocenium Ions and Common Activators. As shown in Figure 1a, the ^1H and ^{19}F NMR spectra of a mixture of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ and excess $MeAl(BHT)_2$ ($[Zr] = 0.02$ M, $[Al] = 0.10$ M) shows no reaction between these two species. Further, the 2D $^1H-^1H$ NOESY spectrum of this mixture (see the Supporting Information) shows no evidence of exchange correlation between Al-Me and Zr-Me (or B-Me) groups despite the use of mixing times as long as 1.0 s. This puts an upper limit on the rate constant for Me exchange between these two compounds of $k = 1.9 \times 10^{-3}$ s^{-1} at 22 °C based on the S:N ratios of the diagonal peaks in this 2D spectrum.[17] This corresponds to a lower limit for $\Delta G^{\ddagger} \geq 21.0$ kcal mol^{-1} at 22 °C. On the other hand, the expected cross-peaks between B-Me and Zr-Me resonances due to competing ion-pair reorganization and borane dissociation are seen (see the Supporting Information). A rough estimate of the total exchange rate constant based on the diagonal versus cross-peak intensities[18] is 0.043 s^{-1}, corresponding to $\Delta\Delta G^{\ddagger} = 19.3$ kcal mol^{-1} at 295 K. This value is in reasonable agreement with data reported in the literature for unbridged ion-pairs of this type.[1]

It is known from the work of Siedle and co-workers that degenerate exchange of Me groups occurs between Cp_2ZrMe_2 and $MeAl(BHT)_2$ with $\Delta G^{\ddagger} = 22.4$ kcal mol^{-1} at 22 °C based on kinetic measurements using ^{13}C-labeled materials.[19]

Surprisingly, the analogous process involving $[Cp_2Zr^{13}Me]$, $[^{13}MeB(C_6F_5)_3]$, and $MeAl(BHT)_2$ appears equally slow at room temperature. Under pseudo-first-order conditions using a 5-fold excess of $MeAl(BHT)_2$ there is limited, if any, scrambling on mixing at 22 °C at $[Zr] = 0.02$ M (see the Supporting Information). Ion-pair thermal instability limited the range of temperature and times over which this reaction could be investigated, but satisfactory data were obtained at 40 °C. Analysis of these data is also complicated by the fact that exchange of Zr-Me and B-Me groups is rapid on the chemical time scale, while the latter resonances are line-broadened at this elevated temperature. Further, competing decomposition of the ion-pair results in disappearance of labeled Zr-Me at a faster rate compared to that at which labeled $MeAl(BHT)_2$ appears.

Thus, the observed rate constant and activation free energy are based on the latter data. An estimate for the pseudo-first-order rate constant for scrambling of the label from Zr-^{13}Me into Al-Me is 4.76×10^{-5} s^{-1}. As $[MeAl(BHT)_2] = 0.106$ M in this experiment, this corresponds to a second-order rate constant of 4.49×10^{-4} M^{-1} s^{-1} or $\Delta G^{\ddagger} = 23.2$ kcal mol^{-1} at 40 °C. Thus, formation of a transient hetero-dinuclear adduct between $[Cp_2ZrMe][MeB(C_6F_5)_3]$ and $MeAl(BHT)_2$ must occur during this exchange process, but it is evident that the equilibrium is quite unfavorable compared to simple AlR_3, and $AlMe_3$ in particular.[5]

$MeAl(BHT)_2$ is inert toward prototypical metallocenium ion-pairs, as illustrated above. It is also unreactive toward Lewis acidic organoboranes used to activate metallocene dialkyls. The ^1H and ^{19}F NMR spectra of excess $MeAl(BHT)_2$ and $B(C_6F_5)_3$ (Figure 1b), the chelating diborane $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$,[20] or the strongly Lewis acidic $9,10\text{-}(C_6F_4)_2[B(C_6F_5)]_2$[21] are unchanged compared to those of the pure compounds.[10f]

$MeAl(BHT)_2$ does react slowly with $[Ph_3C][B(C_6F_5)_4]$ to form a mixture of oligomeric methylaluminum compounds of undetermined structure. The Al-Me resonances are undiminished in intensity during degradation, although they become broad, as do all other resonances (Figure 2a). Additional signals characteristic of aliphatic Me groups appear at δ 0.7−0.9, suggesting degradation or rearrangement of the Ar-^{t}Bu groups during this process. The only readily identifiable product is Ph_3C-H (δ 5.31, Figure 2a), while the corresponding ^{19}F NMR spectra indicate no anion degradation.

In monitoring these reactions, it is apparent that Ph_3CH is formed about 2 times faster than the rate of $MeAl(BHT)_2$ consumption ($k_{obs} = 5.8$ vs 3.0×10^{-4} M^{-1} s^{-1}). Further, only catalytic amounts of $[Ph_3C][B(C_6F_5)_4]$ are required for this reaction. Taken together, the results suggest that $[Ph_3C][B(C_6F_5)_4]$ *initiates* degradation of $MeAl(BHT)_2$, possibly by initial hydride abstraction, but is otherwise uninvolved in the subsequent degradation of this compound. Hydride abstraction by $[Ph_3C][B(C_6F_5)_4]$ would be expected to generate a *p*-quinone methide (eq 1); normally these species are reasonably stable when derived from hindered phenols such as BHT-H,[22] but the Lewis acidic aluminum center would make this species highly

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[17] Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 4605−25.

[18] Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

[19] Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schröpfer, J. N. *Polyhedron* **1990**, *9*, 301−308.

[20] Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244−3245.

[21] Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312−1316.

[22] Filar, L. J.; Winstein, S. *Tetrahedron Lett.* **1960**, 9−16.

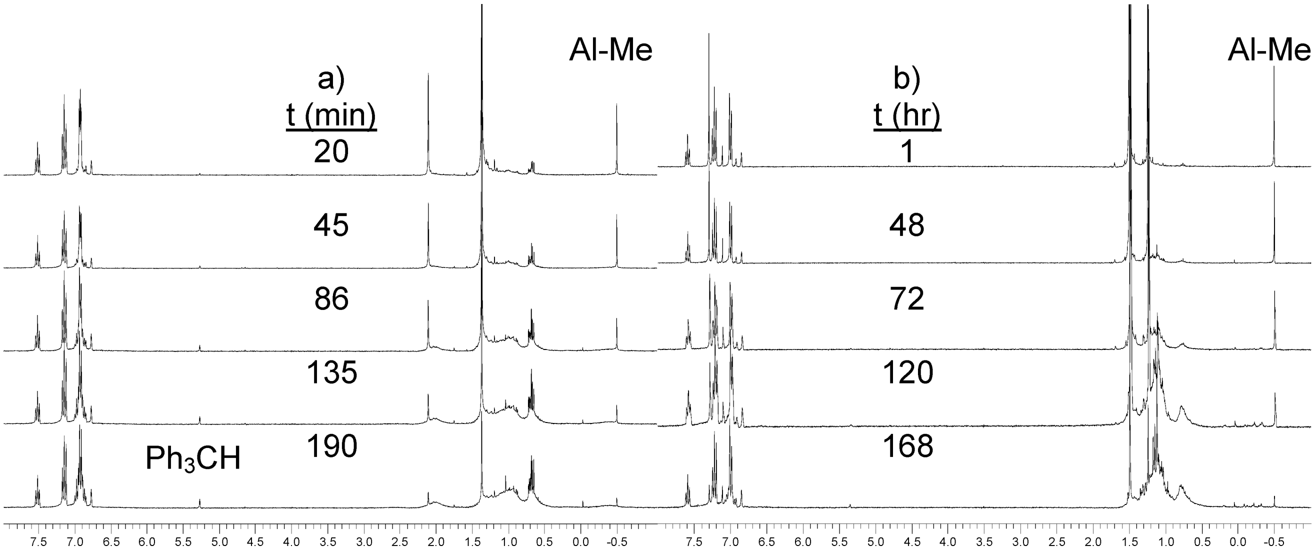
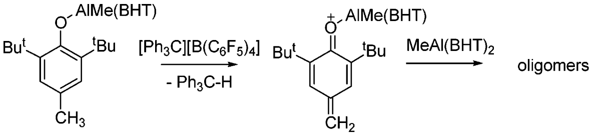


Figure 2. ^{1}H NMR spectra (300 MHz, C_6D_5-Br, 25 °C) of a 1:1 mixture of (a) $[Ph_3C][B(C_6F_5)_4]$ and $MeAl(BHT)_2$ (left) and (b) $[Ph_3C][B(C_6F_5)_4]$ and $MeAl(BHT^*)_2$ (right) as a function of time. Note that the latter units are in *hours* [vs minutes in the case of $MeAl(BHT)_2$].

electrophilic.[23] Since the use of BHT-H in the presence of $AlCl_3$, as a reagent for the electrophilic *tert*-butylation of other aromatic compounds, is known,[24] it is possible this or a related process is involved in the further degradation of $MeAl(BHT)_2$.



(1)

As $MeAl(BHT)_2$ has benzylic C$-$H bonds, which would be most susceptible to either hydrogen or hydride abstraction, we investigated the compatibility of $MeAl(BHT^*)_2$ (BHT* = 2,4,6-tri-*tert*-butylphenoxide) with $[Ph_3C][B(C_6F_5)_4]$. Degradation of this material was much slower (ca. 33× slower) than in the case of $MeAl(BHT)_2$. Although only trace amounts of Ph_3C-H formed in this reaction, it would appear that similar Al byproducts were formed (Figure 2b). Here, however, there was a noticeable loss of Al-Me intensity over time in this experiment.

It is quite possible that the degradation of both of these aluminum alkyls is redox-initiated by $[Ph_3C][B(C_6F_5)_4]$ and in the case of $MeAl(BHT)_2$ is accompanied by hydrogen abstraction by $Ph_3C^\bullet$ to produce Ph_3C-H. We do note in this context that $MeAl(BHT)_2$ is susceptible to oxidative degradation by O_2 where the formation of $BHT^\bullet$ and Al-centered radicals has been invoked.[9c]

Under catalytic conditions using in situ catalyst formation from Cp_2ZrMe_2 and $[Ph_3C][B(C_6F_5)_4]$ in the presence of a large excess of $MeAl(BHT)_2$ or $MeAl(BHT^*)_2$ this degradation reaction does not interfere with catalysis. Thus, nearly identical polymerization activities of 7.2 and 7.8 $\times$ 10^6 g PE/mol Zr $\times$ h were observed when 2.2 μM $[Ph_3C][B(C_6F_5)_4]$ was precontacted with either $MeAl(BHT)_2$ or $MeAl(BHT^*)_2$ ([Al] = 1.0 mM) for 6 min prior to the addition of Cp_2ZrMe_2 ([Zr] = 2.0 μM) into toluene saturated with ethylene at 30 psig at 30 °C.

An earlier report that concluded that $[Ph_3C][B(C_6F_5)_4]$ and $MeAl(BHT)_2$ are incompatible must be in error[10e] since an identical protocol was employed here and the results independently confirmed using the two different scavengers. Further, from the second-order rate constant for degradation ($k_{obs} = 3.0 \times 10^{-4}\ M^{-1}\ s^{-1}$), and the activator and scavenger concentrations used, it can be estimated that minimal degradation of either compound could have occurred (i.e., the extent of $[Ph_3C][B(C_6F_5)_4]$ or $MeAl(BHT)_2$ degradation within 6 min corresponds to a decrease in concentration of $(2-4) \times 10^{-10}$ M).

Mixtures of $MeAl(BHT)_2$ with Al_2Me_6. As indicated in the Introduction, unhindered or less reactive polymerization catalysts can be deactivated by BHT-H,[12] the kinetic hydrolysis product of $MeAl(BHT)_2$.[14] To that end, we considered the use of $R_2Al(OAr)$ (R = Me, etc.) and related compounds as scavengers that would be prone to formation of alkane on hydrolysis. These compounds exist as monomers, dimers, or even higher-order aggregates depending on both R and OAr; when polynuclear, they are almost invariably bridged by the phenoxide group. Structurally characterized examples of mono- and dinuclear compounds have been reported,[25] while other compositions have been characterized by solution and solid-state NMR spectroscopy.[25,26]

The compound $Me_2Al(BHT)$ has been structurally characterized through formation of adducts with donors such as C=O compounds, amines, or phosphines.[27] The equilibrium between $MeAl(BHT)_2$ and Me_3Al, which furnishes $Me_2Al(BHT)$, was studied some time ago by Ittel and co-workers by variable-

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[23] Toteva, M. M.; Moran, M.; Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 8814−8819.

[24] Tashiro, M. *Synthesis* **1979**, *12*, 921−36.

[25] (a) Firth, A. V.; Stewart, J. C.; Hoskin, A. J.; Stephan, D. W. *J. Organomet. Chem.* **1999**, *591*, 185−193. (b) Aitken, C. L.; Barron, A. R. *J. Chem. Crystallogr.* **1996**, *26*, 293−295. (c) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704−8. (d) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A.; Angermund, K.; Betz, P.; Goddard, R.; Krueger, C. *J. Organomet. Chem.* **1991**, *411*, 37−55. (e) Kumar, R.; Sierra, M. L.; De Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484−9. (f) Dzugan, S. T.; Goedken, V. L. *Inorg. Chim. Acta* **1988**, *154*, 169−75.

[26] (a) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *333*, 155−68. (b) Starowieyski, K. B.; Skowronska-Ptasinska, M.; Muszynski, *J. Organomet. Chem.* **1978**, *157*, 379−87. (c) Pasynkiewicz, S.; Starowieyski, K. B.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1973**, *52*, 269−74.

[27] (a) Akakura, M.; Yamamoto, H.; Bott, S. G.; Barron, A. R. *Polyhedron* **1997**, *16*, 4389−4392. (b) Barron, A. R. *IUC, Crystallogr. Symp.* **1991**, *4*, 164−70. (c) Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 597−608. (d) Healy, M. D.; Leman, J. T.; Barron, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 2776−7. (e) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086−97. (f) Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949−54.

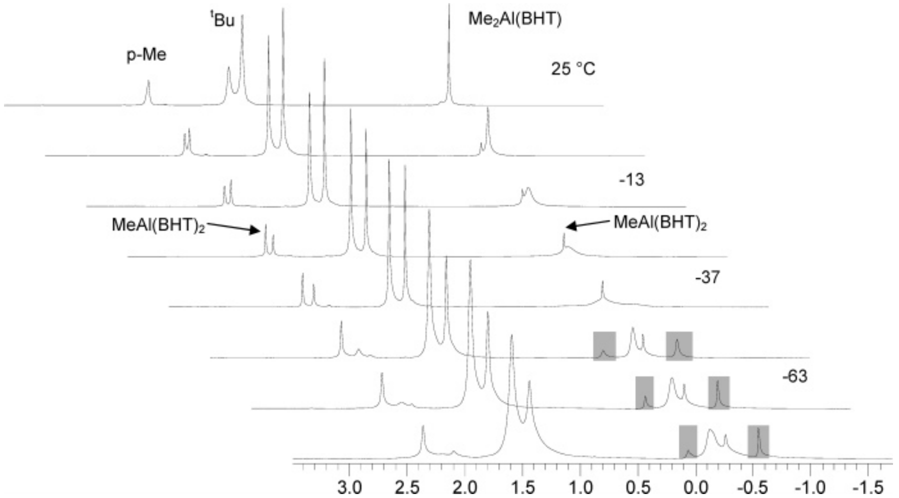


Figure 3. Variable-temperature ^{1}H NMR spectra (400 MHz, toluene-d_8) of a 1:1 mixture of $AlMe_3$ and $MeAl(BHT)_2$ with $[MeAl(BHT)_2]_o$ = 0.500 M. Signals due to $MeAl(BHT)_2$ and Me_2AlBHT are labeled, and those due to Al_2Me_6 are highlighted in gray.

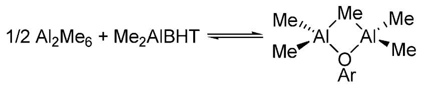
temperature ^{1}H NMR spectroscopy; the low-temperature spectra had to be simulated with reference to assumed equilibria, as the slow exchange limit was not accessible.[9b]

We have reinvestigated this process using variable-temperature ^{1}H and ^{13}C NMR spectroscopy. As shown in Figure 3, the 400 MHz ^{1}H NMR spectrum of a 1:1 mixture of $AlMe_3$ and $MeAl(BHT)_2$ exhibits a set of line-broadened signals characteristic of $Me_2Al(BHT)$ and $MeAl(BHT)_2$ at 25 °C. On cooling, the signals due to Ar-H, Me, and ᵗBu protons sharpen, while the AlMe signal due to $Me_2Al(BHT)$ broadens, and at −13 °C, a set of separate and sharp signals due to $MeAl(BHT)_2$ are seen. The ratio of $Me_2Al(BHT)$ to $MeAl(BHT)_2$ is 2.13:1 at −13 °C.

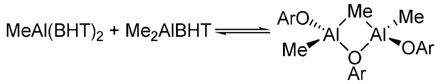
On further cooling, all of the signals due to $Me_2Al(BHT)$ line-broaden, while those due to $MeAl(BHT)_2$ remain sharp (aside from viscosity-induced line-broadening at low temperature in this concentrated solution). The Al-Me signal of $Me_2Al(BHT)$ shows decoalescence behavior and at, for example, −57 °C; separate signals due to the terminal and bridging Me groups of Al_2Me_6 are present (highlighted in gray). In contrast, the Al-Me signal due to $Me_2Al(BHT)$ (as well as the other signals characteristic of this compound) remains broadened even at the lowest temperature investigated. The Al-Me region of the spectrum at −63 °C can be integrated, and from this the relative amounts of the three compounds present can be determined to be $Me_2Al(BHT)$:$MeAl(BHT)_2$:Al_2Me_6 = 6.05:2.00:1, while K_{eq} for the reaction depicted in eq 2 is 33.3 M at this temperature.

$$Al_2Me_6 + 2\ MeAl(BHT)_2 \rightleftharpoons 4\ \text{“}Me_2AlBHT\text{”} \text{ with } K_{eq} = [Me_2AlBHT]^4/[MeAlBHT_2]^2[Al_2Me_6] \quad (2)$$

It is evident from these spectra that there are at least three exchange processes occurring in this system, in addition to the known exchange between the terminal and bridging groups of Al_2Me_6.[28] At lowest temperature, $Me_2Al(BHT)$ is still fluxional on the ^{1}H NMR time scale, while at higher temperature this compound is involved in degenerate Me exchange with Al_2Me_6 (eq 3a) and at still higher temperature, with $MeAl(BHT)_2$ (eq 3b). The latter process may involve degenerate exchange of BHT and Me groups given the broadening of all signals in the ^{1}H NMR spectrum.



(3a)



(3b)

Note that the adduct depicted in eq 3a is similar to that invoked by Ittel and co-workers to explain their temperature-dependent NMR spectra. However, there is no evidence in these spectra for the independent existence of this species.

The variable-temperature ^{13}C NMR spectra were more revealing in terms of the nature of the compounds present. Depicted in Figure 4 are the low (a) and high (b) field regions of the ^{13}C NMR spectra of this mixture at various temperature. The Al-Me region (Figure 4b) mirrors the results just discussed for the ^{1}H NMR spectra over this same temperature range, and assignments are as indicated. At the lowest temperature investigated, it is evident that there is residual exchange between an intense Al-Me signal at ca. −3 ppm and a very weak signal at higher field (ca. −7.5 ppm), while the signals due to Al_2Me_6 and $MeAl(BHT)_2$ are quite sharp at this temperature.

In the low-field region at room temperature, two line-broadened signals are seen at δ 153.3 and 152.6 due to the *ipso* $O-C_{Ar}$ carbons of $Me_2Al(BHT)$ and $MeAl(BHT)_2$, respectively. The signal at higher field due to $MeAl(BHT)_2$ sharpens at low temperature, while the other broadens and shifts to higher field. Concomitantly, a signal at higher field (138.5 ppm due to an *ipso* ᵗBu-C_{Ar} carbon) also line-broadens and shifts to lower field. Although not readily evident, due to overlap with the solvent resonances, a signal at δ 126.7 also shows similar behavior. All of these signals undergo decoalescence, and at low temperature, three signals are resolved at δ 147.4, 140.6, and 132.4 in a ratio of 1:2:1 in these inverse gate-decoupled spectra. In addition a very weak signal is evident at δ 153.6; we suspect there are additional signals present, but they are difficult to reliably detect because of overlap and low sensitivity.

Our interpretation of these results is the lowest temperature exchange process involves monomeric and dinuclear forms of $Me_2Al(BHT)$, where the dinuclear compound is exclusively

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(28) Cerny, Z.; Fusek, J.; Kriz, O.; Hermanek, S.; Sole, M.; Casensky, B. *J. Organomet. Chem.* **1990**, *386*, 157−165.

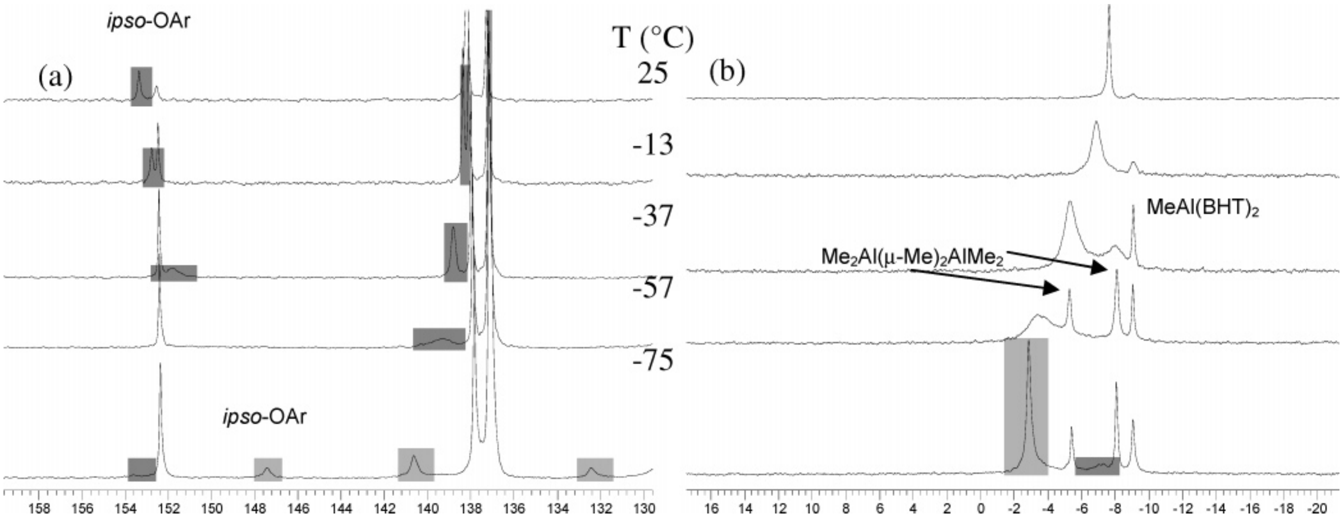
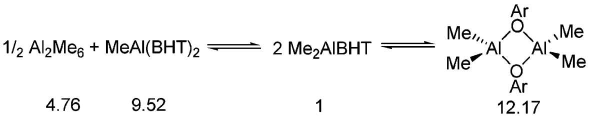


Figure 4. Partial VT ^{13}C NMR spectra (100 MHz, toluene-d_8) of a 1:1 mixture of Al_2Me_6 and $MeAl(BHT)_2$: (a) low-field region; (b) high-field region. Signals due to dinuclear and mononuclear $Me_2Al(BHT)$ are highlighted in light and dark gray, respectively.

phenoxide bridged (eq 4). The very weak signal at lowest field is due to the *ipso* O−C$_{Ar}$ carbons of monomeric $Me_2Al(BHT)$ by analogy with the signal that appears for $MeAl(BHT)_2$ in this same region. The remaining three signals are in a ratio of 1:2:1, and they can be assigned to the *ipso* O−C$_{Ar}$, *ipso* ^{t}Bu-C$_{Ar}$, and *ipso* Me-C$_{Ar}$, respectively, of the dinuclear complex. The upfield chemical shift of the *ipso* O−C$_{Ar}$ is in agreement with other spectroscopic studies of hindered, phenoxide-bridged complexes of this type.[25,26]

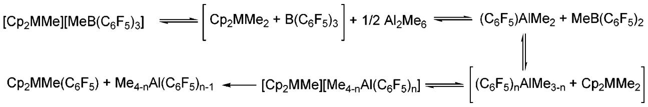


(4)

Taken together, the ^{1}H and ^{13}C NMR spectra indicate that $Me_2Al(BHT)$ is an equilibrating mixture of four different compounds: monomeric $Me_2Al(BHT)$, the symmetrical dinuclear complex $Me_2Al(\mu\text{-}BHT)_2AlMe_2$, while Al_2Me_6 and $MeAl(BHT)_2$ comprise the reactant side of the equilibria depicted in eq 4, where the relative amounts of all species are depicted at −75 °C. Evidently, the position of these equilibria are temperature dependent, and from the room-temperature ^{1}H and ^{13}C NMR spectra it seems probable that the mononuclear form of $Me_2Al(BHT)$ is the dominant species present. This explains, in part, why adducts of this compound can be isolated by treatment of such mixtures with donors.[27]

Mixtures of $MeAl(BHT)_2$, Al_2Me_6, and Metallocenium Ion-Pairs. The experiments just discussed illustrate that significant quantities of Al_2Me_6 are present in mixtures of $MeAl(BHT)_2$ and Al_2Me_6 at least at low temperature. To further investigate this in the context of polymerization catalysis, the behavior of in situ generated ion-pairs, derived from metallocene dimethyl complexes and $B(C_6F_5)_3$, in the presence of mixtures of these two compounds was investigated.

The complexes studied were the *ansa*-metallocene complexes $Me_2Si(Cp)IndMMe_2$ (M = Zr, Hf) and the symmetrical $Me_2SiCp_2ZrMe_2$ complex. Typically, a stock solution of $MeAl(BHT)_2$ and the relevant ion-pair (IP) was prepared in toluene-d_8, and this stock solution was used to prepare solutions differing in the amount of Al_2Me_6. Representative ^{19}F NMR spectra for the $[Me_2Si(Cp)IndMMe][MeB(C_6F_5)_3]$ ion-pairs in the absence and presence of Al_2Me_6 are depicted in Figure 5a). It can be readily seen that the Hf-based IP suffers extensive degradation on addition of 0.5 equiv of Al_2Me_6, while the Zr IP is more stable.[29] In the former case, the principle degradation products are a mixture of $(C_6F_5)_nAlMe_{3-n}$ (and the corresponding IP formed from these alanes)[30] and $(C_6F_5)_2BMe$. These same compounds are also present in smaller quantities in the case of the Zr analogue, and there is also evidence in both spectra of C_6F_5 transfer to the metal (*o*-F at δ 114−115).[30] Thus, the hafnocene IP, which is more prone to $B(C_6F_5)_3$ dissociation, is degraded by the Al_2Me_6 that is present according to the following general scheme:



Note that such a mixture of compounds can still be competent for olefin polymerization, but of course the identity of the active catalyst is now clouded by uncertainty with respect to the nature of the counteranion(s).

The behavior of the hafnocene IP in the presence of various quantities of $MeAl(BHT)_2$ and Al_2Me_6 is depicted in Figure 5b. It can be appreciated from these spectra that IP degradation is much less problematic when $MeAl(BHT)_2$ is present compared to the situation where it is absent. However, at higher ratios of Al_2Me_6:Hf a new IP with a less coordinating $MeB(C_6F_5)_3$ anion ($\Delta\delta = 2.6$ ppm) is generated at the expense of the original ion-pairs. Although not readily evident from Figure 5b, a second set of signals with the *same* Δδ value is present in these spectra in variable amounts with respect to the major set of signals, depending on [Hf]. We attribute this second set of signals to formation of variable amounts of a liquid clathrate phase that forms at these relatively high concentrations (0.01−0.02 M) when the counteranion is rendered less coordinating.[31]

Although the ^{19}F NMR spectra of these mixtures were readily interpreted, the corresponding ^{1}H NMR spectra were complex due to the fluxional and unsymmetrical nature of the various compounds present. For this reason, we studied analogous

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[29] (a) Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745−746. (b) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912.

[30] It is interesting to note that the two isomeric ion-pairs present in the case of M = Zr[10b] react at different rates with Al_2Me_6.

[31] Beck, S.; Geyer, A.; Brintzinger, H.-H. *Chem. Commun.* **1999**, 2477−2478.

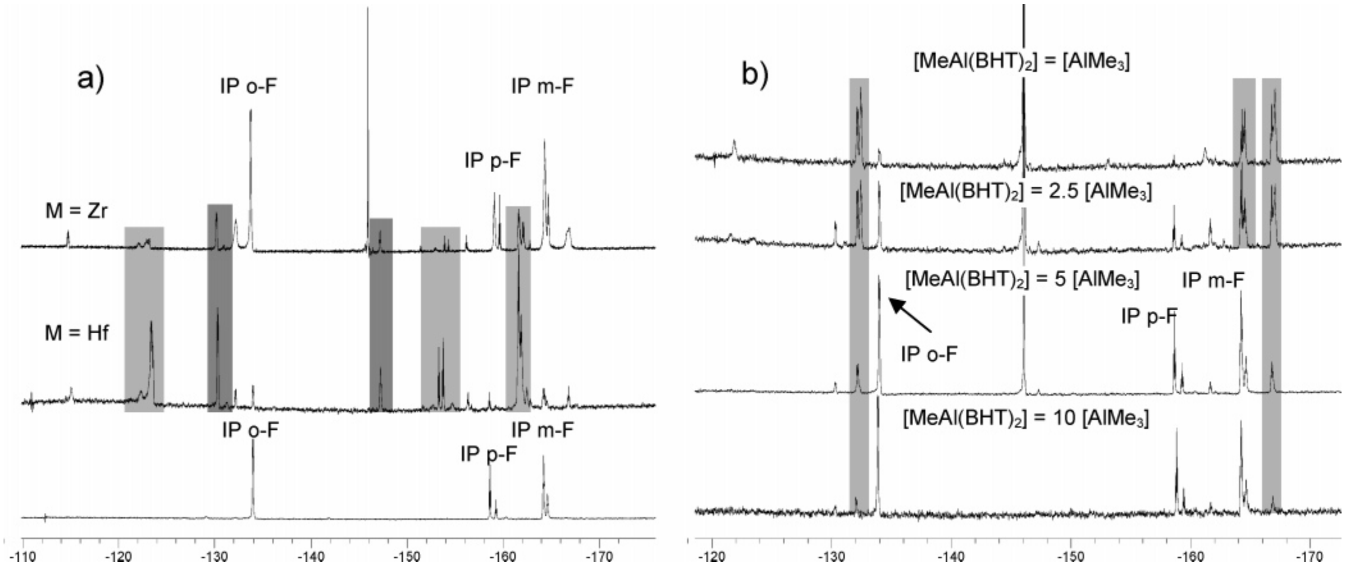

Figure 5. ^{19}F NMR spectra (276 MHz, toluene-d_8) of (a) [Me$_2$SiCp(Ind)MMe][MeB(C$_6$F$_5$)$_3$] (IP: M = Zr, Hf) in the absence (bottom spectrum) and presence of 0.5 equiv of Al$_2$Me$_6$. Signals due to (C$_6$F$_5$)$_n$AlMe$_{3-n}$ [or their adducts with Me$_2$SiCp(Ind)MMe$_2$] and (C$_6$F$_5$)$_2$BMe are highlighted in light and dark gray, respectively, while the *o*- *p*-, and *m*-F signals due to the isomeric ion-pairs are labeled. (b) [Me$_2$SiCp(Ind)HfMe][MeB(C$_6$F$_5$)$_3$] ([Hf] = 0.0125 M) in the presence of various amounts of MeAl(BHT)$_2$ ([Al] = 0.03125 M) and Al$_2$Me$_6$. Signals due to [Me$_2$SiCp(Ind)Hf(μ-Me)$_2$AlMe$_2$][MeB(C$_6$F$_5$)$_3$] adducts are highlighted in light gray.

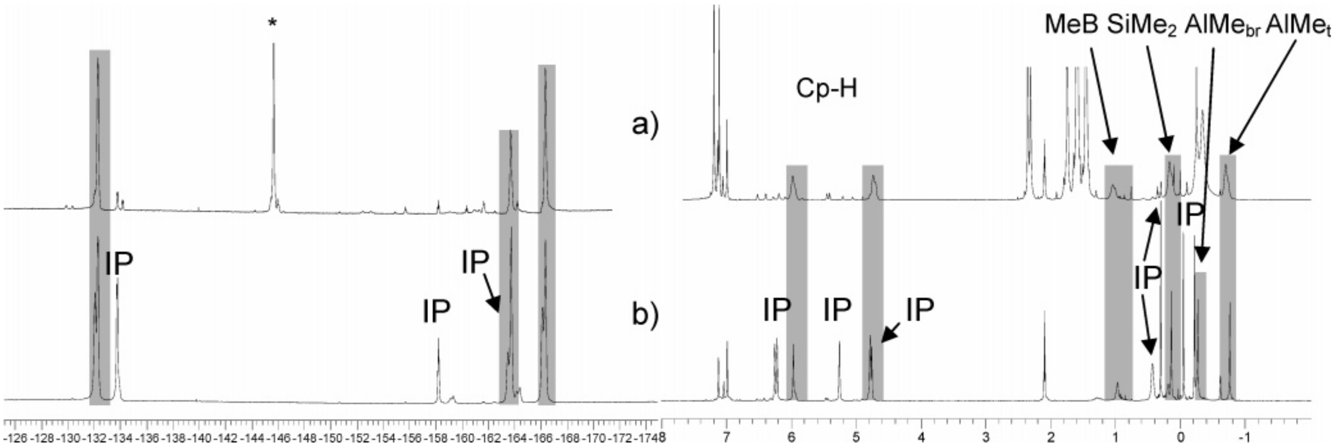

Figure 6. ^{19}F (282 MHz, toluene-d_8, −30 °C) and ^{1}H NMR spectra (300 MHz, toluene-d_8, −30 °C) of (a) a 5:2.5:2 mixture of MeAl(BHT)$_2$, Al$_2$Me$_6$, and [Me$_2$SiCp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] (IP) containing TFX as an internal standard and (b) a ca. 4:1 mixture of [Me$_2$SiCp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] (IP) and Al$_2$Me$_6$. Signals due to the [Me$_2$SiCp$_2$Zr(μ-Me)$_2$AlMe$_2$][MeB(C$_6$F$_5$)$_3$] adduct are highlighted in gray, while signal due to TFX are indicated with an asterisk.

reactions of the more symmetrical IP [Me$_2$SiCp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$], and the ^{1}H and ^{19}F NMR spectra of mixtures of this compound with Al$_2$Me$_6$ and MeAl(BHT)$_2$ are depicted in Figure 6. The behavior seen in the ^{19}F NMR spectra was similar to that for the unsymmetrical ion-pairs discussed above. In particular, at a MeAl(BHT)$_2$:Al$_2$Me$_6$:Zr ratio of 5:2.5:2 formation of an IP with a less coordinating counteranion ($\Delta\delta = 2.6$) was essentially complete.

The room-temperature ^{1}H NMR spectrum of a mixture of MeAl(BHT)$_2$/Al$_2$Me$_6$/Zr (5:2.5:2) was not informative due to exchange broadening, but on cooling, new signals highlighted in gray in Figure 6a were observed. Since there are only two Cp signals and a single SiMe$_2$ resonance, it is evident that this species is symmetrical, consistent with the formation of [Me$_2$SiCp$_2$Zr(μ-Me)$_2$AlMe$_2$][MeB(C$_6$F$_5$)$_3$]. The signals present are identical (aside from their line-width) to those observed for this ion-pair in the presence of 0.25 equiv of Al$_2$Me$_6$ at low temperature (Figure 6b). In this spectrum, separate signals for the bridging and terminal AlMe signals are resolved, while the remaining signals are due to the unsymmetrical contact IP [Me$_2$SiCp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$].[32]

We thus conclude that the principle ion-pair formed in the presence of MeAl(BHT)$_2$ and Al$_2$Me$_6$ is [Me$_2$SiCp$_2$Zr(μ-Me)$_2$AlMe$_2$][MeB(C$_6$F$_5$)$_3$] and that neither MeAl(BHT)$_2$ nor Me$_2$Al(BHT) coordinates to the metal center, or at least to the same extent as Al$_2$Me$_6$. The signals are line-broadened presumably due to exchange of AlMe$_3$, coordinated to Zr, with excess Al$_2$Me$_6$ present in this solution.

The results presented in this section can be interpreted in the following manner. In essence, MeAl(BHT)$_2$ and metallocenium ion-pairs compete for Al$_2$Me$_6$ through formation of Me$_2$Al(BHT) and hetero-dinuclear Al,M adducts, respectively. At sufficiently high MeAl(BHT)$_2$:Al$_2$Me$_6$ ratios, essentially all of the Al$_2$Me$_6$ is sequestered in the form of Me$_2$Al(BHT), where the latter

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[32] (a) Beck, S.; Prosenc, M.-H.; Brintzinger, H.-H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A: Chem.* **1996**, *111*, 67−79. (b) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483−1489.

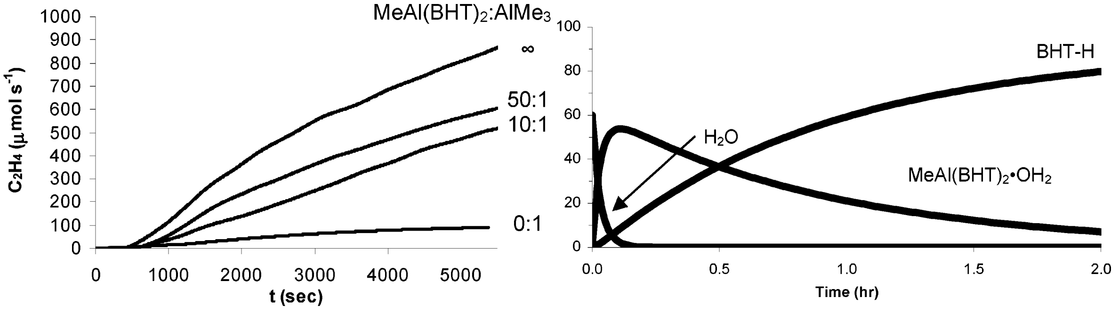

Figure 7. (a) Ethylene consumption vs time for $[Cp_2ZrMe][MeB(C_6F_5)_3]$ for mixtures of $MeAl(BHT)_2$ and Al_2Me_6. Conditions: Toluene solution, 30 °C, 30 psig, $[Zr] = 2.0\ \mu M$, $[Al_2Me_6] = 20\ \mu M$. (b) Simulated consumption of $MeAl(BHT)_2$ assuming $[H_2O]_o = 60\ \mu M$ and $[Al]_o = 600\ \mu M$ based on kinetic data for hydrolysis of $MeAl(BHT)_2$ obtained in THF.[14]

compound, or at least its monomeric form, does not strongly bind to metallocenium ions.

Thus, from a practical perspective, the deleterious effects of Al_2Me_6 on metallocenium ion-catalyzed olefin polymerization should be largely alleviated through the addition of a sufficient excess of $MeAl(BHT)_2$. This concept is only partially realized during actual catalysis of ethylene polymerization by $[Cp_2ZrMe][MeB(C_6F_5)_3]$, where initial monomer uptake versus *t* curves at various ratios of $MeAl(BHT)_2{:}AlMe_3$ are shown in Figure 7. Even at a 50:1 ratio, the activity of this catalyst is still not equivalent to that observed in the absence of $AlMe_3$. However, we suspect that any inhibition of catalysis under these conditions does not result from free $AlMe_3$ but perhaps from weak and reversible interaction of "$Me_2Al(BHT)$" with the metal center during catalysis.

A final comment concerning practical aspects of polymerization experiments using these scavengers deserves mention. This relates to effective and timely removal of protic impurities in autoclave reactors. $MeAl(BHT)_2$ is only sluggishly reactive toward water, and from the rates of hydrolysis measured in THF one can estimate that 4 h of scavenging time would be required to reduce water to sub-micromolar concentrations (see Figure 7b).[14] Although we have been unable to measure the rate of hydrolysis in hydrocarbon solution, it is significantly faster than in THF, though the product distribution is the same; hydrolysis is accompanied by formation of ca. 100 μM BHT-H if, for example. $[H_2O]_o = 60\ \mu M$ (Scheme 1).

It is interesting to note that the reaction of BHT-H with a mixture of Al_2Me_6 and excess $MeAl(BHT)_2$ is much slower than independent reaction of BHT-H with Al_2Me_6. Even when the latter compound is added to about an equimolar amount of BHT-H ([BHT-H] = 0.0091 M) and excess $MeAl(BHT)_2$ ([Al] = 0.0682 M) at 25 °C, the initial ^1H NMR spectra reveal the presence of BHT-H, $MeAl(BHT)_2$, and $Me_2Al(BHT)$ ([Al] = 0.0078 M) with very little CH_4 production (see the Supporting Information).

A plot of $\ln\{[\text{BHT-H}][Me_2Al(BHT)]_o/[\text{BHT-H}]_o[Me_2Al(BHT)]\}$ vs *t* was linear over about 2 half-lives with $k = 5.7 \times 10^{-2}\ M^{-1}\ s^{-1}$. If we assume that $[\text{BHT-H}]_o = [AlMe_3]_o = 100\ \mu M$ with excess $MeAl(BHT)_2$, as in the simulation depicted in Figure 7b, one would predict that decline of BHT-H to 1.0 μM concentration would require in excess of 4800 h for completion!

This is far too slow for practical purposes and dictates that $AlMe_3$ be added *first* to an autoclave reactor to scavenge water. From a practical perspective we use $[AlMe_3] = [H_2O]$ even though this represents a 1.5-fold excess of Al-Me over that required for complete reaction. After a much shorter period of time (typically 1 h or less), a 10- to 100-fold excess of $MeAl(BHT)_2$ is then added, followed by activator and metallocene catalyst.

Under these conditions, scavenging of water is effective (and timely), and as we show here, the effects of any excess Al_2Me_6 are largely mitigated through the addition of a sufficient quantity of $MeAl(BHT)_2$ prior to catalyst/cocatalyst introduction.

Conclusions. The use of sterically hindered aluminum alkyls confers an advantage in the fundamental study of olefin polymerization using metallocene or other early metal catalysts and single-component activators. They represent what one might term weakly interacting scavengers in the sense that they do not strongly inhibit polymerization through formation of heterodinuclear adducts, as seen with conventional alkylaluminum compounds, nor do they readily degrade many activators of interest. Further, as we show here, the deleterious effects of simple alkylaluminum compounds can be largely eliminated through the addition of a sufficient quantity of one of these sterically hindered scavengers; this is important for catalysts that are susceptible to protonolysis by BHT-H, the principle product of $MeAl(BHT)_2$ hydrolysis.

Experimental Section

All materials were obtained from Aldrich Chemical Co. or Strem Chemical Co. and purified as required. All synthetic procedures were conducted under a N_2 atmosphere using Schlenk techniques or in a glovebox. Isolation of solids from supernatant liquids was performed using a filter-tipped cannula or by filtration. Tetrahydrofuran, diethyl ether, toluene, hexane, and dichloromethane were purified by passage through activated La Roche A-2 alumina and Engelhard CU-0226s Q-5 columns.[33]

Routine ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian Mercury or Gemini 300 MHz instrument. Benzene-d_6, toluene-d_8, and bromobenzene-d_5 were distilled from Na or Na/K alloy prior to use. ^1H NMR spectra were referenced with respect to residual protonated solvent, while ^{13}C NMR spectra were referenced with respect to deuterated solvent. ^{19}F NMR spectra were referenced with respect to tetrafluoro-*p*-xylene (TFX: δ −145.69 vs $CFCl_3$ in toluene-d_8). Variable-temperature experiments were performed using Varian Innova 400 MHz or VXR 300 MHz instruments. The spectrometer thermocouple was calibrated to within 5% of actual temperature using a sample of MeOH. IR spectra were obtained on a DigiLab Excalibur FTS 3000 spectrometer and were not calibrated. Elemental analyses were performed by either Oneida Research Services or Galbraith Laboratories.

Tris(perfluorophenyl)borane, donated by Nova Chemicals, was predried in a hexane solution containing 4 Å activated molecular sieves and recrystallized from hexane at −30 °C. 2,4,6-Tri-*tert*-butylphenol was purchased from Aldrich Chemical Co. and was purified by recrystallization from hexane at 0 °C. The compounds

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[33] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

$[(C_6H_5)_3C][B(C_6F_5)_4]$,[34] Cp_2ZrMe_2,[35] $Cp_2Zr^{13}Me_2$,[36] $Me_2SiCp_2ZrMe_2$,[19] $Me_2SiCp(Ind)ZrMe_2$,[10b] and $Me_2SiCp(Ind)HfMe_2$[10b] were prepared according to literature procedures.

Methyl Bis(2,6-di-^{t}Bu-4-methylphenoxy)aluminum. $MeAl(BHT)_2$ was synthesized using a modification of literature procedures.[9] Trimethyl aluminum (3.45 g, 47.9 mmol) was dissolved in 20 mL of *n*-hexane. This solution was slowly added over a period of 5 min via cannula to a rapidly stirred solution of Ar′OH (20.04 g, 90.9 mmol) in 120 mL of *n*-hexane. *Caution: Addition must be done slowly to avoid uncontrolled methane formation.* The solution was stirred for 1 h at 25 °C, during which time a white precipitate separated. The mixture was concentrated to dryness in vacuo at 0.01 mmHg overnight. The crude product (21.3 g, 98% yield) could be used without further purification. Spectroscopic data were consistent with the literature.

Methyl Bis(2,4,6-tri-^{t}Bu-phenoxy)aluminum. $MeAl(BHT^*)_2$ was synthesized using a modification to the literature procedure.[9d] Analogous to the synthesis of $MeAl(BHT)_2$, a solution of 2,4,6-tri-^{t}Bu-phenol (4.94 g, 17.5 mmol) in hexane was rapidly stirred with an excess of $Al(CH_3)_3$ (0.95 g, 13 mmol). The mixture was concentrated to dryness in vacuo at 0.01 mmHg overnight. The crude product (4.85 g, 98% yield) could be used without further purification. Spectroscopic data were consistent with the literature.

Reaction of $[(C_6H_5)_3C][B(C_6F_5)_4]$ with $MeAl(BHT)_2$. In a septum-sealed 5 mm NMR tube, 39 mg (42 μmol) of $[(C_6H_5)_3C][B(C_6F_5)_4]$ was dissolved in 483 μL of bromobenzene-d_5. Twenty milligrams (42 μmol) of solid $MeAl(BHT)_2$ was then added and dissolved. The reaction solution turned deep red. ^1H and ^{19}F NMR spectra were recorded at room temperature.

Reaction of $[(C_6H_5)_3C][B(C_6F_5)_4]$ with $MeAl(BHT^*)_2$. In a septum-sealed 5 mm NMR tube 38.5 mg (41.7 μmol) of $[(C_6H_5)_3C][B(C_6F_5)_4]$ was dissolved in 468 μL of bromobenzene-d_5. Twenty-four milligrams (46 μmol) of solid $MeAl(BHT^*)_2$ was then added and dissolved. The reaction solution slowly turned deep red. ^1H and ^{19}F NMR spectra were recorded at room temperature.

Mixtures of $MeAl(BHT)_2$ and $Al(CH_3)_3$. In a septum-sealed 5 mm NMR tube, 132 mg (0.28 mmol) of $MeAl(BHT)_2$ was weighed and dissolved into a solution of 560 μL of toluene-d_8 containing 20 mg (0.28 mmol) of $Al(CH_3)_3$. The equimolar ratio of $MeAl(BHT)_2$ and $Al(CH_3)_3$ was confirmed by acquiring a ^1H NMR spectrum at room temperature. Low-temperature ^{13}C and ^1H NMR spectra were recorded by cooling the probe to between −30 and −80 °C.

Reaction of $[Me_2SiCp_2ZrMe][MeB(C_6F_5)_3]$[32] with $AlMe_3$. Into separate vials, 100 mg (325 μmol) of $Me_2SiCp_2ZrMe_2$ and 179 mg (350 μmol) of $B(C_6F_5)_3$ were each dissolved into 6.25 mL of toluene-d_8 containing 50 mM TFX standard. The $Me_2SiCp_2ZrMe_2$ solution was added to the $B(C_6F_5)_3$ solution to generate a 26 mM ion-pair solution, which turned from yellow to red upon mixing. In a separate vial, 31 mg (430 μmol) of $AlMe_3$ was weighed and dissolved into 1.00 mL of toluene-d_8 (containing 50 mM TFX), making a 430 mM solution. Into a 5 mm septum-capped NMR tube, 500 μL (13 μmol) of the ion-pair solution was added and cooled to −80 °C. Thirty microliters of the $AlMe_3$ (1.0 equiv, 13 μmol) solution was then syringed in and gently shaken at −80 °C. The NMR tube was then lowered into a precooled probe at −80 °C. ^1H and ^{19}F NMR spectra were acquired at 10 °C increments during slow warming of the probe to 30 °C.

Reaction of $[Me_2SiCp_2ZrMe][MeB(C_6F_5)_3]$ with 5 equiv of a 1:1 Solution of $MeAl(BHT)_2$ and $AlMe_3$. In a vial, 210 mg (440 μmol) of $MeAl(BHT)_2$ was dissolved into 1.0 mL of toluene-d_8 (containing 50 mM TFX) to make a 440 mM solution. Into a 5 mm septum-capped NMR tube, 150 μL of the $MeAl(BHT)_2$ (5.0 equiv, 65 μmol) and 500 μL (13 μmol, 26 mM) of the ion-pair solutions were added. To this solution was then syringed 150 μL of the $AlMe_3$ solution (5.0 equiv, 65 μmol) at 25 °C. The NMR tube was then lowered into a precooled probe at −80 °C. ^1H and ^{19}F NMR spectra were acquired at 10 °C increments during slow warming of the probe to 30 °C.

Reaction of $[Me_2SiCp(Ind)MMe][MeB(C_6F_5)_3]$ (M = Zr or Hf)[10b] with $AlMe_3$ and $MeAl(BHT)_2$. These reactions were performed in a manner similar to the above experiments, with the $[Me_2SiCp(Ind)MMe][MeB(C_6F_5)_3]$ ion-pair[10b] and using various amounts of $AlMe_3$ and $MeAl(BHT)_2$. In each case the $AlMe_3$ was added at 25 °C to a mixture of the ion-pair and $MeAl(BHT)_2$ in the following amounts: [Zr] or [Hf] = [$AlMe_3$] = 0.025 M with [$MeAl(BHT)_2$] = 0.0, 0.025, and 0.25 M. The spectra are depicted in Figure 4b.

Spectroscopic Studies of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ and $MeAl(BHT)_2$. (a) NOESY Spectroscopy. A solution of $MeAl(BHT)_2$ (121 mg, 0.25 mmol) and $B(C_6F_5)_3$ (28 mg, 0.055 mmol) was prepared in 0.612 mL of C_6D_6. To this solution was added 0.305 mL of a solution of Cp_2ZrMe_2 in C_6D_6 (20 mg in 0.47 mL; 0.17 M) so as to give a final solution where [IP] = 0.056 M. A series of NOESY spectra were acquired with different mixing times, the longest of which was $\tau = 1.0$ s. This spectrum and F_1 slices through the relevant diagonal and cross-peaks at δ 0.24 (Zr-Me), 0.08 (B-Me), and −0.34 (Al-Me) are depicted in the Supporting Information.

(b) ^{13}C-Scrambling Experiment. A solution of $MeAl(BHT)_2$ (60 mg, 0.125 mmol) and $B(C_6F_5)_3$ (14 mg, 0.0275 mmol) was prepared in 0.600 mL of C_6D_6. To this solution was added 0.350 mL of a solution of $Cp_2Zr^{13}Me_2$ in C_6D_6 (20 mg in 1.0 mL; 0.079 M) so as to give a final solution where [IP] = 0.029 M. ^1H and ^{19}F NMR spectra were acquired about 5 min after mixing at room temperature and showed trace levels of scrambling between Zr-Me and Al-Me. A ^1H spectrum acquired 10 min later revealed minimal change. These spectra were integrated to record the intensity of (a) the low-field ^{13}C satellite of the ^{t}Bu protons of $MeAl(BHT)_2$ as an internal standard, (b) the two signals due to Zr-^{13}-CH_3, and (c) the ^{13}C satellite at highest field due to the Al-Me protons, as these peaks were of similar intensity and resolved. After ejecting the sample and equilibrating the probe at 40 °C, the sample was reinserted and spectra were recorded over a 2 h period, corresponding to ca. one half-life (see the Supporting Information for representative spectra and integral data as a function of time). At this point there was significant decomposition of the IP as judged by multiple resonances in the Cp region of the ^1H NMR spectrum.

Reaction of BHT-H with a Mixture of $MeAl(BHT)_2$ and Al_2Me_6. A stock solution of $MeAl(BHT)_2$ (22 mg, 0.045 mmol) and BHT-H (1.0 mg, 0.0045 mmol) in 0.692 mL of C_6D_6 containing TFX was prepared. A ^1H NMR spectrum of the mixture was recorded, and then 32 μL of a solution of Al_2Me_6 (0.0505 M in C_6D_6) was added via syringe with shaking and the tube immediately immersed in the probe. An initial spectrum revealed the presence of BHT-H and $Me_2Al(BHT)$ but no methane. Spectra were recorded over a 3 h period, during which time both of these materials were consumed with concomitant production of methane. Selected spectra along with kinetic data are included as Supporting Information.

Polymerization of Ethylene at Various Ratios of Al_2Me_6:$MeAl(BHT)_2$. A 1.0 L autoclave reactor was heated to 100 °C under vacuum and evacuated and refilled 3× with dry N_2 at this temperature. It was allowed to cool to 30 °C under N_2, and then 448−498 mL of dry toluene (impurity level 40 μM as determined by titration of an aliquot using a stock solution of benzophenone ketyl in xylenes/tetraglyme) was added using an overpressure of dry N_2. A solution of Al_2Me_6 in toluene (1.0 mL of 0.01 M) was added via syringe at 30 °C, and the mixture was then saturated with ethylene at 30 psig for 1−2 h. After saturation was complete as detected by calibrated mass flow meter (i.e., zero flow), a solution

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[34] (a) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−1. (b) Doellein, G. US Patent 5,399,781, 1995, 3 pp.

[35] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *32*, 155−164.

[36] Dahmen, K. H.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1988**, *4*, 1212−14..

of MeAl(BHT)$_2$ in toluene (0.01 M in toluene) was added in amounts corresponding to 0:1, 10:1 ([MeAl(BHT)$_2$] = 0.4 mM), or 50:1 ([MeAl(BHT)$_2$] = 2.0 mM) equivalents based on [AlMe$_3$]. In a control experiment no Al$_2$Me$_6$ was added to the reactor, but an equivalent amount of MeAl(BHT)$_2$ was added so as to give [MeAl(BHT)$_2$] = 2.0 mM prior to saturation with ethylene.

A stock solution of [Cp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] (0.001 M in toluene) was prepared, and for each reaction the same fixed quantity of solution (1.0 mL) was added via syringe after a further 1 h of stirring following the addition of MeAl(BHT)$_2$. After a short delay, ethylene uptake was detected and the reactions were stirred at 1000 rpm and 30 °C for several hours until steady state had been achieved. Representative ethylene uptake curves are depicted in Figure 6a.

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Supporting Information Available: Additional NMR spectra for mixtures of MeAl(BHT)$_2$ with various compounds. This information is available free of charge via the Internet at http://pubs.acs.org.

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