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Reaction of AlR_3 with $[CPh_3][B(C_6F_5)_4]$: Facile Degradation of $[B(C_6F_5)_4]^-$ by Transient “$[AlR_2]^+$”

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Trimethylaluminum reacts with $[CPh_3][B(C_6F_5)_4]$ at elevated temperatures to give a mixture of $AlMe_{3-x}(C_6F_5)_x$ compounds, depending on the Al/B ratio. $AlBu^i_3$ reacts significantly faster under β-hydride abstraction. The Al−C_6F_5 species rapidly react with Cp_2ZrMe_2 or $[Cp_2ZrMe]^+$ under C_6F_5 transfer to give poorly active $Cp_2ZrMe(C_6F_5)$; this reaction may have implications for the deactivation of $Cp_2ZrMe_2/AlR_3/[CPh_3][B(C_6F_5)_4]$ olefin polymerization catalysts.

Introduction

As is now well established, highly active olefin polymerization catalysts can be generated by reacting metallocene dialkyls Cp_2MR_2 (M = Ti, Zr, Hf) with cation-generating agents, notably $B(C_6F_5)_3$, $[HNMe_2Ph][B(C_6F_5)_4]$, or $[CPh_3][B(C_6F_5)_4]$, to give complexes in which the highly electrophilic active species $[Cp_2MR]^+$ is stabilized by weakly coordinating but chemically very robust counteranions such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$.[1] Because of the high sensitivity of these catalyst systems toward trace impurities the addition of aluminum alkyls is usually beneficial. For example, we have shown previously that the addition of 1 equiv of $AlMe_3$ stabilizes the 14-electron cation $[Cp_2ZrMe]^+$ by formation of a heterobinuclear complex, $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$,[2] and Chien et al. have developed highly active catalysts based on mixtures of metallocene dichlorides and $[CPh_3][B(C_6F_5)_4]$ in the presence of an excess of $AlMe_3$ or $AlEt_3$.[3]

The success of these catalysts depends on the selective reaction of $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ with the transition metal alkyl complex in preference to reaction with the main group metal alkyl additive. This may seem at first glance surprising since it is not obvious why reactive electrophiles such as $B(C_6F_5)_3$ or CPh_3^+ should fail to react with a strong alkylating reagent such as $AlMe_3$. Indeed, we have shown earlier[4] that the reaction of $B(C_6F_5)_3$ with Cp_2AlMe to give $[AlCp_2]^+[MeB(C_6F_5)_3]^-$ is fast and quantitative even at low temperatures, and Jordan et al.[5] recently reported the facile methyl anion abstraction from (benzamidinato)$AlMe_2$ compounds to give cationic aluminum methyl complexes.

Two reasons attracted our interest in analogous reactions of $AlMe_3$. First, although the $Cp_2MR_2/[CPh_3][B(C_6F_5)_4]/AlR_3$ catalysts mentioned above[2,3] show very high initial activities, there is typically a significant reduction of activity with time. Little is known about the chemistry that underlies such catalyst deactivation processes,[6] and we speculated that a decay of the pentafluorophenylborate anion, possibly with the participation of AlR_3, might be important. Second, while there are numerous cationic aluminum alkyls $[AlR_2(L)_2]^+$ stabilized by N- and O-ligands,[7] with the exception of the metallocenes $[AlCp_2]^+$ and $[AlCp^*_2]^+$ [8] cationic $[AlR_2]^+$ species free of donor ligands are not known, and we were intrigued by the possibility of stabilizing such species with weakly coordinating anions such as $[B(C_6F_5)_4]^-$.

Results

A solution of $[CPh_3][B(C_6F_5)_4]$ in toluene-d_8 was treated with a 10-fold molar excess of $AlMe_3$ and

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warmed to 60 °C. The reaction was monitored by ^1H, ^{11}B, and ^{19}F NMR spectroscopy over 4.5 h. A slow reaction takes place; formation of $MeCPh_3$ is observed, along with BMe_3 [^1H NMR (toluene-d_8, 60 °C) δ 0.74; ^{11}B NMR δ 86.8], and a new set of signals appears in the ^{19}F NMR spectrum, at δ −121.5 (*o*-F), −152.2 (*p*-F), and −160.8 (*m*-F), in addition to unreacted $[CPh_3][B(C_6F_5)_4]$. In the presence of excess $AlMe_3$ the reaction is first-order in $[CPh_3^+]$, with $k_{obs} = 5 \times 10^{-5}\ s^{-1}$ (at 60 °C). In the absence of $AlMe_3$ toluene solutions of $[CPh_3][B(C_6F_5)_4]$ are stable under these conditions.

This observation demonstrates that methyl abstraction from $AlMe_3$ by CPh_3^+ is very much less favorable than with transition metal methyl complexes but occurs slowly at elevated temperatures to give a transient species "$[AlMe_2]^+[B(C_6F_5)_4]^-$", which immediately decomposes to $B(C_6F_5)_3$ and $AlMe_2(C_6F_5)$. Evidently cations such as $[AlMe_2]^+$ (or possibly higher homologues, e.g., $[Al_2Me_5]^+$ or $[Al_3Me_8]^+$, which might be envisaged in the presence of excess $AlMe_3$) are too electrophilic to be stabilized even by $[B(C_6F_5)_4]^-$ and immediately react with abstraction of $C_6F_5^-$. The difference in reactivity between $[AlMe_2]^+$ and the thermally stable complexes $[AlCp_2]^+$ and $[(\text{benzamidinate})AlMe]^+$ is most probably due to the absence of any form of π-donor stabilization in the dialkyl species.

Further ligand exchange between $AlMe_{3-x}(C_6F_5)_x$ and $B(C_6F_5)_3$ can eventually lead to the formation of $Al(C_6F_5)_3$ and BMe_3, which in an open system escapes into the gas phase, thereby shifting the equilibrium:

$$[CPh_3][B(C_6F_5)_4] + AlMe_3 \rightarrow Ph_3CMe + \text{“}[AlMe_2]^+[B(C_6F_5)_4]^-\text{”}$$

$$\text{“}[AlMe_2]^+[B(C_6F_5)_4]^-\text{”} \rightarrow AlMe_2(C_6F_5) + B(C_6F_5)_3$$

$$AlMe_2(C_6F_5) + B(C_6F_5)_3 \rightarrow AlMe(C_6F_5)_2 + BMe(C_6F_5)_2$$

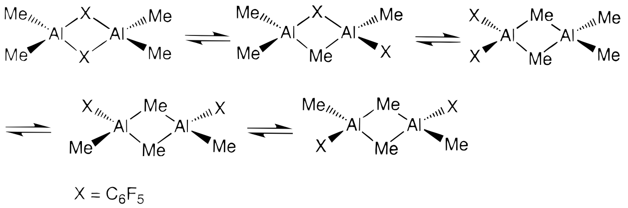
$$AlMe(C_6F_5)_2 + BMe(C_6F_5)_2 \rightarrow Al(C_6F_5)_3 + BMe_2(C_6F_5)$$

$$BMe_2(C_6F_5) + AlMe_3 \rightarrow AlMe_2(C_6F_5) + BMe_3$$

The reaction of $B(C_6F_5)_3$ with $AlMe_3$ in toluene to afford $Al(C_6F_5)_3 \cdot 0.5$toluene and BMe_3 via a similar sequence of ligand redistribution processes has recently been described in a patent application by Biagini et al. as a convenient synthetic method for $Al(C_6F_5)_3$.[9,10]

Under the conditions of the NMR experiment in the presence of an excess of $AlMe_3$ the major product of the reaction between $[CPh_3][B(C_6F_5)_4]$ and $AlMe_3$ is $[AlMe_2(C_6F_5)]_2$. The identity of this species was confirmed by its independent preparation from a 2:1 mixture of $AlMe_3$ and $Al(C_6F_5)_3 \cdot 0.5$toluene. Treating 2 equiv of $AlMe_3$ with $Al(C_6F_5)_3 \cdot 0.5$toluene at 20 °C in toluene-d_8 in an NMR tube causes an immediate shift of the methyl resonance in the ^1H NMR spectrum from δ −0.37 to −0.08 ppm. Upon cooling the sample to −60 °C the methyl signal is split into seven observable peaks (although additional smaller methyl signals appear obscured by more intense peaks), while three sets of C_6F_5 signals are observed in the ^{19}F NMR spectrum. None of the signals are attributable to Al_2Me_6.[11] Warming to −20 °C results in broadening of all the signals in the ^1H and ^{19}F NMR spectra, and at 20 °C the single methyl chemical shift value observed is the averaged chemical shift of the methyl groups of a number of isomers that are in rapid equilibrium with each other (Scheme 1). Similarly, 1:2 mixtures of $AlMe_3$ and $Al(C_6F_5)_3 \cdot 0.5$toluene give predominantly $[AlMe(C_6F_5)_2]_2$. The pertinent NMR data of the C_6F_5 species reported here are collected in Table 1.

Scheme 1



Mixing $Al(C_6F_5)_3 \cdot 0.5$toluene with $AlMe_3$ in a ratio of 1:10 at room temperature in toluene on a preparative scale, followed by removal of the solvent in vacuo with mild heating, leads to the recovery of $Al(C_6F_5)_3 \cdot 0.5$toluene. Isolation of the initial product, $AlMe_2(C_6F_5)$, was not possible due to the evidently very facile ligand exchange and quantitative removal of excess $AlMe_3$ even under these mild conditions. In related recent work, Roesky et al. reported the synthesis of $AlMe_2(C_6F_5)$ by the reaction of $AlMe_2Cl$ with LiC_6F_5 as an uncharacterized intermediate which was converted to $Al(C_6F_5)_3$ by heating to 180 °C in vacuo.[12] Considering the facile ligand exchange in this system (Scheme 1) we find that such high temperatures are not required to shift the equilibrium toward $Al(C_6F_5)_3$.

The ^{19}F NMR chemical shifts of all three aluminum C_6F_5 species $AlMe_{3-x}(C_6F_5)_x$ ($x = 1-3$) are remarkably similar, with changes in the δ value of *para*-F being most indicative, though identification is possibly by ^1H NMR. More pronounced changes are seen when the exchange process is suppressed by adduct formation with diethyl ether. The addition of excess Et_2O to NMR samples of $AlMe_2(C_6F_5)$ in toluene-d_8 at 20 °C results in the formation of $AlMe_2(C_6F_5) \cdot Et_2O$ as the major product, together with small amounts of $AlMe(C_6F_5)_2 \cdot Et_2O$ and $AlMe_3 \cdot Et_2O$. Likewise, addition of Et_2O to $AlMe(C_6F_5)_2$ gives $AlMe(C_6F_5)_2 \cdot Et_2O$ as the major product, with small amounts of $AlMe_2(C_6F_5) \cdot Et_2O$ and $AlMe_3 \cdot Et_2O$ also being detectable. The adducts were characterized by ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectroscopy (Table 1). Surprisingly, although Roesky et al.[12] isolated a crystalline THF adduct of $Al(C_6F_5)_3$, the compound appears not to form a complex with Et_2O in toluene solution, possibly for steric reasons.

To test the suitability of the reaction of $AlMe_3$ with $[CPh_3][B(C_6F_5)_4]$ as a synthetic route for $Al(C_6F_5)_3$, a 10:1 mixture of the two reactants was heated at 65 °C over 14 h. Triphenylethane was produced, and the color of the solution changed from orange to pale yellow.

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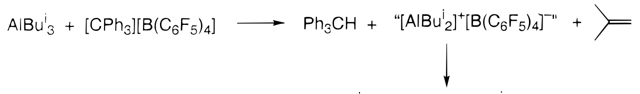
Table 1. ^{1}H and ^{19}F NMR Data of C_6F_5 Compounds

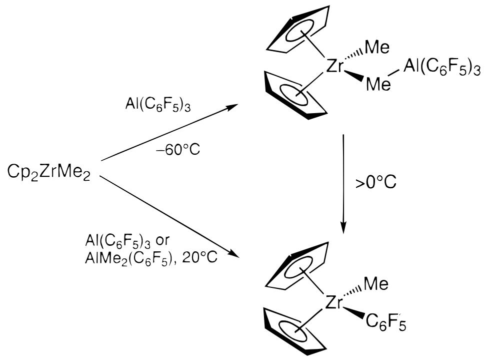
compound	^{1}H NMR	^{19}F NMR (J_{FF}, Hz)		
		o-F	*p*-F	*m*-F[b]
$AlMe_2(C_6F_5)$[a]	−0.08 (Me)	−122.5 (16.9)	−151.9 (br)	−161.0
$AlMe(C_6F_5)_2$[a]	0.04 (Me)	−122.4 (16.9)	−151.4	−161.0
$Al(C_6F_5)_3$·0.5toluene		−122.7 (20.9)[a]	−151.3 (21.2)[a]	−161.1[a]
		−121.9 (21)[c]	−149.6 (21)[c]	−160.4[c]
$AlMe_2(C_6F_5)·OEt_2$[a]	−0.36 (Me) 0.69, 3.31 (Et_2O)	−122.5 (28.2)	−155.1 (19.8)	−161.8
$AlMe(C_6F_5)_2·OEt_2$[a]	−0.18 (Me) 0.88, 3.32 (Et_2O)	−123.1 (28.2)	−152.8 (19.8)	−161.0
$Cp_2ZrMe(\mu\text{-}Me)Al(C_6F_5)_3$ [c]	−0.26 (μ-Me) 0.51 (Zr−Me) 6.44 (Cp)	−124.0 (16.9)	−155.2 (19.8)	−162.6
$Cp_2ZrMe(C_6F_5)$ [a]	0.31 (Me) 5.66 (Cp)	−115.2 (25.4)	−156.7 (19.8)	−162.2

[a] Toluene-d_8, 20 °C. [b] Multiplets or broadened signals. [c] CD_2Cl_2, −60 °C.

Scheme 2



Scheme 3



Removal of the solvent and drying for 4 h in vacuo produced a light brown oily solid. The ^{19}F NMR spectrum shows a major product in approximately 50% yield with chemical shifts identical to an authentic sample of $Al(C_6F_5)_3·0.5$toluene. However, the remaining 50% of the signals were due to other C_6F_5 species which could not be identified, and the reaction is evidently less clean than the reaction of $AlMe_3$ with $B(C_6F_5)_3$.

In contrast to the rather slow reaction between $AlMe_3$ and $[CPh_3][B(C_6F_5)_4]$ which is initiated by *alkyl* abstraction, the reaction of $AlBu^i_3$ with $[CPh_3][B(C_6F_5)_4]$ involves *hydride* abstraction[13] and isobutene elimination (Scheme 2). This reaction proceeds very much faster: at 20 °C a toluene solution of $[CPh_3][B(C_6F_5)_4]$ discolors immediately on addition of $AlBu^i_3$, and the ^{19}F NMR shows that all $[B(C_6F_5)_4]^-$ has been consumed, with formation of BBu^i_3, $BBu^i_2(C_6F_5)$, and $BBu^i(C_6F_5)_2$ (but not, under these conditions, $B(C_6F_5)_3$).

Implications for the Deactivation Process of Metallocene Catalysts. The foregoing results show that the reaction of aluminum alkyls with $[CPh_3][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ can lead to aluminum pentafluorophenyl compounds, with borate degradation in the presence of aluminum alkyls bearing β-hydrogens being particularly facile. As pointed out in the Introduction, catalyst deactivation processes are as yet little understood, and the possible contribution of Al−C_6F_5 species to catalyst deactivation was therefore of interest.

Treatment of Cp_2ZrMe_2 with an equimolar amount of $Al(C_6F_5)_3·0.5$toluene in CD_2Cl_2 at −60 °C leads immediately to the quantitative formation of $Cp_2ZrMe(\mu\text{-}Me)Al(C_6F_5)_3$, according to ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy (Scheme 3). The ^{1}H NMR spectrum shows Cp, Zr−Me, and Zr−Me−Al resonances at δ 6.44, 0.51, and −0.26 ppm, respectively. In the $^{13}C\{^1H\}$ spectrum the Cp and Zr−Me signals are present at δ 113.9 and 40.5 ppm, the μ-Me signal is broad and centered at δ 7.9 ppm. Only one set of C_6F_5 signals in the ^{19}F spectrum are observed (Table 1) which are entirely different from $Al(C_6F_5)_3·0.5$toluene in CD_2Cl_2 at −60 °C (cf. Table 1). Attempts to isolate this product resulted only in the formation of a number of Cp complexes, one of which is identified as $Cp_2ZrMe(C_6F_5)$. We conclude that $Al(C_6F_5)_3$ interacts with Cp_2ZrMe_2 in a way similar to $B(C_6F_5)_3$[14] to give initially zwitterionic methyl-bridged complexes, but that redistribution of C_6F_5 ligands from aluminum to zirconium proceeds much more readily than in the case of $B(C_6F_5)_3$ (Scheme 2), as observed for example by Marks et al., who noted the slow decomposition of $Cp''_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ to $Cp''_2ZrMe(C_6F_5)$ by Me/C_6F_5 exchange with a half-life of 10 h at room temperature [$Cp'' = C_5H_3(SiMe_3)_2$].[15]

At 20 °C a benzene-d_6 solution of Cp_2ZrMe_2 reacts immediately with $Al(C_6F_5)_3$ in a 1:1 molar ratio with formation of two major Cp compounds, one of which was identified as $Cp_2ZrMe(C_6F_5)$, while the other could not be assigned. The formation of $Cp_2Zr(C_6F_5)_2$[16] could not be detected, even in the presence of an excess of $Al(C_6F_5)_3$. By contrast, the reaction of $[Cp_2Zr(\mu\text{-}H)(C_6F_5)]_2$ with $[CPh_3][BBu_n(C_6F_5)_{4-n}]$ has been reported to proceed rapidly to give $Cp_2Zr(C_6F_5)_2$ and other decomposition products.[10] On a preparative scale $Al(C_6F_5)_3·0.5$toluene reacts with Cp_2ZrMe_2 in a 1:3 ratio to give $Cp_2ZrMe(C_6F_5)$ in 54% yield. The same product results from a 1:1 mixture of Cp_2ZrMe_2 and $AlMe_2(C_6F_5)$ in toluene-d_8 at 20 °C; the reaction is quantitative.

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The above discussion shows that under certain circumstances, and particularly if $AlBu^i_3/[CPh_3][B(C_6F_5)_4]$ mixtures are used in catalyst preparation, the transfer of C_6F_5 to zirconium may be facile. The deactivating effect of C_6F_5 was assessed by reacting $Cp_2ZrMe(C_6F_5)$ with $[CPh_3][B(C_6F_5)_4]$ and $B(C_6F_5)_3$, to give $[\{Cp_2Zr(C_6F_5)\}_2(\mu\text{-Me})][B(C_6F_5)_4]$ and $Cp_2Zr(C_6F_5)(\mu\text{-Me})B(C_6F_5)_3$, respectively.[17] Although at comparatively high zirconium concentrations (1 mM) some ethylene polymerization was observed, the activities are very poor compared to Cp_2ZrMe_2/activator mixtures. On the other hand, if conditions that can give rise to "$[AlR_2]^+$" (such as premixing CPh_3^+ with AlR_3) are avoided, the system $Cp_2ZrMe_2/AlR_3/[CPh_3][B(C_6F_5)_4]$ is thermally stable. For example, heating equimolar mixtures of Cp_2ZrMe_2 and $[CPh_3][B(C_6F_5)_4]$ in toluene-d_8 for 1 h at 60 °C, followed by heating for a further 2 h in the presence of $AlMe_3$ ($Al/Zr = 4$), led to a darkening of the samples, but no degradation of the $[B(C_6F_5)_4]^-$ anion was observed by ^{19}F NMR.

Conclusion

Aluminum alkyl cocatalysts in MAO-free metallocene systems are capable of reacting with the catalyst activators $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ at elevated temperatures with formation of $AlMe_{3-x}(C_6F_5)_x$ compounds. The degradation of $[B(C_6F_5)_4]^-$ is initiated by a highly electrophilic transient "$[AlR_2]^+$" species. The value of x depends on the ratio of C_6F_5:Me ligands in the system. Aluminum alkyls carrying β-hydrogens such as $AlBu^i_3$ react with CPh_3^+ under hydride abstraction and alkene elimination; this reaction leads to the rapid consumption of $[B(C_6F_5)_4]^-$ even at ambient temperatures. $Al(C_6F_5)_3$ reacts with Cp_2ZrMe_2 to give the adduct $Cp_2ZrMe(\mu\text{-Me})Al(C_6F_5)_3$ which is stable only at low temperatures and on warming reacts under C_6F_5 transfer from aluminum to zirconium. At room temperature and above Cp_2ZrMe_2 reacts rapidly with $AlMe_{3-x}(C_6F_5)_x$ to give $Cp_2ZrMe(C_6F_5)$. The ethene polymerization activity of $Cp_2ZrMe(C_6F_5)/B(C_6F_5)_3$, mixtures is about 3 orders of magnitude lower that that of $Cp_2ZrMe_2/B(C_6F_5)_3$, an illustration of the deactivating consequence of C_6F_5 transfer reactions.

Experimental Section

All manipulations were carried out with the use of Schlenk, vacuum-line, and glovebox techniques. Light petroleum (bp 40−60 °C), toluene, and diethyl ether were distilled under nitrogen from sodium−potassium alloy. Deuterated solvents were dried over Linde 4 Å molecular sieves and deoxygenated via several freeze−thaw cycles. $AlMe_3$ (97%, Aldrich) was used as purchased. The compounds Cp_2ZrMe_2,[18] $B(C_6F_5)_3$,[19] and $[CPh_3][B(C_6F_5)_4]$[20] were prepared by literature methods. The ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker DPX300 instrument. ^1H and ^{13}C NMR spectra were referenced to residual solvent peaks relative to TMS; ^{11}B and ^{19}F spectra were referenced externally to $BF_3{\cdot}Et_2O$ and $CFCl_3$, respectively.

Synthesis of $Al(C_6F_5)_3{\cdot}0.5$toluene. This compound was prepared by modification of a literature procedure.[9] **CAUTION:** $Al(C_6F_5)_3$ has been reported to detonate on attempted sublimation at elevated temperatures.[21] A solution of $B(C_6F_5)_3$ (3.55 g, 6.94 mmol) in toluene (20 mL) was added to a solution of $AlMe_3$ (0.50 g, 6.94 mmol) in toluene (40 mL) at room temperature. A precipitate formed after 0.5 h, and the reaction was left to stir for 16 h. The solid was isolated and dried under vacuum for 3 h to give $Al(C_6F_5)_3{\cdot}0.5$toluene as a white microcrystalline solid (1.8 g). The filtrate was concentrated and placed in the freezer overnight and provides another 1.5 g, combined yield 3.3 g (5.74 mmol, 83%).

Reaction of $AlMe_3$ with $[CPh_3][B(C_6F_5)_4]$. For monitoring the reaction by NMR, a solution of $[CPh_3][B(C_6F_5)_4]$ (0.014 g, 15 μmol) in toluene-d_8 (0.4 mL) was treated with a solution of $AlMe_3$ (0.6 mL, 0.11 M, 66 μmol) in toluene-d_8 and immediately placed in the spectrometer heated to 60 °C. The reaction was monitored via ^1H and ^{19}F NMR over a period of 4.5 h. Signals for $AlMe_2(C_6F_5)$ grew in and became the major species after 4.5 h. No other products were seen. The reaction is first-order in triphenylmethyl salt, $k_{obs} = 5 \times 10^{-5}\ s^{-1}$.

In a separate experiment, a toluene solution (5 mL) of $[CPh_3][B(C_6F_5)_4]$ (0.202 g, 0.22 mmol) was treated with a toluene solution of $AlMe_3$ (3 mL, 1.5 M, 4.50 mmol). The reagents were heated at 65 °C for 14 h before the solvent was removed, and the light brown oily residue was dried under vacuum for 4 h. A sample of the crude product contained $Al(C_6F_5)_3$ as the major product in 50% yield by ^{19}F NMR spectroscopy. NMR ^{19}F (toluene-d_8) δ −122.7 (d, $J = 20.9$ Hz, 6F, *o*-F), −151.3 (t, $J = 21.2$ Hz, 3F, *p*-F), −161.1 (m, 6F, *m*-F).

Reaction of $AlBu^i_3$ with $[CPh_3][B(C_6F_5)_4]$. An NMR tube containing $[CPh_3][B(C_6F_5)_4]$ (0.012 mmol) was reacted with a solution of $AlBu^i_3$ (0.070 mmol) in toluene-d_8 at 20 °C. The solution turned from orange to colorless *immediately*, and the ^{19}F NMR spectrum contained no signals due to $[B(C_6F_5)_4]^-$. Apart from the reaction products isobutene and triphenylmethane, signals were observed for $AlBu^i_2(C_6F_5)$ [^1H NMR δ 1.99 (m, 1H, CH), 0.97 (d, 6H, $J = 6.5$ Hz, CH_3), 0.28 (d, 2H, $J = 7.2$ Hz, CH_2); ^{19}F NMR δ −120.7 (m, 2F), −152.5 (t, 1F, $J = 19.8$ Hz), −161.6 (m, 2F)], $BBu^i(C_6F_5)_2$ [−130.9 (m, 2F), −147.4 (t, 2F, $J = 21.2$ Hz), −161.1 (m, 2F)], and $BBu^i_2(C_6F_5)$ [-134.3 (m, 2F), −153.3 (t, 1F, $J = 19.7$ Hz), −161.8 (m, 2F)] but not $B(C_6F_5)_3$. The ^{11}B and ^1H NMR spectra show the presence of BBu^i_3 [^1H NMR δ 1.56 (m, 1H, CH), 1.16 (d, 2H, $J = 7.0$ Hz, CH_2), 0.88 (d, 6H, $J = 6.5$ Hz, CH_3); ^{11}B NMR δ 88.1].[22]

Reaction of 2 $Al(C_6F_5)_3{\cdot}0.5$toluene with $AlMe_3$. A solution of $Al(C_6F_5)_3{\cdot}0.5$toluene (43 mg, 76 μmol) in toluene-d_8 (0.5 mL) was treated with a solution of $AlMe_3$ (0.1 mL, 0.38 M, 38 μmol) in toluene-d_8 at 20 °C to form $[AlMe(C_6F_5)_2]_2$. The sample was cooled to −60 °C, and three major and three minor methyl signals could be seen in the ^1H NMR spectrum at δ (rel int) 0.34 (1.2), 0.26 (8.9), 0.09 (7.2), −0.26 (10.0), −0.34 (4.5), −0.51 (3.8), and −0.57 (3.1). Three sets of peaks for C_6F_5 groups are seen in the ^{19}F NMR spectrum, at δ (rel int) −122.4 (40.0), −122.7 (12.6), −123.1 (3.2) (*o*-F), −150.1 (1.6), −151.2 (20.0), −152.4 (6.3) (*p*-F), and −160.1 (3.2), −160.4 (40.0), −160.9 (12.6) (*m*-F). At 20 °C $[AlMe(C_6F_5)_2]_2$ is characterized by the following NMR parameters: ^1H NMR (toluene-d_8, 20 °C) δ 0.04 (s, br, Me); $^{13}C\{^1H\}$ NMR (toluene-d_8, 20 °C) δ 150.0 (dm, $J_{CF} = 236$ Hz, *o*-CF), 142.3 (dm, $J_{CF} = 254$ Hz, *p*-CF), 137.2 (dm, $J_{CF} = 254$ Hz, *m*-CF), −6.9 (Me); ^{19}F NMR (toluene-d_8, 20 °C) δ −122.4 (d, $J = 16.9$ Hz, 6F, *o*-F), −151.4 (s, br, 3F, *p*-F), −161.0 (s, br, 6F, *m*-F).

Formation of $AlMe(C_6F_5)_2{\cdot}Et_2O$. An excess of diethyl ether was added to the above solution at 20 °C. ^1H NMR

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[17] A mixture of 50 μmol $Cp_2ZrMe(C_6F_5)$ and 50 μmol $B(C_6F_5)_3$ in toluene (50 mL) at 50 °C under 1 bar ethene gave 0.2 g of PE after 1 h, corresponding to a productivity of 4 kg PE (mol Zr)$^{-1}{\cdot}$bar$^{-1}{\cdot}$h^{-1}. Although recrystallized $Cp_2ZrMe(C_6F_5)$ was used, the possibility of the presence of traces of Cp_2ZrMe_2 cannot be entirely discounted.

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(toluene-d_8, 20 °C): δ 3.32 (q, $J = 7.0$ Hz, 4H, OCH_2CH_3), 0.88 (t, $J = 7.0$ Hz, 6H, OCH_2CH_3), −0.18 (t, $^5J_{HF} = 1.2$ Hz, 3H, Me−Al). $^{13}C\{^1H\}$ (toluene-d_8, 20 °C): δ 67.1 (OCH_2CH_3), 14.5 (OCH_2CH_3), −6.91 (s, br, Me-Al). ^{19}F (toluene-d_8, 20 °C): δ −123.1 (d, $J = 28.2$ Hz, 6 F, *o*-F), −152.8 (t, $J = 19.8$ Hz, 3 F, *p*-F), −161.0 (m, 6 F, *m*-F). Small amounts of $AlMe_2(C_6F_5)\cdot Et_2O$ (see below) and $AlMe_3\cdot Et_2O$ are also present. $AlMe_3\cdot Et_2O$: ^1H (toluene-d_8, 20 °C) δ −0.51 (s, 9H, Me−Al); $^{13}C\{^1H\}$ (toluene-d_8, 20 °C) δ −7.7 (s, br, Me−Al). The diethyl ether signals quoted are a time-averaged value of all $AlMe_{3-x}(C_6F_5)_x\cdot Et_2O$ species and free diethyl ether in equilibrium.

Reaction of $Al(C_6F_5)_3\cdot 0.5$toluene with $2AlMe_3$. A solution of $Al(C_6F_5)_3\cdot 0.5$toluene (43 mg, 76 μmol) in toluene-d_8 (0.2 mL) was treated with a solution of $AlMe_3$ (0.4 mL, 0.38 M, 152 μmol) in toluene-d_8 and placed in the spectrometer at 20 °C. The sample was cooled to −60 °C, and at least seven separate methyl signals could be seen, which coalesce to one singlet at 20 °C. $[AlMe(C_6F_5)_2]_2$: ^1H NMR (toluene-d_8, 20 °C) δ −0.08 (s, br, 3H, Me); $^{13}C\{^1H\}$ NMR (toluene-d_8, 20 °C) δ 150.1 (dm, $J_{CF} = 249$ Hz, *o*-C), 142.3 (dm, $J_{CF} = 249$ Hz, *p*-CF), 137.2 (dm, $J_{CF} = 249$ Hz, *m*-CF), −7.3 (Me); ^{19}F NMR (toluene-d_8, 20 °C) δ −122.5 (d, $J = 16.9$ Hz, 6F, *o*-F), −151.9 (s, br, 3F, *p*-F), −161.0 (s, br, 6F, *m*-F).

Formation of $AlMe_2(C_6F_5)\cdot Et_2O$. An excess of diethyl ether was added to the above solution. ^1H NMR (toluene-d_8, 20 °C): δ 3.31 (q, $J = 7.0$ Hz, 4 H, OCH_2CH_3), 0.69 (t, $J = 7.2$ Hz, 6H, OCH_2CH_3), −0.36 (t, $^5J_{HF} = 1.1$ Hz, 6H, Me−Al). $^{13}C\{^1H\}$ (toluene-d_8, 20 °C): δ 67.4 (OCH_2CH_3), 13.4 (OCH_2CH_3), −8.1 (s, br, Me−Al). ^{19}F (toluene-d_8, 20 °C): δ −122.5 (d, $J = 28.2$ Hz, 6F, *o*-F), −155.1 (t, $J = 19.8$ Hz, 3F, *p*-F), −161.8 (m, 6F, *m*-F). Small amounts of $AlMe(C_6F_5)_2\cdot Et_2O$ and $AlMe_3\cdot Et_2O$ are also present.

Generation of $Cp_2ZrMe(\mu\text{-}Me)Al(C_6F_5)_3$. A solution of Cp_2ZrMe_2 (12 mg, 48 μmol) in CD_2Cl_2 (0.6 mL) was treated with $Al(C_6F_5)_3\cdot 0.5$toluene (29.4 mg, 51 μmol) in an NMR tube at −78 °C and then placed in the spectrometer cooled to −60 °C. An immediate reaction occurs providing a quantitative conversion to $Cp_2ZrMe(\mu\text{-}Me)Al(C_6F_5)_3$. ^1H NMR (CD_2Cl_2, −60 °C): δ 6.44 (s, 10H, Cp), 0.51 (s, 3H, Zr−Me), −0.26 (s, 3H, Me−Al). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 149.8 (dm, $J_{CF} = 234$ Hz, *o*-CF), 141.0 (dm, $J_{CF} = 249$ Hz, *p*-CF), 136.7 (dm, $J_{CF} = 226$ Hz, *m*-CF), 113.9 (Cp), 40.5 (Zr−Me), 7.9 (br, Me−Al). ^{19}F NMR (CD_2Cl_2, −60 °C): δ −124.0 (d, $J = 16.9$ Hz, 6H, *o*-F), −155.2 (t, $J = 19.8$ Hz, 3F, *p*-F), −162.6 (m, 6F, *m*-F).

Generation of $Cp_2Zr(C_6F_5)(\mu\text{-}Me)B(C_6F_5)_3$. A sample of $Cp_2ZrMeC_6F_5$ (19 mg, 0.053 mmol) in CD_2Cl_2 (0.3 mL) was treated with $B(C_6F_5)_3$ (28.5 mg, 0.056 mmol) in CD_2Cl_2 (0.3 mL) at −78 °C and placed in the spectrometer at −50 °C. Immediate formation of $Cp_2Zr(C_6F_5)(\mu\text{-}Me)B(C_6F_5)_3$ was observed. The $Zr-C_6F_5$ moiety shows hindered rotation at low temperature. ^1H NMR (CD_2Cl_2): δ 0.56 (bs, 3H, B−Me), 6.60 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR: δ 116.1 (Cp), 33.8 (B−Me). ^{11}B NMR: δ −11.1. ^{19}F NMR (−80 °C): δ 112.6 (d, 1F, $J = 28.0$ Hz, *o*-F of $Zr-C_6F_5$), −114.1 (d, 1F, $J = 28.0$ Hz, *o*-F of $Zr-C_6F_5$), −132.7 (d, 6F, $J = 22.5$ Hz, *o*-F of $B-C_6F_5$), −152.3 (t, 1F, $J = 19.8$ Hz, *p*-F of $Zr-C_6F_5$), −158.2 (t, 3F, $J = 21.2$ Hz, *p*-F of $B-C_6F_5$), −159.4 (m, 1F, *m*-F of $Zr-C_6F_5$), −160.0 (m, 1F, *m*-F of $Zr-C_6F_5$), −163.3 (m, 6F, *m*-F of $B-C_6F_5$).

Generation of $[\{Cp_2Zr(C_6F_5)\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$. A sample of $Cp_2ZrMeC_6F_5$ (16 mg, 0.045 mmol) in CD_2Cl_2 (0.3 mL) was treated with $[CPh_3][B(C_6F_5)_4]$ (0.024 mmol) in CD_2Cl_2 (0.3 mL) at −78 °C and placed in the spectrometer at −50 °C. There was a slow reaction to give $[\{Cp_2Zr(C_6F_5)\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$. Complete conversion took 160 min at −30 °C. ^1H NMR (CD_2Cl_2): δ 6.56 (s, 20H, Cp), −0.029 (bs, 3H, μ-Me). $^{13}C\{^1H\}$ NMR: δ 115.0 (Cp), μ-Me not observed. ^{11}B NMR: δ −14.5. ^{19}F NMR (−80 °C): δ 113.1 (d, 2F, $J = 25.0$ Hz, *o*-F of $Zr-C_6F_5$), −119.3 (d, 2F, $J = 25.0$ Hz, *o*-F of $Zr-C_6F_5$), −132.1 (m, 8F, *o*-F of $B-C_6F_5$), −152.2 (t, 2F, $J = 19.8$ Hz, *p*-F of $Zr-C_6F_5$), −158.3 (m, 2F, *m*-F of $Zr-C_6F_5$), −159.3 (m, 2F, *m*-F of $Zr-C_6F_5$), −160.9 (m, 4F, *p*-F of $B-C_6F_5$), −164.9 (m, 8F, *m*-F of $B-C_6F_5$).

Reaction of $Al(C_6F_5)_3\cdot 0.5$toluene with Cp_2ZrMe_2 at 20 °C. A C_6D_6 solution of Cp_2ZrMe_2 (24 mg, 95 μmol) was treated with $Al(C_6F_5)_3\cdot 0.5$toluene (18.5 mg, 32 μmol) in an NMR tube at room temperature. An immediate reaction occurs providing a quantitative conversion to $Cp_2ZrMe(C_6F_5)$.

In a preparative scale reaction two separate Schlenk tubes were charged with Cp_2ZrMe_2 (0.641 g, 2.55 mmol) in one and $Al(C_6F_5)_3\cdot 0.5$toluene (0.467 g, 0.85 mmol) in the other. Both were dissolved in toluene (ca. 10 mL). The $Al(C_6F_5)_3$ solution was added to Cp_2ZrMe_2 at 20 °C. The reaction mixture was stirred for 10 min before filtering and cooling to −78 °C over 48 h. A pale yellow precipitate was isolated, washed twice with light petroleum, and dried in vacuo, to yield $Cp_2ZrMe(C_6F_5)$ (0.55 g, 1.36 mmol, 54%). ^1H NMR (C_6D_6, 20 °C): δ 5.66 (s, 10H, Cp), 0.31 (t, $^5J_{HF} = 4.1$ Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 145.4 (dm, $J_{CF} = 226$ Hz, *o*-CF), 139.5 (dm, $J_{CF} = 251$ Hz, *p*-CF), 136.8 (dm, $J_{CF} = 255$ Hz, *m*-CF), 111.4 (Cp), 45.4 (t, $^4J_{CF} = 6.0$ Hz, Me). ^{19}F NMR (C_6D_6, 20 °C): δ −115.2 (d, $J = 25.4$ Hz, 6H, *o*-F), −156.7 (t, $J = 19.8$ Hz, 3F, *p*-F), −162.2 (m, 6F, *m*-F). MS (EI): *m*/*e* (%) 402 (2) (M^+), 387 (80) [$M^+ - Me$], 239 (85) [$M^+ - C_6F_5$], 220 (100) [Cp_2Zr].

Reaction of $AlMe_2(C_6F_5)$ with Cp_2ZrMe_2. A sample of $AlMe_2(C_6F_5)$ (228 μmol), prepared from $Al(C_6F_5)_3\cdot 0.5$toluene (43 mg, 76 μmol) and $AlMe_3$ (0.4 mL, 0.38 M, 152 μmol) in toluene-d_8 as discussed above, was added to Cp_2ZrMe_2 (57 mg, 228 mmol) at 20 °C. An immediate reaction takes place with quantitative conversion to $Cp_2ZrMe(C_6F_5)$ and $AlMe_3$, identified by comparison with authentic samples.

Thermal Stability of $[Cp_2ZrMe][B(C_6F_5)_4]$. In a control experiment, 13 mg (14 μmol) of $[CPh_3][B(C_6F_5)_4]$ and Cp_2ZrMe_2 (14 μmol) were mixed in an NMR tube at room temperature in 0.5 mL of toluene-d_8. The ^{19}F NMR spectrum of the mixture was monitored at 60 °C for 1 h; there was no indication of anion degradation. Next, $AlMe_3$ (66 μmol) was added and heating was continued for another 2 h. No change in the signals for $[B(C_6F_5)_4]^-$ was observed.

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