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Synthesis and Characterization of $[(C_5Me_4H)_2Al]^+$, an Initiator for the Polymerization of Isobutene. X-ray Crystal Structures of $[(C_5Me_4H)_2Al(\mu\text{-}Cl)]_2$ and $[(C_5Me_4H)_2Al][B(C_6F_5)_4]$

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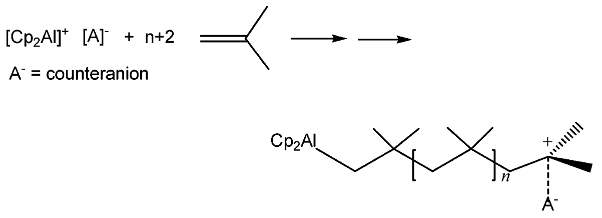
The octamethylaluminocenium cation $[Cp'_2Al]^+$ ($Cp' = C_5Me_4H$) was formed both by halide abstraction in the reaction between $[Cp'_2AlCl]_2$ and $AlCl_3$ and by cyclopentadienide abstraction in the reaction between Cp'_3Al and $[CPh_3][B(C_6F_5)]_4$. $[Cp'_2Al]^+$ is less thermally stable than $[Cp^*_2Al]^+$ ($Cp^* = C_5Me_5$) but is more active as an initiator for isobutene polymerization. The X-ray crystal structures of $[Cp'_2AlCl]_2$ and $[Cp'_2Al][B(C_6F_5)_4]$ are reported.

Introduction

Organoaluminum cations are of interest as initiators for ring-opening polymerization of alkene oxides[1] and carbocationic alkene polymerization[2] and as potential catalysts for the coordination/insertion polymerization of alkenes.[3] Stable, two-coordinate organoaluminum cations are rare since their electronic and coordinative unsaturation, the very properties that make them attractive as potential catalysts, also make them especially vulnerable to decomposition. Those that have been isolated and structurally characterized have been stabilized either by the presence of bulky, sterically protecting hydrocarbyl ligands on the aluminum or by inert, weakly coordinating counteranions.[4] Among this group is the decamethylaluminocenium cation $[Cp^*_2Al]^+$ ($Cp^* = C_5Me_5$), first isolated by Schnöckel and co-workers from the reaction between $[Cp^*Al]_4$ and $AlCl_3$.[5] The counteranion in this case was $[Cp^*AlCl_3]^-$. Other synthetic approaches to $[Cp^*_2Al]^+$ were later reported by us[6] and by Jutzi and co-workers.[7] The importance of steric stabilization by the bulky Cp* ligand is underscored by the poor stability of $[Cp_2Al][MeB(C_6F_5)_3]$, formed by Bochmann and co-workers from the reaction between Cp_2AlMe and $B(C_6F_5)_3$.[2] This species decomposes in CH_2Cl_2 solution at temperatures above −20 °C. Below this temperature it is a highly active initiator for the carbocationic polymerization of isobutene and isoprene, even at −78 °C. By contrast, $[Cp^*_2Al][MeB(C_6F_5)_3]$ is a poor initiator for isobutene polymerization, exhibiting no activity below −20 °C.[6]

Equation 1 illustrates how the aluminocenium cation is presumed to initiate the polymerization.[2,8] Coordination of an isobutene molecule to the aluminum generates a carbenium ion, from which the polymer is propagated. The striking effect of cyclopentadienyl ligand size on the stability and activity of the aluminocenium cation prompted us to explore the possibility of fine-tuning the stability and activity of the cation by varying the number of methyl substituents on its cyclopentadienyl rings. For this purpose, we pursued the synthesis of the octamethylaluminocenium cation $[Cp'_2Al]^+$ ($Cp' = C_5Me_4H$). As described herein, methanide ion abstraction from Cp'_2AlMe by $B(C_6F_5)_3$ in the manner demonstrated for Cp_2AlMe and Cp^*AlMe was not a viable route to the cation. Therefore, an alternate synthetic route to the octamethylaluminocenium cation was sought. Toward this goal, we developed the new compound $[Cp'_2AlCl]_2$ (**1**). We also demonstrated, for the first time, the abstraction of a cyclopentadienyl anion from a metal by the trityl cation.



(1)

Results and Discussion

We initially explored methanide anion abstraction from Cp'_2AlMe by $B(C_6F_5)_3$ as a potential route to $[Cp'_2Al][MeB(C_6F_5)]$ since this approach was successful for preparing aluminocenium cations from Cp_2AlMe[2] and Cp^*_2AlMe.[6] Unlike Cp_2AlMe and Cp^*_2AlMe, Cp'_2AlMe is not isolable because it undergoes ligand redistribution in toluene to form Cp'_3Al (identified by ^1H and ^{27}Al NMR spectroscopy) and possibly $Cp'AlMe_2$.

An equivalent of $B(C_6F_5)_3$ was added to the product mixture from the 2:1 reaction between $Cp'Na$ and $MeAlCl_2$ to determine if the equilibria might be shifted in favor of selective formation of $[Cp'_2Al][MeB(C_6F_5)_3]$; however, an ill-defined mixture of products was obtained instead. Therefore, we pursued a dicyclopentadienylaluminum halide precursor as a potential precursor to a $[Cp'_2Al]^+$ salt.

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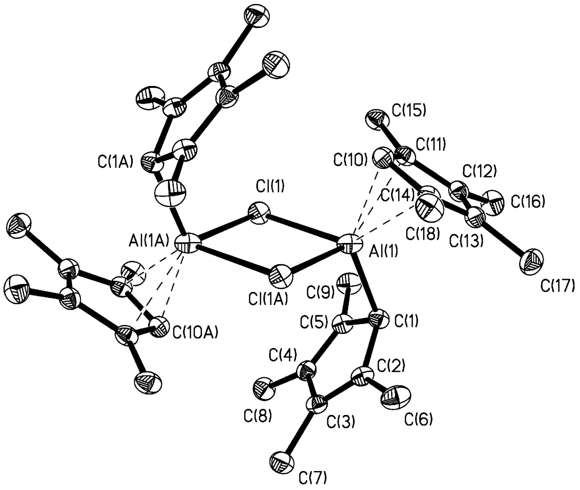

Figure 1. Thermal ellipsoids diagram (30%) of $[\eta^1,\eta^3\text{-}Cp'_2Al\text{-}\mu\text{-}Cl]_2$ (**1**). Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for Compounds 1 and 3

	1	3
formula	$C_{36}H_{52}Al_2Cl_2$	$C_{48}H_{31}AlBBrF_{20}$
mol wt	609.64	1105.43
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	8.622(17)	22.644(5)
b (Å)	10.595(2)	23.988(5)
c (Å)	10.614(2)	17.049(3)
α (deg)	108.88(3)	90
β (deg)	111.74(3)	107.02(3)
γ (deg)	92.98(3)	90
V (Å^3)	835.7(4)	8855(3)
Z	1	8
T (K)	203(2)	84(2)
λ (Å)	0.71073	0.71073
ρ_{calc} (Mg/m^3)	1.211	1.658
μ (mm^{-1})	0.270	1.069
cryst size (mm^3)	0.25 × 0.15 × 0.146	0.18 × 0.08 × 0.08
θ range (deg)	2.07 to 25.25	1.57 to 27.50
index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-12 \leq l \leq 12$	$-29 \leq h \leq 29$, $-31 \leq k \leq 31$, $-22 \leq l \leq 21$
no. reflns collected	8693	58 723
no. indep reflns	3011 [R(int) = 0.0248]	10 166 [R(int) = 0.1092]
no. data/restraints/ params	3011/0/189	10 166/78/562
GOF	1.054	1.018
R_1 [$I > 2\sigma(I)$]^a	0.0385	0.0687
wR_2 [$I > 2\sigma(I)$]^b	0.0995	0.1454
largest diff peak, hole (e·Å^{-3})	0.308, −0.235	0.709, −0.788

^{a} $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Al(1)−C(1)	1.997(2)	C(4)−C(5)	1.349(3)
Al(1)−C(10)	2.046(2)	C(10)−C(11)	1.438(3)
Al(1)−C(11)	2.355(2)	C(10)−C(14)	1.440(3)
Al(1)−C(14)	2.346(2)	C(11)−C(12)	1.401(3)
C(1)−C(2)	1.485(3)	C(12)−C(13)	1.417(3)
C(1)−C(5)	1.495(3)	C(13)−C(14)	1.499(3)
C(2)−C(3)	1.351(3)	Al(1)−Cl(1)	2.3511(11)
C(3)−C(4)	1.461(3)	Al1−Cl(1A)	2.3409(9)
C(4)−C(5)	1.349(3)		
Cl(1A)−Al(1)−Cl(1)	84.86(3)		
Al(1A)−Cl(1)−Al(1)	95.14(3)		

^{a}Symmetry generation = $-x + 1$, $-y + 1$, $-z + 1$.

Synthesis and Structural Characterization of $[Cp'_2Al(\mu\text{-}Cl)]_2$. $[Cp'_2Al(\mu\text{-}Cl)]_2$, **1**, was formed via ligand redistribution between Cp'_3Al and $AlCl_3$, which were combined in a 2:1 ratio in dichloromethane. Efforts to form **1** by reacting $AlCl_3$ with Cp'_2Mg were unsuccessful, possibly due to the tendency of the aluminum compound to form a matrix with the $MgCl_2$ byproduct. Although the ^1H NMR spectra of **1** in C_6D_6 and $CDCl_3$ indicated the presence of multiple species due to ligand redistribution, single crystals of **1** crystallized from a chloroform solution of the compound in 42% yield. The molecular structure of the compound is shown in Figure 1. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively.

The molecule sits on a center of inversion in the crystal, so each half of the dimer is related by symmetry. The aluminum bears one η^1 and one η^3 Cp′ ring. The Al−C(1) σ-bond distance is slightly shorter, by 0.04−0.05 Å, than the distance between Al and C(10), the shortest bond with the η^3 ring. C(11) and C(14) of the η^3 ring are 0.3 Å more distant from the aluminum than C(10). C(12) and C(13) are 0.3−0.4 Å farther still. Whereas the η^1 ring exhibits discrete single and double C−C bond lengths, with single-bond lengths of 1.461(3)−1.495(3) Å and double-bond lengths of 1.349(3) and 1.351(3) Å, the C−C bond lengths in the η^3 ring, ranging from 1.401(3)−1.499(3) Å, are delocalized.

Only a small number of chloride-bridged cyclopentadienylaluminum compounds have been structurally characterized: $[(\eta^5\text{-}C_5Me_4Et)(Ph)Al\text{-}\mu\text{-}Cl]_2$,[9] $[(\eta^5\text{-}C_5Me_4Et)(Cl)Al\text{-}\mu\text{-}Cl]_2$,[9] $[(\eta^3\text{-}C_5Me_5)(Cl)Al\text{-}\mu\text{-}Cl]_2$,[10] $[(\eta^3\text{-}C_5Me_5)(CH_3)Al\text{-}\mu\text{-}Cl]_2$,[11] and $[(\eta^3\text{-}C_5Me_5)(i\text{-}Bu)Al\text{-}\mu\text{-}Cl]_2$.[11] The hapticities of the cyclopentadienyl ring in these compounds vary between η^3 and η^5 in the solid state. There are no striking structural differences between **1** and these other compounds.

Compound **1** is stable indefinitely in the solid state below −20 °C under nitrogen. At room temperature the solid turns purple over the course of a week. ^1H and ^{27}Al NMR spectra of solutions of the compound in $CDCl_3$ and CD_2Cl_2 exhibit ligand redistribution and ionization products from **1**. Four distinct resonances at δ = 103, 70, −37, and −113 were observed in the ^{27}Al NMR spectrum. The resonance at 103 ppm is consistent with the reported chemical shift of $[AlCl_4]^-$.[12] We attribute the −113 ppm resonance to $[Cp'_2Al]^+$ due to its extreme upfield shift,[13] similar to that of $[Cp^*_2Al]^+$ (δ −115)[5] and $[Cp_2Al]$ (δ −128).[2]

Synthesis and Structural Characterization of $[Cp'_2Al][B(C_6F_5)_4]$. Since $AlCl_3$ itself can serve as a halide-abstracting agent, we also examined the reaction between Cp'_3Al and $AlCl_3$ in a 1:2 ratio in CH_2Cl_2, instead of the 2:1 ratio used to generate **1**. This reaction afforded a brown solid that exhibited resonances for $[Cp'_2Al]^+$, $[AlCl_4]^-$, and **1** in the ^1H and ^{27}Al NMR spectra of a sample in $CDCl_3$. Efforts to crystallize the aluminocenium salt from this mixture afforded only crystals of **1**.

When Cp'_3Al and $AlCl_3$ were combined in a 1:2 ratio in bromobenzene and the solution was layered with hexane, a pink, crystalline product was obtained in 55% yield. We tentatively formulate this compound as $[Cp'_2Al][AlCl_4]$ (**2**) (eq 2) on the

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Table 3. Selected Bond Lengths (Å) for 3

Al1−C25	2.105(4)	C28−C29	1.437(6)
Al1−C26	2.142(4)	Al2−C34	2.154(16)
Al1−C27	2.168(4)	Al2−C35	2.093(12)
Al1−C28	2.167(4)	Al2−C36	2.031(12)
Al1−C29	2.131(4)	Al2−C37	2.060(15)
C25−C29	1.423(6)	Al2−C38	2.141(17)
C25−C26	1.426(7)		
C26−C27	1.427(6)	Al−(centroid 1)	1.765
C27−C28	1.430(6)	Al−(centroid 2)	1.708/1.836

basis of its spectroscopic data. ^{1}H and ^{27}Al NMR spectra of the compound in bromobenze-d_5 revealed signals for only [Cp′$_2$Al]$^+$ (δ −113) and [AlCl$_4$]$^-$ (δ 103). The ^{1}H NMR spectrum showed Cp′ methyl resonances at 1.65 and 1.73 ppm and a Cp′ allylic proton resonance at 5.85 ppm. Efforts to elucidate the molecular structure of **2** from X-ray diffraction data were unsuccessful.

$$2\mathrm{Cp'_3Al} + 4\mathrm{AlCl_3} \xrightarrow{\mathrm{C_6H_5Br}} 3[\mathrm{Cp'_2Al}]^+[\mathrm{AlCl_4}]^- \quad (2)$$

(**2**)

Ligand redistribution occurred immediately when **2** was dissolved in CDCl$_3$. Two sets of Cp′ methyl signals (δ 1.91, 2.02; 2.14, 2.23) and two Cp′ allylic proton peaks (δ 5.77, 6.46) were observed in the ^{1}H NMR spectrum. There was a slight splitting in the δ 6.46 resonance that is reminiscent of the splitting observed in the Cp* methyl resonance in the ^{1}H NMR spectra of [Cp*$_2$Al]$^+$ salts.[6,7] We believe that this splitting is associated with ion pairing since it is solvent and temperature dependent.

Compound **2** initiates the polymerization of isobutene in CH$_2$Cl$_2$; however, due to ligand redistribution, we could not rule out the involvement of [AlCl$_2$]$^+$ [8] or [Cp′AlCl]$^+$ as initiators of the polymerization. With the knowledge that a [Cp′$_2$Al]$^+$ salt was isolable, we sought an alternate route to an aluminocenium salt with an inert counteranion. Although the trityl cation is best known for its ability to abstract hydride and methyl anions from metals, it proved to also be competent at abstracting a [Cp′]$^-$ group from Cp′$_3$Al. Clear, light pink crystals of [Cp′$_2$Al][B(C$_6$F$_5$)$_4$], **3**, were isolated in 43% yield from the reaction between Cp′$_3$Al and [CPh$_3$][B(C$_6$F$_5$)$_4$] in a bromobenzene/hexane solvent mixture (eq 3). The pink coloration of the crystals could be due to the presence of trace impurities. An X-ray crystal structure determination was performed on the compound. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 3, respectively.

$$\mathrm{Cp'_3Al} + [\mathrm{Ph_3C}]^+[\mathrm{B(C_6F_5)_4}]^- \xrightarrow{\mathrm{C_6H_5Br}} [\mathrm{Cp'_2Al}]^+[\mathrm{B(C_6F_5)_4}]^- \quad (3)$$

(**3**)

The asymmetric unit of the crystal contains two symmetry unique half aluminocenium cations, a [B(C$_6$F$_5$)$_4$]$^-$ counteranion, and a 50% disordered bromobenzene molecule from the solvent of crystallization. Thermal ellipsoid drawings of the two aluminocenium ions are shown in Figure 2. One aluminocenium cation is linear with staggered η^5 Cp′ rings. The centroid−Al bond distance is 1.765 Å (vs 1.78 Å for [Cp*$_2$Al]), and a 180 °C centroid−Al−centroid angle is imposed by the symmetry of the crystal. The second aluminocenium cation is disordered. Two orientations of the Cp′ were identified in this cation and modeled as rigid groups using the coordinates of the ordered aluminocenium cation. Both octamethylcyclopentadienyl ligands are η^5 bonded to aluminum, but the centroid−Al−centroid angle deviates from linearity and is 174.7° for both disordered models. The centroid−Al−centroid bond lengths are inequivalent. One is 0.06 Å shorter and the other is 0.07 Å shorter than the Al(1)−centroid bond length in the ordered, linear molecule. The disorder suggests that the Cp′ rings may be wagging back and forth as a result of their inadequate steric shielding of the low-coordinate, electrophilic aluminum center.

The stability of compound **3** in both bromobenzene-d_5 and CDCl$_3$ solvents was monitored by ^{1}H and ^{27}Al NMR spectroscopy. The compound was stable in bromobenzene-d_5 at room temperature for over a week. It was stable in CDCl$_3$ at −20 °C for more than 48 h and gradually decomposed as the temperature was warmed to 20 °C. The cation [Cp′$_2$Al]$^+$ exhibits an ^{27}Al NMR chemical shift of δ −113 in both CDCl$_3$ and bromobenzene-d_5. A splitting of the allylic peak was observed in the room-temperature ^{1}H NMR spectra of the compound in CDCl$_3$ that was not seen in brombenzene-d_5.

Isobutene Polymerization. The isobutene polymerization activities of compound **3** and [Cp*$_2$Al][MeB(C$_6$F$_5$)$_3$] were compared under similar conditions. Whereas **3** activated the polymerization of isobutene at −20 °C in CH$_2$Cl$_2$, [Cp*$_2$Al][MeB(C$_6$F$_5$)$_3$] was completely inactive at this temperature. This was confirmed in both NMR scale and preparative experiments. Reaction of 10 mL of isobutene with 58 μg of **3** in 5 mL of CH$_2$Cl$_2$ for 3 h at at −20 °C, followed by quenching with methanol, yielded 3.2 g of polyisobutene as a viscous oil. A similar scale reaction using [Cp*$_2$Al][MeB(C$_6$F$_5$)$_3$] afforded 2.1

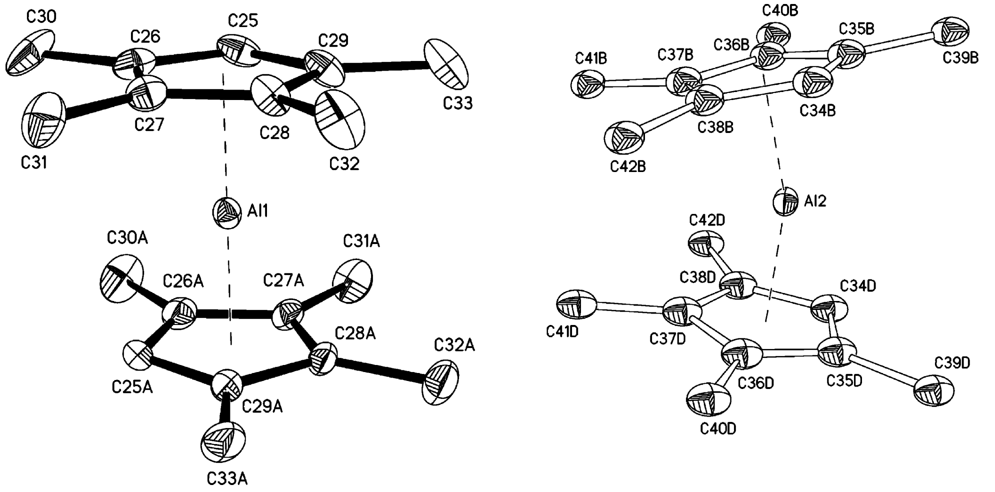

Figure 2. Thermal ellipsoid drawing (30%) of [η^5,η^5-Cp′$_2$Al]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**3**). Hydrogen atoms are omitted and only one of the disordered models for Al2 is shown for clarity.

g of polyisobutene after being run overnight at room temperature. These results combined with the results from Bochmann's group indicate the following relative initiator activities: $[Cp_2Al]^+ \gg [Cp'_2Al]^+ > [Cp^*_2Al]^+$. They also offer strong evidence that the aluminocenium cation is indeed the initiator for the polymerization, as opposed to protons generated by trace amounts of water. Furthermore, these results show that activity of the aluminocenium initiator is highly sensitive to the number of methyl substituents on its cyclopentadienyl rings.

Summary and Conclusions

In summary, the inaccessibility of Cp'_2AlMe necessitated the development of a alternate route to $[Cp'_2Al]^+$ besides methyl anion abstraction by $B(C_6F_5)_3$. Toward this goal, $Cp_2'AlCl$ (**1**) was prepared as a potential precursor to the $[Cp'_2Al]^+$ cation via a ligand redistribution reaction between Cp'_3Al and $AlCl_3$. Chloride ligand abstraction from **1** by $AlCl_3$ appears to afford $[Cp'_2Al][AlCl_4]$. Neither **1** nor $[Cp'_2Al][AlCl_4]$ maintains their integrity in solution, however, equilibrating to mixtures of **1**, $[Cp'_2Al][AlCl_4]$, and Cp'_3Al. An alternate route to $[Cp'_2Al]^+$ was found involving an unprecedented abstraction of a cyclopentadienyl anion from Cp'_3Al by $[Ph_3C][B(C_6F_5)_4]$. $[Cp'_2Al][B(C_6F_5)_4]$ (**3**) is less stable thermally than $[Cp^*_2Al][MeB(C_6F_5)_3]$ but is more active as an initiator of the carbocationic polymerization of isobutene. We attribute the relative activities of the aluminocenium cations ($[Cp_2Al]^+ \gg [Cp_2Al]^+ \gg [Cp^*_2Al]^+$) as initiators primarily to the steric influence of their cyclopentadienyl rings. The bulkier substituted rings should make access to the aluminum center by substrates such as isobutene more difficult and should also interfere with intermolecular decomposition pathways, which is reflected in the relative thermal stabilities of these cations.

Experimental Section

General Considerations. All experiments were performed under inert atmosphere conditions through a combination of glovebox, high-vacuum, and Schlenk line techniques. All solvents were dried over alumina columns and stored in line-pots over sodium/benzophenone or CaH_2 for CH_2Cl_2 and $CHCl_3$ solvents. Argon was purified by passage over an oxytower BASF catalyst (Aldrich) and 4A molecular sieves. NMR spectra were recorded on IBM NR-300 (300 MHz ^1H; 75.4 MHz, ^{13}C; 78 MHz, ^{27}Al) and Bruker Avance 500 (500 MHz, ^1H; 125 MHz, ^{13}C; 470 MHz, ^{19}F; 130 MHz, ^{27}Al) spectrometers. All chemical shifts are reported in ppm and referenced to the solvent (^{13}C, ^1H) or $Al(OH)_3$ (^{27}Al, external reference, 0 ppm). Deuterated solvents were dried over activated 4A molecular sieves. Elemental analyses were determined by Desert Analyses (Tucson, AZ).

Tetramethylcyclopentadiene was prepared from 3-pentanone and acetaldehyde as described in the literature.[14] Aluminum trichloride was purified by sublimation before use.

$[Cp'_2AlCl]_2$ (1). Aluminum trichloride (0.135 g, 1.01 mmol) was added with a sidearm solid dispenser to a solution of Cp'_3Al (0.78 g, 2.0 mmol) in 30 mL of methylene chloride at −78 °C. The mixture was warmed to room temperature slowly and stirred for 3 h. The solvent was removed from the resulting clear yellow solution under reduced pressure, leaving behind a white solid. The white solid product was washed with 20 mL of petroleum ether and dried under vacuum (yield 0.38 g, 42%). Two major species were observed in the ^1H NMR spectrum of **1** as a result of ligand redistribution in $CDCl_3$. ^1H NMR (300 MHz, 297 K, $CDCl_3$): δ 1.95/1.97 (2s, 6H, $(C_5(CH_3)_4)$); 2.00/2.03 (2s, 6H, $(C_5(CH_3)_4)$); 3.28/4.45(2s, 1H, (Me_4C_5H)). $^{13}C\{^1H\}$ NMR (75 MHz): δ 11.67, 12.10, 13.91 $(C_5(CH_3)_4)$; 123.51 (Me_4C_5H). Anal. Found (calcd): C, 68.49 (69.94); H, 7.93 (7.34). Due to the thermal instability of the compound, the carbon value was consistently low upon reanalysis.

$[Cp'_2Al]^+[AlCl_4]^-$ (2). Aluminum trichloride (0.268 g, 2.01 mmol) was added from a sidearm solid dispenser to a solution of Cp'_3Al (0.39 g, 1.0 mmol) in 20 mL of bromobenzene at room temperature. The pinkish reaction mixture was stirred for 30 min. Slow diffusion of hexane into the mixture at room temperature yielded a pink, clear, crystalline solid after 24 h. The pink solid was isolated by decanting off the bromobenzene solvent and rinsed with petroleum ether, then dried under vacuum (yield 0.37 g, 56%). ^1H NMR(300 MHz, 297 K, bromobenzene-d_5): δ 1.65 (s, 6H, $(C_5(CH_3)_4)$); 1.73 (s, 6H, $(C_5(CH_3)_4)$); 5.85 (s, 1H, (Me_4C_5H)). $^{13}C\{^1H\}$ NMR (75 MHz): δ 27.21 $(C_5(CH_3)_4)$; 103.70, 118.79 (Me_4C_5H). ^{27}Al NMR (78 MHz): δ −113 $[Cp'_2Al^+]$; 103 $[AlCl_4^-]$. Anal. Found (calcd) for $C_{18}H_{26}Al_2Cl_4$: C, 46.04 (49.3); H, 5.74 (5.93). The analysis is most consistent with the formulation given for **2**. The presence of some cocrystallized bromobenzene in the crystals could account for the low carbon value.

$[Cp'_2Al]^+[B(C_6F_5)_4]^-$ (3). $Ph_3CB(C_6F_5)_4$ (0.786 g, 0.85 mmol) was added through a solid dispenser to a solution of Cp'_3Al (0.34 g, 0.87 mmol) in 20 mL of bromobenzene at room temperature. The mixture appeared reddish-purple and then changed to a brownish-yellow color and was stirred for 30 min. Slow diffusion of hexane into the mixture at room temperature afforded a pink, clear, crystalline solid after 36 h. The pink solid was isolated by decanting bromobenzene solvent and rinsed with petroleum ether (yield 0.35 g, 43%). ^1H NMR (300 MHz, 297 K, $CDCl_3$): δ 2.19 (s, 6H, $(C_5(CH_3)_4)$); 2.25 (s, 6H, $(C_5(CH_3)_4)$); 6.25(d, 1H, (Me_4C_5H)). $^{13}C\{^1H\}$ NMR(75 MHz): δ 10.72, 12.52 $(C_5(CH_3)_4)$ 107.46 (Me_4C_5H); 127.74, 130.90, 132.40$(B(C_6F_5)$. ^{27}Al NMR(78 MHz): −113. ^{19}F NMR (282 MHz): −132, −163, −166 $(B(C_6F_5)$. ^{11}B NMR (54 MHz): δ −13.6. Anal. Found (calcd) for $C_{40}H_{26}AlBF_{20}\cdot C_6H_5Br$: C, 49.26 (48.90); H, 2.98 (2.69).

Isobutene Polymerizations by 3 and by $[Cp^*_2Al][MeB(C_6F_5)_3]$. Compound **3** (83 mg, 0.058 mmole) was dissolved in 5 mL of CH_2Cl_2 in a 200 mL two-neck round-bottom flask. Isobutene (10 mL) was condensed into the solution of **3** cooled to −78 °C. The reaction mixture was warmed to −20 °C, stirred for 3 h at that temperature, and then quenched with 0.5 mL of MeOH. A viscous polymer was observed after additional MeOH was added to the reaction. The reaction was warmed to room temperature, and the solvent was removed under reduced pressure, leaving a red-brown viscous oil. This material was redissolved in CH_2Cl_2, and the red-brown organic layer was washed twice with distilled water, which did not remove the color caused by impurities from the catayst. After removal of the CH_2Cl_2, the oil was further dried in a 60 °C oven, yielding 3.25 g of polyisobutene, which was identified by its ^1H NMR spectrum. ^1H NMR (300 MHz, 297 K, $CDCl_3$): δ.1.056 (CH_3), δ.1.35 (CH_2)).[15]

The reaction between 47.8 mg (0.058 mmol) of $[Cp^*_2Al][MeB(C_6F_5)_3]$ and isobutene (10 mL) under identical experimental conditions did not yield any polymer.

X-ray Crystal Structure Determinations. For both compounds **1** and **3**, crystals were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[16] Data for **1** and **3** were collected at 203(2) and 84(2) K, respectively, using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a LT-2A low-temperature device (203(2) K) or a Cryocool NeverIce low-temperature device (84(2) K). Data for each crystal were measured using omega scans

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of 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.84 Å for **1** and 0.77 Å for **3**. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[17] software and refined using SAINTPlus[18] on all observed reflections. Data reduction and correction for *Lp* and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[19] The structures were solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[20] The structures for **1** and **3** were solved in the space groups $P\bar{1}$ (# 2) and $C2/c$ (# 15), respectively, by analysis of systematic absences. In the structure determination for **3**, the bromobenzene solvent was disordered and modeled as a rigid body using coordinates obtained from the Cambridge Structure Database with each orientation at 46% and 54% occupancy. The second aluminocinium cation is also disordered. Two orientations of the Cp′ ligand were identified and modeled as rigid groups using the coordinates of the ordered aliminocenium cation. The occupancies of both orientations were refined at 50%. Soft restraints were applied to the disordered carbon atom thermal displacement parameters, and all atoms were refined aniostropically. No decomposition was observed during data collection for either crystal.

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Supporting Information Available: CIF files the X-ray crystal structures of compounds **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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