Organometallics **2000,** *19,* 3361−3367

Bis(permethylcyclopentadienyl)aluminum Compounds: Precursors to $[Cp^*_2Al]^+$ but Not to Cp^*_3Al

Christopher T. Burns,[†] Pamela J. Shapiro,*,[†] Peter H. M. Budzelaar,[‡]
Roger Willett,[§] and Ashwani Vij[‡]

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, Inorganic Chemistry, University of Nijmegen, P.O. Box 9010, 6500 GL, Nijmegen, The Netherlands, and Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

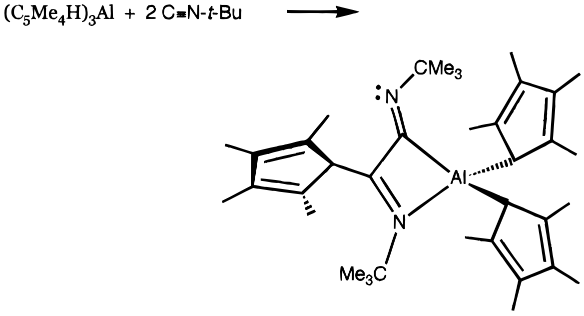
Received February 23, 2000

Replacement of only two chloride ligands occurs when $AlCl_3$ is reacted with 3 equiv of either Cp*Na or Cp*K, forming Cp^*_2AlCl (**1**) [$Cp^* = C_5Me_5$]. This compound dissociates a chloride ion in polar solvents such as methylene chloride. Clean formation of decamethylaluminocenium salts could not be accomplished by abstraction of a chloride ligand from **2** with silver salts, $LiB(C_6F_5)_4$, or $NaB(C_6F_5)_4$. However, reaction of Cp^*_2AlMe (**2**) with $B(C_6F_5)_3$ cleanly affords the salt $[Cp^*_2Al]^+[B(C_6F_5)_3Me]^-$ (**3**). X-ray crystal structures of both **2** and **3** are reported. In the solid state, **2** exhibits a bis-dihapto ring coordination similar to that of $(\eta^2\text{-}C_5H_5)_2AlMe$. The molecular structure of **3** shows complete methyl anion abstraction from the aluminum. The decamethylaluminocenium salt is more stable in solution than its nonmethylated analogue; however, it is also considerably less active as an initiator for the cationic polymerization of isobutene.

Introduction

Besides its importance in transition metal chemistry and homogeneous catalysis, the cyclopentadienyl ligand, in its various guises, has also played a prominent role in the advancement of main group metal and nonmetal chemistry. The ability of sterically encumbered cyclopentadienyl ligands such as the pentamethylcyclopentadienyl ligand and other polysubstituted cyclopentadienyl ligands to support unusual oxidation states, low molecularities, and low coordination numbers has allowed chemists to demonstrate interesting, new modes of bonding and reactivity among the main group elements.[1−6]

In our work with cyclopentadienylaluminum compounds, we have found that increasing the steric bulk of the cyclopentadienyl rings through the introduction of methyl substituents influences the manner in which the rings coordinate to the aluminum.[7] More intriguing, however, is the effect of steric factors on the reactivity of the cyclopentadienyl−aluminum linkages. Whereas Cp_3Al merely coordinates *tert*-butyl isocyanide,[8a] even at elevated temperatures, $(C_5Me_4H)_3Al$ inserts two molecules of *tert*-butyl isocyanide between the aluminum and one of its rings to form $(\eta^1\text{-}C_5Me_4H)_2Al\{C({=}N^tBu)C({=}N^tBu)(C_5Me_4H)\}$ (eq 1).[8b] Similar reactivity between $(1,2,4\text{-}Me_3C_5H_2)_3Al$ and *tert*-butyl isocyanide has been identified by ^1H NMR.[9] Given the enhanced



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[†] University of Idaho.

[‡] University of Nijmegen.

[§] Washington State University.

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10.1021/om000173x CCC: $19.00

reactivities exhibited by these polymethylated, homoleptic cyclopentadienylaluminum compounds, we were interested in preparing and examining the properties of the most highly methylated species possible, Cp^*_3Al ($Cp^* = C_5Me_5$).

Since Cp^*_3Ga had been prepared previously by the reaction of KCp* and $GaCl_3$,[10] we expected to be able to prepare the aluminum analogue in a similar manner; however, we have found aluminum to be resistant to the coordination of three Cp* rings. At best, we have coordinated two Cp* ligands to the aluminum in the compounds Cp^*_2AlCl (**1**) and Cp^*_2AlMe (**2**). The reactivity of these Cp^*_2Al compounds offers some clues as to why aluminum does not accommodate a third Cp* ring. We believe that, rather than coordinating a third cyclopentadienyl anion, the aluminocenium cation prefers to adopt the more stable, bis-η^5 sandwich structure first observed in 1993 by Schnöckel and co-workers for $[Cp^*_2Al][Cp^*AlCl_3]$.[2a] The results that led us to this conclusion are described herein along with the syntheses of **1** and **2**, an X-ray crystal structure determination of **2**, and the synthesis and structure of the permethylaluminocenium salt $[Cp^*_2Al][MeB(C_6F_5)_3]$ (**3**), which is considerably less active than its nonmethylated aluminocenium analogue in the initiation of cationic olefin polymerization.

Results

Synthesis and Solution Behavior of Cp^*_2AlCl. Attempts to synthesize Cp^*_3Al by reacting 1.5 molar equiv of decamethylmagnesocene with $AlCl_3$ in a manner analogous to that used for the synthesis of Cp_3Al ($Cp = C_5H_5$) produced a mixture of products which included unreacted Cp^*_2Mg, $[Cp^*_2AlCl]_x$, and at least two other unidentified Cp*-containing species. To have a greater thermodynamic driving force for the exchange of Cl with Cp* on the aluminum, Cp*Na and Cp*K were tried, especially since Cp*K had been used by Schumann and co-workers to prepare Cp^*_3Ga from $GaCl_3$.[10] Instead of forming Cp^*_3Al, 3 molar equiv of either Cp*Na or Cp*K reacted with $AlCl_3$ to produce $[Cp^*_2AlCl]_x$, **1**, exclusively, and 1 equiv of unreacted Cp*Na or Cp*K was recovered. Compound **1** was prepared previously by Roesky and co-workers by the reaction of $[Cp^*AlCl_2]_2$ with 2 equiv of Cp*K.[11] A dimeric structure of the compound was assumed by the authors, in analogy with the structures of $[Cp^*AlCl_2]_2$ and $[Cp^*(Ph)AlCl]_2$. We have so far been unable to establish the molecularity of this compound either by molecular weight determination or by crystallographic methods.

The tendency of **1** to dissociate a chloride ligand, particularly in more polar solvents, is revealed in its ^{27}Al NMR solution spectra in C_6D_6, $CDCl_3$, and CD_2Cl_2 (Figure 1). Qualitatively, the intensity of the ^{27}Al signal at δ −114 due to $[Cp^*_2Al]^+$ increases with increasing solvent polarity. The ^{27}Al NMR spectrum of a solution of **1** in C_6D_6 at 297 K exhibits a strong, broad signal at δ −3 ($W_{1/2} \approx 1400$ Hz). A weak signal at δ −114 due to $[Cp^*_2Al]^+$ is also visible just above the baseline noise (Figure 1a). By contrast, a solution of **1** in CD_2Cl_2 exhibits an intense ^{27}Al signal at δ −114. The broad, comparatively weaker, downfield signal, originally at δ −3, broadens and disappears altogether into the shoulder of the signal from the NMR probe (Figure 1c). We

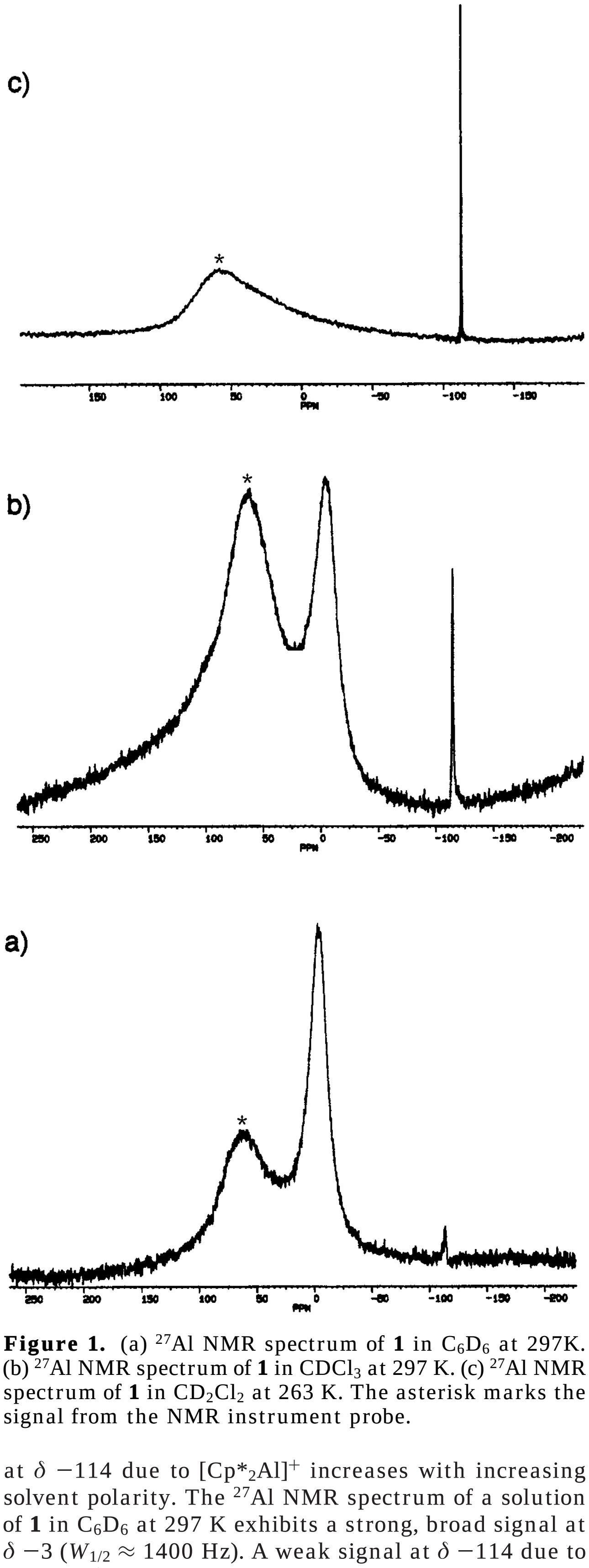

Figure 1. (a) ^{27}Al NMR spectrum of **1** in C_6D_6 at 297K. (b) ^{27}Al NMR spectrum of **1** in $CDCl_3$ at 297 K. (c) ^{27}Al NMR spectrum of **1** in CD_2Cl_2 at 263 K. The asterisk marks the signal from the NMR instrument probe.

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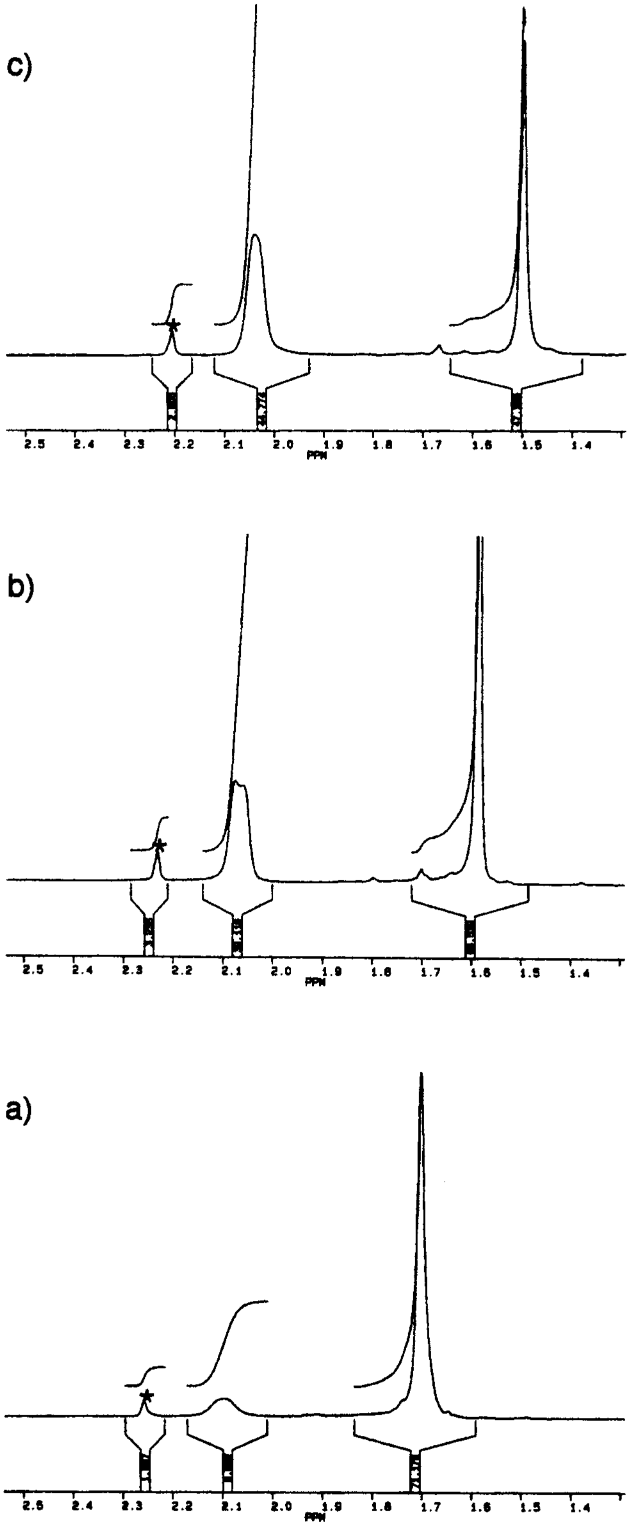


Figure 2. ^1H NMR spectra of **1** in CD_2Cl_2 at (a) 297 K, (b) 258 K, (c) 218 K. The asterisked peak is a toluene impurtity in the sample, which was used as a internal standard to ensure that the net integration of the Cp* peaks remained constant as the temperature of the sample was lowered.

believe that this shifting of the downfield signal is associated with the dynamics of chloride ion exchange between $[Cp*_2AlCl]_x$ and $[Cp*_2AlCl_2]^-$ (eq 2) and that the ^{27}Al NMR resonance for $[Cp*_2AlCl_2]^-$ must be obscured by the probe signal.

Solvent effects are also observed in ^1H NMR spectra of **1** in C_6D_6 and CD_2Cl_2. Whereas there is only one resonance at δ 1.8 for a C_6D_6 solution of **1** at 297 K, there are two signals, a major peak at δ 1.7, and a broad, less intense signal at δ 2.1 (Figure 2a) in a ratio of 8:1, respectively, for a solution of **1** in CD_2Cl_2. As the CD_2Cl_2 sample is cooled, the intensity of the major peak decreases and the signal shifts upfield to δ 1.5 at 218 K (Figure 2c). The minor peak also shifts upfield slightly, and its intensity increases until at 218 K it has the same area as the δ 1.5 resonance.

We attribute the δ 2.1 resonance to the aluminocenium cation since its chemical shift is similar to that of $[Cp*_2Al][MeB(C_6F_5)_3]$ in CD_2Cl_2 (vide infra). As can be seen in the ^1H NMR spectrum at 248 K, this signal splits (Figure 2b) and then collapses back to a single peak at 218 K. This splitting is also observed in the ^1H NMR spectrum of $[Cp*_2Al][MeB(C_6F_5)_3]$ described below.

We attribute the upfield resonance to $[Cp*_2AlCl_2]^-$ since a ^1H NMR spectrum of a CD_2Cl_2 solution of **1** combined with an equivalent of [PPN]Cl (bis(triphenylphosphoranylidene)ammonium chloride) exhibits a resonance at δ 1.6. Thus, the variable-temperature ^1H and ^{27}Al NMR spectra of **1** in CD_2Cl_2 indicate the ionization equilibrium shown in eq 2.

$$2\,[Cp*_2AlCl]_x \rightleftharpoons x\,[Cp*_2Al]^+ + x\,[Cp*_2AlCl_2]^- \quad (2)$$

Ligand redistribution also takes place, as indicated by our isolation of X-ray quality crystals of $[Cp*_2Al][Cp*AlCl_3]$ from a methylene chloride solution of **1** layered with pentane. The structure of this salt has been reported previously by Schnöckel and co-workers.[2a] Efforts to introduce the less bulky tetramethylcyclopentadienyl ligand by reacting $Cp*_2AlCl$ with $Na(C_5Me_4H)$ produced an ill-defined mixture of species, most likely resulting from cyclopentadienyl ligand redistribution.

Synthesis and Molecular Structure of $Cp*_2AlMe$. In analogy with the synthesis of **1**, $MeAlCl_2$ was reacted with 2 equiv of Cp*Na to afford $Cp*_2AlMe$ (**2**) as a white microcrystalline solid. An X-ray crystal structure determination revealed that **2** adopts a bis-dihapto coordination geometry in the solid state akin to the less crowded Cp_2AlMe.[8a] Crystallographic data for **2** are listed in Table 1, and selected bond distances and angles are listed in Table 2. The molecule lies on two crystallographic mirror planes, and a disordering of the rings about one of the mirror planes was indicated by very large atomic displacement parameters on the cyclopentadienyl methyl groups and an unlikely C−C distance of 1.19 Å between the cyclopentadienyl carbons coordinated to the aluminum when an ordered model was used. Introduction of a disorder consisting of rotation of the rings by ±16° improved the refinement, although the displacements of the ring methyl groups remained quite large, as can be seen from the ORTEP drawing of one orientation in the disorder in Figure 3a. The disorder of the rings appears to be driven by steric factors arising from nonbonded interactions between methyl groups on carbons C(4) and C(5) on opposite Cp* rings. This can best be seen from the ball-and-stick view of the structure in Figure 3b. The steric strain experienced by those methyl groups is also manifested in their degree of bending away from the cyclopentadienyl ring

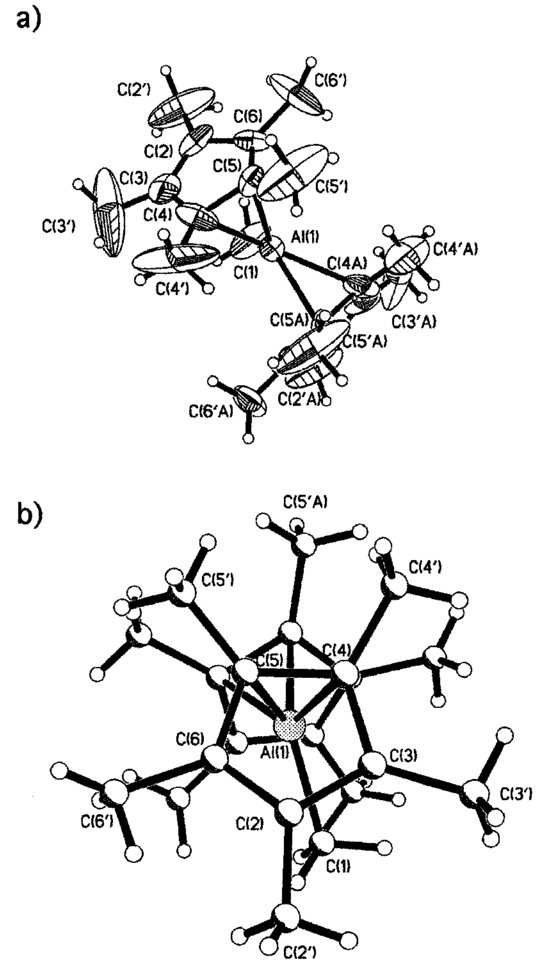


Figure 3. (a) ORTEP drawing of the molecular structure of (η^2-C_5Me_5)$_2$AlCH$_3$ (**2**). Thermal ellipsoids are at 30% probability. (b) Ball-and-stick view of **2** showing staggered arrangement of Cp* rings.

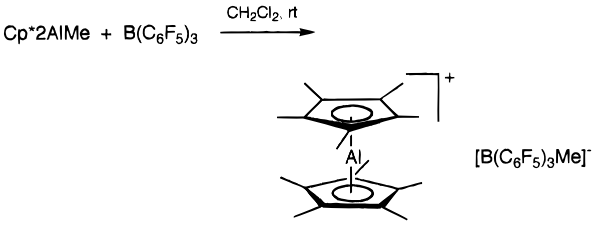
plane, with C(4)−C(5)−C(4′)−C(5′) forming a dihedral angle of 18.6° to C(4)−C(5)−C(3)−C(6). A dihedral angle of 60.4° between the two cyclopentadienyl ring planes is created by their bis-dihapto geometry. The cyclopentadienyl rings are not completely planar, however, with a maximum deviation of 0.081 Å from the plane. The distortion in the ring plane arises from a folding of C(2) away from the Al−CH$_3$ region, forming an angle of 12° with a fold along C(3) and C(6). There are also large deviations among the C−C bond lengths within the ring, C(2)−C(3) (1.37(3) Å) and C(5)−C(6) (1.37(2) Å) being substantially shorter than the other C−C bonds in the ring as if to form a more localized 1,3-diene structure.

Ab initio calculations at the RHF/6-31G* level on the model complexes Cp*AlH$_2$ and Cp*AlMe$_2$ indicate η^2 ground-state geometries, with shortest Al−C(ring) distances of 2.128 and 2.132 Å for the former compound and 2.140 and 2.146 Å for the latter, in close agreement with corresponding Al−C(4) distance of 2.143(13) Å in the molecular structure of **2**. Nevertheless, as has been previously shown for the (C_5H_5)Al complexes, the preference for an η^2 structure is very slight, and calculations at the RHF/3-21G(*) level show that slippage of the Cp* ring to other hapticities should be extremely facile, with barriers from 2 to 6 kcal/mol.[7] Indeed, other peralkylcyclopentadienylaluminum(III) compounds exhibit η^5, η^3, and η^1 ring coordination geometries in the solid state[4b,11−14] and in solution.[15]

As is typical with cyclopentadienylaluminum compounds, very simple ^{1}H and ^{13}C NMR solution spectra are exhibited by **2** due to its fluctionality. Two signals are observed in the ^{1}H NMR spectrum of **2** in C_6D_6 at δ 1.92 and −1.58 for the Cp* ring methyls and the Al-bound methyl group, respectively. The slight upfield shift of the Al−Me in **2** relative to Cp$_2$AlMe can be attributed to the greater electron-releasing properties of Cp* relative to Cp. Signals for only the quarternary and primary cyclopentadienyl ring carbons are observed in the ^{13}C NMR spectrum of **2**. As with Cp$_2$AlMe,[16] a ^{13}C signal for the methyl group of **2** is not observed, presumably due to extreme broadening by the quadrupolar Al nucleus (I = 5/2).

Synthesis and Molecular Structure of [Cp*$_2$Al][B(C_6F_5)$_3$Me]. Given the tendency of **1** to dissociate a chloride ligand, we sought to convert it to a permethylaluminocenium salt by replacement of the chloride ligand with a noncoordinating anion. Although the permethylaluminocenium cation can be generated by reacting **1** with either LiB(C_6F_5)$_4$[17] or NaB(C_6F_5)$_4$, the reaction is accompanied by considerable decomposition, and we have so far been unable to isolate the permethylaluminocenium salt cleanly in this manner. Similar problems with decomposition were encountered with the silver salts AgBF$_4$ and AgOTf.

As an alternative approach to the permethylaluminocenium cation, we followed Bochmann's example for generating Cp$_2$Al$^+$ from Cp$_2$AlMe[16] and reacted **2** with B(C_6F_5)$_3$ (eq 3). The reaction proceeds cleanly to afford



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[Cp*$_2$Al][MeB(C_6F_5)$_3$] (**3**), which is more stable in solution than its (C_5H_5) analogue. By contrast, reaction of **2** with [Ph$_3$C][B(C_6F_5)$_4$][18] produces Ph$_3$CH, presumably via hydrogen abstraction from a Cp* ring. The aluminum-containing product of this reaction has not been identified. Over time it converts to the aluminocenium cation; however, the reaction is not clean.

The 500 MHz ^{1}H NMR spectrum of **3** in CDCl$_3$ at 297 K exhibits a splitting in the signal for the Cp* hydrogens. This persists as the sample is heated to 50 °C but collapses to a single peak when the sample is cooled to −20 °C, behavior that is similar to that of the alumi-

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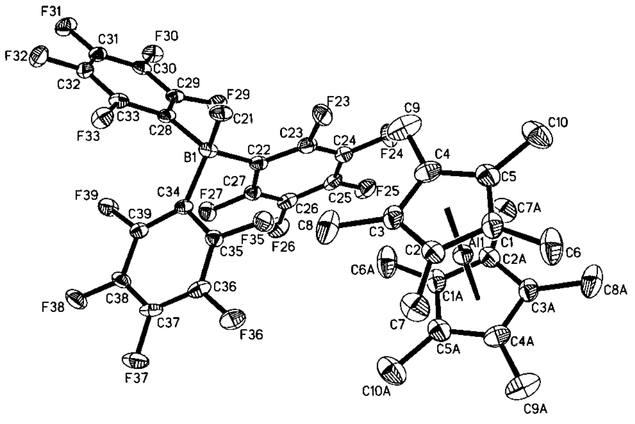

Figure 4. ORTEP drawing of the molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Al]^+[MeB(C_6F_5)_3]^-$. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.

nocenium cation generated from the dissociation of $[Cp^*{}_2AlCl]_x$ in CD_2Cl_2 (Figure 2b, vide supra). No changes are observed in the borate methyl resonance at δ 0.48 in this temperature range; nor are there any peculiarities or changes in the ^{19}F and ^{27}Al NMR spectra of the sample over this temperature range. We are currently investigating solvent effects on this mysterious splitting in the Cp* ^1H NMR signal of **3**. There is no evidence in the variable-temperature ^{19}F NMR spectra for ion pairing or coupling to a fluorine atom of the borate anion. We suspect that the splitting is caused by slippage of one of the Cp* rings from its η^5-hapticity and that at lower temperature the aluminocenium cation assumes the more stable bis-pentahapto sandwich geometry exhibited in its crystal structure (vide infra). Further experiments are underway to explore this hypothesis.

The ^{27}Al NMR spectrum of **3** in $CDCl_3$ exhibits a single, sharp signal at δ −114, and the ^{11}B NMR spectrum exhibits a signal at δ −34 vs H_3BO_3, consistent with the formulation of the compound as an ion pair. X-ray quality crystals of **3** were obtained from a methylene chloride solution of the compound layered with pentane and cooled at −78 °C. Crystallographic data are listed in Table 1, and selected bond lengths and angles are listed in Table 3. The asymmetric unit consists of two independent aluminocenium cations, with each aluminum atom lying on an inversion center, and a borate counteranion. An ORTEP drawing of the structure of one ion pair is shown in Figure 4. The structure of the permethylaluminocenium cation, with its 180° (ring-centroid)−Al−(ring-centroid) angle and 36° staggering of the Cp* rings, is similar to that found by Schnöckel and co-workers for $[Cp^*{}_2Al][Cp^*AlCl_3]$ and is of higher symmetry than that found for the cation in $[Cp^*{}_2Al]^+[\{Ph(Me)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]^-$, another permethylaluminocenium salt that we recently reported.[19] The B(1)−C(21) bond length of 1.650(7) Å is comparable to that of other free $[MeB(C_6F_5)_3]^-$ counteranions that have been structurally characterized.[20] There is no evidence for residual Al- - - Me interaction in the structure, the closest Al−C(21) methyl) contact being 5.95 Å. No interactions between the fluorine atoms and the aluminum centers are apparent either, the shortest Al−F distance being 5.07 Å for Al(2)−F(30).

Compound **3** can be stored for months at −17 °C under an N_2 atmosphere with no apparent decomposition. Over days at room temperature it turns dark purple, and there is evidence for the elimination of Cp*H in the ^1H NMR spectrum. Unlike its Cp analogue, which decomposes readily in CD_2Cl_2 solution upon warming to 20 °C, **3** is stable at room temperature in $CDCl_3$ for months, exhibiting a gradual purple discoloration over time but little accompanying decomposition. In addition to being more stable than its Cp analogue, compound **3** is also considerably less active as an initiator for the cationic polymerization of isobutene and isoprene. Whereas $[Cp_2Al][MeB(C_6F_5)_3]$ is most active at initiating isobutene polymerization in CH_2Cl_2 at −78 °C and is less active at higher temperatures due to decomposition of the catalyst,[16] **3** is essentially inactive at −78 °C but initiates cationic olefin polymerization at room temperature. Reaction of 10 mL of isobutene with approximately 50 μg of **3** in 5 mL of CH_2Cl_2 overnight at room temperature afforded 2.1 g of polymer with $M_n = 8000$ and $M_w/M_n = 2.2$. Catalyst decomposition during the course of the polymerization reaction was indicated by the development of a purple tinge to the reaction over time. Essentially no polymer was obtained when the reaction was quenched after 20 min. Carrying out the reaction under similar conditions, but instead with approximately 40 mg of $[Cp^*{}_2AlCl]_x$ (**1**) as catalyst, afforded only 0.04 g of polymer, consistent with fact that **1** dissociates only partially to the permethylaluminocenium cation in methylene chloride.

Discussion and Conclusions

We have commented previously on the delicate balance between ionicity, π-bonding, and steric repulsion that is manifested in the preferred hapticities of cyclopentadienylaluminum complexes.[7,21] Changing the number of methyl substituents on the cyclopentadienyl ring or changing the electron-withdrawing/donating properties of additional ligands on the aluminum has been shown to tip the balance from primarily covalent σ-bonding (η^1), to covalent π-bonding (η^2, η^3, η^5), to a primarily ionic interaction between the aluminum atom and its cyclopentadienyl ring (η^5). Even more remarkable are the effects of methyl substituents on the cyclopentadienyl ring on the reactivity of the cyclopentadienyl−aluminum linkage as well as its ability to even form.

It appears that our inability to prepare $Cp^*{}_3Al$ using methods that were successful for the synthesis of $(C_5Me_4H)_3Al$ and $Cp^*{}_3Ga$ is associated with the preference of $[Cp^*{}_2Al]^+$ for a bis-pentahapto sandwich geometry, making addition of a third permethylcyclopentadienyl anion thermodynamically unfavorable in the case of $Cp^*{}_2AlCl$. Consistent with this idea is Schnöckel's reaction of Cp*Al with $AlCl_3$ to produce $[Cp^*{}_2Al][Cp^*AlCl_3]$, presumably via a $Cp^*{}_3Al$ intermediate.[2a] Further support comes from chemistry recently reported by Jutzi and co-workers, in which decamethylsilicocene

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reacts with AlX_3 (X = Cl, Br) to form the permethylaluminocenium salts $[Cp^*_2Al]^+[AlX_4]^-$ exclusively.[22] Also noteworthy is the isolation of the side product $[Al(\eta^5\text{-}C_5Me_5)_2][Li(\eta^5\text{-}C_5Bz_5)_2]$ by Dohmeier et al. in the ligand exchange reaction between $Li(C_5Bz_5)$ and $Al(C_5Me_5)$.[23]

Failure of the aluminum to undergo chloride for cyclopentadienide metathesis has been encountered by us in another reaction in which $Al(O^iPr)Cl_2$ undergoes only a single metathesis with $(Me_4CH)_2MgCl$ to form $[Cl(C_5Me_4H)Al]_2(\mu\text{-}O^iPr)_2$ and $(C_5Me_4H)MgCl$, even though a similar reaction with Cp_2Mg affords the double metathesis product, $[Cp_2Al]_2(\mu\text{-}O^iPr)_2$.[24] In this case, steric blocking of the Al−Cl sites in the dimer by the tetramethylcyclopentadienyl ligands is the likely deterrent to further metathesis.

The contrasting behavior of gallium and aluminum with respect to gallium's ability to form Cp^*_3Ga and aluminum's inability to form Cp^*_3Al is noteworthy and reflects the greater tendency of Al(III) to form π-interactions with its cyclopentadienyl rings as compared with Ga(III), which exhibits a preference for localized σ-bonding.[25] This difference in bonding is undoubtedly associated with the greater electronegativity of Ga(III) relative to Al(III).[26]

The effect of steric factors on increasing the stability of $[Cp^*_2Al]^+$ relative to $[Cp_2Al]^+$ and decreasing its effectiveness at activating cationic olefin polymerization is not surprising. It highlights the possibility of varying the ring substituents of the aluminocenium cation to fine-tune its activity in initiating cationic olefin polymerization and in other Lewis-acid-catalyzed reactions.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques as described elsewhere.[2] Aluminum trichloride (Aldrich) was sublimed prior to use. Dichloromethylaluminum was handled as a solid, which was obtained by removing the solvent from a 1.0 M hexane solution (Aldrich). Pentamethylcyclopentadiene was prepared from 2,3,4,5-tetramethyl-2-cyclopentenone (Aldrich) as described by Marks and co-workers. Tris(pentafluorophenyl)borane was both prepared and purchased (Boulder Scientific). Cp*K was prepared by deprotonating Cp*H with potassium hexamethyldisilazide.

Cp^*_2AlCl, 1. Aluminum trichloride (0.67 g, 5.0 mmol) was added to a solution of Cp*Na (1.58 g, 10 mmol) in 50 mL of toluene at −78 °C, and the reaction mixture was slowly warmed to room temperature and stirred overnight. The clear yellow solution was filtered to remove NaCl. The NaCl was rinsed repeatedly with toluene, and the toluene was removed under reduced pressure, leaving behind a white solid with traces of a yellow oil. Petroleum ether (25 mL) was vacuum transferred into the reaction flask. The yellow oil dissolved upon warming the flask to room temperature, resulting in a clear yellow solution with a suspended white solid. More $(Cp^*)_2AlCl$ precipitated out as a white solid upon cooling the flask to −78 °C for 1 h. The white solid was isolated by cold filtration and dried under vacuum (yield 1.24 g, 74%). ^1H NMR (300 MHz, 297 K, C_6D_6): 1.79 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR: (118.8 ($C_5(CH_3)_5$), 12.3 ($C_5(CH_3)_5$). ^{27}Al NMR (vs external H_3AlO_3): −3.0. Anal. Calcd for $C_{20}H_{30}AlCl$: C, 72.16; H, 9.08. Found: C, 72.01; H, 9.02.

Cp^*_2AlMe, 2. Solid dichloromethylaluminum (0.9 g, 8 mmol) was added to a solution of Cp*Na (2.5 g, 16 mmol) in 50 mL of toluene at room temperature, and the reaction mixture was stirred overnight. The NaCl was removed from the reaction mixture by filtration and rinsed with toluene. The volatiles were removed from the filtrate under reduced pressure, leaving a yellow-tinged, white residue. The residue was dissolved in 25 mL of peteroleum ether and cooled to −78 °C to afford a white, microcrystalline solid, which was isolated by cold filtration (yield 1.3 g, 50%). ^1H NMR (300 MHz, C_6D_6): δ 1.92 (s, 30H, $C_5(CH_3)_5$, −1.58 (s, 3H, $AlCH_3$). $^{13}C\{^1H\}$ NMR: 118.7 ($C_5(CH_3)_5$, 11.3 ($C_5(CH_3)_5$. ^{27}Al NMR (vs external H_3AlO_3): δ 70. Anal. Calcd for $C_{21}H_{33}Al$: C, 80.72; H, 10.64. Found: C, 80.67; H, 10.75.

$[Cp^*_2Al][MeB(C_6F_5)_3]$, 3. At room temperature, **2** (0.359 g, 1.15 mmol) was added via a sidearm addition tube to a solution of $B(C_6F_5)_3$ (0.589 g, 1.15 mmol) in 50 mL of methylene chloride, and the reaction mixture was stirred for 30 min. The methylene chloride was removed under vacuum, leaving a tan solid. Addition of petroleum ether to the solid afforded a white precipitate and a gold-colored mother liquor. The white solid, **3**, was isolated by filtration and washed twice with petroleum ether (yield 0.792 g, 83%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.13, 2.10 (2s, 30H, $C_5(CH_3)_5$, 0.48 (s, 3H, BCH_3). $^{13}C\{^1H\}$ NMR: 118 ($C_5(CH_3)_5$, 9.0 ($C_5(CH_3)_5$. ^{27}Al NMR (vs external H_3AlO_3): δ −114. ^{11}B NMR (C_6D_6, vs external H_3BO_3): δ −34. ^{19}F NMR (470.6 MHz, $CDCl_3$, vs external $CFCl_3$): δ −133.1 (d, *o*-F, $^3J_{FF}$ = 19.8 Hz), −165.3 (t, *p*-F, $^3J_{FF}$ = 20.7 Hz), −167.8 (m, *m*-F). Anal. Calcd for $C_{39}H_{33}AlBF_{15}$: C, 56.82; H, 4.03. Found: C, 56.42; H, 3.89.

X-ray Crystal Structure Determinations. Crystals of **2** were grown from a saturated hexamethyldisiloxane solution, and a suitable crystal was mounted in a glass capillary under nitrogen.

Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating around −54 °C. A total of 1271 frames of data were collected using ω scans with a scan width of 0.3° per frame for 45 s. Additional parameters are available in the cif file. The first 50 frames were recollected at the end of data collection to monitor for decay. No decomposition of the crystals during data collection was indicated. Cell parameters were retrieved using SMART software (V. 4.050, Bruker Analytical X-ray Systems, Madison, WI, 1995) and refined using SAINT (V. 4.050, Bruker Analytical X-ray Systems, Madison, WI, 1995) on all observed reflections. Data reduction was performed using the SAINT software, which corrects for *Lp* and decay. Absorption corrections were applied using SADABS (Siemens Area Detector Absorption Correction Program). The structure was solved in the space group $P42_1m$ by direct methods using the SHELXS-97 program (Sheldrick, G. M., University of Göttingen, Germany, 1997). In this space group, the Al and C(1) methyl groups sit on the intersection of two mutually perpendicular mirror planes, with the cyclopentadienyl ring sitting athwart one of the mirror planes. With an ordered model, there were two factors that pointed toward the presence of disorder: (1) very large atomic displacement parameters on the cyclopentadienyl methyl groups indicative of disorder, and (2) a very short ring C−C distance of 1.19 Å between the two carbon atoms bonded to the aluminum. Hence, a disorder of the cyclopentadienyl rings was introduced, and refinement proceeded smoothly by the least-squares method on F^2 using SHELXL-97, which is incorporated in

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SHELXTL-PC V 5.10 (PC/UNIX-Version, Bruker Analytical X-ray Systems, Madison, WI, 1995). The disorder consisted of a rotation by ±16° about the normal to the cyclopentadienyl ring. No disorder of the Al or C(1) position was introduced. The cyclopentadienyl methyl groups were constrained to ideal C_{3v} symmetry.

Crystals of **3** were grown by slow diffusion of pentane into a methylene chloride solution of the compound cooled at −78 °C. A suitable crystal was mounted on a pin with silicon grease, and the pin was mounted on a goniometer head.

Data collection was similar to that for **2**, except that the ω scans were collected with a scan width of 0.3° per frame for 30 s. Data reduction and absorption corrections were performed using the methods listed above. The structure was solved by the direct method.

All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by geometrical methods and refined as a riding model.

Isobutene Polymerization Experiments. In a typical experiment, 50−60 μmol of **3** was dissolved in 5 mL of methylene chloride in a thick-walled, glass vessel. Approximately 10 mL of isobutene was condensed into the reaction vessel at −78 °C. The reaction was allowed to warm to room temperature and stirred overnight. Methanol (0.5−1 mL) was added to quench the reaction. Additional methanol precipitated the polymer as a white, gummy material which was separated from the solvent. The polymer was washed twice with 10% nitric acid, then with distilled water. It was then reprecipitated as a white powder from a methylene chloride solution at −78 °C and dried in a 60 °C oven. Yield of polymer was 2.1 g.

Acknowledgment. Support of this work by the University of Idaho Seed Grant program is gratefully acknowledged. The establishment of a Single-Crystal X-ray Diffraction Laboratory and the purchase of a 500 MHz NMR spectrometer were supported by the M. J. Murdock Charitable Trust of Vancouver, WA, the National Science Foundation, and the NSF-Idaho EPSCoR Program. We thank Mr. Zheng Hao for experimental contributions and Dr. Emilio Bunel (DuPont) for GPC analyses. We also thank Dr. Gary Knerr for his assistance with the NMR experiments.

Supporting Information Available: Tables of crystallographic data, positional parameters, bond lengths and angles, thermal parameters, and atomic parameters of hydrogen atoms for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000173X