*Organometallics* **2006,** *25,* 3721−3729

# Activation of Tantalocene(V) Alkyl and Alkylidene Complexes with Strong Organo Lewis Acids and Application to Polymerization Catalysis

Wesley R. Mariott, Laura O. Gustafson, and Eugene Y.-X. Chen*

*Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872*

*Received March 22, 2006*

This work reexamines the reaction of the tantalocene trialkyl complex $Cp_2TaMe_3$ with the strong organo Lewis acids (LAs) $E(C_6F_5)_3$ ($E = B$, Al) under various reaction conditions, investigates the activation of Schrock's alkylidene complex $Cp_2Ta({=}CH_2)Me$ with $Al(C_6F_5)_3$, and employs the alkylidene complex for the polymerization of functionalized alkenes such as methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide (DMAA). Three cationic and zwitterionic tantalocene complexes have been isolated and structurally characterized, the cation $[Cp_2TaMe_2]^+[MeB(C_6F_5)_3]^-$ (**1**), the zwitterion $Cp_2Ta^+[CH_2Al(C_6F_5)_3^-]Me$ (**2**), and the cation $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+[Al(C_6F_5)_4]^-$ (**3**). Complex **3**, which is formed by the unusual nucleophilic attack of a $C_6F_5$ group within the aluminate moiety in **2** on $Al(C_6F_5)_3$ present in excess, consists of a cationic portion that can be viewed as a hybrid of two extreme structures: $Cp_2Ta^+[CH_2Al(C_6F_5)_2]Me$ and the cationic tantalocene alkylidene−LA adduct $[Cp_2Ta({=}CH_2)MeAl(C_6F_5)_2]^+$. The investigation into the scope of such a unique reaction type shows it to be specific to the aluminate/alane ($Al^-/Al$) pair. All three isolated complexes are inactive for polymerization of MMA and DMAA; however, the combination of $Cp_2Ta({=}CH_2)Me$ with 2 equiv of $Al(C_6F_5)_3$ is highly active, producing high-molecular-weight polymers presumably via an $Al^-/Al$ bimolecular propagation process.

## Introduction

Polymerization of functionalized alkenes such as methacrylates,[1] acrylates,[2] and acrylamides[3] catalyzed by group 4 metallocene and related complexes has attracted increasing attention due to the demonstrated remarkable versatility and control of most of these polymerization systems in terms of both catalyst structure and polymer architecture. In contrast, applications of group 5 metallocene and related complexes, especially tantalocenes(V), to the polymerization of these functionalized alkenes are scarce. Half-sandwich tantalum bis(diene) complexes, upon activation with suitable activators, are active for the polymerization of methyl methacrylate (MMA);[4] trimethyltantalocene, $Cp_2TaMe_3$, in combination with 2 equiv of $Al(C_6F_5)_3$ is active and highly active for MMA polymerization in toluene and 1,2-dichlorobenzene, respectively, whereas other tantalocene/cocatalyst combinations, such as $Cp_2TaMe_3/Al(C_6F_5)_3$, $Cp_2TaMe_3/xB(C_6F_5)_3$ ($x = 1, 2$), and $Cp_2TaMe_3/[Ph_3C][B(C_6F_5)_4]$, exhibit no activity for MMA polymerization in both types of solvents.[5]

Our earlier investigations into how these cocatalysts activate $Cp_2TaMe_3$ provided knowledge for an understanding of the activity or inactivity of the above tantalocene(V)/LA systems. The 1:1 reaction of $Cp_2TaMe_3$ and $E(C_6F_5)_3$ ($E = B$, Al) in polar, halogenated solvents such as $C_6D_5Br$ and $CD_2Cl_2$ leads to clean formation of the corresponding ion pair $[Cp_2TaMe_2]^+[MeE(C_6F_5)_3]^-$,[5b] whereas the reaction of $Cp_2TaMe_3$ with 2 equiv of $Al(C_6F_5)_3$ in either arene (benzene and toluene) or polar chlorinated (bromobenzene) solvents affords a unique cationic

---

* To whom correspondence should be addressed. E-mail: eychen@lamar.colostate.edu.

(1) For leading examples since 2000, see: (a) Rodriguez-Delgado, A.; Chen, E. Y.-X. *Macromolecules* **2005**, *38*, 2587−2594. (b) Kostakis, K.; Mourmouris, S.; Kotakis, K.; Nikogeorgos, N.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3305−3314. (c) Lian, B.; Lehmann, C. W.; Navarro, C.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 2466−2472. (d) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2004**, *126*, 4897−4906. (e) Stojcevic, G.; Kim, H.; Taylor, N. J.; Marder, T. B.; Collins, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5523−5526. (f) Strauch, J. W.; Fauré, J.-L.; Bredeau, S.; Wang, C.; Kehr, G.; Fröhlich, R.; Luftmann, H.; Erker, G. *J. Am. Chem. Soc.* **2004**, *126*, 2089−2104. (g) Chen, E. Y.-X. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3395−3403. (h) Karanikolopoulos, G.; Batis, C.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3761−3774. (i) Ferenz, M.; Bandermann, F.; Sustmann, R.; Sicking, W. *Macromol. Chem. Phys.* **2004**, *205*, 1196−1205. (j) Rodriguez-Delgado, A.; Mariott, W. R.; Chen, E. Y.-X. *Macromolecules* **2004**, *37*, 3092−3100. (k) Jensen, T. R.; Yoon, S. C.; Dash, A. K.; Luo, L.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14482−14494. (l) Chen, E. Y.-X.; Cooney, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7150−7151. (m) Mariott, W. R. Chen, E. Y.-X. *J. Am. Chem. Soc.* **2003**, *125*, 15726−15727. (n) Jin, J.; Mariott, W. R.; Chen, E. Y.-X. *J. Polym. Chem. Part A: Polym. Chem.* **2003**, *41*, 3132−3142. (o) Batis, C.; Karanikolopoulos, G.; Batis, C.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 9763−9774. (p) Karanikolopoulos, G.; Batis, C.; Pitsikalis, M.; Hadjichristidis, N. *Macromol. Chem. Phys.* **2003**, *204*, 831−840. (q) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2002**, *124*, 5612−5613. (r) Jin, J.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 13−15. (s) Bandermann, F.; Ferenz, M.; Sustmann, R.; Sicking, W. *Macromol. Symp.* **2001**, *174*, 247−253. (t) Karanikolopoulos, G.; Batis, C.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 4697−4705. (u) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943−7944. (v) Frauenrath, H.; Keul, H.; Höcker, H. *Macromolecules* **2001**, *34*, 14−19. (w) Nguyen, H.; Jarvis, A. P.; Lesley, M. J. G.; Kelly, W. M.; Reddy, S. S.; Taylor, N. J.; Collins, S. *Macromolecules* **2000**, *33*, 1508−1510. (x) Bandermann, F.; Ferenz, M.; Sustmann, R.; Sicking, W. *Macromol. Symp.* **2000**, *161*, 127−134. (y) Cameron, P. A.; Gibson, V.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329−4335. (z) Stuhldreier, T.; Keul, H.; Höcker, H. *Macromol. Rapid Commun.* **2000**, *21*, 1093−1098.

(2) (a) Mariott, W. R.; Rodriguez-Delgado, A.; Chen, E. Y.-X. *Macromolecules* **2006**, *39*, 1318−1327. (b) Kostakis, K.; Mourmouris, S.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3337−3348. (c) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875−1883. (d) Deng, H.; Soga, K. *Macromolecules* **1996**, *29*, 1847−1848.

(3) (a) Mariott, W. R.; Chen, E. Y.-X. *Macromolecules* **2005**, *38*, 6822−6832. (b) Mariott, W. R.; Chen, E. Y.-X. *Macromolecules* **2004**, *37*, 4741−4743.

(4) (a) Matsuo, Y.; Mashima, K.; Tani, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 960−962. (b) Mashima, K. *Macromol. Symp.* **2000**, *159*, 69−76.

(5) (a) Mariott, W. R.; Hayden, L. M.; Chen, E. Y.-X. *ACS Symp. Ser.* **2003**, *857*, 101−111. (b) Feng, S.; Roof, G. R.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 832−839.

10.1021/om060258j CCC: \$33.50

tantalocene $\mu$-Me dialuminate complex, $[Cp_2TaMe_2]^+[(C_6F_5)_3Al-Me-Al(C_6F_5)_3]^-$, which was structurally characterized.[6] Since the other combinations above produce the same tantalocene cation $[Cp_2TaMe_2]^+$ paired with non-dialuminate anions and are inactive for the MMA polymerization, the polymerization activity of the $Cp_2TaMe_3/2Al(C_6F_5)_3$ system was thus attributed not to the cation but to the $\mu$-Me dialuminate anion-mediated bimolecular propagating process.[5a] We earlier invoked the formation of the analogous $\mu$-Me diborate anion on the basis of $^1H$ and $^{19}F$ NMR data of the resulting phase-separated mixture derived from the reaction of $Cp_2TaMe_3$ with $B(C_6F_5)_3$ in $C_6D_6$ or $C_7D_8$ and the structure of the aluminate analogue.[6] One might wonder, however, why the combination of $Cp_2TaMe_3$ with excess $B(C_6F_5)_3$ is ineffective for MMA polymerization if the species formed are analogous to the $\mu$-Me dialuminate. Recent reports by Collins and Piers that such a diborate anion was not detected by NMR from either the reaction of $B(C_6F_5)_3$ with $[Bu_4N]^+[MeBC_6F_5)_3]^-$ in $C_6D_6/CD_2Cl_2$ (5/1 v/v)[7] or the reaction of $[(Me_3Si)_2N]_3ZrMe$ (or $Cp_2ZrMe_2$) with the chelating diborane 1,2-$[B(C_6F_5)_2]_2C_6F_4$ [8] cast further doubt on the original report of the diborate species. Most recently, Royo and co-workers showed that the reaction of the half-sandwich tantalum tetramethyl complex $Cp^*TaMe_4$ with 1 equiv of $B(C_6F_5)_3$ forms the corresponding cation $[Cp^*TaMe_3]^+$ paired with the methylborate anion $[MeB(C_6F_5)_3]^-$.[9] These questions and observations prompted our current reinvestigation of the reaction of $Cp_2TaMe_3$ with $E(C_6F_5)_3$ under varied reaction conditions, including concentration, solvent, temperature, ratio, and scale, as well as by isolation and structural characterization.

Another readily available tantalocene(V) complex that could potentially lead to an active system for the MMA polymerization, upon appropriate activation, is Schrock's methyl methylidene complex $Cp_2Ta(=CH_2)Me$,[10] which contains both alkyl and nucleophilic alkylidene ligands. Piers et al.[11] investigated the reactions of this methylidene complex with $HB(C_6F_5)_2$ and $B(C_6F_5)_3$ as well as isolated and structurally characterized the reaction products arising from attack of the borane by the methylidene ligand, the latter reaction of which produces the zwitterionic tantalocene complex $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$. In our continued quest for active group 5 metallocene systems for the polymerization of functionalized alkenes, we found that $Cp_2Ta(=CH_2)Me/xE(C_6F_5)_3$ ($E = B$, $x = 1, 2$; $E = Al$, $x = 1$) systems are inactive for MMA polymerization but a combination of $Cp_2Ta(=CH_2)Me$ with 2 equiv of $Al(C_6F_5)_3$ is highly active. Prompted by this observation, we investigated the reaction of $Cp_2Ta(=CH_2)Me$ with $Al(C_6F_5)_3$ and discovered that the reaction product depends on the stoichiometry; while the 1:1 reaction gives the analogous zwitterionic complex $Cp_2Ta^+[CH_2Al(C_6F_5)_3^-]Me$ (**2**), the reaction with excess $Al(C_6F_5)_3$ affords the cationic complex $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+[Al(C_6F_5)_4]^-$ (**3**), involving unusual nucleophilic attack of a $C_6F_5$ group within the aluminate moiety in **2** at $Al(C_6F_5)_3$.

## Experimental Section

**Materials and Methods.** All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line (typically $10^{-5}-10^{-7}$ Torr), or in an argon- or nitrogen-filled glovebox (typically <1.0 ppm oxygen and moisture). NMR-scale reactions (typically on a 0.02 mmol scale in ~0.7 mL of an NMR solvent) were conducted in Teflon-valve-sealed J. Young type NMR tubes. HPLC grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for THF, $Et_2O$, and $CH_2Cl_2$) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-$d_6$ and toluene-$d_8$ were degassed, dried over sodium/potassium alloy, and filtered before use, whereas $CDCl_3$, $C_6D_5Br$, $CD_2Cl_2$, and 1,2-dichlorobenzene (DCB) were degassed and dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, $^1H$; 75 MHz, $^{13}C$; 282 MHz, $^{19}F$) or a Varian Inova 400 spectrometer. Chemical shifts for $^1H$ and $^{13}C$ spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane, whereas $^{19}F$ NMR spectra were referenced to external $CFCl_3$. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

The reagents $TaCl_5$, CpTl, $Ph_3CBF_4$, and $NaNH_2$ were purchased from Alfa Aesar, while $ZnMe_2$ (10 wt % in hexanes), $Me_4PBr$, and $AlMe_3$ (neat) were purchased from Strem Chemical Co.; they were used as received. Methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMAA) were purchased from Aldrich Chemical Co. and TCI America, respectively; they were purified by first degassing and drying over $CaH_2$ overnight, followed by vacuum distillation; final purification of MMA involved titration with neat tri-*n*-octylaluminum to a yellow end point[12] followed by a second vacuum distillation. The purified monomers were stored in brown bottles over activated Davison 4 Å molecular sieves (for DMAA) in a −30 °C freezer inside the glovebox.

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and further purified by recrystallization from hexanes at −30 °C. Tris(pentafluorophenyl)alane, $Al(C_6F_5)_3$, as a 0.5 toluene adduct, $Al(C_6F_5)_3 \cdot 0.5C_7H_8$, on the basis of the elemental analysis for the vacuum-dried sample, was prepared by the ligand exchange reaction of $B(C_6F_5)_3$ and $AlMe_3$ in a 1:3 toluene/hexanes solvent mixture in quantitative yield;[5b] this is the modified synthesis based on literature procedures.[13] *Extra caution should be exercised when handling this material, especially the unsolvated form, because of its thermal and shock sensitivity*. Literature procedures were employed for the preparation of the following compounds or metallocene complexes: $[Ph_3C][B(C_6F_5)_4]$,[14] $Cp_2TaMe_3$ ($Cp = \eta^5$-$C_5H_5$),[10] $Cp_2Ta(=CH_2)Me$,[10] and $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$.[11b]

**Isolation of $[Cp_2TaMe_2]^+[MeB(C_6F_5)_3]^-$ (1).** In an argon-filled glovebox, a 30 mL glass reactor was equipped with a stir bar and charged with $Cp_2TaMe_3$ (53.4 mg, 0.150 mmol), $B(C_6F_5)_3$ (76.8 mg, 0.150 mmol), and 15 mL of $CH_2Cl_2$. The resulting clear yellow reaction mixture was stirred for 30 min at ambient temperature, after which all volatiles were removed in vacuo to give a pale yellow

---

[6] Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541−5543.

[7] Al-Humydi, A.; Garrison, J. C.; Youngs, W. J.; Collins, S. *Organometallics* **2005**, *24*, 193−196.

[8] Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695−3698.

[9] While we were revising our paper, the following report appeared: Sánchez-Nieves, J.; Royo, P.; Mosquera, M. E. G. *Organometallics* **2006**, *25*, 2331−2336.

[10] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc*. **1978**, *100*, 2389−2399.

[11] (a) Cook, K. S.; Piers, W. E.; Patrick, B. O.; McDonald, R. *Can. J. Chem.* **2003**, *81*, 1137−1148. (b) Cook, K. S.; Piers, W. E.; Rettig, S. J.; McDonald, R. *Organometallics* **2000**, *19*, 2243−2245. (c) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575−1577.

[12] Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127−134.

[13] (a) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Catal., A: Chem.* **1998**, *132*, 231−239. (b) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U.S. Pat. 5,602,269, 1997.

[14] (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571. (b) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. EP 0,426,637, 1991.

microcrystalline solid. This solid was washed with 3 × 2 mL of hexanes and dried under vacuum for 2 h, yielding 116 mg (89%) of the pure title complex as a pale yellow microcrystalline solid. Anal. Calcd for $C_{31}H_{19}BF_{15}Ta$: C, 42.88; H, 2.21. Found: C, 43.14; H, 2.28.

$^1H$ NMR ($CD_2Cl_2$, 23 °C): $\delta$ 6.44 (s, 10H, $C_5H_5$), 0.64 (s, 6H, Ta−*Me*), 0.47 (s, br, 3H, B−*Me*). $^{19}F$ NMR ($CD_2Cl_2$, 23 °C): $\delta$ −131.50 (d, $^3J_{FF}$ = 20.6 Hz, 6F, *o*-F), −163.37 (t, $^3J_{FF}$ = 20.6 Hz, 3F, *p*-F), −166.00 (m, 6F, *m*-F). $^{13}C$ NMR ($CD_2Cl_2$, 23 °C): $\delta$ 148.81 (d, $^1J_{CF}$ = 241.5 Hz, $C_6F_5$), 138.03 (d, $^1J_{CF}$ = 243.5 Hz, $C_6F_5$), 136.97 (d, $^1J_{CF}$ = 242.8 Hz, $C_6F_5$), and 129.52 (s, br) for $C_6F_5$ carbons, 112.92 ($C_5H_5$), 57.13 (Ta−*Me*), 10.49 (B−*Me*).

**Isolation of $Cp_2Ta^+[CH_2Al(C_6F_5)_3^-]Me$ (2).** In an argon-filled glovebox, a 30 mL glass reactor was equipped with a stir bar and charged with $Cp_2Ta({=}CH_2)Me$ (34.0 mg, 0.100 mmol), $Al(C_6F_5)_3\cdot(C_7H_8)_{0.5}$ (57.4 mg, 0.100 mmol), and 5 mL of toluene. The resulting clear dark green solution was stirred for 30 min at ambient temperature, after which all volatiles were removed in vacuo, affording a dark green sticky residue. This residue was washed with 5 × 2 mL of hexanes and dried under vacuum to yield 81.9 mg (94%) of the pure title complex as a dark green solid. Anal. Calcd for $C_{30}H_{15}AlF_{15}Ta$: C, 41.50; H, 1.74. Found: C, 41.56; H, 1.59.

$^1H$ NMR ($C_6D_5Br$, 23 °C): $\delta$ 5.76 (s, 10H, $C_5H_5$), 3.77 (s, br, 2H, $CH_2$), 0.09 (s, 3H, $CH_3$). $^{19}F$ NMR ($C_6D_5Br$, 23 °C): $\delta$ −121.17 (d, $^3J_{FF}$ = 19.6 Hz, 6F, *o*-F), −154.71 (t, $^3J_{FF}$ = 20.3 Hz, 3F, *p*-F), −161.45 (m, 6F, *m*-F). $^{13}C$ NMR ($C_6D_5Br$, 23 °C): $\delta$ 150.34 (d, $^1J_{CF}$ = 231.1 Hz, $C_6F_5$), 141.18 (d, $^1J_{CF}$ = 251.0 Hz, $C_6F_5$), 137.25 (d, $^1J_{CF}$ = 254.0 Hz, $C_6F_5$), 109.89 ($C_5H_5$), 31.51 ($CH_3$). The $CH_2$ carbon and ipso carbon of the $C_6F_5$ group could not be assigned with confidence, due to their aluminum-broadened peaks and overlapping with the NMR solvent peaks; the HMQC experiment gave a $^1J_{CH}$ value of 126.0 Hz for the $CH_2$ group.

**Synthesis of $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+[Al(C_6F_5)_4]^-$ (3).** In an argon-filled glovebox, a 25 mL Schlenk flask was equipped with a stir bar and charged with $Cp_2Ta({=}CH_2)Me$ (34.0 mg, 0.100 mmol) and $Al(C_6F_5)_3\cdot0.5C_7H_8$ (0.230 g, 0.400 mmol). The flask was sealed, removed from the glovebox, and interfaced to a Schlenk line in a 23 °C water bath, after which 5 mL of bromobenzene was added via gastight syringe. The reaction mixture was stirred at 23 °C for 24 h, during which time the solution gradually changed from light green to dark green. All volatiles were removed in vacuo, and the resulting sticky green residue was dried for an additional 2 h before being taken into a glovebox and washed with 3 × 1 mL of cold (−30 °C) toluene followed by 3 × 2 mL of hexanes. The residue was dried extensively under vacuum, affording 115.5 mg (83%) of the pure title complex as a dark green solid. Anal. Calcd for $C_{48}H_{15}Al_2F_{30}Ta$: C, 41.28; H, 1.08. Found: C, 41.02; H, 1.09.

$^1H$ NMR ($C_6D_5Br$, 23 °C): $\delta$ 8.96 (s, br, 2H, $CH_2$), 5.85 (s, 10H, $C_5H_5$), 0.47 (s, 3H, $CH_3$). $^{19}F$ NMR ($C_6D_5Br$, 23 °C): $\delta$ −120.51 (d, $^3J_{FF}$ = 21.1 Hz, 4F, *o*-F, $Al(C_6F_5)_2$), −121.87 (d, $^3J_{FF}$ = 18.8 Hz, 8F, *o*-F, $Al(C_6F_5)_4$), −147.02 (s, br, 2F, *p*-F, $Al(C_6F_5)_2$), −156.41 (t, $^3J_{FF}$ = 20.0 Hz, 4F, *p*-F, $Al(C_6F_5)_4$), −157.42 (m, 4F, *m*-F), −162.78 (m, 8F, *m*-F, $Al(C_6F_5)_4$).

**General Polymerization Procedures.** Polymerizations were carried out in 30 mL glass reactors at ambient temperature (∼25 °C) inside an argon-filled glovebox in either toluene or DCB. For activated complex polymerizations, $Cp_2Ta({=}CH_2)Me$ (8.0 mg, 23.4 $\mu$mol) and $Al(C_6F_5)_3\cdot0.5C_7H_8$ (26.9 mg, 46.8 $\mu$mol) were dissolved in 5 mL of solvent and the mixtures stirred for 10 min at ambient temperature before the addition of MMA (1.00 mL, 9.35 mmol) to the vigorously stirred solution. The solution was stirred for 30 min, after which the reaction was quenched by the addition of 5 mL of 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 30 min, filtered, and washed with methanol. The polymer product was collected and dried in a vacuum oven at 50 °C overnight to a constant weight. Activated monomer polymerizations were performed in a similar manner, but for these runs a solution of $Al(C_6F_5)_3$ in MMA was added via pipet to a vigorously stirred solution of $Cp_2Ta({=}CH_2)Me$ in 5 mL of solvent. Polymerizations of DMAA were carried out in a manner similar to the MMA polymerizations, except for different workup procedures. When a DMAA polymerization was quenched by the addition of 5 mL of 5% HCl-acidified methanol, the quenched mixture was precipitated into 100 mL of diethyl ether, this mixture was stirred for 30 min, and the solvent was decanted off. An additional 75 mL of diethyl ether was used to wash the polymer product and then decanted. The product was dried in a vacuum oven at 50 °C overnight, dissolved in a minimum amount of $CH_2Cl_2$ or methanol, and precipitated into a 10-fold excess of diethyl ether, and this mixture was stirred for 30 min, filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C overnight to a constant weight.

**Polymer Characterizations.** Gel permeation chromatography (GPC) analyses of the polymers were carried out at 40 °C and a flow rate of 1.0 mL/min, with $CHCl_3$ as the eluent, on a Waters University 1500 GPC instrument equipped with four 5 $\mu$m PL gel columns (Polymer Laboratories) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (version 2002); number-average molecular weights and polydispersities of polymers are given relative to PMMA standards. NMR spectra of the resulting polymers were recorded in $CDCl_3$ and analyzed according to literature procedures.[15]

**X-ray Crystallographic Analyses of 1−3.** Single crystals of complexes **1**−**3** suitable for X-ray diffraction were grown from a $CH_2Cl_2$ solution layered with hexanes, a 1:1 toluene−hexanes solvent mixture, and a 10:1 toluene−$CH_2Cl_2$ solvent mixture, respectively, all at −30 °C inside the freezer of a glovebox. The crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/$10^{-6}$ Torr for 24 h) after the mother liquors were decanted and then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on $F^2$ for all reflections.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions, except for the bridging methylene and methyl hydrogen atoms in **2** and **3**, which were located by the difference Fourier synthesis and refined. There are one $CH_2Cl_2$, one toluene, and two $CH_2Cl_2$ crystallization solvent molecules in the lattice in complexes **1**−**3**, respectively. Selected crystal data and structural refinement parameters are collected in Table 1.

## Results and Discussion

**Reaction of $Cp_2TaMe_3$ with $E(C_6F_5)_3$ (E = B, Al): Reexamination.** Mixing of $Cp_2TaMe_3$ with 1 equiv of $B(C_6F_5)_3$ in nonpolar hydrocarbon solvents such as $C_6D_6$ and $C_7D_8$ (28.6 mM) at ambient temperature initially formed light yellow suspensions which turned gradually to yellow oily precipitates in about 15 min. The resulting phase-separated mixture showed two sets of signals in $^1H$ and $^{19}F$ NMR spectra at ambient temperature, both assignable to the $[MeB(C_6F_5)_3]^-$ anion or a closely related anion moiety. In the $^1H$ NMR ($C_6D_6$, 23 °C) spectrum, the separation between the two broad singlet *Me*B peaks is 0.38 ppm ($\delta$ 1.33 vs 0.95 ppm), whereas the separations between two Cp ($\delta$ 5.04 and 5.01 ppm) and *Me*Ta peaks ($\delta$

---

(15) (a) Bulai, A.; Jimeno, M. L.; de Queiroz, A.-A. A.; Gallardo, A.; Roman, J. S. *Macromolecules* **1996**, *29*, 3240−3246. (b) Ferguson, R. C.; Ovenall, D. W. *Macromolecules* **1987**, *20*, 1245−1248. (c) Subramanian, R.; Allen, R. D.; McGrath, J. E.; Ward, T. C. *Polym. Prepr.* **1985**, *26*, 238−240.

(16) SHELXTL, Version 6.12; Bruker Analytical X-ray Solutions, Madison, WI, 2001.

**Table 1. Crystal Data and Structure Refinement Details for $1\cdot CH_2Cl_2$, $2\cdot C_7H_8$, and $3\cdot 2CH_2Cl_2$**

| | **1**·$CH_2Cl_2$ | **2**·$C_7H_8$ | **3**·$2CH_2Cl_2$ |
|---|---|---|---|
| empirical formula | $C_{32}H_{21}BCl_2F_{15}Ta$ | $C_{37}H_{23}AlF_{15}Ta$ | $C_{50}H_{19}Al_2Cl_4F_{30}Ta$ |
| formula wt | 953.15 | 960.48 | 1566.36 |
| temp/K | 173(2) | 100(2) | 173(2) |
| wavelength/Å | 0.710 73 | 0.710 73 | 0.710 73 |
| cryst syst | orthorhombic | orthorhombic | triclinic |
| space group | $P2_12_12_1$ | *Pbca* | $P\bar{1}$ |
| $a$/Å | 12.6003(10) | 19.9908(11) | 12.2991(10) |
| $b$/Å | 15.4046(12) | 16.7232(9) | 14.0265(11) |
| c/Å | 16.4304(13) | 20.0723(11) | 16.5511(13) |
| α/deg | 90 | 90 | 87.396(2) |
| $\beta$/deg | 90 | 90 | 78.182(2) |
| $\gamma$/deg | 90 | 90 | 68.632(20 |
| V/Å$^3$ | 3189.2(4) | 6710.4(6) | 2601.3(4) |
| $Z$ | 4 | 8 | 2 |
| calcd density/Mg m$^{-3}$ | 1.985 | 1.901 | 2.000 |
| abs coeff/mm$^{-1}$ | 3.727 | 3.415 | 2.499 |
| $F$(000) | 1840 | 3728 | 1512 |
| cryst size/mm$^3$ | 0.30 × 0.20 × 0.08 | 0.54 × 0.24 × 0.11 | 0.19 × 0.14 × 0.06 |
| $\theta$ range for data collecn/deg | 1.81−28.44 | 1.88−28.33 | 2.79−38.07 |
| index ranges | $-16 \le h \le 16$, | $-26 \le h \le 25$, | $-21 \le h \le 21$, |
| | $-20 \le k \le 20$, | $-22 \le k \le 22$, | $-24 \le k \le 24$, |
| | $-21 \le l \le 21$ | $-26 \le l \le 26$ | $-28 \le l \le 28$ |
| no. of rflns collected | 30 175 | 61 163 | 254 589 |
| no. of indep rflns | 7807 ($R_{int} = 0.0328$) | 8313 ($R_{int} = 0.0304$) | 28 325 ($R_{int} = 0.0412$) |
| completeness to $\theta$/% | 98.3 | 99.4 | 99.5 |
| no. of data/restraints/params | 7807/0/460 | 8313/0/495 | 28 325/1/796 |
| goodness of fit on $F^2$ | 1.022 | 1.059 | 1.011 |
| final $R$ indices ($I > 2\sigma(I)$) | | | |
| R1 | 0.0236 | 0.0251 | 0.0337 |
| wR2 | 0.0495 | 0.0587 | 0.0928 |
| $R$ indices (all data) | | | |
| R1 | 0.0280 | 0.0398 | 0.0408 |
| wR2 | 0.0509 | 0.0679 | 0.0972 |
| largest diff peak, hole/e Å$^{-3}$ | 1.311, −0.583 | 1.065, −0.460 | 2.304, −2.919 |

−0.38 and −0.40 ppm) are only marginal. The diagnostic *o*-, *p*-, and *m*-fluorine patterns and chemical shifts for a typical free $[MeB(C_6F_5)_3]^-$ type anion in the $^{19}F$ NMR spectrum are also seen as sharp peaks in pairs with only marginal separations: $\delta$ −131.99 vs −132.36 (d, $^3J_{FF} = 21.2$ Hz, *o*-F), −163.98 vs −164.05 (t, $^3J_{FF} = 21.4$ Hz, *p*-F), and −166.57 vs −166.64 (m, *m*-F). The ratio of these two sets of peaks changes with time when monitored over a period of 15 min to 18 h and also with varied concentration (28.6, 14.3, and 7.15 mM). The reactions of $Cp_2TaMe_3$ in a 1:2 ratio with $B(C_6F_5)_3$ and a 1:1 ratio with $Al(C_6F_5)_3$ also gave phase-separated mixtures, exhibiting similar doubling of the peaks in $^1H$ and $^{19}F$ NMR spectra. An exception is the reaction of $Cp_2TaMe_3$ with $Al(C_6F_5)_3$ in a 1:2 ratio, which cleanly generates in either benzene or toluene the $\mu$-Me dialuminate complex $[Cp_2TaMe_2]^+[(C_6F_5)_3Al{-}Me{-}Al(C_6F_5)_3]^-$ as colorless crystals.[6]

When the 1:1 reaction of $Cp_2TaMe_3$ and $B(C_6F_5)_3$ was carried out in polar halogenated solvents such as $C_6D_5Br$ and $CD_2Cl_2$, a homogeneous solution was obtained, the NMR spectra of which indicated clean formation of the corresponding ion pair $[Cp_2TaMe_2]^+[MeB(C_6F_5)_3]^-$ (**1**).[5b] The noncoordinating nature of the anion $[MeB(C_6F_5)_3]^-$ in **1** is inferred by the diagnostic observation of a small chemical shift difference of <3 ppm ($\Delta(m,p\text{-F}) = 2.6$ ppm in **1**) between the *p*- and *m*-fluorines.[17] The preparative-scale reaction in $CH_2Cl_2$ afforded the analytically pure **1** in 89% isolated yield, and its molecular structure has been confirmed by X-ray diffraction analysis, featuring unassociated cation, $[Cp_2TaMe_2]^+$, and anion, $[MeB(C_6F_5)_3]^-$, pairs (Figure 1). The 1:1 reaction with $Al(C_6F_5)_3$ in $C_6D_5Br$ occurs analogously, to generate cleanly the aluminate derivative $[Cp_2TaMe_2]^+[MeAl(C_6F_5)_3]^-$.[5b] [The use of $C_6D_5Br$, instead of $CD_2Cl_2$, for this reaction is noteworthy; $CD_2Cl_2$ is not suitable for the reaction involving the unsolvated $Al(C_6F_5)_3$ or $Al(C_6F_5)_3\cdot 0.5C_7H_8$, as $CH_2Cl_2$ decomposes $Al(C_6F_5)_3$ via facile chloride abstraction to form $(C_6F_5)_2AlCl$, which has been structurally characterized as a dimer in the solid state.[18] Conversely, $CH_2Cl_2$ presents no problems for reactions involving base adducts such as $THF\cdot Al(C_6F_5)_3$ and $MMA\cdot Al(C_6F_5)_3$.] The 1:2 reactions with $E(C_6F_5)_3$ are drastically different, however, depending on E; while the reaction of $Cp_2TaMe_3$ with 2 equiv of $Al(C_6F_5)_3$ cleanly produces the crystalline $\mu$-Me dialuminate complex, the reaction with 2 equiv of $B(C_6F_5)_3$ affords the same product, **1**, as in the 1:1 reaction, along with excess $B(C_6F_5)_3$ and a small amount of $MeB(C_6F_5)_2$. Additionally, the reaction of $Cp_2TaMe_3$ with 1 equiv of $B(C_6F_5)_3$ and 1 equiv of $Al(C_6F_5)_3$ together did not produce the plausible $\mu$-Me borate−aluminate mixed anion $[(C_6F_5)_3B{-}Me{-}Al(C_6F_5)_3]^-$.

With the fully characterized **1** on hand, the nature of the second set of NMR signals appearing in arene solvents can be understood. Redissolving the crystals of **1** or the isolated liquid clathrate phase, obtained from a preparative-scale reaction of $Cp_2TaMe_3$ with $B(C_6F_5)_3$ in toluene, back into $C_6D_6$ gave identical NMR spectra exhibiting a doubling of NMR signals similar to that observed in the reaction carried out in arene solvents; the switch to $CD_2Cl_2$ afforded cleanly only one set of peaks identical with those for the isolated **1** in $CD_2Cl_2$. Variable-temperature $^1H$ NMR experiments of **1** in $C_7D_8$ (28.6 mM) also showed only one set of peaks at temperatures ≥60 °C (Figure 2); VT $^{19}F$ NMR spectra corresponded to the same trend. It is clear from these results that the observation of the second set of peaks from the reaction in arene solvents at ambient

---

(17) (a) Klosin, J.; Roof, G.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686. (b) Horton, A. D.; de With, J.; van der Linder, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672−2674.

(18) Chakraborty, D.; Chen, E. Y.-X. *Inorg. Chem. Commun.* **2002**, *5*, 698−701.

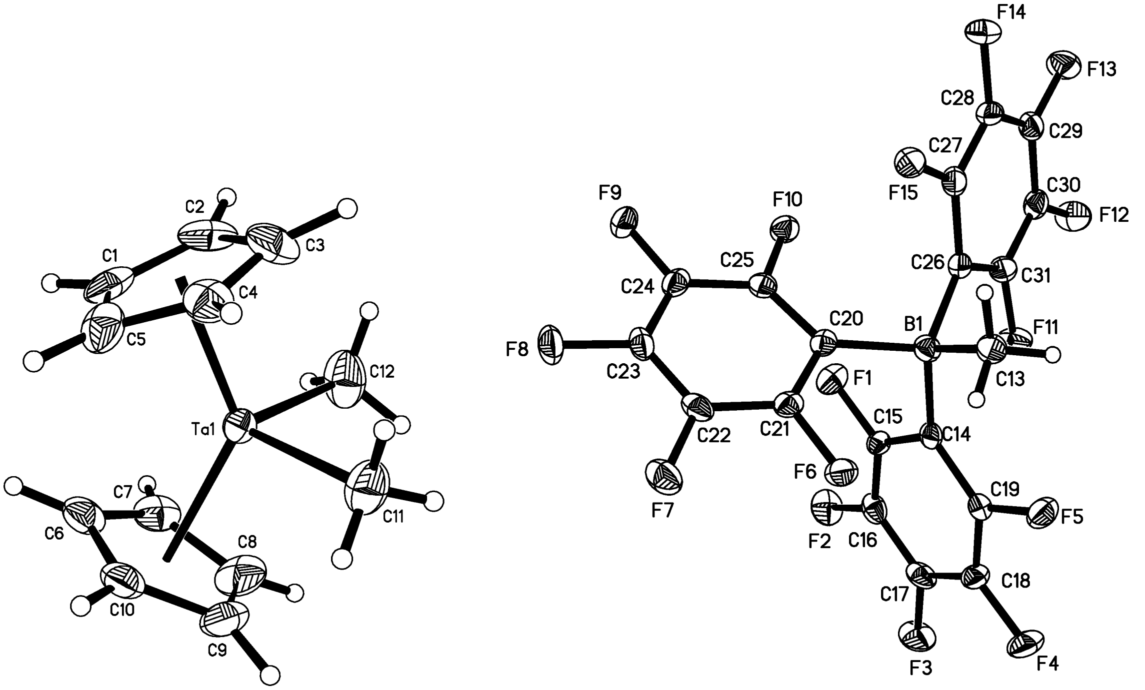


**Figure 1.** Molecular structure of complex **1**. Selected bond lengths (Å): Ta−C(11) = 2.178(3), Ta−C(12) = 2.170(4), B−C(13) = 1.634(5), B−C(14) = 1.658(5), B−C(20) = 1.659(5), B−C(26) = 1.661(5). Selected bond angles (deg): C(11)−Ta−C(12) = 97.0 (1), C(13)−B−C(14) = 114.8(3), C(13)−B−C(20) = 109.0(3), C(13)−B−C(26) = 103.9(3), C(14)−B−C(20) = 103.7(3), C(14)−B−C(26) = 111.7(3), C(20)−B−C(26) = 114.1(3).

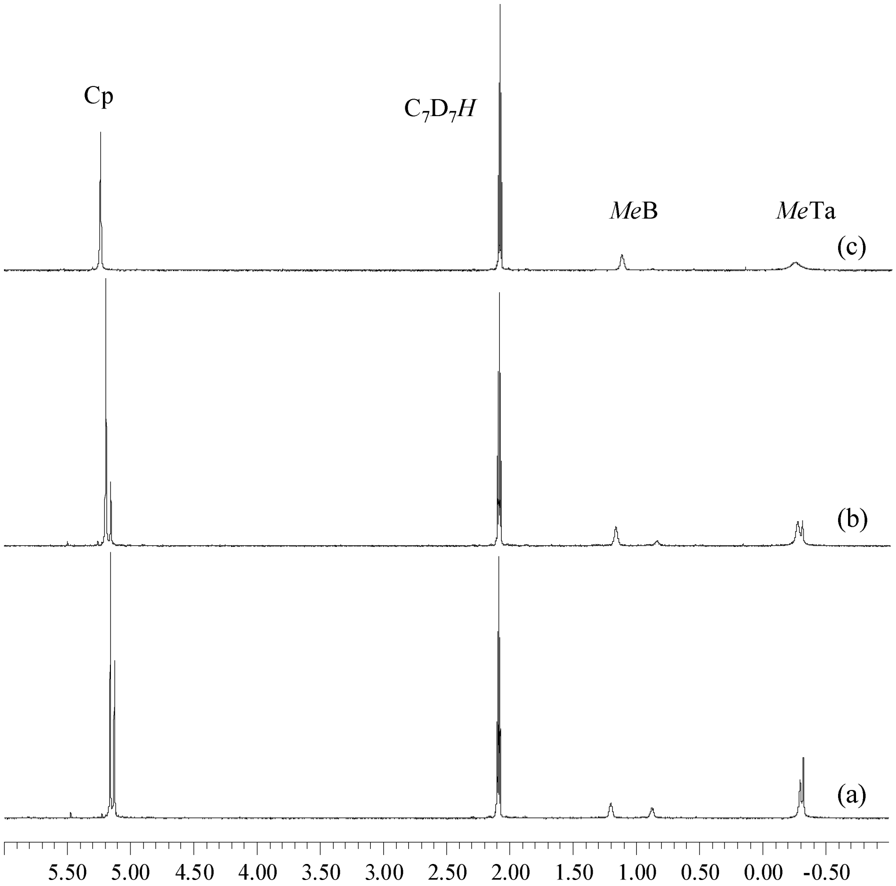
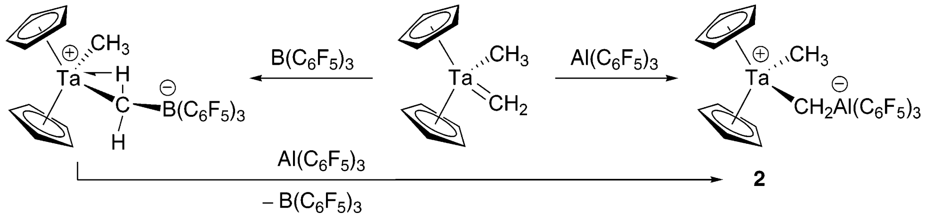


**Figure 2.** $^1$H NMR spectra of **1** in $C_7D_8$ at 25 °C (a), 40 °C (b), and 60 °C (c).

temperature is not due to the formation of the plausible $\mu$-Me diborate species but, rather, simply to the clathrate phase of ionic aggregates that are in slow exchange and can also give rise to decent NMR signals with chemical shifts different from those of the monomeric form in solution. Thus, we previously erred when attributing the second set of NMR signals to the plausible $\mu$-Me diborate species.[6] Consequently, the stability of such $\mu$-alkyl diborate anions must be questioned. The larger covalent radius of aluminum compared to that of boron, reflected by considerably longer distances of typical Al−C bonds (with

**Scheme 1**



electrostatic character) than B−C bonds (more covalent in nature), likely better accommodates the steric crowding of two $Al(C_6F_5)_3$ moieties connected by the small Me group for the facile formation of $[(C_6F_5)_3Al-Me-Al(C_6F_5)_3]^-$; on the other hand, isolation, or even detection, of $\mu$-Me boron-containing dinuclear anions, such as $[(C_6F_5)_3B-Me-Al(C_6F_5)_3]^-$ and $[(C_6F_5)_3B-Me-B(C_6F_5)_3]^-$, still remains elusive.

**Reaction of $Cp_2Ta({=}CH_2)Me$ with 1 Equiv of $Al(C_6F_5)_3$.** Piers and co-workers[11b] showed that the reaction of $Cp_2Ta({=}CH_2)Me$ with $B(C_6F_5)_3$ in toluene rapidly produces the zwitterionic tantalocene complex $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$, in which the cationic Ta center is stabilized by a strong α-agostic interaction involving one of the C−H bonds of the electron-rich methylene unit (Scheme 1). We found that the reaction with 1 equiv of $Al(C_6F_5)_3$ in toluene occurs analogously, affording the zwitterionic tantalocene aluminate derivative $Cp_2Ta^+[CH_2Al(C_6F_5)_3^-]Me$ (**2**; Scheme 1); treatment of the borate derivative with 1 equiv of $Al(C_6F_5)_3$ in $C_6D_5Br$ also leads to complex **2** as the major product (vide infra). As in the reaction with $B(C_6F_5)_3$, electrophilic attack of $Al(C_6F_5)_3$ at the methylidene carbon causes a drastic high-field shift of the sharp peak at 10.14 ppm ($C_6D_6$) for the methylidene protons in $Cp_2Ta({=}CH_2)Me$ to a now aluminum-broadened peak at 3.77 ppm in $C_6D_5Br$ (3.64 ppm in $CD_2Cl_2$ or 3.63 ppm in $C_7D_8$) for the methylene protons in **2**; furthermore, the $^{19}F$ NMR chemical shifts of the resulting product are consistent with alkyl tris(pentafluorophenyl)aluminate formation.[19] However, unlike the case for the structure of the borate derivative, there is no solution NMR evidence (the $^1J_{CH}$ value of the $CH_2$ group is 126.0 Hz) for the presence of an α-agostic interaction in this aluminate derivative, arguing that the charge separation in **2** is less extensive than for the borate analogue. The molecular structure of **2** has been confirmed by X-ray diffraction (Figure 3), in which both $CH_2$ hydrogens were located and refined.

The absence of an α-agostic interaction in the solid-state structure of **2** is evident by the observation of the normal, similar C−H distances for both H(12) hydrogens (C(12)−H(12a) = 0.973(3) Å, C(12)−H(12b) = 0.929(3) Å), normal, similar angles for both Ta−C(12)−H(12) vectors (Ta−C(12)−H(12a) = 105.0 (17)°, Ta−C(12)−H(12b) = 105.6 (17)°), and large, nonbonding Ta−H distances for both H(12) hydrogens (Ta−H(12a) = 2.538(3) Å, Ta−H(12b) = 2.520 Å). As in the borate derivative, the $Ta-CH_2$ distance is notably shorter than the $Ta-CH_3$ distance by ~0.1 Å (Ta−C(11) = 2.202(3) Å, Ta−C(12) = 2.106(3) Å). The metric parameters of the $-CH_2Al(C_6F_5)_3$ aluminate moiety compare well with those of the $\mu$-Me aluminate moiety $-MeAl(C_6F_5)_3$ observed in group 4 metallocene cationic complexes.[19] Considerably larger distances of Al−C bonds in **2** as compared to the corresponding B−C bonds in the borate derivative (e.g., $Al-CH_2$(bridging) = 2.008(3) Å, $B-CH_2$ = 1.661(7) Å) presumably alleviate the steric interactions between the $-Al(C_6F_5)_3$ moiety and Cp rings, resulting in an approximately 12° smaller Ta−C(12)−E vector angle in **2** than in the borate derivative; these results are consistent with the conclusion that the degree of charge separation in **2** is less than in the borate derivative.

**Reaction of $Cp_2Ta({=}CH_2)Me$ with Excess $Al(C_6F_5)_3$.** The outcome of the reaction of $Cp_2Ta({=}CH_2)Me$ with excess (2−4 equiv) $E(C_6F_5)_3$ depends on E. Thus, the reaction with excess $B(C_6F_5)_3$ in $C_6D_6$ or $CD_2Cl_2$ gave the same adduct, $Cp_2Ta^+$-$[CH_2B(C_6F_5)_3^-]Me$, as in the 1:1 reaction, along with the unreacted excess borane. However, the reaction with excess $Al(C_6F_5)_3$ in $C_6D_5Br$ slowly but cleanly converted the rapidly formed adduct **2** to a new species over a 24 h period. The $^1H$ NMR spectrum of this new species exhibits a broad signal at 8.96 ppm for the $CH_2$ moiety attached to an Al center, reflecting a 5.2 ppm downfield shift as compared with **2**, while the Me protons were also shifted downfield, although only by ~0.4 ppm. Interestingly, its $^{19}F$ NMR spectrum exhibits two sets of $Al-C_6F_5$ peaks corresponding to a neutral alane-like structure ($\delta$ −120.51 (d, 4F, *o*-F), −147.02 (s, br, 2F, *p*-F), −157.42 (m, 4F, *m*-F)) and an anionic aluminate-like structure ($\delta$ −121.87 (d, 8F, *o*-F), −156.41 (t, 4F, *p*-F), −162.78 (m, 8F, *m*-F)), the integrals of which show two $C_6F_5$ groups for the neutral species and four $C_6F_5$ groups for the aluminate anion. The spectroscopic data of this new species are consistent with the structure $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+[Al(C_6F_5)_4]^-$ (**3**), depicted in Scheme 2, and its formation is proposed to resemble the established nucleophilic attack of the Me group within the

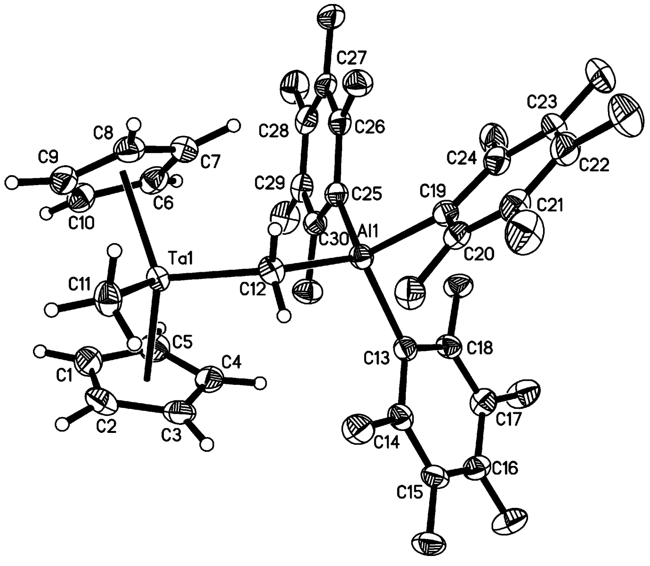


**Figure 3.** Molecular structure of complex **2**. Selected bond lengths (Å): Ta−C(11) = 2.202(3), Ta−C(12) = 2.106(3), Al−C(12) = 2.008(3), Al−C(13) = 2.035(3), Al−C(19) = 2.033(3), Al−C(25) = 2.025(3). Selected bond angles (deg): Ta−C(12)−Al = 133.2 (1), C(11)−Ta−C(12) = 95.5(1), C(12)−Al−C(13) = 115.0(1), C(12)−Al−C(19) = 107.9(1), C(12)−Al−C(25) = 110.0(1), C(13)−Al−C(19) = 102.2(1), C(13)−Al−C(25) = 109.3(1), C(19)−Al−C(25) = 112.3(1).

---

[19] (a) Stahl, N. G.; Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10898−10909. (b) Liu, Z.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 2915−2916. (c) Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745−746.

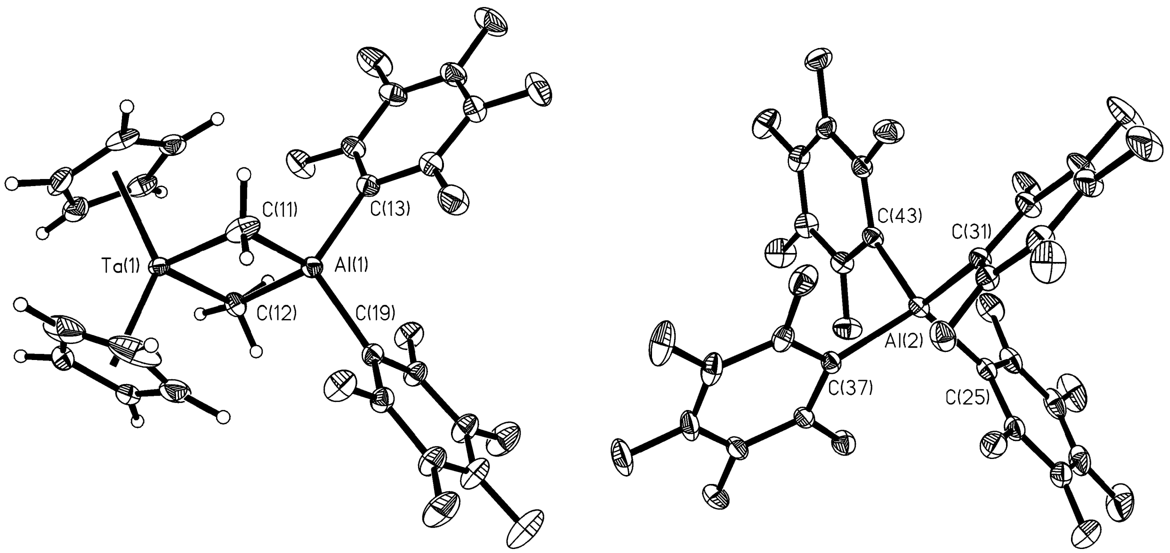
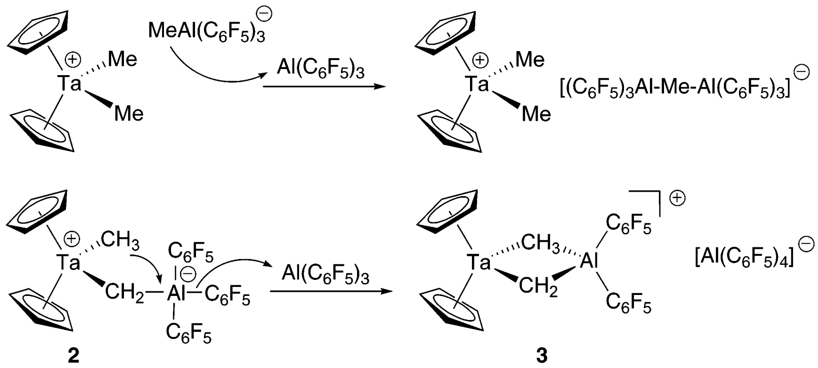


**Figure 4.** Molecular structure of complex **3**. Selected bond lengths (Å): Ta−C(11) = 2.129(2), Ta−C(12) = 2.290(2), Al(1)−C(11) = 2.111(2), Al(1)−C(12) = 2.149(2), Al(1)−C(13) = 1.981(2), Al(1)−C(19) = 1.979(2), Al(2)−C(25) = 2.021(2), Al(2)−C(31) = 2.008(2), Al(2)−C(37) = 2.025(2), Al(2)−C(43) = 2.011(2). Selected bond angles (deg): C(11)−Ta−C(12) = 96.51(7), Ta−C(11)−Al(1) = 83.30(7), Ta−C(12)−Al(1) = 78.72 (6), C(11)−Al(1)−C(12) = 101.47(9), C(11)−Al(1)−C(13) = 108.64(9), C(11)−Al(1)−C(19) = 116.22(8), C(12)−Al(1)−C(13) = 114.03(8), C(12)−Al(1)−C(19) = 103.46(8), C(13)−Al(1)−C(19) = 112.58(8), C(25)−Al(2)−C(31) = 115.66(8), C(25)−Al(2)−C(37) = 99.60(7), C(25)−Al(2)−C(43) = 111.72(8), C(31)−Al(2)−C(37) = 112.67(8), C(31)−Al(2)−C(43) = 103.86(8), C(37)−Al(2)−C(43) = 113.77(8).

**Scheme 2**



free $[MeAl(C_6F_5)_3]^-$ anion at $Al(C_6F_5)_3$ to form the $\mu$-Me dialuminate complex.[6] Specifically, when nucleophilic moieties such as Me(Al) are absent within the aluminate moiety in **2**, a commonly regarded as chemically robust, resistant-to-electrophilic-attack $C_6F_5$ group attacks $Al(C_6F_5)_3$ to form the tetrakis(pentafluorophenyl)aluminate anion, $[Al(C_6F_5)_4]^-$, followed by nucleophilic linking of Me(Ta) to the resulting neutral alane, producing an $\mu$-Me, $\mu$-$CH_2$ tantalocene cation. Direct abstraction of either the Me(Ta) or the anionic $-CH_2Al(C_6F_5)_3$ moiety in **2** by excess $Al(C_6F_5)_3$ would generate a 14-electron tantalocene dication; however, this reaction produced no evidence for the formation of such a species, presumably due to instability of such a dication, steric inaccessibility of $Al(C_6F_5)_3$ to Me(Ta) or (Ta)$CH_2$(Al), or a combination of both factors.

The solid-state structure (Figure 4) determined by X-ray diffraction confirmed the molecular structure of **3**, shown in Scheme 2. There are two $CH_2Cl_2$ (crystallization solvent) molecules in the crystal lattice, and the cation $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+$ and tetrakis anion $[Al(C_6F_5)_4]^-$ exist as unassociated ion pairs. The metric parameters based on the located and refined hydrogens attached to the bridging carbons show no evidence for any α-agostic interaction. The Ta−$CH_2$ distance is notably shorter than the Ta−$CH_3$ distance by ~0.16 Å (Ta−C(11) = 2.129(2) Å, Ta−C(12) = 2.290(2) Å); this difference is more pronounced than that found in the zwitterionic tantalocene aluminate **2**, but the Ta−$CH_2$ distance in **3** is still longer than that in the parent complex $Cp_2Ta({=}CH_2)Me$[20] by ~0.1 Å. As one goes from **2** to **3**, which is accompanied by heterometallacycle formation, the Ta−$CH_2$ and Ta−$CH_3$ distances are shortened and lengthened by ~0.07 and 0.18 Å, respectively, while the Al−$CH_2$ distance is lengthened by ~0.1 Å. The Al−$CH_3$ distance in **3** (Al(1)−C(12) = 2.149(2) Å) is quite comparable to some of the Al−$CH_3$ (bridging) distances found in $(C_6F_5)_3Al_2(CH_3)_3$.[17a] Overall, these structural data argue that the cationic portion of **3** could be viewed as a hybrid of two extreme structures, $Cp_2Ta^+[CH_2Al(C_6F_5)_2]Me$ and $[Cp_2Ta({=}CH_2)MeAl(C_6F_5)_2]^+$; the latter structure, formally an adduct of the neutral Lewis acid $MeAl(C_6F_5)_2$ with the tantalocene methylidene cation $[Cp_2Ta({=}CH_2)]^+$ that is isoelectronic with neutral titanocenes methylidene complex $[Cp_2Ti({=}CH_2)]$, is particularly interesting because it resembles the Tebbe reagent $Cp_2Ti(CH_2)ClAlR_2$,[21] being considered an adduct of $[Cp_2Ti({=}CH_2)]$ with $ClAlR_2$.

---

[20] Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578−6579.

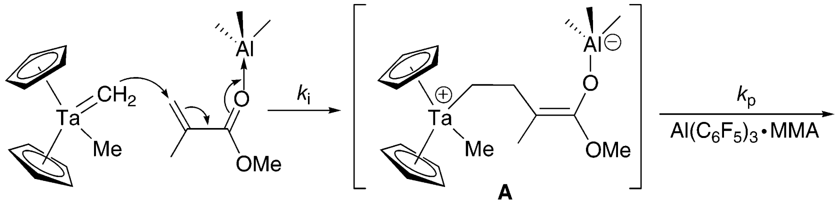
[21] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611−3613.

**Table 2. MMA Polymerization Results by $Cp_2Ta({=}CH_2)Me/2Al(C_6F_5)_3$ [a]**

| run no. | temp (°C) | activation mode | reacn solvent | yield (%) | $10^4M_n$ [b] (g/mol) | PDI[b] ($M_w/M_n$) | [*rr*][c] (%) | [*mr*][c] (%) | [*mm*][c] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 25 | monomer | toluene | 93 | 68.5 | 1.43 | 72.9 | 25.4 | 1.7 |
| 2 | 25 | monomer | DCB | 13 | 8.95 | 1.50 | 72.8 | 25.6 | 1.6 |
| 3 | 25 | complex | toluene | 0 | | | | | |
| 4 | 25 | complex | DCB | >99 | 41.5 | 1.65 | 72.0 | 26.2 | 1.8 |
| 5 | 0 | complex | DCB | >99 | 49.7 | 1.67 | 74.9 | 22.8 | 2.3 |

[a] Conditions: solvent, 5.0 mL; reaction time, 30 min; $[M]_0:[Al]_0:[Ta]_0 = 400:2:1$; monomer activation mode, addition of the premixed M + Al (5 min) to a Ta solution; complex activation mode, addition of M to the premixed Ta + Al solution (10 min); DCB = 1,2-dichlorobenzene. [b] Number average molecular weight ($M_n$) and polydispersity index (PDI) determined by GPC relative to PMMA standards. [c] Methyl triad distribution determined by $^1H$ NMR spectroscopy in $CDCl_3$.

**Scheme 3**



The scope of the reaction of the zwitterionic adducts $Cp_2Ta^+[CH_2E(C_6F_5)_3^-]Me$ with $E(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ has also been investigated. As mentioned earlier, there is no further reaction between $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$ and $B(C_6F_5)_3$. Treatment of $Cp_2Ta^+[CH_2Al(C_6F_5)_3^-]Me$ (**2**) with $[Ph_3C][B(C_6F_5)_4]$ in $CD_2Cl_2$ resulted in no reaction over 24 h, nor did mixing of **2** with $B(C_6F_5)_3$. Interestingly, when $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$ was treated with $Al(C_6F_5)_3$ in $C_6D_5Br$, the aluminate adduct **2** was gradually generated as a major product via apparent B/Al exchange within the $-CH_2B(C_6F_5)_3^-$ moiety (Scheme 1), with concomitant formation of $B(C_6F_5)_3$ and a minor amount of $[Al(C_6F_5)_4]^-$. Overall, the reaction type depicted in Scheme 2 seems to be specific to the aluminate/alane ($Al^-/Al$) pair: for example, the reaction of **2** with $Al(C_6F_5)_3$.

**Polymerization of MMA and DMAA.** Only the species derived from the alkylidene complex $Cp_2Ta({=}CH_2)Me$ were examined for the polymerization of MMA and DMAA in this study, whereas the MMA polymerization by the species derived from the alkyl complex $Cp_2TaMe_3$ had been previously investigated.[5] First, control runs with either $Cp_2Ta({=}CH_2)Me$ or $E(C_6F_5)_3$ (E = B, Al) alone under the polymerization conditions employed in this study (see Table 2) yielded no polymeric products. Second, the following complexes or systems also exhibited no activity for polymerization of MMA: adduct **2** (either isolated or readily generated by in situ mixing of $Cp_2Ta({=}CH_2)Me$ with 1 equiv of $Al(C_6F_5)_3$), complex **3** (with or without 1 equiv of $Al(C_6F_5)_3$), and the complex or mixture derived from the mixing of $Cp_2Ta({=}CH_2)Me$ with 1 or 2 equiv of $B(C_6F_5)_3$ (which generates $Cp_2Ta^+[CH_2B(C_6F_5)_3^-]Me$ or this complex plus the unreacted borane). Third, the system based on $Cp_2Ta({=}CH_2)Me$ and 2 equiv of $Al(C_6F_5)_3$ is, however, uniquely active for MMA polymerization, the results of which are summarized in Table 2 and discussed below.

Polymerization by the $Cp_2Ta({=}CH_2)Me/2Al(C_6F_5)_3$ system is highly sensitive to the reaction medium and addition sequence of the reagents involved. When the monomer activation mode (monomer is premixed with the alane followed by its addition to a Ta solution) is executed, the polymerization is highly active in toluene, producing a high-molecular-weight ($M_n = 6.85 \times 10^5$, $M_w/M_n = 1.43$) polymer of moderate syndiotacticity ([*rr*] = 72.9%) in 93% isolated yield within 30 min (run 1, Table 2). Interestingly, the polymer yield dropped significantly to only 13% for the same reaction time period when the solvent was changed from toluene to DCB (run 2 vs run 1). In contrast, when the complex activation mode (complex is premixed with the alane followed by addition of monomer) is employed, the polymerization in toluene is inactive, while the polymerization in DCB is highly active, giving a quantitative yield of polymer (run 4 vs run 3). Lowering the temperature of the polymerization in DCB from ambient temperature to 0 °C apparently did not affect the activity but notably increased the resulting polymer molecular weight and syndiotacticity (run 5 vs 4). Polymerization of DMAA in DCB follows the same trend, with high activity (>99% yield in 30 min) for the complex activation mode and no activity for the monomer activation mode.

The observation that neither $Cp_2Ta({=}CH_2)Me$ nor complexes **2** and **3** are active for MMA polymerization clearly points to the critical role played by $Al(C_6F_5)_3$ in the high activity of the $Cp_2Ta({=}CH_2)Me/2Al(C_6F_5)_3$ system. In the activated monomer polymerization, chain initiation presumably involves nucleophilic attack of the electron-rich methylidene moiety at the activated monomer $Al(C_6F_5)_3{\cdot}MMA$ to generate an active enolaluminate species[22] (**A**) that participates in the aluminate/alane bimolecular propagation steps, as depicted in Scheme 3. Attempts to acquire MALDI-TOF MS spectra of low-molecular-weight polymer samples for chain-end group analysis were unsuccessful because the molecular weights were still too high even with low [monomer]/[initiator] ratios of 50 and 20, indicative of the currently ill-controlled polymerization system. On the other hand, NMR monitoring of the reaction of $Cp_2Ta({=}CH_2)Me$ and $2Al(C_6F_5)_3$ premixed with 10 equiv of MMA in $C_7D_8$ showed the rapid formation of PMMA by $^1H$ NMR and three $C_6F_5$-group-containing aluminum species by $^{19}F$ NMR, including the neutral $Al(C_6F_5)_3{\cdot}MMA$ (or ·PMMA) adduct ($\delta$ −122.66 (*o*-F), −151.62 (*p*-F), −160.83 (*m*-F)) and the two anionic aluminate species **A** ($\delta$ −122.04 (*o*-F), −153.66 (*p*-F), −161.84 (*m*-F)) and **B** ($\delta$ −119.98 (*o*-F), −154.40 (*p*-F), −162.20 (*m*-F)). The $^{19}F$ NMR chemical shifts of **A** are consistent with an enol aluminate moiety, whereas those of **B** are consistent with its decomposition product, $[(C_6F_5)_3Al{-}OMe{-}Al(C_6F_5)_3]^-$. The reaction of $Cp_2Ta({=}CH_2)Me$ with 2 equiv of $Al(C_6F_5)_3{\cdot}MMA$ in $C_7D_8$ formed the same three alane and aluminate species, as shown by $^{19}F$ NMR, while the reaction in $CD_2Cl_2$ gave the majority of species **B**. Thus, the instability of such enol aluminate active species, especially in polar chlorinated solvents, explains the low initiator efficiency for

---

(22) Rodriguez-Delgado, A.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2005**, *127*, 961−974.

the polymerization in toluene and low monomer conversion for the reaction in DCB. On the other hand, in the activated complex polymerization, the relevant species of interest are in situ generated **2** and excess (1 equiv) $Al(C_6F_5)_3$, as the reaction of $Cp_2Ta({=}CH_2)Me$ with 2 equiv of $Al(C_6F_5)_3$ in $\leq$10 min produced these two species, plus a trace amount of **3**, which is inactive (as is the **3**/$Al(C_6F_5)_3$ system, vide supra). NMR monitoring of the reaction of $Cp_2Ta({=}CH_2)Me/2Al(C_6F_5)_3$ (i.e., **2**/$Al(C_6F_5)_3$) with 1 or 10 MMA in $C_6D_5Br$ indicated the formation of, in addition to **2**, the same aluminate species (**A** and **B**) as those observed in the reaction by the monomer activation sequence in $C_7D_8$, suggesting the same propagating species involved. However, the key difference is that in the activated complex polymerization the initiator $Cp_2Ta({=}CH_2)$ is "stored or trapped" as the transient adduct **2**, which can reactivate (reinitiate) the system in DCB when the enol aluminate active species is rapidly depleted by decomposition, thereby driving to a quantitative monomer conversion. Apparently, the initiation by the **2**/$Al(C_6F_5)_3$ system is not possible in toluene, as this system is inactive in this solvent.

## Conclusions

We have isolated and structurally characterized three cationic and zwitterionic tantalocene complexes, including $[Cp_2TaMe_2]^+[MeB(C_6F_5)_3]^-$ (**1**), $Cp_2Ta^+[CH_2Al(C_6F_5)_3{}^-]Me$ (**2**), and $[Cp_2Ta(CH_2)MeAl(C_6F_5)_2]^+[Al(C_6F_5)_4]^-$ (**3**), over the course of our reexamination of the reaction of $Cp_2TaMe_3$ with $E(C_6F_5)_3$ under various reaction conditions and investigation into the activation of the alkylidene complex $Cp_2Ta({=}CH_2)Me$ with $Al(C_6F_5)_3$. The combination of $Cp_2Ta({=}CH_2)Me$ with 2 equiv of $Al(C_6F_5)_3$ has been shown to be highly active for the polymerizations of MMA and DMAA, producing high-molecular-weight polymers via the proposed aluminate/alane bimolecular propagating process. The current investigation also corrected the previous erroneous attribution of the NMR signals derived from the liquid clathrate phase of ionic aggregates to the formation of the $\mu$-Me diborate species and presented a cautionary note when analyzing NMR spectra of ion pairs as phase-separated mixtures in certain NMR solvents. Perhaps the most interesting finding of this work is that complex **3** is formed apparently by unusual nucleophilic attack of a $C_6F_5$ group, commonly regarded as chemically robust, resistant to electrophilic attack, within the aluminate moiety in **2** at $Al(C_6F_5)_3$ present in excess to give the tetrakis aluminate anion $[Al(C_6F_5)_4]^-$, which somewhat resembles the formation of the $\mu$-Me dialuminate anion $[(C_6F_5)_3Al{-}Me{-}Al(C_6F_5)_3]^-$ by nucleophilic attack of the Me group within the free $[MeAl(C_6F_5)_3]^-$ anion at $Al(C_6F_5)_3$. The investigation into the scope of this unique reaction shows that it is specific to the aluminate/alane ($Al^-$/Al) pair; such anion reactivity may also apply to olefin polymerization systems where aluminum-containing anions are ubiquitous and aluminum LAs are typically present in excess with respect to the cation and anion.

**Acknowledgment.** Funding for this work was provided by the National Science Foundation and Colorado State University. We thank Prof. Scott Collins of the University of Akron for sharing results and insightful discussions with us, as well as Boulder Scientific Co. for the gift of $B(C_6F_5)_3$. W.R.M. and L.O.G. gratefully acknowledge an ARCS/Hach Graduate Fellowship and the NSF-REU program, respectively.

**Supporting Information Available:** Tables and CIF files giving crystallographic data for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060258J