

“Double Activation” of Constrained Geometry and *ansa*-Metallocene Group 4 Metal Dialkyls: Synthesis, Structure, and Olefin Polymerization Study of Mono- and Dicationic Aluminate Complexes

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Strong organo-Lewis acids such as $B(C_6F_5)_3$ and a number of its derivatives¹ play vital roles in generating highly active, single-site homogeneous olefin polymerization catalysts.² In sharp contrast, the aluminum analogue, $Al(C_6F_5)_3$,³ has attracted much less attention, despite its higher alkylidene affinity.^{4–6} Bochmann et al.⁵ have disclosed that, unlike relatively stable $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ complexes⁷ derived from methide abstraction from the zirconocene dimethyl by $B(C_6F_5)_3$,⁸ the aluminum analogue undergoes very facile C_6F_5 -transfer to Zr above 0 °C to form $Cp_2ZrMe(C_6F_5)$, resulting in diminished polymerization activity.

Cocatalytic systems derived from $Al(C_6F_5)_3$ in combination with a second component for high-temperature, homogeneous solution olefin polymerization processes have been previously described.⁹ We communicate here the very unusual cocatalytic features of $Al(C_6F_5)_3$.¹⁰ These attributes include the unprecedented “double activating” ability of $Al(C_6F_5)_3$ for the formation of dicationic group 4 constrained geometry¹¹ and *ansa*-metallocene¹² bis-aluminate complexes. In contrast to the $B(C_6F_5)_3$ activation, use of multiple equivalents of $Al(C_6F_5)_3$ substantially enhances exothermicities and efficiencies of olefin polymerization catalyzed by the constrained geometry and *ansa*-metallocene catalysts.

While donor-stabilized dicationic group 4 metal (M) complexes with a general formula of $[Cp_2MD_2]^{2+}X_2^-$ (D = neutral donor

ligand; X = anion) are known,¹³ isolation and characterization of dicationic structures absent of donor ligands are challenging and of great interest. Green et al.¹⁴ recently reported NMR spectroscopic evidence for the formation of a dication-like zirconocene stabilized by metal–arene interactions by treating $(p\text{-MeC}_6\text{H}_4\text{CMe}_2\text{Cp})_2\text{ZrMe}_2$ with 2 equiv of $B(C_6F_5)_3$ at –60 °C in CD_2Cl_2 which reverts to the monocationic species and neutral $B(C_6F_5)_3$ above –40 °C in solution. Most recently, Stephan et al.¹⁵ reported a crystallographically characterized non-Cp bis-borate-zwitterionic complex $[(t\text{Bu}_3\text{P}=\text{N})_2\text{Ti}\{\mu\text{-MeB(C}_6\text{F}_5)_3\}_2]$ generated from the reaction of $[(t\text{Bu}_3\text{P}=\text{N})_2\text{TiMe}_2]$ with an excess of $B(C_6F_5)_3$ in CH_2Cl_2 . The formation of such a species in the presence of excess $B(C_6F_5)_3$ was considered to be a catalyst deactivation pathway, as the bis-borate adduct exhibits negligible polymerization activity while the corresponding mono-borate adduct is a very active catalyst.

Although the reaction of $B(C_6F_5)_3$ with either the constrained geometry titanium dimethyl $Me_2Si(\eta^5\text{-Me}_4\text{C}_5)(t\text{-BuN})TiMe_2$ (CGC-TiMe₂) or the *ansa*-metallocene dimethyl *rac*- $Me_2Si(\eta^5\text{-Ind})_2\text{-ZrMe}_2$ (SBI-ZrMe₂) proceeds rapidly and quantitatively in hydrocarbon solvents to produce the corresponding monocationic complexes, reaction with an excess of $B(C_6F_5)_3$ does not affect the abstraction of the second CH_3^- group.¹⁶ This behavior is likewise observed for bis-Cp-type dimethyl zirconocenes⁷ and Cp-based titanocenes.¹⁵ However, unlike the reaction of Cp_2ZrMe_2 with $Al(C_6F_5)_3$, reaction of CGC-TiMe₂ and SBI-ZrMe₂ with 1 equiv of $Al(C_6F_5)_3$ proceeds cleanly in hydrocarbon solvents to produce the corresponding *stable* and *isolable* cationic complexes CGC-TiMe($\mu\text{-Me}$) $Al(C_6F_5)_3$ (**1**) and SBI-ZrMe($\mu\text{-Me}$) $Al(C_6F_5)_3$ (**2**), respectively.¹⁷ The substantially enhanced solution stability of these complexes ($t_{1/2}$ = 5 and 16 days for **1** and **2**, respectively, at room temperature) versus the bis-Cp analogue is attributable to stronger anion coordination to these sterically more open and coordinatively more unsaturated metal centers having *ansa*-bridged ligation. Singly activated species **1** and **2** exhibit lower olefin polymerization efficiencies than the borane analogues.

The crystal structure of complex **1**¹⁸ reveals the pseudo-tetrahedral coordination sphere about Ti. The Ti–CH₃ (bridging) distance is 2.332(3) Å which is longer than the Ti–CH₃ (terminal) distance by 0.235 Å. The Ti–H₃C–Al vector is nearly linear with an angle of 169.0(2)°. Another noteworthy feature of complex **1** is that two of the bridging methyl hydrogens exhibit relatively close contacts to Ti, with Ti–H distances of 2.21(3) and 2.24(3) Å and acute Ti–C(bridging)–H angles of 71(2) and 73(2)°, indicative of α -agostic interactions, compared to a nonbonding distance of 2.36 (3) Å for the third methyl hydrogen atom.

The most striking feature of the abstractive chemistry of $Al(C_6F_5)_3$ is its ability to effect the removal of the second metal–methyl groups to form the corresponding dicationic bis-aluminate complexes CGC-Ti[($\mu\text{-Me}$) $Al(C_6F_5)_3$]₂ (**3**) and SBI-Zr[($\mu\text{-Me}$) $Al(C_6F_5)_3$]₂ (**4**).¹⁷ Thus, addition of a second equivalent of $Al(C_6F_5)_3$ to a toluene solution of **1** or **2** causes an immediate color change from yellow **1** to orange **3** or from yellow **2** to deep red **4**. NMR spectroscopic data of **3** and **4** are consistent

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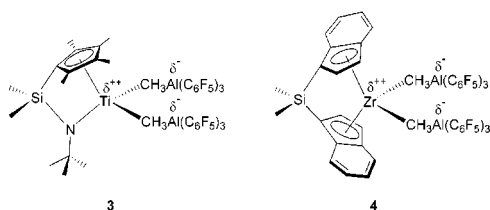
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(18) See Supporting Information for crystallographic data for **1**.

with symmetry changes of the complexes from previously C_1 -symmetric **1** and **2** to C_s -symmetric **3** and to C_2 -symmetric **4**, as a result of bis-aluminate adduct formation.¹⁷



A crystallographic study confirms the structure of the doubly activated dicationic bis-aluminate complex **4** (Figure 1)¹⁹ in which the two $\text{Al}(\text{C}_6\text{F}_5)_3$ groups are almost symmetrically bound to the two bridging methyl groups. The two $\text{Zr}-\text{H}_3\text{C}-\text{Al}$ vectors are close to linearity with angles of $163.3(2)$ and $169.7(1)^\circ$. The ionic character of **4** is unambiguously established by the $\text{Zr}-\text{CH}_3$ distances (2.431(2) Å and 2.454(2) Å) which are both substantially longer than the $\text{Zr}-\text{CH}_3$ (terminal) distances of 2.24(2) Å in an F-bridged aluminate complex $\text{SBI-ZrMe}^+(\text{PBA})^-$ ²⁰ and of 2.223(6) Å in $(\text{Me}_5\text{C}_5)_2\text{ZrCH}_3^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$,⁷ and by the relatively “normal” $\text{Al}-\text{CH}_3$ distances (2.084(2) Å and 2.059(2) Å), compared to the average $\text{Al}-\text{C}$ (aryl) distances (2.001(2) Å and 2.012(2) Å) in **4** and the $\text{Al}-\text{CH}_3$ distance (2.033(3) Å) in **1**. The positions of the hydrogen atoms of the μ -methyl groups in **4** were located and refined, and two of the three bridging methyl hydrogens of each μ -methyl group were slightly closer to the Zr center than the third by 0.17 Å, indicative of weak $\text{Zr}-\text{methyl}$ α -agostic interactions.

To investigate the influence of the catalyst double activation on polymerization characteristics, ethylene and 1-octene were copolymerized at 140°C using CGC-TiMe_2 and SBI-ZrMe_2 activated with one or multiple equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Al}(\text{C}_6\text{F}_5)_3$, respectively.¹⁶ In varying the $\text{B}(\text{C}_6\text{F}_5)_3$:pre-catalyst ratio from 1 to 4, polymerization characteristics are not noticeably affected, nor are the polymer properties (exotherm: $0.2-2.1^\circ\text{C}$; efficiency: $1.22-1.43$ g polymer/ μg Ti; M_w : $76.5-66.1$ K; density: $0.900-0.897$). In contrast, variation of the $\text{Al}(\text{C}_6\text{F}_5)_3$:pre-catalyst ratio from 1 to 4 causes substantially increased both initial polymerization exothermicity (from 0.3 to 30.6°C with the same amount of pre-catalyst or less) and overall polymerization efficiency (from 0.32 to 2.40 g polymer/ μg Ti).²¹ Similar low-density elastomers were produced in all cases but with noticeably higher molecular weights (by $\sim 50\%$ with narrow PDI of $1.96-2.06$), compared with polymers produced using $\text{B}(\text{C}_6\text{F}_5)_3$ activation. Likewise, similar polymerization behavior is observed with catalyst SBI-ZrMe_2 , which, however, produced relatively high-density polymers ($d = 0.926$). Multiple equivalents of $\text{Al}(\text{C}_6\text{F}_5)_3$ also very effectively activate *rac*-dimethylsilane-bis(2-methyl-4-phenylindenyl)zirconium(II)-1,4-diphenyl-1,3-butadiene²² in a $0.25/0.125$ μmol activator/pre-catalyst ratio to produce isotactic polypropylene of $T_m = 157.8^\circ\text{C}$ with 4.46×10^6 g polymer/g Zr efficiency at a 70°C polymerization temperature,

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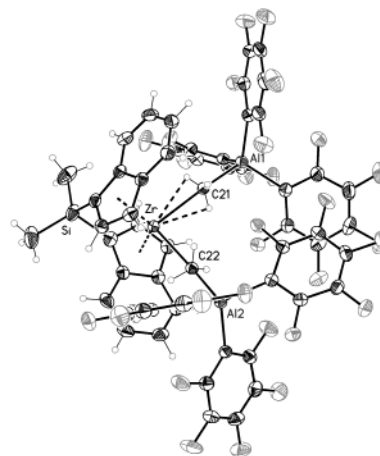
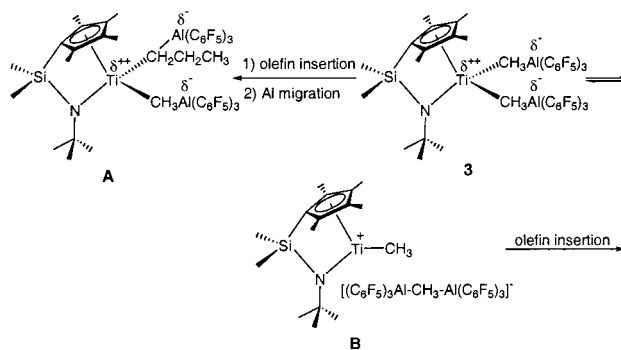


Figure 1. Molecular structure of **4**. The F atoms of the anion portion are not labeled for clarity.

compared to 0.14×10^6 g polymer/g Zr polymerization efficiency when activated with $\text{B}(\text{C}_6\text{F}_5)_3$ under similar conditions.

It is tempting to suggest that double activation lowers the initiation/propagation barriers via a pathway in which olefin inserts into either lengthened $\text{Ti}-\text{Me}$ bond, followed by migration of the Al moiety back to the Lewis basic α -carbon (A). Alternatively,



one can also speculate on the equilibrium formation of an ion pair (B) having a μ -Me bridged dinuclear anion $[(\text{C}_6\text{F}_5)_3\text{Al}-\text{CH}_3-\text{Al}(\text{C}_6\text{F}_5)_3]^-$ under high-temperature polymerization conditions. Although such species have not been detected in the activation chemistry of group 4 complexes, such anions paired with tantalocene cations have been observed and characterized by X-ray diffraction analysis in the activation of group 5 metallocenes.²³

Unlike $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Al}(\text{C}_6\text{F}_5)_3$ is capable of producing the dicationic constrained geometry and *ansa*-metallocene group 4 complexes which are far more efficient olefin polymerization catalysts than the corresponding mono-cationic catalysts.

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Supporting Information Available: Experimental details, complete X-ray crystallographic data for complexes **1** and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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