

Cationic Aluminum Alkyl Complexes Incorporating Amidinate Ligands. Transition-Metal-Free Ethylene Polymerization Catalysts

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Cationic aluminum species of the general type AlX_2^+ (L = neutral 2-electron donor, X = anionic 2-electron donor) and the corresponding base-stabilized adducts $\text{AlX}_2(\text{L}')^+$ (L' = labile Lewis base) are of interest for application in catalysis and synthesis because the combination of an electrophilic cationic Al center and a potentially reactive Al–X bond should promote coordination and activation of a range of substrates.¹ Known cationic aluminum compounds include 5- to 7-coordinate (chelate) AlX_2^+ species containing polydentate ether/amine or tetradentate Schiff-base ligands,^{2,3} 4-coordinate species incorporating chelating ligands,⁴ (amine)₂ AlX_2^+ compounds,⁵ $\text{AlX}_2(\text{THF})_4^+$ complexes ($\text{X} = \text{H}, \text{Cl}$),⁶ and $(\text{C}_5\text{R}_5)_2\text{Al}^+$ aluminocenium cations.⁷ Here we describe a strategy for the design of reactive 3-coordinate cationic aluminum alkyl compounds which are capable of polymerizing ethylene.

Neutral, d^0 , group 4 metal L_nMR_2 complexes (L_n = ancillary ligands, e.g. Cp_2) can be activated for olefin polymerization and other reactions by conversion to $\text{L}_n\text{MR}(\text{L}')^+$ or L_nMR^+ cations.⁸ We reasoned that $(\text{L}-\text{X})\text{AlR}_2$ compounds containing a suitable bidentate, monoanionic ancillary ligand $\text{L}-\text{X}^-$ could be ionized to $(\text{L}-\text{X})\text{AlR}(\text{L}')^+$ or $(\text{L}-\text{X})\text{AlR}^+$ cations using methods developed for transition metal systems. N,N' -Dialkylamidinates, $\text{RC}(\text{NR}')_2^-$, are attractive ligands for this application because they possess the correct charge and metal binding properties and can be sterically and electronically tuned by modification of the R and R' groups. Several neutral Al compounds containing $\text{MeC}(\text{NSiMe}_3)_2^-$, $\text{PhC}(\text{NSiMe}_3)_2^-$, or $\text{MeC}(\text{N}^i\text{Pr})_2^-$ ligands have been described,⁹ and we have developed general routes to $\{\text{RC}(\text{NR}')_2\}\text{AlMe}_2$ compounds ($\text{R} = \text{Me}, \text{R}' = ^i\text{Pr}, \text{Cy}; \text{R} = ^i\text{Bu}, \text{R}' = ^i\text{Pr}, \text{Cy}, \text{SiMe}_3$).¹⁰

The reaction of $\{\text{MeC}(\text{N}^i\text{Pr})_2\}\text{AlMe}_2$ (**1a**) with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ ¹¹ at 23 °C in CD_2Cl_2 results in the formation of a new aluminum complex, $[\mathbf{2a}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, and consumption of half of the boron activator (by ¹¹B NMR). The analogous reaction employing 0.5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ produces $[\mathbf{2a}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ in 83% isolated yield (white solid) with total consumption of the boron reagent. The reaction of **1a** and 1.0 or 0.5 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ¹² under similar conditions yields $[\mathbf{2a}][\text{B}(\text{C}_6\text{F}_5)_4]$ and MeCPh_3 . The variable temperature ¹H and ¹³C NMR spectra of $[\mathbf{2a}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ and $[\mathbf{2a}][\text{B}(\text{C}_6\text{F}_5)_4]$ are identical except for the anion resonances, and establish that **2a**⁺ is the dinuclear Me-bridged cation $\{[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlMe}_2(\mu\text{-Me})\}^+$ (Scheme 1). The –20 °C ¹H NMR spectrum of **2a**⁺ contains two singlets at δ –0.15 and –0.57 in a 2:1 intensity ratio, which are assigned to the terminal and bridging methyl groups, respectively. These signals coalesce to a broad singlet (δ –0.38) at 23 °C, indicating that bridge/terminal methyl exchange is rapid under these conditions. The ¹H NMR spectrum of a solution of $[\mathbf{2a}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ containing 0.5 equiv of **1a** ($\text{CD}_2\text{-Cl}_2$, 23 °C) contains resonances for each component which are identical with those observed for separate solutions of the components, implying that the bridge/terminal exchange of **2a**⁺ is intramolecular. ¹H NMR spectra of **2a**⁺ below –60 °C are more complex and are consistent with the presence of a 1:1 mixture of two slowly exchanging rotamers (anti-Me and gauche-Me).¹³

The formation of **2a**⁺ from **1a** involves initial generation of the 3-coordinate $\{\text{MeC}(\text{N}^i\text{Pr})_2\}\text{AlMe}^+$ cation, which is rapidly trapped by adduct formation with **1a**. Bochmann found that analogous metallocene species $\{\text{Cp}_2\text{M}(\text{Me})\}_2(\mu\text{-Me})^+$ ($\text{M} = \text{Ti}, \text{Cp} = \text{indenyl}; \text{M} = \text{Zr or Hf}, \text{Cp} = \text{C}_5\text{H}_5, \text{Me}_2\text{Si}(\text{indenyl})_2 \text{ or } \text{C}_2\text{H}_4(\text{indenyl})_2$), are formed in a similar manner; however, in contrast to **2a**⁺, these species are converted to $\text{Cp}_2\text{M}(\text{Me})^+$ cations by reaction with additional activator under mild conditions.¹⁴ Recently Marks isolated several dinuclear cationic metallocenes of this type.¹⁵

Replacement of the amidinate methyl substituent of **1a** by a ^tBu group in **3a,b** (Scheme 2) causes an 8° reduction in the Al–N–R' bond angles and thus increases the steric congestion at Al.¹⁰ We anticipated that this effect would disfavor the formation of dinuclear cations. Indeed, the reaction of **3a,b** with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ generates the base free ion pairs $\{[{}^t\text{BuC}(\text{NR}')_2]\text{AlMe}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**4a,b**) in quantitative NMR yield (Scheme 2). The ¹H and ¹³C NMR spectra of **4a,b** contain resonances for the NR' groups which are consistent with C_s -symmetric structures. The ¹H NMR spectra (CD_2Cl_2 , 23 °C) of **4a** and **4b** both contain a $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ resonance at δ 1.67, which is significantly downfield from the free anion resonance (δ 0.5).¹¹ Additionally, the ¹³C and ¹⁹F NMR spectra of **4a,b** contain two sets of C_6F_5 resonances (2:1 ratio in the ¹⁹F NMR spectrum). These data for **4a,b** are consistent with structures in which the anion coordinates to Al by a B–Me–Al bridge and rotation about the B–Me–Al linkage is slow due to steric crowding. Initial efforts to isolate **4b** gave $\{^t\text{BuC}(\text{NCy})_2\}\text{Al}(\text{Me})(\text{C}_6\text{F}_5)$, showing that anion degradation can occur in these systems. Efforts to isolate **4a,b** are continuing.

Lewis base adducts $\{\text{RC}(\text{NR}')_2\}\text{Al}(\text{Me})(\text{L}')^+$ have been

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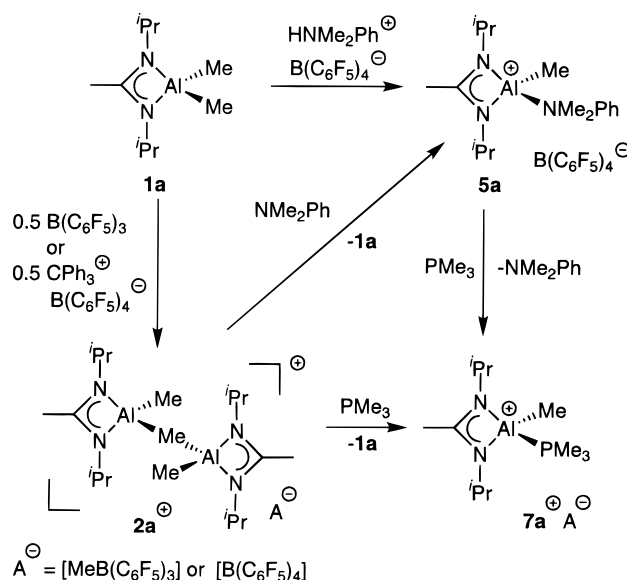
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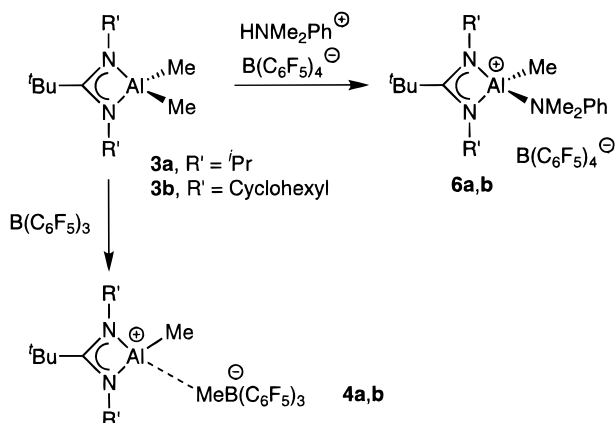
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Scheme 1



Scheme 2



generated in NMR scale reactions. The reactions of **1a** or **3a,b** with 1 equiv of $[HNMe_2Ph][B(C_6F_5)_4]$ ¹⁶ yield the corresponding amine adducts $\{[RC(NR')_2]Al(Me)(NMe_2Ph)\}[B(C_6F_5)_4]$ (**5a**, **6a,b**; Schemes 1 and 2). The ¹H and ¹³C NMR spectra of **5a** and **6a,b** (23 °C) contain amine resonances which are shifted from those of the free amine, and resonances for the R' groups which imply C_s-symmetric structures. These results are consistent with amine coordination to Al. The reaction of **[2a]**- $[MeB(C_6F_5)_3]$ with 0.5 equiv of NMe₂Ph generates a 1:1 mixture of **1a** and **5a**. Similarly, the reaction of **[2a]**- $[MeB(C_6F_5)_3]$ or **5a** with excess PMe₃ generates the phosphine adduct $\{[MeC(N^iPr)_2]AlMe(PMe_3)\}[A^-]$ (**7a**⁺, A⁻ = MeB(C₆F₅)₃⁻ or B(C₆F₅)₄⁻), with liberation of 1 equiv of **1a** or NMe₂Ph. These ligand exchange reactions show that the order of Lewis basicity toward $\{MeC(N^iPr)_2\}AlMe^+$ is PMe₃ > NMe₂Ph > **1a** > A⁻.

One potential application of $\{RC(NR')_2\}AlR^+$ cations is as transition-metal-free olefin polymerization catalysts. Neutral aluminum alkyls catalyze the oligomerization of ethylene to C₈–C₁₄ α-olefins at ethylene pressures above 80 atm and temperatures of 90–120 °C.¹⁷ Monomeric AlR₃ species catalyze the chain growth by repetitive insertion, and the low molecular weight results from rapid β-H elimination.^{1a,18} Recently, on the basis of comparisons of group 4 metal Cp₂MR⁺ and (C₂B₉H₁₁)CpMR catalysts, we proposed that a cationic charge on the active species should inhibit β-H elimination by

strengthening the M–C bond (other factors being equal).¹⁹ In initial studies, we have found that CD₂Cl₂ solutions of **[2a]**- $[MeB(C_6F_5)_3]$ (50 °C) or **4a** (23 °C) polymerize ethylene (≤1 atm) with low activity. Toluene solutions of **4a** polymerize ethylene (2 atm) to solid polyethylene at 60 °C (activity = 700 g PE/(mol·h·atm); M_w = 176 100; M_w/M_n = 2.84; DSC mp 138.2 °C). More active catalysts are generated by activation of **3a** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in toluene (2 atm of ethylene; 60 °C: activity 2480 g PE/(mol·h·atm); M_w = 272 200; M_w/M_n = 3.30; DSC mp 139.6 °C; 85 °C: activity 3050 g PE/(mol·h·atm); M_w = 184 700; M_w/M_n = 2.23; DSC mp 138.2 °C). Our current interpretation of these results is that 3-coordinate $\{RC(NR')_2\}AlR^+$ cations are the active species in these polymerizations, and that the activities are strongly influenced by coordination of $\{RC(NR')_2\}AlMe_2$ or A⁻ to these species and, in the MeB(C₆F₅)₃ systems, by anion degradation. The high molecular weights and narrow molecular weight distributions are consistent with a single site catalyst with a high $k_{chain-growth}/k_{chain-transfer}$ ratio.

This work establishes that $\{MeC(N^iPr)_2\}AlMe_2(\mu-Me)^+$ and $\{RC(NR')_2\}AlMe(L)^+$ cations and $\{[{}^tBuC(NR')_2]AlMe\}[MeB(C_6F_5)_3]$ ion pairs are formed by alkyl abstraction from $\{RC(NR')_2\}AlMe_2$, and suggests that $\{RC(NR')_2\}AlR^+$ cations are active species in ethylene polymerization. Efforts to isolate base free $\{[RC(NR')_2]AlR\}[A]$ salts and to develop even more reactive Al-based catalysts are in progress.

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Supporting Information Available: Synthetic procedures, characterization data for new compounds, and a listing of ethylene polymerization results (10 pages). See any current masthead page for ordering and Internet access instructions.

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