

Simple Generation of Cationic Aluminum Alkyls and Alkoxides Based on the Pendant Arm Tridentate Schiff Base

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The prepared in situ methyl(chloro)aluminum complex (**2**) from Me_2AlCl and the pendant arm tridentate Schiff base (H-SchNMe_2) was used to generate the methylaluminum cationic species $[(\text{SchNMe}_2)\text{AlMe}]^+$ in further reaction with 1 equiv of AlCl_3 or NaBPh_4 as the chloride abstracting reagents. The exposure of the resulting methylaluminum cationic species to an excess of dry dioxygen at 0°C afforded the alkoxyaluminum cationic species, $[(\text{SchNMe}_2)\text{AlOMe}]^+$ or $[(\text{SchNMe}_2)\text{AlOPh}]^+$. The alkoxyaluminum cations proved to be a very efficient catalyst in the polymerization of ϵ -caprolactone.

Cationic aluminum complexes have been very intensively investigated over the past few years with the main aim of developing catalysts for the polymerization of olefins.^{1–3} A range of neutral dialkylaluminum chelate complexes containing N,N -1 and O,N -bidentate² as well as N,N,N -3 and O,N,N -tridentate⁴ spectator ligands have been used to generate three- or four-coordinate alkylaluminum cationic complexes upon further reaction with $[\text{CPh}_3][\text{BPh}_4]$, $[\text{HNMe}_2\text{Ph}]$, $[\text{B}(\text{C}_6\text{F}_5)_4]$, or $\text{B}(\text{C}_6\text{F}_5)_3$ as the alkyl abstracting reagents. These various cationic aluminum alkyls were found to be active to a certain

degree in the polymerization of ethylene,^{1a,b,f–h,2b,3,4a,5} methyl methacrylate,^{1a,g,i} or heterocyclic monomers.^{1g,i,2b} Nevertheless, knowledge about the reactivity and potential application of these species is very limited, and undoubtedly, the chemistry of well-defined cationic aluminum alkyls is just emerging.⁶ On the other hand, aluminum alkoxides have attracted much attention on account of their rich structural and bonding features and potential applications. However, cationic aluminum species with a terminal alkoxide or aryloxy group are lacking, and only very recently, Jordan reported the synthesis and molecular structure of the first example of cationic dinuclear species with the bridging alkoxide group, $\{(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-O}^i\text{Pr})\}_2^{2+}$ ($\text{ATI} = N,N$ -diisopropylamino-troponimate ligand).^{1d} Herein we describe a simple method for the synthesis of alkylaluminum and alkoxyaluminum cationic species employing inexpensive reagents as well as demonstrate that the resulting alkoxyaluminum cations are very efficient catalyst in the polymerization of ϵ -caprolactone.

Treatment of Me_2AlCl with 1 equiv of pendant arm tridentate Schiff base **1** (H-SchNMe_2) at low temperature afforded the putative methyl(chloro)aluminum complex **2** (Scheme 1). The prepared in situ **2** was used to generate the methylaluminum cationic species in further reaction with 1 equiv of AlCl_3 or NaBPh_4 as the chloride abstracting reagent.^{7,8} The reaction with AlCl_3 proceeded smoothly at

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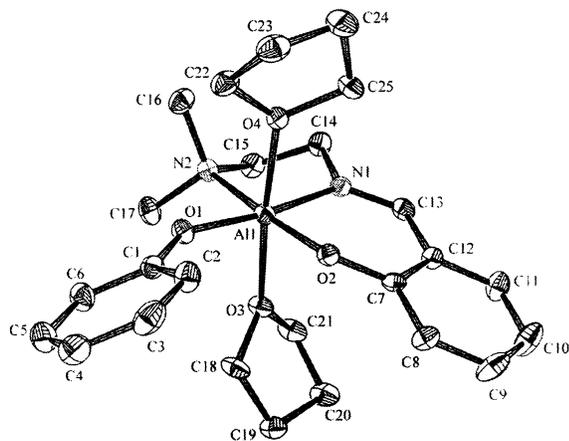


Figure 1. Molecular structure of the [(Sch-NMe₂)Al(OPh)(THF)₂]⁺ cation as 30% ellipsoids; BPh₄⁻ anion is omitted for clarity.

C=N group.¹³ The latter fact is well expressed by a marked difference between the two Al–N bonds, with that to the imine nitrogen being significantly shorter (1.985(2) Å) than that to the amine nitrogen (2.122(2) Å). The multinuclear NMR spectra are consistent with the solid-state structure being maintained in solution (Supporting Information). According to our knowledge, compound **8** comprises the first structurally authenticated mononuclear cationic aluminum species with a terminal alkoxide group. While we have not succeeded in the structure characterization of “base-free” **6** and **7**, the molecular structure of **8** is not less interesting than the former compounds as it mimics a potential intermediate in the ring-opening polymerization of heterocyclic monomers.

Indeed, compounds **6** and **7**, resulting from the oxygenation of a mixture of **4** and **5**, appeared to be highly reactive in the polymerization of ϵ -caprolactone (ϵ -CL). The polymerization took place rapidly (Al/ ϵ -CL = 1/50, temp = 40 °C), and the great increase in viscosity of the solution was observed after 15 min with 95% conversion after 1 h. For example, the MALDI TOF spectrum of P- ϵ -CL obtained with generated in situ cationic alkoxides **6** and **7** as initiators shows two sets of signals, each one representing the monomodal weight distribution with 114 Da mass difference (M_w/M_n , 1.30) (Figure 2). The masses of residual groups were found to be 32 and 94 Da, which correspond to a hydroxy group and methyl ester and phenyl ester end-groups, respectively. Interestingly, when the putative salt [(SchNMe₂)-

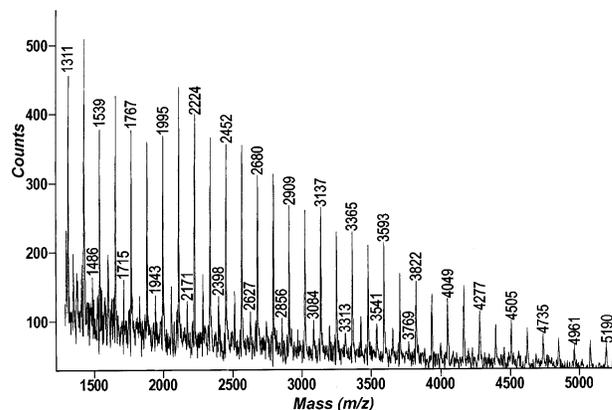


Figure 2. MALDI TOF spectrum of polycaprolactone obtained with the mixture of **6** and **7** as initiators.

AlOMe][AlCl₄] (**9**) (the product resulting from the oxygenation of **3**) was used as catalyst for polymerization of ϵ -CL, the MALDI TOF spectrum of the resulting P- ϵ -CL revealed one set of signals with monomodal weight distribution (M_w/M_n , 1.24) and the end-group of 32 Da corresponding to a hydroxy and a methyl ester group (Figure 1S, Supporting Information). These data also demonstrate that only the terminal alkoxide or aryloxide group is involved in the polymerization process and the aryloxide associated with the Schiff base ligand acts as a spectator functionality, which is consistent with the already mentioned weakening of the Lewis basicity of this aryloxide oxygen. The above observations additionally confirm the presence of an equilibrium between **4** and **5** (Scheme 2), as well as strongly indicate that both the Al–Me and Al–Ph bonds undergo oxidation to the Al–OMe and Al–OPh units, which are able to initiate the polymerization of ϵ -CL.

In conclusion, we have found a simple and relatively inexpensive method for the generation of alkylaluminum and alkoxyaluminum cationic species, based on readily available organoaluminum Schiff base complexes and effective anion abstractors such as AlCl₃ or NaBPh₄. The resulting alkoxide cationic species appeared to be very efficient initiators in the polymerization of ϵ -caprolactone.

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Supporting Information Available: Text giving synthetic procedures and characterization of **2–9**, MALDI-TOF spectrum of polycaprolactone obtained with **9** as catalyst, and X-ray crystallographic files for **8** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) For an extended discussion on the role of the π -interaction within the salicylideneimine extended π -system on the structure of the group 13 organometallic complexes, see: Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopeć, T.; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *22*, 3773.