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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 $[(SchNMe_2)AlMe]^+$ 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, $[(SchNMe_2)AlOMe]^+$ or $[(SchNMe_2)AlOPh]^+$. The alkoxylaluminum 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*-bidentate[2] as well as *N*,*N*,*N*-[3] and *O*,*N*,*N*-tridentate[4] spectator ligands have been used to generate three- or four-coordinate alkylaluminum cationic complexes upon further reaction with $[CPh_3][BPh_4]$, $[HNMe_2Ph]$, $[B(C_6F_5)_4]$, or $B(C_6F_5)_3$ 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 aryloxide 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, $\{(^iPr_2\text{-ATI})Al(\mu\text{-}O^iPr)\}_2^{2+}$ (ATI = *N*,*N*-diisopropylamino-troponiminate 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 alkoxylaluminum 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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(7) It is worth noting that, for example, attempts of Nöth and co-workers to prepare the low-coordinate aluminum cations by reaction of the aluminum halide adducts with $NaBPh_4$ were unsuccessful and resulted in phenylation products: Krossing, I.; Nöth, H.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* **1998**, 927.

(8) The chloride was abstracted from higher-coordinate salen-type (N_2O_2)-AlCl complexes to form higher coordinate cationic aluminum complexes; see for example ref 6.

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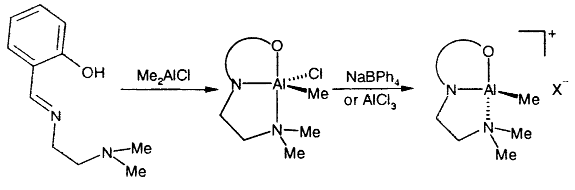
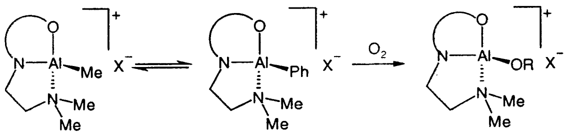
Scheme 1



1 2 X = $AlCl_4$ (**3**) or BPh_4 (**4**)

ambient temperature, while that with $NaBPh_4$ required prolonged reaction time. The resulting ionic compounds $[(SchNMe_2)AlMe][AlCl_4]$ (**3**) and $[(SchNMe_2)AlMe][BPh_4]$ (**4**) were characterized by multinuclear NMR spectroscopy. The ^1H NMR spectrum of **3** shows a sharp singlet at −0.82 ppm due to the Al−Me protons. The ionic character of salt **3** is evidenced by the ^{27}Al NMR spectrum, which shows two signals at 102 ppm ($w_{1/2} = 60$ Hz) and 97 ppm ($w_{1/2} = 100$ Hz). The lower field sharp signal is characteristic for the $AlCl_4^-$ anion,[9] which nicely confirms the abstraction of the Cl^- anion from **2**. The second resonace was assigned to the $[(SchNMe_2)AlMe]^+$ cation; however, the observed chemical shift is not univocally indicative for the metal center coordination number, and does not allow us to distinguish between the monomeric or higher coordinate cationic species. We note that the tendency of methylaluminum cations supported by the O,N-bidentate Schiff base to form the dimeric species was recently nicely demonstrated by Dagorne et al.[2b] In the case of the reaction involving $NaBPh_4$, the ^{11}B NMR spectrum of the postreaction mixture revealed the presence of two sharp signals at −6.6 ppm ($w_{1/2} = 20$ Hz) and at −11.7 ppm ($w_{1/2} = 37$ Hz) corresponding to the BPh_4^- and $BMePh_3^-$ anions, respectively.[9] However, the corresponding ^1H NMR spectrum is relatively complex in contrast to that of **3**, and several signals in the region characteristic for Al−Me protons, two broad signals of the B−Me protons, and two well resolved singlets of the CH=N proton could be distinguished. The above observations imply the presence of two cationic species, $[(SchNMe_2)AlMe]^+$ and $[(SchNMe_2)AlPh]^+$ (Scheme 2), which was further confirmed by the oxygenation and polymerization reactions (vide infra). Furthermore, a complex character of the ^1H NMR spectrum may also suggest the presence of higher aggregates in solution (vide supra). Unfortunately, difficulties in isolating the alkylaluminum ionic species precluded their structural characterization by X-ray crystallography.

Scheme 2



4, X = BPh_4 **5**, X = $MeBPh_3$ R = Me (**6**) or Ph(**7**), X = BPh_4 or $MeBPh_3$

There has been our continued interest in the controlled oxygenation of main group metal alkyls,[10] which may be regarded as one of the most promising methods for the synthesis of metal alkoxides. Thus, we examined the interaction of the methylaluminum cations with dioxygen. The exposure of the methylene chloride solution of **4** and **5** to an excess of dry O_2 at 0 °C for several hours affords a mixture of alkoxyaluminum cationic species, $[(SchNMe_2)AlOMe]^+$ (**6**) and $[(SchNMe_2)AlOPh]^+$ (**7**) (Scheme 2). The ^1H NMR spectrum of the postreaction mixture reveals the presence of a methyl group bound to oxygen and the lack of the Al−Me group, which implies complete oxygenation of the Al−C bond. The ^{27}Al NMR spectrum contains a single resonance at 35 ppm, which indicates the presence of a five-coordinate aluminum center.[9] The latter result suggests that the $[(SchNMe_2)AlOR]^+$ species might adopt a weakly associated dimeric structure with bridging alkoxide groups. The ^{11}B NMR spectrum of the postreaction mixture shows two resonances characteristic for BPh_4^- and $BMePh_3^-$ anions, which confirms the presence of an equilibrium between **4** and **5** in solution (Scheme 2). We were not able to obtain crystals of **6** or **7** suitable for X-ray crystallography using aromatic solvents. However, the corresponding crystalline material was obtained from a THF solution, and the X-ray analysis revealed a new salt, $[(SchNMe_2)Al(OPh)(THF)_2][BPh_4]$ (**8**) (Figure 1).[11]

The six-coordinate aluminum center in the $[(SchNMe_2)Al(OPh)(THF)_2]^+$ cation is stabilized by the tridentate Schiff base, occupying equatorial positions along with the phenoxy group, and two THF molecules in axial positions. The Al−O distances associated with THF are long at 2.024(2) and 2.062(2) Å. The terminal aryloxide Al−O(1) distance of 1.760(2) Å is short and is only marginally longer than the corresponding distances previously reported for neutral, monomeric, four-coordinate, sterically crowded aluminum aryloxides.[12] The aryloxide Al−O(2) distance (1.813(2) Å) associated with the Schiff base ligand is slightly longer and is controlled by the π-interaction of the aryloxide oxygen lone pair with the salicylideneimine extended π-system which substantially weakens the Lewis basicity of the oxygen atom and simultaneously strengthens the basicity of the chelating

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(11) Crystal data for $[(SchNMe_2)Al(OPh)(THF)_2][BPh_4]$ (**8**), $C_{49}H_{56}Al_1B_1N_2O_4\ C_4H_8O$: triclinic, space group $P1$ (No. 2), $a = 12.2830(2)$ Å, $b = 12.6830(2)$ Å, $c = 15.1880(3)$ Å, $\alpha = 87.6130(10)°$, $\beta = 68.9840(10)°$, $\gamma = 88.8800(10)°$, $U = 2206.73(7)$ Å^3, $Z = 2$, $F(000) = 466$, $D_c = 0.655$ g m^3, R1 = 0.0445, wR2 = 0.0853 for 3695 reflections with $I_o > 2\sigma(I_o)$. The structure was solved by direct methods using the SHELXS97 program (Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1997) and was refined by full-matrix least-squares on F^2 using the program SHELXL97 (Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1997). H-atoms were included in idealized positions and refined isotropically. The GOF on F^2 was equal to 1.080. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the final stage of refinment. The residual electron density = 0.25/−0.26 e Å^{-3}.

(12) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63.

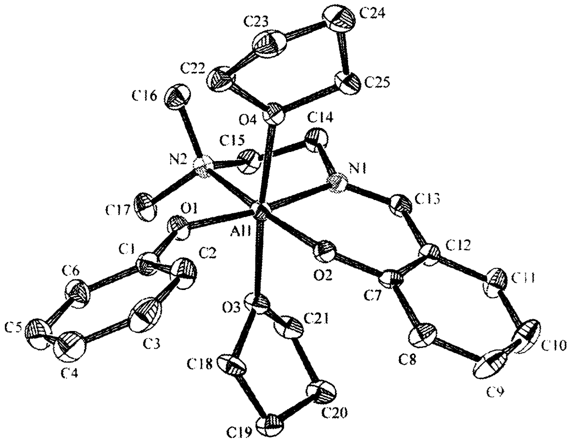

Figure 1. Molecular structure of the $[(\text{Sch-NMe}_2)\text{Al(OPh)(THF)}_2]^+$ cation as 30% elipsoids; BPh_4^- anion is omitted for clearity.

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 mixtrure 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 $[(\text{SchNMe}_2)\text{AlOMe}][\text{AlCl}_4]$ (**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.

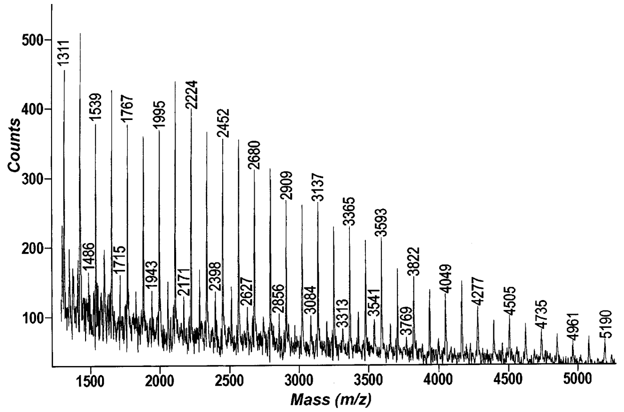

Figure 2. MALDI TOF spectrum of polycaprolactone obtained with the mixture of **6** and **7** as initiators.

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 Shiff base complexes and effective anion abstractors such as AlCl_3 or NaBPh_4. 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.