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Methoxyaryl substituted aluminum ketiminate complexes and its activity in ring opening polymerization processes

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ABSTRACT

The synthesis of dimethyl aluminum ($\mathbf{L^oAlMe_2}$) and chloromethyl aluminum ($\mathbf{L^oAlMeCl}$) complexes containing ketiminate ligand $[(2\text{-MeO})C_6H_4]N(H)C(Me) = CHC(Me) = O$ (L^oH) is reported along with the preparation of $\mathbf{L^o{}_3Al}$ from L^oH and $LiAlH_4$, and ionic $\mathbf{[L^{o\prime}Al(thf)_3]I}$ from $\mathbf{L^oAlMe_2}$ and I_2. In the later complex the pseudooctahedral geometry of the aluminum ion by terdentate ligand $\{[(2\text{-O})C_6H_4]NC(Me) = CHC(Me) = O\}^{2-}$ ($L^{o\prime}$), originated from L^o ligand by the methyl group abstraction, and three THF molecules are observed. Structures of these complexes were determined by X-ray techniques. The activity of $\mathbf{L^oAlMe_2}$ and $\mathbf{L^oAlMeCl}$ as initiators of ring opening polymerization of ε-caprolactone, trimethylene carbonate and L-lactide, and (co)polymerization of cyclohexene oxide and carbon dioxide was studied.

Coordination compounds of main group metals nowadays serve in a vast majority of catalytically driven organic chemistry transformations as well as the single site precursors for material chemistry applications. The necessity for stabilization of usually very reactive Lewis acid centers by a variety of ligands led to the development and great success of Schiff base and derived Salen and Salen-like ligands [1]. Further discoveries have prompted the research in the area of β-diketiminate ligands which are structurally related to the Salen ones but much higher delocalization of π-electrons is expected through the diaza metalla core (Scheme 1A). A logical step would be to combine both these systems in the ketiminate ligand and use them for similar applications in order to compare structure of complexes, reactivity and catalytic activity of prepared species. One could expect slightly asymmetric bonding of the ligand with open space for extra coordination of adjacent donors to the metal center from the oxo side and thus the enhanced reactivity, and moreover a cooperative effect of possible coordination to the second metal in a bimetallic or "ate" system. Next, the free ligands are easily prepared by addition of 1,3-dione or its aldol derivative with one equivalent of an amine (most likely a bulky aniline). One of the most studied main group elements in this respect is aluminum which is able in the form of its Schiff base/Salen [1,2] or β-diketiminate complexes that catalyze several organic chemistry transformations, and even mononuclear Al(I) species [3] with great synthetic potential could be synthesized. In the series of ketiminate ligands, various complexes were prepared and structurally characterized. Bifunctional ketiminate aluminum complexes, in terms of the presence of an extra donor site in the chain or ring system of the nitrogen substituent, have also been reported [4]. The extra donors could be employed in the form of neutral amino- or oxo-groups or negatively charged alkoxy or phenoxy substituent where a formation of five- or six-membered cycle with coordinated or covalently bound aluminum is reported. The main application observed for this class of complexes is a polymerization leading to biodegradable polymers [5].

In this paper, we report the synthesis, structure and activity of bifunctional aluminum ketiminate complexes for ring opening polymerization of ε-caprolactone, trimethylene carbonate and L-lactide and (co)polymerization of epoxides and CO_2.

The desired aluminum(III) ketiminate complexes were prepared by a straightforward method via the methane or dihydrogen elimination (Scheme 2) pathways from L^oH. The first reaction led to the formation of complexes $\mathbf{L^oAlMe_2}$ and $\mathbf{L^oAlMeCl}$, respectively, in moderate yield. On the other hand, in the case of attempts to synthesize aluminum hydrido complexes via the reaction of L^oH with $LiAlH_4$, a mixture of compounds which are presumably composed of two L^o ligands and an aluminum hydride was obtained. Along with these species, the single crystalline material of $\mathbf{L^o{}_3Al}$ was obtained in about 30% yield. To the best of our knowledge, the first tri(ketiminate) aluminum complex analogous to $\mathbf{L^o{}_3Al}$ has been prepared very recently from ketimine and $AlMe_3$ under harsh conditions [6]. The last reaction has been performed, according to the literature [7], in order to prepare the diiodo aluminum complex from $\mathbf{L^oAlMe_2}$ and diiodine. In this case, an immediate reaction was observed visually, but the isolated product was surprisingly $\mathbf{[L^{o\prime}Al(thf)_3]I}$ (Scheme 2) as a product of abstraction of methyl groups

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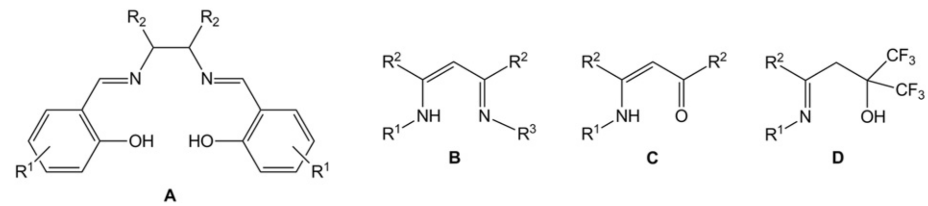
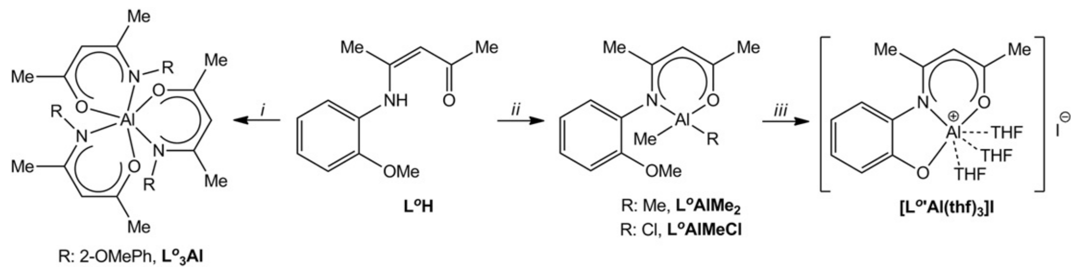


Scheme 1. Types of discussed *N*,*O*- and *N*,*N*-chelating proligands; A) Salen, B) β-diketimine, C) ketimine and D) Schiff base.



Scheme 2. Reaction pathways, *i*) $^1/_3$ $LiAlH_4$/$-^1/_3$ LiH, H_2; *ii*) $AlMe_3$ or $AlMe_2Cl$/$-CH_4$; *iii*) I_2/THF (prepared from **L°AlMe₂**).

from the aluminum atom as well as from the ligand's methoxy substituent, and thus the novel five membered alumina-aza-oxa cycle is formed via the covalent bond. Similar process was observed earlier for abstraction of methyl group promoted by a presence of a Lewis acid [7a,8].

Measured ^{1}H and ^{13}C NMR spectra (see Supplementary information) of both compounds containing one ketiminate ligand, and its comparison with the spectra of free L°H, proved the formation of complexes of suggested geometry with pseudotetrahedral vicinity of Al atoms and the methoxy group being non-coordinated. This is well visible from the chemical shift values of resonances (~3.3 ppm in ^{1}H and ~55 ppm in ^{13}C NMR spectra) attributed to the methoxy group which is practically the same as is found for L°H. The resonances (~ −0.4/−11 ppm) for methyl groups attached to the aluminum center are very close to the values found for similar complexes [7,9]. Nearly the same comparison can be carried out for resonances of the middle CH group of NC_3O skeleton (~5/100 ppm). On the other hand the resonances which were assigned to the carbonyl group are shifted in these complexes from values for L°H (195.4 ppm) to 182 ppm which resemble the contribution of the electron density of the oxygen atom to the bidentate coordination of the ligand to the metal. In cases of the rest of the complexes only broad resonances were observed in both ^{1}H and ^{13}C NMR spectra probably as a product of a dynamic behavior in solution. Attempts to measure more resolved ^{1}H NMR spectra of **L°₃Al** in solution of THF-d_8 at variable temperatures failed because of its low solubility at low temperatures. As already reported [7a], also the signals found in the spectra of **[L°′Al(thf)₃]I** are not well resolved, probably due to the changing number of coordinated THF molecules.

Structures of **L°AlMe₂** and **L°AlMeCl** were determined in the solid state on a single crystalline material revealing the pseudotetrahedral geometries of aluminum in both compounds (Figs. 1 and 2). The characteristic interatomic distances and angles found for that compounds, Al1–N1 and O1–Al1, are similar as analogous distances found in the literature for corresponding complexes [9,10] from the separations of N1–C3, C2–C1 and C1–O1 atoms, respectively; one can conclude that the localization of the π-electron density is taking place between those atoms in the central ring system.

The last two complexes, **L°₃Al** and **[L°′Al(thf)₃]I** (Figs. 3 and 4), have the deformed octahedral coordination vicinity of the aluminum atom, with three nearly iso-bidentately bound ligands in the first case, and a terdentate ligand, ketimine and phenolate, together with three THF molecules around the aluminum cation which is compensated by iodine anion in the second case. The only reported compound with three ketiminate ligands, prepared by the reaction of trimethyl aluminum and

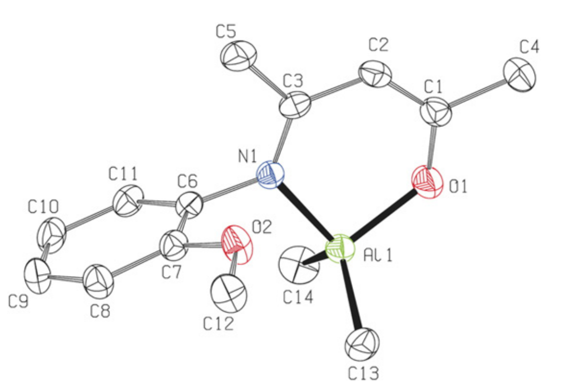


Fig. 1. Molecular structure of **L°AlMe₂** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: C6–N1 1.4397(18), N1–C3 1.3189(19), C3–C2 1.423(2), C2–C1 1.367(2), C1–O1 1.299(2), O1–Al1 1.7967(12), Al1–N1 1.9347(13), Al1–C13 1.9616(17), Al1–C14 1.9507(17); C1–O1–Al1 128.24(11), O1–Al1–N1 95.22(6), Al1–N1–C3 124.30(10).

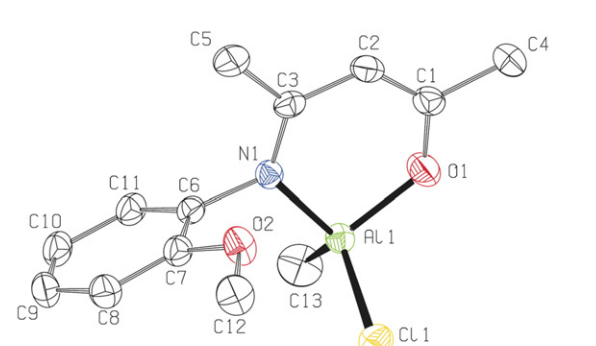


Fig. 2. Molecular structure of **L°AlMeCl** (ORTEP view, 50% probability level). Hydrogen atoms and the position of disordered AlMeCl group are omitted for clarity. Selected interatomic distances [Å] and angles [°]: C6–N1 1.443(2), N1–C3 1.322(2), C3–C2 1.427(3), C2–C1 1.359(3), C1–O1 1.306(2), O1–Al1 1.784(4), Al1–N1 1.908(4), Al1–Cl1 2.145(3), Al1–C13 1.938(10); C1–O1–Al1 127.86(17), O1–Al1–N1 96.36(16), Al1–N1–C3 124.10(17).