ARTICLE

Unique Reactivity of α-ketiminopyridine Ligand with Metal-Alkyls. Synthesis and ROP of ε-Caprolactone

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The α-ketimininopyridine ligand 2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N (L^1) was studied in reactions with metal-alkyls such as MeLi, Et_2Zn, Me_3Al and Me_2AlCl. The reaction of L^1 with MeLi led exclusively to the formation of [2-((H_2C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]Li·$(THF)_2$ (**1**·$(THF)_2$) with deprotonated ketimine methyl group as a product of a methane elimination. The treatment of L^1 with Et_2Zn provided, at the first stage, only complex [2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$ZnEt_2$ (**2**). Nonstability of **2** led to the ethane elimination along with the deprotonation of ketimine methyl group, which further yielded [2-((H_2C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]ZnEt (**3**). In contrast, Me_3Al reacted with L^1 in carboalumination fashion and [2-(($Me)_2$C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$AlMe_2$ (**4**) was isolated. In the case of Me_2AlCl, a ionic specie {[2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$AlMe_2$}$^+$ {Me_2AlCl_2}$^-$ (**5**) was formed as a result of a spontaneous dissociation of Me_2AlCl initiated by the ligand L^1. Since compounds **2**-**5** contain a metal-alkyl fragment, they were used as pre-catalysts in ROP of ε-caprolactone, as well as compound **1**·$(THF)_2$.

Introduction

Aliphatic polyesters, such as poly(ε-caprolactone) (PCL) and polylactide (PLA), as well their copolymers are recently of great interest due to their biodegradable and biocompatible properties.[1] They are used in many industries, especially in medicine, pharmacy, as packaging materials and other fields.[2] One of the synthetic approach for producing these polymers is based on the ROP of cyclic esters initiated by metal complexes.[3] In industry, most linear aliphatic polyesters are produced by ROP in the presence of $Sn(Oct)_2$.[3] However, tin compounds are relatively toxic and difficult to completely remove from the polymers, which is a major limitation especially for medical application. Therefore lithium, zinc or aluminum alkoxides have attracted an attention due to its low toxicity and good control over the polymerization.[4] Suitable precursors for producing these metal alkoxides are most frequently metal-alkyls MR_n (M = Li, Zn, Al; R = Me, Et, Bu) supported by either anionic or or neutral N-donor ligands[5].

The family of the popular N-donor ligands is represented by 2,6-disubstituted pyridines, where DIMPY ligand (2,6-[(Me)C=N(C_6H_3-2,6-iPr_2)]$_2C_5H_3N$) is the prominent example of this family.[6] After Gibson and Brookhart reported DIMPY-stabilized iron and cobalt species in combination with MAO as highly active catalytic systems for olefin polymerization,[7] an attention of chemists has focused on transition metal-alkyl derivatives of DIMPY ligand.[8] DIMPY as a non-innocent ligand with strong π electron-acceptor properties weakens the electron-rich M-R bond, resulting in a diverse reactivity of these complexes. Therefore, only a few DIMPY-stabilized polyalkyl metal complexes of a general formula [(DIMPY)MR_n] (M = Mn, Fe) have been isolated.[8e,9] However, as already mentioned, most such complexes are subject to subsequent reactions. For lithium-, zinc- and aluminium-alkyls, a pyridine N-alkylation,[10] a pyridine C2- and C4-alkylation,[11] carbometallation of (Me)C=N bond[11b,12] or deprotonation of a ketimine methyl group[10b,c] has been reported (Chart 1). The different reactivity is influenced by the nature of the metal centre, character of alkyl groups and reaction conditions.

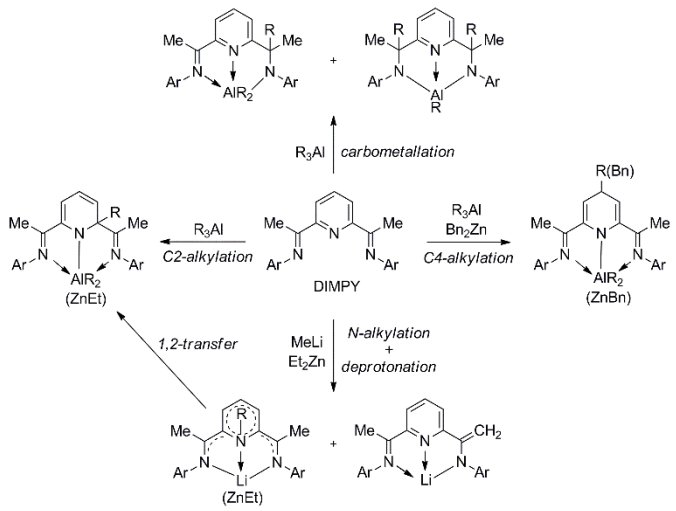

Chart 1 Reactivity of DIMPY-supported lithium-,zinc- and aluminium-alkyls

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For the reaction of DIMPY with MeLi, an equilibrium between the N-alkylated product and η^1-*N*-aza-enolate-lithium derivative was observed, which depends on the temperature, the ratio of reactants and the solvent.[10b,c] In a similar way, the treatment of DIMPY with diethylzinc also resulted in N-alkylated product, in which, however, 1,2-transfer of the ethyl is preferred over the deprotonation of the ketimine methyl group.[10c] On the other hand, C4-alkylation took place with diallyl- and dibenzylzinc.[11a] The divergent chemistry of DIMPY-supported alkyl-metals is comprehensively reflected within alkyl-aluminium complexes, in which C2- and C4-alkylation is observed as well as a carboalumination of (Me)C=N group.[12]

Surprisingly, despite the presence of an alkyl-metal bond in these compounds, there is no mention of their use as pre-catalysts, in combination with alcohol, for ROP cyclic esters in the literature.

DIMPY has been also found to be a suitable ligand for the stabilization of rare earth metal complexes[13] and, in particular, for a spontaneous dissociation of the main group metal halides MX_n providing $[(DIMPY)MX_{n-1}]^+$ $[MX_{n+1}]^-$ species (M = Al, Ga, Ge, Sn; X = Cl, I) (Chart 2A).[12c,14] Later on, it was reported that α-ketiminopyridine ligand L^1 (L^1 = 2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N) behaves in the same fashion as DIMPY yielding ionic complexes $[(L^1)MCl]^+$ $[MCl_3]^-$ (M = Ge, Sn) (Chart 2B).[15]

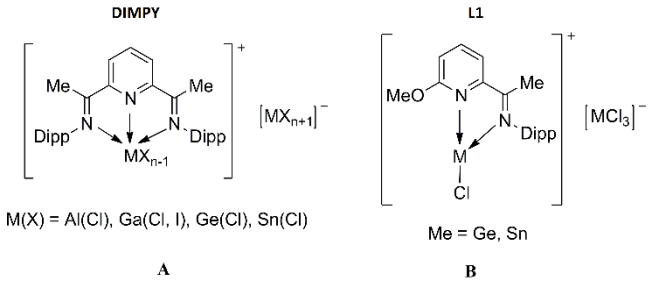


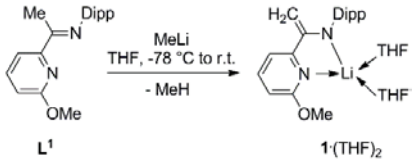
Chart 2 Spontaneous dissociation of MX_n (M = Al, Ga, Ge, Sn; X = Cl, I) initiated by DIMPY (**A**) or α-ketiminopyridine ligand L^1 (**B**)

As a part of comprehensive study on the chemistry of α-ketiminopyridine ligands, we report here the reactivity of L^1 with metal-alkyls (MeLi, Et_2Zn, Me_3Al and Me_2AlCl) in order to compare the effect of the OMe group replacing one (Me)C=N group in DIMPY. Depending on metal-alkyls the possibility of carbometallation of (Me)C=N group, deprotonation of the ketimine methyl group, spontaneous dissociation or only complexation will be discussed. The isolation of well-defined compounds allowed us to study their catalytic activity in ROP of ε-caprolactone.

Results and discussion

Synthesis and characterization of complexes

In our study, the treatment of a THF solution of L^1 with 1 eq. of MeLi at -78 °C yielded exclusively compound [2-((H$_2$C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]Li·$(THF)_2$ (**1**·$(THF)_2$) with deprotonated ketimine methyl group as a product of a methane elimination (Scheme 1). Thus, **1**·$(THF)_2$ can be considered as the η^1-*N*-aza-enolate-lithium derivative.



Scheme 1 Synthesis of compound **1**·$(THF)_2$

Compound **1**·$(THF)_2$ was isolated as orange-red crystals and was characterized by the help of ^{1}H, ^{13}C and ^{7}Li NMR spectroscopy. The ^{1}H NMR spectrum of **1**·$(THF)_2$ revealed two singlets at δ 3.62 and 4.48 ppm associated with the new terminal vinylic fragment *H$_2$C*=C-N. In ^{13}C NMR spectrum of **1**·$(THF)_2$ the vinylic *H$_2$C*=C-N group resonates at δ 73.3 ppm. Similar signals were detected also in parent compound derived from DIMPY (^{1}H NMR: 3.80 and 4.49 ppm, ^{13}C NMR: 76.6 ppm)[10b] and were assigned to the *H$_2$C*=C-N moiety. The ^{7}Li NMR spectrum of **1**·$(THF)_2$ contained one signal at δ 2.29 ppm.

The molecular structure of **1**·$(THF)_2$ was determined by single-crystals X-ray diffraction analysis and is depicted in Figure 1. Crystallographic data of **1**·$(THF)_2$ are summarized in Table S1 of the Supporting Information.

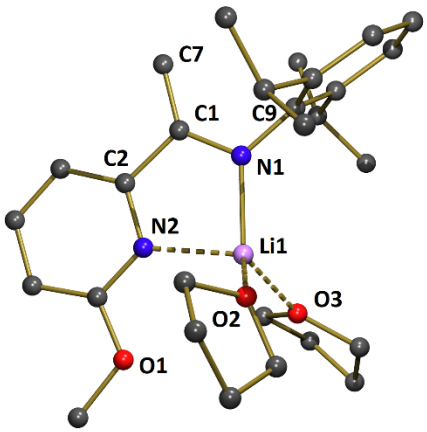
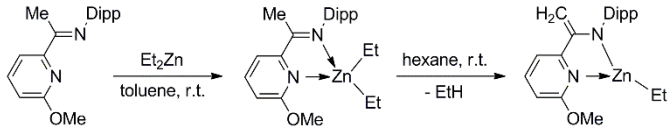


Fig. 1 Molecular structure of **1**·$(THF)_2$. Selected bond distances (Å) and bond angles (°): N1-Li1 1.958(4), N2-Li1 2.044(4), O2-Li1 1.962(4), O3-Li1 1.962(5), O1-Li1 3.141(4), C1-C7 1.359(3), C1-N1 1.355(3), C9-N1 1.412(3), N1-Li1-N2 82.64(15), N1-Li1-O2 122.9(2), N2-Li1-O3 114.0(2), C2-C1-C7 118.80(19), N1-C1-C7 127.2(2), C2-C1-N1 114.05(18).

The central lithium Li1 atom is tetra-coordinated by two nitrogen atoms N1 and N2 and two oxygen atoms O2 and O3 originating from two THF molecules. The coordination arrangement of the central lithium Li1 atom can be described as a distorted tetrahedron. The deviation from the ideal tetrahedral arrangement is demonstrated in particular by the N1-Li1-N2 bond angle (82.64(15)°). The C1–C7 bond distance (1.359(3) Å) is somewhat longer than the double C=C bond ($\sum_{covDB}$(C,C) = 1.34 Å)[17] and the C1–N1 bond distance (1.355(3) Å) is significantly shorter than the single C-N bond ($\sum_{covSB}$(C,N) = 1.46 Å)[17]. These structural parameters suggest overlapping of the N1-lone pair with C1–C7 double bond and thus the presence of the aza-enolate anion.[16] The Li1-N1 bond distance (1.958(4) Å) is then typical for related aza-enolate-lithium derivatives.[16a,b,g] The Li1-N2 bond distance (2.044(4) Å) is very close to that in DIMPY-stabilized derivative (2.033 Å)[10b] and indicates the strong N→Li coordination.

Data obtained from multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis clearly confirm that the reaction of L^1 with MeLi yields exclusively η^1-*N*-aza-enolate-lithium derivative **1**·$(THF)_2$ as the only product of the reaction. This fact contrasts with the reaction of the DIMPY ligand with MeLi, which provides the mixture of η^1-*N*-aza-enolate-lithium derivative and N-methylated product.[10b,c]

The above result prompted us to examine the reactivity of L^1 with other metal-alkyls, such as Et_2Zn, Me_3Al and Me_2AlCl. Interestingly, the reaction of L^1 with Et_2Zn provided, at the first stage, only complex [2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$ZnEt_2$ (**2**) (Scheme 2). The standing of **2** in hexane solution led to a change in colour from dark red to dark green during 3 days and η^1-*N*-aza-enolate-zinc derivative [2-((H_2C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]ZnEt (**3**) was isolated as the product of ethane elimination (Scheme 2).



Scheme 2 Synthesis of compounds **2** and **3**

The ethyl groups of Zn-Et fragment resonate as a quartet at δ 0.14 ppm and a triplet at δ 1.16 ppm in the ^{1}H NMR spectrum of **2**. The fact that the ketimine (Me)C=N methyl remained unchanged in **2** is reflected by the observation of a singlet for methyl protons at δ 2.11 ppm. In the ^{13}C NMR spectrum of **2**, the ketimine (*Me*)C=N methyl group resonates at δ 13.5 ppm. On the other hand, the ^{1}H NMR and ^{13}C NMR spectra of **3** revealed the absence of a signal for the ketimine (*Me*)C=N methyl group. The signals characteristic for the vinylic *H_2C*=C-N group resonate in two singlets at δ 3.98 and 4.74 ppm in the ^{1}H NMR spectrum and at δ 81.5 ppm in the ^{13}C NMR spectrum of **3**. The broad signals at δ 0.87 ppm and δ 1.55 ppm were assigned to the ethyl group of Zn-Et fragment, when the integral intensity is in molar ratio 1:1 with other signals of L^1.

The molecular structures of **2** and **3** were unambiguously determined by single-crystal X-ray diffraction analysis and are depicted in Figure 2. Crystallographic data of **2** and **3** are summarized in Table S2 and S3 of the Supporting Information.

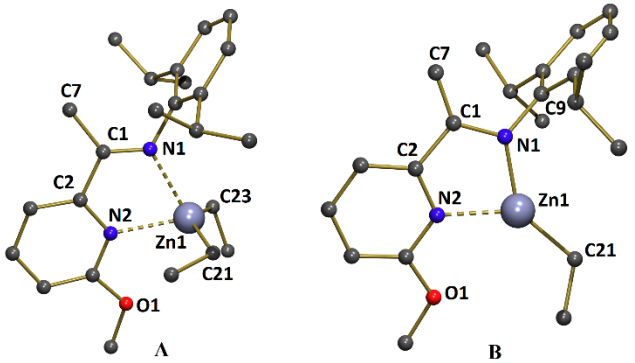


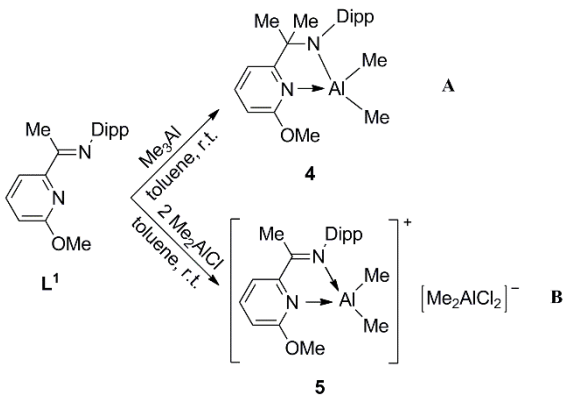
Fig. 2 Molecular structures of **2** and **3.** Selected bond distances (Å) and bond angles (°): **A**) for compound **2**: N1-Zn1 2.2733(14), N2-Zn1 2.2104(15), C21-Zn1 2.013(2), C23-Zn1 1.9973(19), O1-Zn1 3.1344(14), C1-C7 1.505(3), C1-N1 1.285(2), N1-Zn1-N2 72.67(5), N2-Zn1-C21 103.03(7), N1-Zn1-C23 109.22(7), C21-Zn1-C23 136.95(8), C7-C1-N1 125.26(18), C2-C1-N2 116.69(16). **B**) for compound **3**: N1-Zn1 1.929(2), N2-Zn1 2.052(2), C21-Zn1 1.945(4), O1-Zn1 3.1167(19), C1-N1 1.369(4), C1-C7 1.361(5), C9-N1 1.426(3), N1-Zn1-N2 81.90(9), N1-Zn1-C21 141.07(10), N2-Zn1-C21 136.99(11), C2-C1-C7 120.4(3), N1-C1-C7 125.5(2), C2-C1-N1 114.1(3).

The central zinc Zn1 atom is tetra-coordinated by two nitrogen atoms N1 and N2 and two carbon atoms C21 and C23 and adopts a distorted tetrahedral arrangement in **2**. The N1-Zn1-N2 bond angle (72.67(5)°) indicates the largest deviation from the ideal tetrahedral arrangement. The Zn1-N1 (2.2733(14) Å) and Zn1-N2 (2.2104(15) Å) bond distances fall to the region typical for N→Zn coordination bonds found in *N*,*N*-supported diethylzinc species (range 2,181 – 2.666 Å).[18] Similarly, the Zn1-C21 (2.013(2) Å and Zn1-C23 (1.9973(19) Å) bond distances corresponds to the zinc-carbon bond distances found in *N*,*N*-chelated diethylzinc complexes (range 1.993 – 2.170 Å).[18] The fact that the ketimine (Me)C=N moiety remained without any chemical transformation is evidenced by the C1-C7 (1.505(3) Å) and C1–N1 (1.285(2) Å) bond distances, which are typical single C-C ($\sum_{covSB}$(C,C) = 1.50 Å)[17] and double C=N bond ($\sum_{covDB}$(C,N) = 1.27 Å)[17].

On the other hand, the central zinc Zn1 atom is tri-coordinated by two nitrogen atoms N1 and N2 and the carbon atom C21 and adopts a trigonal planar arrangement in **3**. The deviation from the ideal trigonal planar arrangement is demonstrated in particular by the C21-Zn1-N1 bond angle (141.07(10)°). The C1–C7 bond distance (1.361(5) Å) is somewhat longer than the double C=C bond ($\sum_{covDB}$(C,C) = 1.34 Å)[17] and the C1–N1 bond distance (1.369(4) Å) is significantly shorter than the single C-N bond ($\sum_{covSB}$(C,N) = 1.46 Å)[17]. These structural parameters suggest overlapping of the N1-lone pair with C1–C7 double bond and thus the presence of the aza-enolate anion.[16] The Zn1–N1 bond distance (1.929(2) Å) corresponds to the covalent single Zn-N bond (($\sum_{covSB}$(Zn,N) = 1.89 Å)[17], while the Zn1–N2 bond distance (2,052(2) Å) shows the strong N→Zn coordination.

The results showed a unique behaviour of the L^1 toward Et_2Zn. While DIMPY stabilized dialkylzinc complexes undergo C4-alkylation[11a] or N-alkylation with subsequent 1,2-transfer[10c], the reaction of Et_2Zn with L^1 afforded **2** as a rare example of isolable α-ketiminopyridine-stabilized dialkylzinc. Furthermore, **3** is the first example of α-ketiminopyridine-zinc specie, in which the deprotonation of the ketimine methyl group take place.

The diverse reactivity of L^1 to metal-alkyl reagents was also observed within the reaction with Me_3Al and Me_2AlCl. The reaction of L^1 with Me_3Al afforded compound [2-((Me)$_2$C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$AlMe_2$ (**4**) as the product of the carboalumination of the ketimine (Me)C=N functional group (Scheme 3A). In contrast, the treatment of L^1 with two equivalents of Me_2AlCl yielded compound {[2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$AlMe_2$}$^+$ {Me_2AlCl_2}$^-$ (**5**) as a result of a spontaneous dissociation of Me_2AlCl initiated by L^1 (Scheme 3B).



Scheme 3 Synthesis of compounds **4** and **5**

Compounds **4** and **5** were isolated as white powder materials and were characterized by the help of ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction analysis (for **4**). The Al-*Me* groups resonate at δ = -0.14 ppm in the ^{1}H NMR spectrum of **4**, while a signal with δ = 1.35 ppm was assigned to methyl groups of the $(Me)_2C$-N fragment. The successful reduction of the ketimine (Me)C=N to an amine $(Me)_2C$-N moiety was proved by the ^{13}C NMR spectrum of **4**, in which no signal of the ketimine carbon atom was found, but a signal at δ = 63.2 ppm was attributed to the $(Me)_2C$-N fragment. On the other hand, the presence of the ketimine (Me)C=N group in **5** is proved by the observation of a singlet at δ = 2.32 ppm corresponding to (*Me*)C=N methyl group in the ^{1}H NMR spectrum and a signal at δ = 178.6 ppm corresponding to (Me)*C*=N carbon atom in the ^{13}C NMR spectrum of **5**. The ^{1}H NMR spectrum of **5** revealed two singlets with δ = -0.39 and -0.1 ppm showing the presence of Me_2Al^+ and $Me_2AlCl_2^-$ fragments in **5**. The integral intensity of these signals is in molar ratio 2:1 toward (*Me*)C=N methyl group. This finding agrees with related ionic species $[(L)AlR_2]^+$ $[R_2AlX_2]^-$ (L is *N*-donor ligand), in which Me_2Al^+ and $Me_2AlCl_2^-$ fragments resonate in range δ = -0.02 – (-0.81) ppm.[19]

The molecular structure of **4** is depicted in Figure 3. Crystallographic data of **4** are summarized in Table S4 of the Supporting Information.

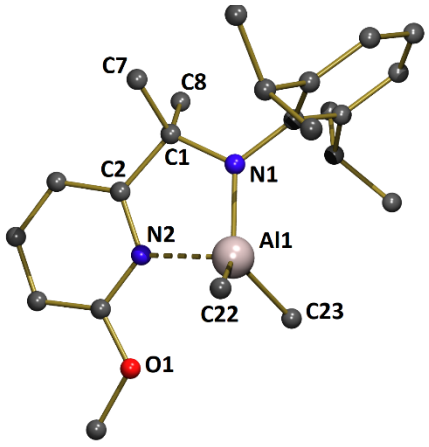


Fig. 3 Molecular structures of **4**. Selected bond distances (Å) and bond angles (°): N1-Al1 1.8403(14), N2-Al1 1.9671(13), C22-Al1 1.9614(18), C23-Al1 1.9591(18), O1-Al1 3.0298(13), C1-N1 1.478(2), N1-Al1-N2 84.86(6), N1-Al1-C22 118.95(8), N2-Al1-C23 109.20(7), C2-C1-N1 107.37(13), N1-C1-C7 113.70(13), N1-C1-C8 112.94(13).

The central aluminum Al1 atom is tetra-coordinated by two nitrogen atoms N1 and N2 and two carbon atoms C22 a C23 and adopts a distorted tetrahedral arrangement in **4**. The deviation from the ideal tetrahedral arrangement is demonstrated in particular by the N1-Al1-N2 bond angle (84.86(6)°). The C1-N1 bond distance (1.478(2) Å) corresponds to the single C-N bond. ($\sum_{covSB}$(C,N) = 1.46 Å).[17] In addition, the C2-C1-N1 bond angle (107.37(13)°) indicates sp^3 hybridization of the C1 carbon atom. The Al1-N1 (1.8403(14) Å) and Al1-N2 (1.9671(13) Å) bond distances are shorter than the covalent single Al-N bond ($\sum_{covSB}$(Al,N) = 1.97 Å)[17] and reflect the presence Al-N covalent and strong N→Al coordination bond, respectively.

The behaviour of L^1 toward Me_3Al, and thus the formation of **4**, is not surprising because carboalumination is a typical reaction in the chemistry of DIMPY and other α-iminopyridine ligands.[20] On the other hand, the formation of **5** is unique. Despite the fact that the spontaneous dissociation of R_2AlX providing $[(L)AlR_2]^+$ $[R_2AlX_2]^-$ is described for several *N*,*N*-chelating ligands (L),[19] a similar reaction has not been reported for DIMPY and α-iminopyridine ligands. The only mention of a similar ion pair is the calculated intermediate $[(DIMPY)AlEt(Cl)]^+$ $[Et_3AlCl]^-$ in C2- and C4-alkylation of DIMPY with Et_2AlCl.[12c] Thus, the synthesis of **5** suggests that Me_2AlCl reacts with L^1 more as a main group metal halide than as a metal-alkyl.

Because compounds **2**-**5** possess a metal-alkyl fragment, they should be promising pre-catalysts for ROP of cyclic esters. Therefore, they were subjected to catalytic tests in ROP of ε-caprolactone, as well as compound **1**·$(THF)_2$.

ROP of ε-caprolactone

All polymerization tests were performed in toluene solution. The polymerization reactions were carried out at 30 °C, 55 °C and 80 °C in molar ratios of [pre-catalyst]:[monomer] = 1:100, 1:250 and 1:500. In all reactions, benzyl alcohol (BzOH) was added as a co-initiator in a molar ratio of 1:1 compared to the pre-catalyst. Results on polymerization tests are summarized in Table 1.

Polymerization tests employing **1**·$(THF)_2$ as the pre-catalyst have shown that **1**·$(THF)_2$ is inactive in the presence of benzyl alcohol as a coinitiator. This fact probably has its origin in the high sensitivity of **1**·$(THF)_2$ to protic agents associated with the rapid decomposition of the pre-catalyst. For this reason, subsequent polymerization tests were performed in the absence of benzyl alcohol. Table 1 (Entry 1 and 2) summarizes the results of the ROP of ε-caprolactone using **1**·$(THF)_2$ as the pre-catalyst. For molar ratio [**1**·$(THF)_2$]:[ε-caprolactone] = 1:100, a quantitative polymerization occurred almost immediately after the **1**·$(THF)_2$ was added to the monomer solution at 30 °C and 55 °C. However, the number average molecular weights M_n of PCL (13200 g/mol for 30 °C and 7700 g/mol for 55 °C) differ from the calculated theoretical values. Moreover, the polydispersity indexes (PDI) are very high (6.81 for 30 °C and 3.34 for 55 °C), which clearly indicates poor control over the polymerization. When the molar ratio [**1**·$(THF)_2$]:[ε-

caprolactone] was increased to 1:250 and 1:500, **1**·$(THF)_2$ proved to be completely inactive.

Attempts to test zinc compounds **2** and **3** as ROP pre-catalysts of ε-caprolactone failed because of high instability of **2** and **3**. Compound **2** rapidly decomposes in *vacuo* and since an application of *vacuo* is an integral part of the polymerization setup, tests involving **2** could not be performed. Similarly, handling of **3** after its isolation and characterization led to the rapid decomposition of **3**.

On the other hand, compound **4** was found to be a good pre-catalyst at molar ratios [**4**]:[BzOH]:[ε-caprolactone] = 1:1:100 and 1:1:250. As expected, the increasing polymerization temperature has a positive effect on the monomer conversion. At a molar ratio of 1:1:100, the monomer conversion at 30 °C is 42% in 1.5 hours (Table 1, run 3), at 55 °C complete conversion is then achieved in 1 hour (Table 1, run 6) and at 80 °C almost complete conversion in 30 minutes (Table 1, run 9). A similar trend is then found for a molar ratio of 1:1:250 (Table 1, run 4, 7 and 10), with the difference that at 30 °C compound **4** is no longer able to initiate the polymerization. The molecular weights M_n of PCL correspond relatively well to the calculated theoretical values. PDIs (1.11-1.36) indicate good control over the polymerization. At a molar ratio 1:1:500, **4** is active only at 80 °C with a conversion of 12.5% after 1 hour (Table 1, run 11). However, the experimental M_n does not agree with the calculated theoretical M_n, neither the PDI indicates good control over the polymerization.

Despite **5** has more Lewis acidic character, this compound is completely catalytically inactive at 30 °C, regardless of the [**5**]:[BzOH]:[ε-caprolactone] molar ratio (Table 1, run 12-14). The catalytic activity does not start until the reaction temperature rises to 55 °C (Table 1, run 15-16). As can be seen, **5** shows excellent catalytic activity at a temperature of 80 °C, especially at a molar ratio [**5**]:[BzOH]:[ε-caprolactone] = 1:1:100 and 1:1:250, where the conversion reaches 100% after one hour (Table 1, run 18-19). The molecular weight M_n of PCL at a molar ratio of 1:1:100 corresponds quite well to the theoretical values. However, at a molar ratio of 1:1:250, the deviation is larger, and in addition, PDIs are too high for the polymerization to be considered as controlled.

Based on these data, it is clear that the best pre-catalyst for ROP of ε-caprolactone is compound **4**, where the PCL show a very good agreement of the experimental molecular weight of M_n with the theoretical one. In addition, the PDIs clearly demonstrate the uniform nature of the polymers.

Table 1. ROP of e-caprolactone catalysed by **1**·$(THF)_2$, **4** and **5**.

run	pre-catalyst	T [°C]	[ε-CL]:[cat]:[BzOH]	t [h]	conv [%][a]	$M_{n,th.}$ [g/mol][b]	$M_{n,GPC}$ [g/mol][c]	PDI
1	**1**·$(THF)_2$	30	100:1:0	1	100	11400	13 200	6.81
2	**1**·$(THF)_2$	55	100:1:0	1	100	11400	7 700	3.34
3	**4**	30	100:1:1	1.5	42	4 900	4 280	1.11
4	**4**	30	250:1:1	1.5	0	-	-	-
5	**4**	30	500:1:1	1.5	0	-	-	-
6	**4**	55	100:1:1	1	100	11 520	14 340	1.36
7	**4**	55	250:1:1	1	35	5 810	6 400	1.25
8	**4**	55	500:1:1	1	0	-	-	-
9	**4**	80	100:1:1	0.5	97	11 180	9 760	1.31
10	**4**	80	250:1:1	0.5	91,5	26 220	22 210	1.25
11	**4**	80	500:1:1	1	12,5	7 240	3 950	2.90
12	**5**	30	100:1:1	1.5	0	-	-	-
13	**5**	30	250:1:1	1.5	0	-	-	-
14	**5**	30	500:1:1	1.5	0	-	-	-
15	**5**	55	100:1:1	1	24	2 850	-	-
16	**5**	55	250:1:1	1	6	1 820	-	-
17	**5**	55	500:1:1	1	0	-	-	-
18	**5**	80	100:1:1	0.5	100	11 520	14 370	2.76
19	**5**	80	250:1:1	1	100	28 640	32 030	2.62
20	**5**	80	500:1:1	1	0	-	-	-

a) measured by the ^{1}H NMR spectroscopy

b) calculated M_n of PCL (g/mol): [ε-CL]:[cat] · conv · M(ε-CL) + M(BzOH)

c) experimental M_n values were determined by GPC analysis in THF solution using polystyrene standards and corrected by factor 0.56[21]

A kinetic study of ε-caprolactone by using **4** was performed by removing 0.5 mL sample from the reaction mixture and analyzing it by the ^{1}H NMR spectroscopy at the appropriate time under the conditions [**4**]:[BzOH]:[ε-caprolactone] = 1:1:100 at 30 °C in toluene. The polymerization rate of the ROP of ε-caprolactone exhibited approximate first-order dependence on the ε-caprolactone concentration (Figure 4).

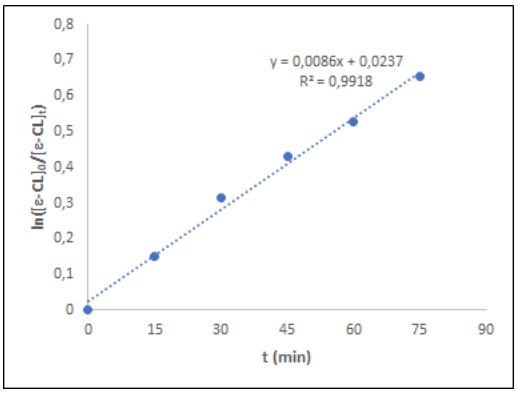


Fig. 4 Plot of $\ln[\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t$ versus time when using **4** as pre-catalyst.

To shed light on the role BzOH in the ROP of ε-caprolactone catalyzed by **4**, the stoichiometric reaction of **4** with BzOH in NMR tube was carried out. The ^{1}H NMR spectroscopic study showed that BzOH attacks the Al-N bond in **4** and amino-derivative of L^1 and a specie based on $[Me_2(BzO)Al]$ are formed (Figure S12). The intrinsic initiator for the ROP of ε-caprolactone is therefore $[Me_2(BzO)Al]$ specie. To determine the mechanism of polymerization, the reaction was performed under the conditions [**4**]:[BzOH]:[ε-caprolactone] = 1:1:5. ^{1}H NMR monitoring of the reaction mixture showed a signal at δ = 5.04 ppm corresponding to the benzyl group as the end group in the resulting oligomer (Figure S13). In addition, this signal was also present in the ^{1}H NMR spectra of all isolated polymers (Figure S14). Thus, it can be clearly stated that the polymerization proceeds by a coordination-insertion mechanism with the $[Me_2(BzO)Al]$ specie as the active initiator.

Conclusions

In this paper we reported the reactivity of DIMPY related α-ketiminopyridine ligand 2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N (L^1) toward metal-alkyl reagents such a MeLi, Et_2Zn, Me_3Al and Me_2AlCl. It has been shown that the replacing of one (Me)C=N group in DIMPY by OMe group has a significant influence on this reactivity. While the reactions involving DIMPY ligand are complex and several products have been isolated for each reagent, the ligand L^1 always provides exclusively one product. The results further showed that the reactivity of L^1 toward Et_2Zn and Me_2AlCl is completely different compared to DIMPY.

The reaction of L^1 with MeLi led to the methane elimination and [2-((H$_2$C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]Li·$(THF)_2$ (**1**·$(THF)_2$) was isolated as the only product of the reaction. The treatment of Et_2Zn with L^1 afforded, at the first stage, [2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]ZnEt2 (**2**) as a rare example of isolable α-ketiminopyridine-stabilized dialkylzinc. Furthermore, the ethane elimination was observed in **2** affording [2-((H$_2$C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]ZnEt (**3**) as the first example of α-ketiminopyridine-zinc specie with the deprotonated ketimine methyl group. The unique behaviour of L^1 has been also reflected in reactions with Me_3Al and Me_2AlCl. It has been demonstrated that L^1 undergoes by carboalumination providing [2-((Me)$_2$C-N(C_6H_3-2,6-iPr_2))-6-(CH_3O)C_5H_3N]$AlMe_2$ (**4**). On the other {[2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]$AlMe_2$}$^+$ {Me_2AlCl_2}$^-$ (**5**) was isolated as the product spontaneous dissociation of Me_2AlCl.

All compounds **1**-**5** were further used as the pre-catalysts for ROP of ε-caprolactone. Polymerization tests indicated the compound **4** as the most suitable pre-catalyst, since the obtained PCL showed narrow PDIs and good agreement of the experimental molecular weight of M_n with the theoretical one.

Experimental section

General consideration

All moisture and air sensitive reactions were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried using Pure Solv–Innovative Technology equipment. Starting compound L^1 was prepared according to the literature.[15] MeLi (1.6M), $AlMe_3$ (1M), $AlMe_2Cl$ (1M) and $ZnEt_2$ (1M) were purchased from Sigma Aldrich and used as received. Elemental analyses were performed on an LECO-CHNS-932 analyser. The ^{1}H, ^{13}C and ^{7}Li NMR spectra were recorded on Bruker 500 NMR spectrometer at 298 K in C_6D_6. The ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent. The ^{7}Li NMR spectra were referenced externally to LiCl.

Syntheses

Synthesis of [2-((H$_2$C)C-N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]Li·$(THF)_2$ (1·$(THF)_2$). A Et_2O solution of MeLi (0.52 mL, 1.6M) was added to a stirred solution of L^1 (0.256 g, 0.82 mmol) in THF (15 mL) at -78 °C. The reaction mixture was warmed up and stirred for 1 hour at room temperature. After that the resulting orange solution was concentrated under reduced pressure and small amount of hexane was added. The storage of the solution at -20 °C afforded **1**·$(THF)_2$ as orange-red crystalline material suitable for X-ray diffraction analysis. Yield: 0.31 g (83 %). For **1**·$(THF)_2$: mp = 99-101 °C. Anal.Calcd.for $C_{28}H_{41}N_2O_3Li$ (MW 460.58): C, 73.0; H, 8.9. Found: C, 72.8; H, 8.8. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): *δ (ppm)* 1.28 (d, 6H, CH_3(*i*Pr), ^3J(^{1}H, ^{1}H) = 6.8 Hz), 1.30 (bs, 8H, CH_2-THF), 1.58 (d, 6H, CH_3(*i*Pr), ^3J(^{1}H, ^{1}H) = 6.8 Hz), 3.22 (s, 3H, OCH_3), 3.48 (bs, 8H, OCH_2-THF), 3.62 (s, 1H, =CH_2), 3.79 (sept, 2H, C*H*(*i*Pr), ^3J(^{1}H, ^{1}H) = 6.8 Hz), 4.48 (s, 1H, =CH_2), 5.98 (d, 1H, Py-*H*, ^3J(^{1}H, ^{1}H) = 7.9 Hz), 7.13 (t, 1H, Py-*H*, ^3J(^{1}H, ^{1}H) = 7.8 Hz), 7.23 (t, 1H, Ar-*H*, ^3J(^{1}H, ^{1}H) = 7.5 Hz), 7.39 (d, 2H, Ar-*H*, ^3J(^{1}H, ^{1}H) = 7.5 Hz), 7.69 (d, 1H, Py-*H*, ^3J(^{1}H, ^{1}H) = 7.8 Hz). ^{13}C NMR (C_6D_6, 125.72 MHz, 25 °C): *δ (ppm)* 24.8 (*C*H$_3$(*i*Pr)), 25.1 (*C*H$_2$-THF), 25.5 (*C*H$_3$(*i*Pr)), 27.7 (*C*H(*i*Pr)), 53.8 (O*C*H$_3$), 67.5 (O*C*H$_2$-THF), 73.3 (=*C*H$_2$), 101.1, 114.7, 120.8, 122.9, 138.7, 143.7, 153.3, 156.8, 162.7, (Ar-*C*), 163.2 (*C*=CH$_2$). ^{7}Li NMR (C_6D_6, 125.72 MHz, 25 °C): *δ (ppm)* 2.29

Synthesis of [2-((Me)C=N(C_6H_3-2,6-iPr_2))-6-(OMe)C_5H_3N]ZnEt_2 (2). A hexane solution of Et_2Zn (1.13 mL, 1M) was added to a stirred solution of L^1 (0.35 g, 1.13 mmol) in toluene (3 mL) at room temperature. The reaction mixture was stirred for 1 hour. The storage of the solution at -20 °C afforded **2** as deep red

crystalline material suitable for X-ray diffraction analysis. Yield: 0.38 g (78 %). For **2**: mp = 120-122 °C (decomp.). Anal.Calcd.for $C_{24}H_{36}N_2OZn$ (MW 433.96): C, 66.4; H, 8.4. Found: C, 66.1; H, 8.1. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ *(ppm)* 0.14 (q, 4H, CH_2(Et), $^3J(^1H, ^1H)$ = 8.2 Hz), 1.10 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 7.0 Hz), 1.15 (t, 6H, CH_3(Et), $^3J(^1H, ^1H)$ = 8.2 Hz), 1.18 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 7.0 Hz), 2.11 (s, 3H, CH_3), 2.91 (sept, 2H, C*H*(*i*Pr), $^3J(^1H, ^1H)$ = 7.0 Hz), 3.66 (s, 3H, OCH_3), 6.52 (d, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 8.2 Hz), 7.07 (t, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 7.6 Hz), 7.16-7.18 (m, 3H, Ar-*H*), 7.87 (d, 1H, Ar-*H*, $^3J(^1H, ^1H)$ = 8.2 Hz). ^{13}C NMR (C_6D_6, 500.13): δ *(ppm)* 8.9 (*C*H_2(Et)), 13.5 (*C*H_3), 20.0 (*C*H_3(*i*Pr)), 25.8 (*C*H_3(Et)), 26.2 (*C*H_3(*i*Pr)), 31.4 (*C*H(*i*Pr)), 55.8 (O*C*H_3), 114.9, 117.3, 126.2, 127.1, 131.0, 138.9, 141.8, 149.5, 166.5 (Ar-*C*), 169.5 (*C*=N).

Synthesis of [2-((H$_2$C)C-N(C$_6$H$_3$-2,6-iPr$_2$))-6-(OMe)C$_5$H$_3$N]ZnEt (3). A compound **2** (0.3 g, 0.69 mmol) was dissolved in hexane (10 mL) and stirred for 3 days at room temperature. During that time the colour of the solution changed from deep red to dark green. The storage of the solution at room temperature afforded **3** as green crystals suitable for X-ray diffraction analysis. Yield: 0.42 g (74 %). For **3**: mp = 155-158 °C. Anal.Calcd.for $C_{22}H_{30}N_2OZn$ (MW 403.90): C, 65.4; H, 7.5. Found: C, 65.2; H, 7.3. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ *(ppm)* 0.96 (bs, 2H, CH_2(Et), 1.39 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 6.5 Hz), 1.45 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 6.5 Hz), 1.64 (bs, 3H, CH_3(Et), 3.05 (s, 3H, OCH_3), 3.58 (sept, 2H, C*H*(*i*Pr), $^3J(^1H, ^1H)$ = 6.5 Hz), 3.98 (s, 1H, CH_2=C), 4.74 (s, 1H, CH_2=C), 5.72 (d, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 7.9 Hz), 6.97 (t, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 7.9 Hz), 7.31-7.41 (m, 4H, Ar-*H* + Py-*H*). ^{13}C NMR (C_6D_6, 500,13): δ *(ppm)* 1.2 (*C*H_2(Et)), 12.4 (*C*H_3(Et)), 24.0 (*C*H_3(*i*Pr)), 25.4 (*C*H_3(*i*Pr)), 28.1 (*C*H(*i*Pr)), 54.7 (O*C*H_3), 81.5 (=*C*H_2), 102.3, 113.4, 123.5, 124.7, 140.9, 145.1, 145.7, 151.3, 156.3 (Ar-*C*), 162.4 (*C*=CH_2).

Synthesis of [2-((Me)$_2$C-N(C$_6$H$_3$-2,6-iPr$_2$))-6-(CH$_3$O)C$_5$H$_3$N]AlMe$_2$ (4). A hexane solution of Me_3Al (1.48 mL, 2M) was added to a stirred solution of L^1 (0.46 g, 1.48 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred overnight. After that all volatiles were removed under reduced pressure and the resulting residue was dissolved in toluene (20 mL). The insoluble material was filtered off, the toluene filtrate was evaporated and the residue was washed with small amount of cold hexane (5 mL) affording **2** as pale yellow powder material. Single-crystals suitable for X-ray diffraction analysis were grown from saturated toluene-hexane solution of **4** at -20 °C. Yield: 0.44 g (78 %). For **2**: mp = 175-178 °C. Anal.Calcd.for $C_{23}H_{35}N_2OAl$ (MW 382.52): C, 72.2; H, 9.2. Found: C, 72.1; H, 9.1. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ *(ppm)* -0.15 (s, 6H, Al(CH_3)$_2$, 1.33 (br, 6H, (CH_3)$_2$C), 1.36 (br, 12H, CH_3(*i*Pr), 2.96 (s, 3H, OCH_3), 3.98 (br, 2H, C*H*(*i*Pr)), 5.55 (d, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 7.6 Hz), 6.50 (d, 1H, Py-*H*, $^3J(^1H, ^1H)$ = 7.1 Hz), 6.94 (br, 1H, Py-*H*), 7.25-7.28 (m, 3H, Ar-*H*). ^{13}C NMR (C_6D_6, 125.72 MHz, 25 °C): δ *(ppm)* -6.4 (Al(*C*H_3)$_2$), 24.6 ((*C*H_3)$_2$C), 28.6 (*C*H_3(*i*Pr)), 28.7 (*C*H_3(*i*Pr)), 31.3 (*C*H(*i*Pr)), 56.1 (O*C*H_3), 64.3 (*C*(CH$_3$)$_2$N), 103.4, 114.0, 124.4, 125.2, 143.6, 143.8, 152.0, 163.1, 172.4 (Ar-*C*).

Synthesis of {[2-((Me)C=N(C$_6$H$_3$-2,6-iPr$_2$))-6-(OMe)C$_5$H$_3$N]AlMe$_2$}$^+$ {Me$_2$AlCl$_2$}$^-$ (5). A hexane solution of Me_2AlCl (3.41 mL, 1M) was added to a stirred solution of L^1 (0.53 g, 1.70 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred for 1 hour. After that all volatiles were removed under reduced pressure and the resulting residue was dissolved in toluene (20 mL). The insoluble material was filtered off, the toluene filtrate was evaporated and the residue was washed with small amount of hexane (5 mL) affording **5** as pale yellow powder material. Yield: 0.60 g (71 %). For **5**: mp = 230-233 °C (decomp.). Anal.Calcd.for $C_{24}H_{38}Al_2Cl_2N_2O$ (MW 495.44): C, 58.2; H, 7.7. Found: C, 58.0; H, 7.5. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ *(ppm)* -0.39 (s, 6H, Al(CH_3)$_2$), -0.01 (s, 6H, Al(CH_3)$_2$, 1.10 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 6.7 Hz), 1.24 (d, 6H, CH_3(*i*Pr), $^3J(^1H, ^1H)$ = 6.7 Hz), 2.35 (s, 3H, C(CH_3)=N), 2.62 (sept, 2H, C*H*(*i*Pr), $^3J(^1H, ^1H)$ = 6.7 Hz), 3.60 (s, 3H, OCH_3), 7.10-7.13 (m, 3H, Ar-*H*), 7.26 (d, 1H, Ar-*H*, $^3J(^1H, ^1H)$ = 7.9 Hz), 8.04 (d, 1H, Ar-*H*, $^3J(^1H, ^1H)$ = 7.2 Hz), 8.43 (t, 1H, Ar-*H*, $^3J(^1H, ^1H)$ = 7.9 Hz). ^{13}C NMR (C_6D_6, 125.72 MHz, 25 °C): δ *(ppm)* -11.0 (Al(*C*H_3)$_2$), -3.0 (Al(*C*H_3)$_2$), 19.5 (C(*C*H_3)=N), 24.7 (*C*H_3(*i*Pr)), 26.0 (*C*H_3(*i*Pr)), 29.3 (*C*H(*i*Pr)), 58.8 (O*C*H_3), 115.2, 123.0, 126.2, 128.9, 130.6, 135.3, 141.8, 150.1, 164.6 (Ar-*C*), 179.5 (*C*(CH$_3$)=N).

Ring-Opening Polymerization of ε-caprolactone Using 1–5 as Pre-catalysts. Typical polymerization procedures in the presence of one equivalent of benzyl alcohol (Table 1, run 3) are as follows. A toluene solution of **4** (0.005 mmol, 5.0 mL toluene) and BzOH (0.005 mmol) were added into a Schlenk tube and stirred for 1.5 hour at 30 °C. The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution. After removal of the volatiles, the residue was subjected to 1H NMR analysis. Monomer conversion was determined by calculation of the integration of monomer vs polymer methylene resonance in the 1H NMR (CDCl3, 500 MHz) spectrum. The polymer was purified by dissolving the crude samples in CH3Cl and precipitating into cold methanol (100 mL). The obtained polymers were dried to a constant weight, and the dry polymer samples were analyzed by GPC.

Crystallography

The X-ray data for colorless crystals of **1**, **3** and **4** (see Tables S1, S3 and S4) were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN[22]. The absorption was corrected by multi-scan method - SADABS. Structures were solved by direct methods (Sir92)[23]and refined by full matrix least-square based on F^2 (SHELXL97)[24].

Full-set of diffraction data for **2** (see Table S2) was collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Cu (Cu/Kα radiation; λ = 1.54178 Å) or Mo (Mo/Kα radiation; λ = 0.71073 Å) microfocus X-ray (IμS) sources, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection.

The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.[25]

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). H atoms in methyl, methylene, moieties and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, and 0.93Å. Disordered parts of isopropyl and coordinated THF molecules in **1** were treated by standard methods.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 2036881-2036884 for **1 - 4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Conflicts of interest

There are no conflicts to declare.

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