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Simple generation of neutral bimetallic aluminium and zinc alkyls Schiff bases bridged by a central resorcinol moiety

Research Article

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Abstract: Aluminium and zinc complexes bearing the N,O-chelating Schiff base ligand 4,6-bis-1-(2-(dimethylamino)ethylimino)ethyl)benzene-1,3-diol, ($C_6H_2(OH)_2(NCH_2CH_2NMe_2)_2$) (**1a**), have been synthesized. Bimetallic aluminium and zinc alkyl complexes (**2a** - **4a**) were prepared by treatment of the hexadentate **1a** with the appropriate amount of $AlMe_3$, $ZnMe_2$ and $ZnEt_2$, respectively. **2a** has been characterized crystallographically, it lies on a crystallographic two-fold rotation axis and each aluminium centre adopts a five coordinate geometry. Complex **2a** was tested as a catalyst in the ring-opening polymerisation of ε-caprolactone. We describe here the synthesis of two neutral ligands (**1a** and $(C_6H_2(OH)_2(C_6H_5NH_2)$ $(C{=}O(CH_3))$ (**1b**)) and demonstrate their application in the synthesis of molecular aluminium and zinc derivatives.

Keywords: *Aluminium methyl • Zinc alkyl • Schiff bases • DAR • Binuclear complex*

1. Introduction

Schiff base ligands are easily synthesized and form complexes with almost all metal ions, many of their complexes show high catalytic activity [1]. Monometallic Al complexes containing a series of phenoxy-imine ligands or NN Schiff base ligands have been reported [2-11]. The monometallic pendant-arm single Schiff base complexes of aluminium provide active centers for ethylene polymerization due to the liability of the pendant donor arm, thus allowing a pathway for ethylene to approach the aluminium centre [6]. So far, considerable attention has been paid to the synthesis, structural determinations, and catalytic activity of metal complexes based on aluminium and zinc [12-15]. Among the reported catalysts, bimetallic complexes are relatively few [16-19], and those reported for binuclear zinc alkyl, aryl and aryloxide involved Cl, N and O bridging ligands [20-22].

The bifunctional carbonyl compound 4,6-diacetylresorcinol (DAR) serves as precursor for the generation of symmetrical Schiff bases which are either di- or tetra-basic with two symmetrical sets of either O_2N or N_2O tridentate chelating sites [23-27]. Nevertheless, dinuclear Al(III) and Zn(II) alkyl complexes with 1,3-dihydroxybenzene bridging motifs are lacking.

Here we have synthesized the new double and single-Schiff-base ligands **1a** and **1b**, respectively, as shown in Scheme 1, starting from DAR by Schiff-base condensation with two equivalents of the appropriate amine. The resulting ligand (**1a**) provides hexadentate [N_2O] binding pockets which are bridged by a central resorcinol moiety, while (**1b**) provides both tridentate N_2O and bidentate OO chelating sites.

2. Experimental Procedure

2.1. Chemicals and physical measurement

All manipulations were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried from the appropriate drying agent, distilled, degassed

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and stored over 4 Å sieves. Chemicals were purchased from Sigma-Aldrich Company Ltd. and diethyl zinc was procured from Acros organics. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer or a Varian 500 MHz spectrometer. The ^{1}H and ^{13}C NMR spectroscopy chemical shifts are given relative to residual solvent peaks.

2.2. Synthesis of the compounds

2.2.1. Synthesis of Schiff base ligand, 1a

The Schiff base ligand was prepared by the addition of 2-dimethylaminoethylamine (5.14 mmol, 0.56 mL) to a colorless solution of (1,3-diacetyl-4,6-dihydroxybenzene ((resodiacetophenone, (RDP)) in the molar ratio 2:1 (0.5 g, 2.57 mmol) in ethanol (50 mL). The solution was refluxed for 4 h, at which time the color had changed to yellow. The volatile components were removed by rotary evaporation to give a yellow oil. Washing with pentane (3×10) mL resulted in the precipitation of a yellow powder. The precipitate was collected by filtration, washed with pentane then diethylether and finally dried in vacuo overnight (yield: 0.55 g, 64.2%). Anal.Calc. for $C_{18}H_{30}N_4O_2$: C, 64.64 ; H, 9.04 ; N, 16.75. Found: C, 64.01 ; H,8.81; N15.19, EI MS: m/z 334 (38%). ^{1}H NMR (500 MHz, DMSO) δ: 2.18(12H, s, $N(CH_3)_2$), 2.38(6H, s, C-CH_3), 3.31(4H, s, br, CH_2CH_2), 3.58(4H, s, CH_2CH_2), 5.73(1H, s, Ar-H), 7.79(1H, s, Ar-H), 17.14(2H, s, Ar-OH). ^{13}C NMR (500 MHz, DMSO) δ: 13.98($C\underline{C}H_3$), 44.67(CH_2CH_2), 45.21($N(CH_3)_2$), 58.47(CH_2CH_2), 105.35 (C-H), 109.83 ($\underline{C}$-CCH_3), 132.70 (C-H)),172.53(C=N and C-OH).

2.2.2. Synthesis of 2a

To a stirred solution of **1a** (0.2g, 0.60 mmol) in toluene (30 mL) was added drop wise $AlMe_3$ (0.6 mL of a 2 M solution in hexanes) at 25ºC. The color of the solution changed from dark yellow to light yellow and an off white powder precipitated immediately. The exothermic reaction was left to stir for 1 h. Filtration and washing with toluene (5 mL) afforded **2a** as an off white powder, pure by ^{1}H NMR spectroscopy. The obtained solid was dissolved in THF and crystallized at -20ºC to give colorless crystals of **2a**. (Yield: 0.25 g, 93.3%). Anal.Calc. for $C_{22}H_{40}Al_2N_4O_2$: C, 59.17 ; H, 9.03 ; N, 12.55. Found: C, 59.50; H, 9.15; N, 12.31. EI MS: m/z 446 (32%). ^{1}H NMR (500 MHz, DMSO) δ: -1.09 (12H, s, $AlCH_3$), 2.13(12H, s, $N(CH_3)_2$, 2.36(6H, s, C-CH_3), 2.72(4H, t, ^{3}J=6.6, CH_2CH_2), 3.63(4H, t, ^{3}J=6.5, CH_2CH_2), 5.62(1H, s, Ar-H), 7.93(1H, s, Ar-H).

2.2.3 Synthesis of 3a

To a stirred solution of **1a** (0.2 g, 0.60 mmol) in toluene (30 mL) was added drop wise $ZnMe_2$ (0.6 mL of a 2 M solution in hexanes) at 25ºC. The color of the solution changed from dark yellow to light brown and an off-white powder precipitated immediately. The exothermic reaction was left to stir for 2 h. Filtration and drying under vacuum afforded **3a** as an off white powder, pure by ^{1}H NMR spectroscopy. (Yield: 0.24 g, 81.7%). Anal. Calc. for **3a** $C_{20}H_{34}N_4O_2Zn_2$: C, 48.69 ; H, 6.95 ; N, 11.36. Found: C, 48.83; H, 7.04; N, 11.21. ^{1}H NMR (399 MHz, DCM) δ: -0.99 (6H, s, $ZnCH_3$), 2.31(6H, s, C-CH_3), 2.48(12H, s, $N(CH_3)_2$, 2.75(4H, t, ^{3}J=6.0, CH_2CH_2), 3.60(4H, t, ^{3}J=5.9, CH_2CH_2), 5.99(1H, s, Ar-H), 7.49(1H, s, Ar-H). ^{13}C NMR (399 MHz, DCM) δ: -18.23($ZnCH_3$), 19.33($C\underline{C}H_3$), 45.46($N(CH_3)_2$), 47.10(CH_2CH_2), 58.74(CH_2CH_2), 112.12, 116.58, 125.9, 128.72, 129.53 and 136.46 (Ar-C), 173.19 (C=N).

2.2.4 Synthesis of 4a

To a stirred solution of **1a** (0.2 g, 0.60 mmol) in toluene (30 mL) was added drop-wise $ZnEt_2$ (1.2 mL of 1 M solution in hexane) at 25ºC. A white powder precipitated immediately. The exothermic reaction was left to stir for 1 h. Filtration and drying under vacuum afforded **4a** as a white powder pure by ^{1}H NMR spectroscopy. (Yield: 0.26 g, 85%). Anal.Calc. $C_{22}H_{38}N_4O_2Zn_2$: C, 50.68; H, 7.35; N, 10.75. Found: C, 50.57; H, 7.48; N, 10.70. ^{1}H NMR (500 MHz, DCM) δ: -1.91(4H, q, J=7.9, $ZnC\underline{H}_2CH_3$), -0.82(6H, t, $ZnCH_2C\underline{H}_3$), 2.31(6H, s, C-CH_3), 2.48(12H, s, $N(CH_3)_2$, 2.75(4H, t, ^{3}J=6.0, CH_2CH_2), 3.60(4H, t, ^{3}J=5.9, CH_2CH_2), 5.99(1H, s, Ar-H), 7.49(1H, s, Ar-H). ^{13}C NMR (500 MHz, DCM) δ: -2.86($ZnCH_2\underline{C}H_3$), 13.67($Zn\underline{C}H_2CH_3$) 19.53($C\underline{C}H_3$), 45.78($N(CH_3)_2$), 47.31(CH_2CH_2), 59.26(CH_2CH_2), 112,47, 116.95, 126.01, 128.93, 129.74 and 135.37 (Ar-C), 173.24 (C=N).

2.2.5 Synthesis of Schiff base 1b

The Schiff base ligand was prepared by the addition of o-phenylenediamine (5.15 mmol, 0.56 g) to a colorless solution of RDP in the molar ratio 2:1 (0.5 g, 2.57 mmol) in ethanol (50 mL). The solution was refluxed for 5 h, at which time the color changed to yellow. The precipitate was collected by filtration and recrystallised from hot toluene and finally dried in vacuo overnight (yield based on RDP: 0.63 g, 86%). Anal.Calc. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.67; H, 5.58; N, 159.86, EI MS: $M^{+\cdot}$ m/z 284 (20%), M^{+}-Me m/z 269 (100%). ^{1}H NMR (500 MHz, DMSO) δ: 2.25(3H, s, C-CH_3), 2.49(3H, s, C-CH_3), 4.89(4H, s, NH_2), 6.12(1H, s, Ar-H(DAR)), 6.47-6.71(1H, s, Ar-H(o-phenylenediamine), 8.21(1H, s, Ar-H(DAR)), 12.69 (1H, s, Ar-OH), 16.11(1H, s, Ar-OH). ^{13}C NMR (500 MHz, DMSO) δ: 16.96, 27.17 ($C\underline{C}H_3$), 112.80-141.04 (Ar-C), 165.88, 172.00 and 174.01(C=N and C-OH), 203.08 (C=O).

2.2.6 Synthesis of 3b

To a stirred solution of **1b** (0.1 g, 0.35 mmol) in toluene (30 mL) was added drop-wise $ZnMe_2$ (0.35 mL of a 2 M solution in hexanes) at 25ºC. The color of solution changed from dark yellow to light brown and an off white powder precipitated immediately. The exothermic reaction was left to stir for 2 h. Filtration and drying under vacuum afforded **3b** as an off-white powder, pure by ^{1}H NMR spectroscopy. (Yield: 0.12 g, 75.0%). Anal. Calc. for **3b** $C_{18}H_{20}N_2O_3Zn_2$: C, 48.79; H, 4.55; N, 6.32. Found: C, 48.84; H, 4.57; N, 6.37. ^{1}H NMR (399 MHz, DCM) δ: -1.27 (3H, s, $ZnCH_3$), -1 (3H, s, $ZnCH_3$), 2.19 (3H, s, C-CH_3), 2.28 (3H, s, C-CH_3), 4.54 (2H, s, NH_2), 5.65 (1H, s, Ar-H(DAR)), 6.60-6.23 (4H, m, Ar-H(o-phenylenediamine), 8.16 (1H, s, Ar-H(DAR)).

2.3. Typical polymerization procedure [22]

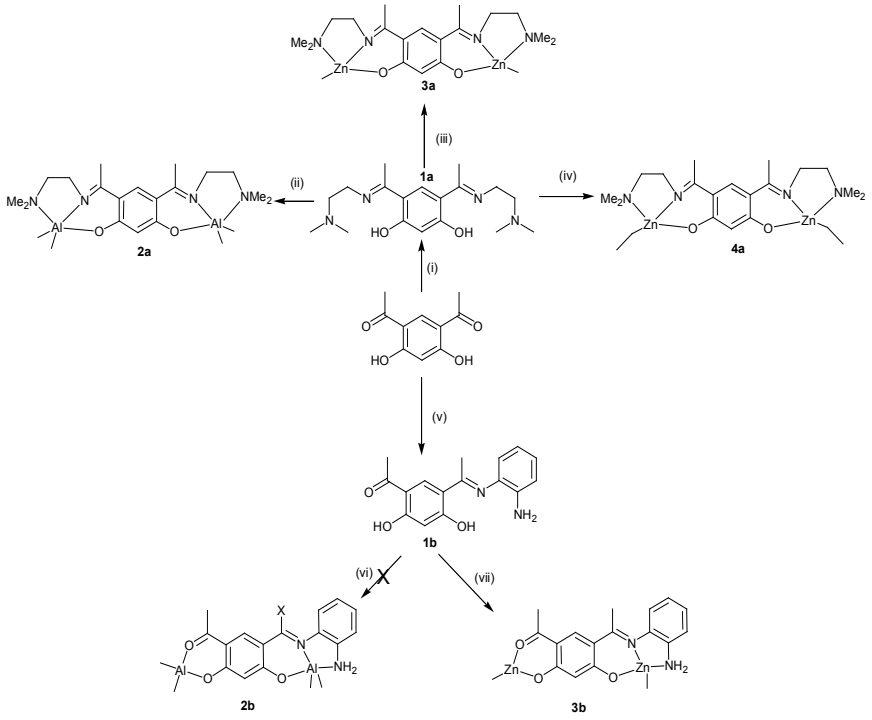
A solution of aluminium complex **2a** in toluene was injected to a solution of ε-caprolactone (ε-CL) in toluene kept at 60ºC. The concentration of ε-CL was 1 M. The molar ratio of [ε-CL] / [**2a**] = 300:1. 1 mL of polymerization aliquots were withdrawn at appropriate time intervals under the protection of nitrogen and quenched with methanol. After removal of the volatiles, the residue was subjected to ^{1}H NMR analysis. Monomer conversion was determined by observing the integration of monomer *vs.* polymer methylene resonance in the ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum.

2.4. Crystal structure determination

Single crystals of **2a** were grown by crystallization at -20ºC from THF. The data for the complex were collected at 173(2) K. Data collection: COLLECT [31]; cell refinement: HKL DENZO and SCALEPACK [32]; data reduction: HKL SCALEPACK and DENZO [32]; program(s) used to solve structure: SHELXS97 [33]; program(s) used to refine structure: SHELXL97 [33]; molecular graphics: ORTEP-3 for Windows) [34]; software used to prepare material for publication: WinGX [35]. CCDC 784404 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

The Schiff base ligand 4,6-bis-1-(2-(dimethylamino)ethylimino)ethyl)benzene-1,3-diol ($C_6H_2(OH)_2(NCH_2CH_2NMe_2)_2$), **1a**, was accessed in moderate yield (> 64%) *via* standard imine condensation reaction between 4,6-diacetyl resorcinol with two equivalents of 2-dimethylaminoethylamine in a ratio 1:2 to give the symmetrical bis-azomethine **1a**, obtained as yellow powder. The ^{1}H NMR spectrum of the ligand exhibited the disappearance of the phenolic DAR peak at δ 12.50 ppm and the appearance of a new phenolic peak down field at δ 17.14 ppm, the formation



Scheme 1. Synthesis of **1a** and **1b** and their metal complexes. (i) 2 $NH_2CH_2CH_2NMe_2$, reflux 4 h, EtOH; (ii) 2 $AlMe_3$, toluene; (iii) 2 $ZnMe_2$, toluene; (iv) 2 Zn Et_2, Toluene; (v) 2 o-phenylenediamine, reflux 5 h, EtOH; (vi) 2 $AlMe_3$, toluene; (vii) 2 $ZnMe_2$, toluene

Table 1. Crystal data, bond lengths [Å] and angles [°] for **2a**

Crystal data			
Empirical formula	$C_{22}H_{40}Al_2N_4O_2$	F(000)	968
Formula weight	446.54	Crystal size	0.42 x 0.20 x 0.20 mm^3
Temperature	173(2) K	Theta range for data collection	3.50 to 27.09°.
Wavelength	0.71073 Å	Index ranges	-35<=h<=35, -9<=k<=9, -15<=l<=15
Crystal system	Monoclinic	Reflections collected	17968
Space group	C2/c (No.15)	Independent reflections	2700 [R(int) = 0.053]
Unit cell dimensions		Reflections with I>2sigma(I)	2480
a = 27.7413(7) Å	α= 90°.	Completeness to theta = 27.09°	98.2%
b = 7.5898(2) Å	β= 101.621(2)°.	Refinement method	Full-matrix least-squares on F^2
c = 12.0513(3) Å	γ = 90°.	Data / restraints / parameters	2700 / 0 / 140
Volume	2485.40(11) $Å^3$	Goodness-of-fit on F^2	1.066
Z	4	Final R indices [I>2sigma(I)]	R1 = 0.040, wR2 = 0.109
Density (calculated)	1.19 $Mg\ m^{-3}$	R indices (all data)	R1 = 0.044, wR2 = 0.113
Absorption coefficient	0.14 mm^{-1}	Largest diff. peak and hole	0.26 and -0.34 e.$Å^{-3}$

Bond distances/Å		Bond angles/°	
Al-O	1.8376(10)	O-Al-C(12)	100.06(6)
Al-C(12)	1.9780(15)	O-Al-C(11)	95.83(6)
Al-C(11)	1.9959(16)	C(12)-Al-C(11)	117.44(7)
Al-N(1)	2.0182(12)	O-Al-N(1)	88.63(5)
Al-N(2)	2.3138(13)	C(12)-Al-N(1)	111.38(6)
O-C(2)	1.3029(15)	C(11)-Al-N(1)	129.21(7)
N(1)-C(5)	1.3082(16)	O-Al-N(2)	162.29(5)
N(1)-C(7)	1.4851(16)	C(12)-Al-N(2)	93.04(6)
		C(11)-Al-N(2)	88.55(6)

of azomethine methyl protons at δ 2.38 ppm instead of the acetyl methyl protons at δ 2.60 ppm and the appearance of two non-equivalent ethyl protons of the dimethylaminoethylamine moiety indicate the formation of **1a**, this was further supported by ^{13}C NMR spectrum, elemental analysis and EI-MS.

To demonstrate that the **1a** compound described above can be used in the synthesis of coordination complexes, a brief investigation into the application of **1a** as a ligand precursor in aluminium and zinc chemistry was conducted. The reaction between the neutral **1a** with alkyl-aluminium and -zinc compounds in toluene proceeded *via* protonolysis of the phenolic oxygen and an alkane elimination leads to the formation of the complexes in good yields to afford the bis(aluminium methyl), bis(zinc methyl and ethyl) Al(L)Me_2 (**2a**), Zn(L)Me_2 (**3a**) and Zn(L)Et_2 (**4a**) respectively, [L = $C_6H_2(O)_2(NCH_2CH_2NMe_2)_2$] (Scheme 1).

The mass spectrum and elemental analysis of **2a** were consistent with two 'AlMe_2' units attached to the Schiff base ligand. The ^1H NMR spectrum of **2a** shows a sharp singlet at -1.09 ppm due to the Al-Me protons as predicted for a symmetrically substituted Al-centre.

Crystals of **2a**, suitable for X-ray structure determination, were grown from THF at -20ºC. The molecular structure is shown in Fig. 1, Table 1. Selected bond lengths and angles are given in Table 1. Deprotonated **1a** is seen to act as a hexadentate ligand, binding to each aluminium atom *via* the phenolic oxygen and the imino and amino nitrogen atoms. Monomeric molecules of **2a** lie on a crystallographic two-fold rotation axis. The amino nitrogen N2-Al bond length [2.3138(13) Å] being substantially longer than that of the imino one N1-Al [2.0182(12) Å], The azomethine C=N bond retains its double bond character [N1-C5, 1.30852(16) Å]. These bonds, however, are comparable to the related single Schiff base chelate [(3,5-Bu^t_2-2-(O)C_6H_2CHNNL)$AlMe_2$] [L = $CH_2CH_2NMe_2$] [6]. The geometry of the five-coordinate Al(III) centre by quantative method (τ = 0.55) cannot be reasonably defined as either square pyramidal (sqp) or trigonal bipyramidal (tbp). For example the O-Al-N2 (axial) angles, expected to be 180° for tbp is rather narrow, 162.29(5)°. Similar deviations are found in the structure of previously reported five-coordinate, chelated aluminium complexes [28].

The Al–C12 , Al-C11 and Al-O bond distances [1.9780(15) ,1.9959(16) and 1.8376(10) Å], are longer than those recently reported for the four coordinate $AlMe_2$ complex [Me_2Al[O-2,4-But_2-6-{(2,6-Pri2C_6H_3)N=CH}C_6H_2] [Al–C: 1.955(2) and 1.949(3) Å; Al-O: 1.7688(17) Å] and may indicate weaker coordination, however, the Al-O bond length is within the range suggested for σ-bond coordination [5]. The multinuclear NMR spectra are consistent with the solid-state structure being maintained in solution.

The binuclear symmetrical zinc alkyl complexes **3a** and **4a** were formulated on the basis of ^1H, ^{13}C NMR spectroscopy and elemental analysis. A single resonance for the methyl and ethyl protons were observed in the ^1H NMR spectra at δ -0.99 ppm for $ZnCH_3$ in **3a** and δ -1.91 and -0.82 ppm for $ZnCH_2CH_3$ in **4a**, which was also supported by a single resonance signal in the ^{13}C NMR spectra. Further evidence for a symmetrical solution-state geometry is implied by the single azomethine

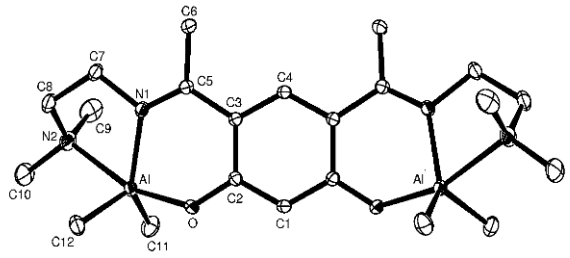


Figure 1. Molecular structure of $[Al_2(C_6H_2(O)_2(NCH_2CH_2NMe_2)_2)(Me)_2]$, **2a**

methyl resonances of the compounds at δ 2.31 ppm for both **3a** and **4a** in the ^{1}H NMR spectra. According to these data, the Zn(II) ion in both complexes are four-coordinate and may adopt a distorted tetrahedral geometry.

The structure of **1b** was confirmed by NMR spectroscopy, which confirmed the isolation of an unsymmetrical single Schiff base as the first major insoluble product isolated from ethanol. Further confirmation of ligand structure was supported by microanalysis and EI-MS. Attempts to isolate Al complex 2b were unsuccessful, however the Zn methyl was isolated in good yield. The reaction of dimethyl zinc with **1b** in a molar ratio of 2:1 leads to the expected methyl zinc complex **3b**, which can be stabilized without donor ligands. For **3b**, two methyl resonances were observed at -1.27 and -1.00 ppm and a down-field shift in the NH_2 resonance from δ 4.89 to 4.54 ppm indicating its coordination to one of the Zn atoms having a distorted tetrahedral geometry, while the other Zn atom may adopt a trigonal geometry. The structure of **3b** was further supported by elemental analysis. **3b** represents a rare example of a mixed four and three-coordinate monomeric zinc(II) methyl complex [29]; however, attempts to grow single crystals suitable for X-ray analysis were unsuccessful. The isolated complexes were stable at ambient temperature, air and moisture-sensitive powders, poorly soluble in aliphatic hydrocarbons (pentane, hexane) and aromatic hydrocarbons (benzene, toluene), and very soluble in dichloromethane, DMSO and THF.

2a is moderately reactive in the polymerization of ε-caprolactone (ε-CL). The polymerization took place rapidly (Al/ε-CL) 1/300, (temp, 60 °C), and the great increase in viscosity of the solution was observed after 1 h with 100% conversion after 4 h based on ^{1}H NMR spectroscopy.

4. Conclusion

In conclusion, we have found a simple and relatively inexpensive method for the generation of alkyl-aluminium and -zinc neutral species, based on readily available 4,6-diacetylresorcinol core. The resulting Al methyl species appeared to be efficient initiators in the polymerization of ε-caprolactone. It has been known that the activity toward ring-opening polymerization of L-lactide is Mg>Zn>Al [30], so it might be predicted that **3a** and **4a** will be more efficient initiators.

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