



Synthesis and characterization of multidentate ethylene bridged pyrrole- and ketoamine-morpholine aluminum compounds. Structure, theoretical calculation and catalytic study

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ABSTRACT

Pyrrole and keto-amine based morpholine ligands are conveniently synthesized and their corresponding Al-compounds are afforded accordingly. The combination of **1**, {C₄H₃NH-2-[CH=NCH₂CH₂N(CH₂CH₂)₂O]} and two equivalents of PhNCO generates compound **3**, {C₄H₃N(CONPh)CH-N(CONPh)(CH₂)₂NC₄H₄O} in relatively high yield. In addition, reacting **1** with one and two equivalents of AlMe₃ in toluene render mono- and di-aluminum compounds, AlMe₂{C₄H₃N[2-CH=NCH₂CH₂N(CH₂CH₂)₂O]} (**4**) and AlMe₂{C₄H₃N[2-CH=NCH₂CH₂N(CH₂CH₂)₂O]AlMe₃} (**5**), respectively. Similarly, reactions of morpholine bounded keto-amine ligands OMeCHCMeNHCH₂CH₂N(CH₂CH₂)₂O (**2a**) and OPhCHCMeNHCH₂CH₂N(CH₂CH₂)₂O (**2b**) with one and two equivalents of AlMe₃ result the formation of mono- and di-aluminum compounds, AlMe₂{OCRCHCMeN[CH₂CH₂N(CH₂CH₂)₂O]} (**6a**, R = Me; **6b**, R = Ph) and AlMe₂{OCRCHCMeN[CH₂CH₂N(CH₂CH₂)₂O]·AlMe₃} (**7a**, R = Me; **7b**, R = Ph), respectively in moderate yield. Compounds **1**, **3**, **4** and **6b** are subjected to X-ray diffraction analysis to ensure the geometry around Al atom. All the aluminum compounds could effectively commence the ring-opening polymerization (ROP) of ϵ -caprolactone in a well-controlled manner with molecular weight distributions (PDI = 1.08–1.37).

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1. Introduction

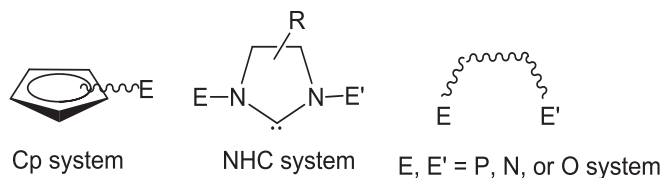
Polycaprolactone, an aliphatic polyester, is an important polymer due to its versatile applicability and mechanical properties (controlled degradability, miscibility with other polymers, biocompatibility) and it can be made inexpensively [1,2]. It is prepared by ring opening polymerization of ϵ -caprolactone monomers using initiators such as stannous octanoate [3–5]. However, the toxicity of tin metal has raised the concern for using polycaprolactone in any bio-related material industry [6–8]. Therefore, using bio-friendly metal as initiators for the ring opening polymerization of cycloesters has attracted a large interest in the past decades and been reviewed [9–15]. Among these initiators aluminum [16–20] is considered as friendly metal which shows

remarkable activity towards lactone ring opening polymerization. Therefore, design of new ligands and their corresponding aluminum complexes raise interest for significant contribution on the ring opening polymerization chemistry.

Investigating new ligand design [21–30] for chelation of new organometallic derivatives and analyzing their applications represents an important issue among organometallic chemists. Scheme 1 represents some examples of ligand architectures incorporated earlier; such as Cp based [31–35], NHC (N-heterocyclic carbene) mediated [36–42], and chelating ligands [43–49]. To concise interest on different ligand systems, we have before focused our attention on the synthesis and reactivity study of symmetrical and asymmetrical substituted pyrrole [50–54] and keto-amine [55–57] ligands (Scheme 2) with various main group or transition metals. The ability to simply and independently vary the steric and electronic properties of a given ligand may provide a wealth of opportunities to influence reactivity, stability, catalysis and other important properties at the metal center. As an extension

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Scheme 1. Ligands used in synthesizing organometallic compounds.

of our previous work [50–57]. We now synthesize new pyrrole-morpholine and keto-amine-morpholine precursors *via* the linkage of an ethylene chain. Interestingly, these two ligand systems show multiple coordinating sites and pursue possible reactive unsaturated bonds (Scheme 3). The ethylene linked morpholine fragment may also bind the metal center *via* nitrogen or oxygen donor atom. In exploring metal-organic system, the synthesis, characterization and X-ray crystal structures of pyrrole and keto-amine linked morpholine ligands and their corresponding aluminum derivatives are discussed. We also assess the influence of Al-derivatives as initiators towards ROP of ϵ -caprolactone [58–62].

2. Results and discussion

2.1. Synthesis and characterization

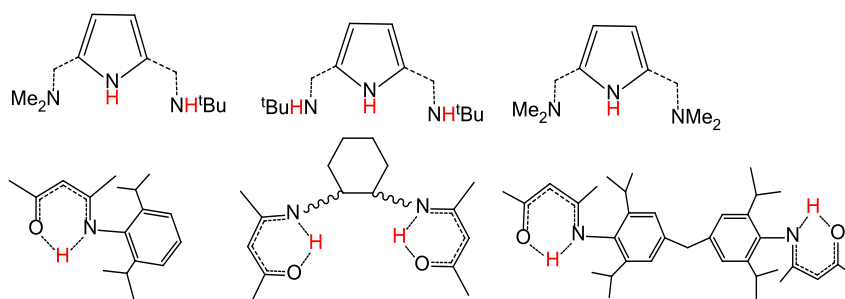
The pyrrole and keto-amine ligands containing ethylene bridged morpholine **1**, **2a** and **2b** and their corresponding aluminum compounds as shown in Scheme 4 are synthesized and characterized. Reacting pyrrole-2-carboxaldehyde with 4-(2-aminoethyl) morpholine in 1,2-dichloroethane results a pale yellow solid {C₄H₃NH-2-[CH=NCH₂CH₂N(CH₂CH₂)₂O]} (**1**) in high yield. The ¹H and ¹³C NMR spectra of **1** show characteristic proton and carbon resonances of imine CH=N fragment at δ 8.03 and 152.8, respectively. When 4-(2-aminoethyl)morpholine reacts with 2,4-pentanedione or benzoylacetone in methanol produces keto-amine-morpholine ligands OCMcCHCMeNHCH₂CH₂N(CH₂CH₂)₂O

(**2a**) and OPhCHCMeNHCH₂CH₂N(CH₂CH₂)₂O (**2b**), respectively, in moderate yield. The characteristic methine proton and carbon of keto-amine backbone are evident in the ¹H and ¹³C NMR spectra at δ 4.41 and 94.0 for **2a** and at δ 5.62 and 92.3 for **2b**.

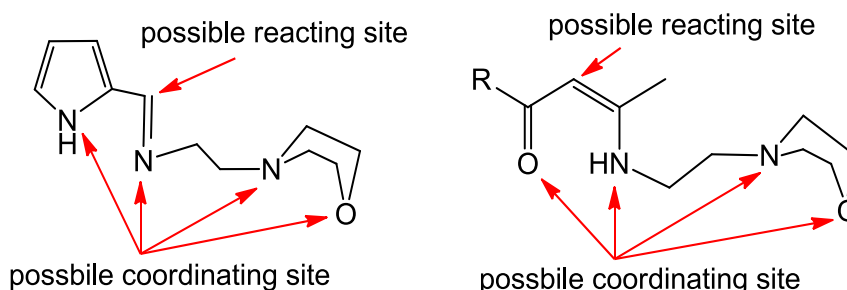
Reacting compound **1** with two equivalents of PhNCO, a 1,1-disubstituted phenylurea compound, {C₄H₃N(CONPh)CH-N(CONPh)(CH₂)₂NC₄H₄O} (**3**) was generated in relatively high yield (Scheme 4). Compound **3** shows a proton resonance at δ 10.34 for CONH fragment and two carbon resonances at δ 148.9 and 157.2 for two urea NCON fragments. A plausible reaction mechanism for the formation of **3** is depicted in Scheme 5. The pyrrole N–H bond is coupled to the C=N bond of the first equivalent of PhNCO to yield an intermediate **3*** [63,64]. Then, two possible routes are proposed where route (a) the intramolecular hydroamination of amide N–H to C=N bond followed by a consecutive hydroamination with another equivalent of PhNCO to generate compound **3**** or route (b) a consecutive nucleophilic attack of **3*** with another equivalent of PhNCO to form a zwitterionic intermediate **3***** followed by proton rearrangement to give the final product **3**.

Reacting the ethylene bridged bidentate pyrrole-morpholine ligand **1** with one and two equivalents of AlMe₃ in toluene afford the mono- and di-aluminum compounds, AlMe₂{C₄H₃N[2-CH=NCH₂CH₂N(CH₂CH₂)₂O]} (**4**) and AlMe₂{C₄H₃N[2-CH=NCH₂CH₂N(CH₂CH₂)₂O]AlMe₃} (**5**), respectively (Scheme 4). Alternatively, compound **5** can be obtained by adding one more equivalent of AlMe₃ to compound **4**. The ¹H NMR spectrum of **4** shows a resonance at δ –0.44 for the AlMe₂ fragment and two multiplets at δ 3.60 and 2.09 for the CH₂ protons of morpholine ring. The ¹H NMR spectrum of compound **5** shows two singlets with an integration ratio of 3 to 2 at δ –0.36 and –0.44 for the AlMe₃ and AlMe₂ fragments [65]. We observe that compounds **4** and **5** are quite thermal stable which remain unchanged while dissolving in C₆D₆ and heating at 60 °C for 72 h, monitored by ¹H NMR spectra.

Similarly, the ethylene bridged keto-amine-morpholine ligands **2a** and **2b** react with one and two equivalents of AlMe₃ to produce mono- and di-aluminum compounds, AlMe₂{OCRCHCMeN[CH₂CH₂N(CH₂CH₂)₂O]} (**6a**, R = Me; **6b**, R = Ph) and



Scheme 2. Pyrrole and keto-amine ligand systems.



Scheme 3. The possible reaction sites of ligands **1** and **2**.

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