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# Synthesis and characterization of tri-dentate pyrrole-morpholine ligands and their corresponding aluminum, magnesium, and zinc compounds

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## ABSTRACT

A series of metal compounds containing tri-dentate monoanionic pyrrole-morpholine ligands was synthesized and characterized. The reaction of $O(CH_2CH_2)_2NH\cdot HCl$, pyrrole and formaldehyde generated a new type of tri-dentate pyrrole-morpholine ligand, $C_4H_2NH\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}$ (**1**), in high yield. The reaction of **1** with one equivalent of $AlMe_3$ and $ZnMe_2$ in toluene generated $AlMe_2\{C_4H_2N\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}\}$ (**2**) and $\{ZnMe\{C_4H_2N\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}\}\}_2$ (**4**), respectively, in moderate yield. The reaction of two equivalents of **1** with $Mg^nBu_2$ in THF generated a bis-pyrrolyl Mg compound, $Mg\{C_4H_2N\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}\}_2(THF)$ (**3**), in moderate yield. Compound **4** is sensitive to air and moisture and it decomposed into a hexa-Zn compound, $\{(ZnMe)_2\{C_4H_2N\text{-}\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}(\mu^4\text{-}O)_2(\mu^2\text{-}ZnMe)_2\}$ (**5**), when a small amount of moisture leaked into the flask during the recrystallization process. Compounds **1**–**4** were characterized by $^1H$ and $^{13}C$ NMR spectra and the structures of **1**, **3**, and **5** were also determined by single crystal X-ray diffractometry. Compounds **2** and **3** were tested as initiators for the ring opening polymerization of ε-caprolactone and **3** showed excellent activity.

## Introduction

Multidentate ligands are often used in organometallic chemistry because of their versatile bonding modes and stability toward metals [1–6]. Therefore, a novel system of multidentate ligand is crucial for the success of a research project. Among these multidentate ligands, pincer type ligands [7–10] have attracted much attention because of their ability to bind metals via a central atom and two side arms.

Morpholine [11] is a chemical produced by the dehydration of diethanolamine with sulfuric acid and is used in water treatment, optical brightener, pharmaceutical and agricultural industries. More importantly, the price of morpholine is quite affordable for use as a starting material for the synthesis of the corresponding derivatives. We are interested in using pyrrole-based bi- and tri-dentate ligands, as shown in Scheme 1, to form a series of metal complexes and to study both their reactivity toward organic molecules and their potential as initiators for cyclic esters [12,13]. To extend the bonding potential, we combined pyrrole and morpholine molecules to develop a series of tri-dentate pyrrole-morpholine ligands and their corresponding metal complexes. The tri-dentate pyrrole-morpholine ligands can bind to the metal via the N and O atoms of the pyrrole and oxazines, as shown in Scheme 2. We herein report the synthesis and characterization of a series of metal compounds containing this new tri-dentate pyrrole-morpholine ligand and the ring opening polymerization of ε-caprolactone using compounds **2** and **3**.

## Results and discussion

### *Synthesis and characterization of **1**–**5***

A new type of tridentate pyrrole ligand containing morpholine fragments was synthesized according to Scheme 3. Morpholine was

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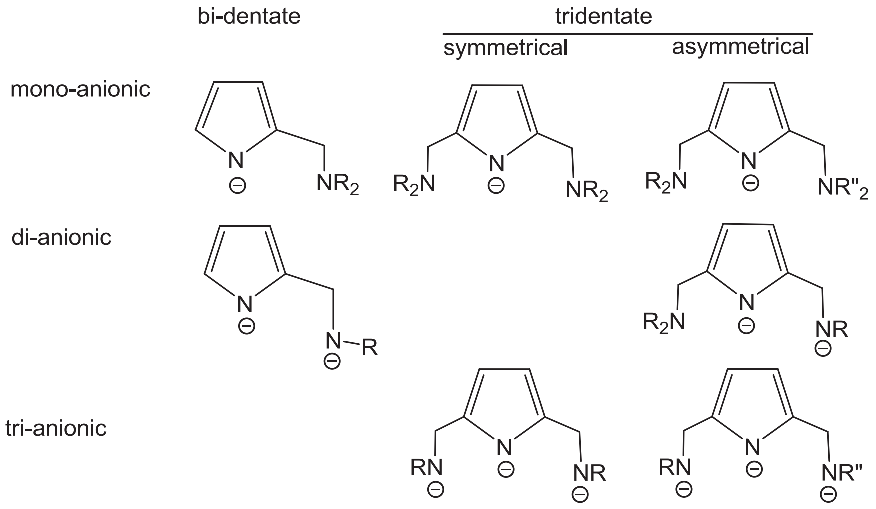
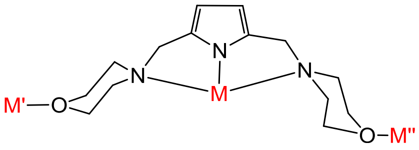


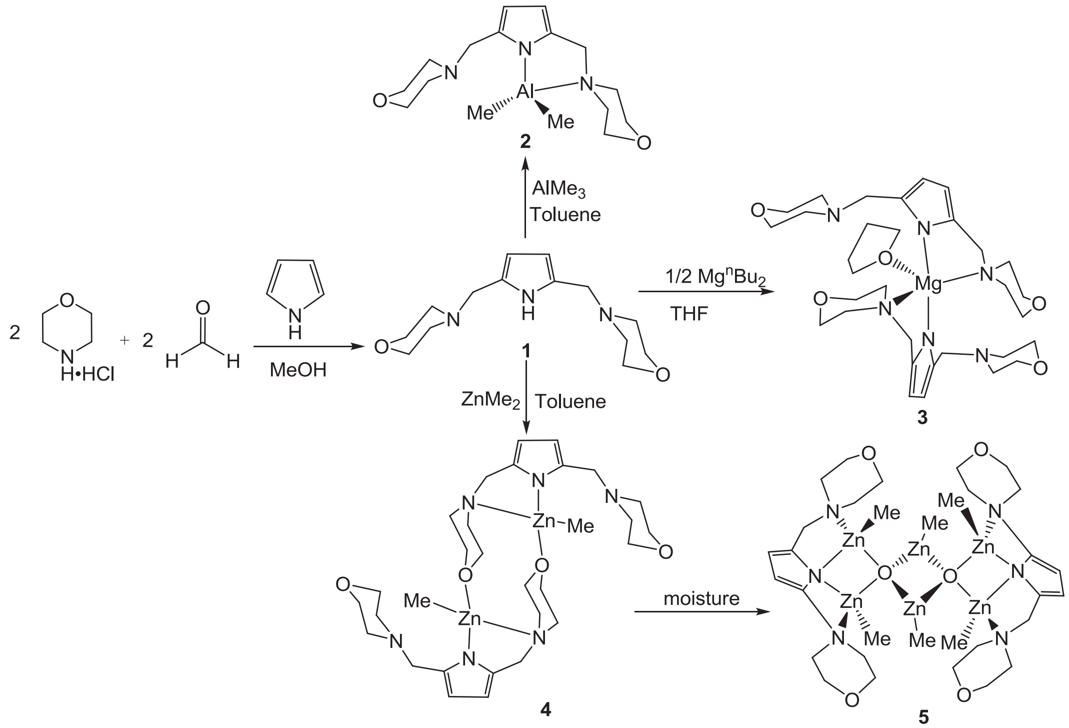
**Scheme 1.** Ligand design of pyrrole-based ligands.



**Scheme 2.** Possible bonding sites of the tri-dentate pyrrole-morpholine ligand.

converted into its corresponding hydrochloric salt, $O(CH_2CH_2)_2NH \cdot HCl$, and added to a methanol solution of pyrrole and formaldehyde to generate the desired tri-dentate pyrrole-morpholine ligand, $C_4H_2NH\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}$ (**1**), in 81% yield. Compound **1** was characterized using $^1H$ and $^{13}C$ NMR spectroscopy and single crystal X-ray diffractometry. A characteristic resonance for the methylene of the side chain substituent $CH_2N(CH_2CH_2)_2O$ in the $^1H$ and $^{13}C$ NMR spectra in $CDCl_3$ shows a singlet at $\delta$ 3.35 and 55.8, respectively. The tri-dentate symmetrical ligand **1** shows only one resonance at $\delta$ 5.85 for the two CH protons of the pyrrole ring and two triplets at $\delta$ 2.35 and 3.63 for the $CH_2$ protons of the morpholine ring.

The reaction of the tri-dentate pyrrole ligand **1** with one equivalent of $AlMe_3$ in toluene generated an aluminum dimethyl compound, $AlMe_2\{C_4H_2N\{2,5\text{-}[CH_2N(CH_2CH_2)_2O]_2\}\}$ (**2**), in moderate yield after work-up (Scheme 3). Compound **2** shows a singlet at $\delta$ 3.62 in the $^1H$ NMR spectrum in $CDCl_3$ for the methylene protons of the side chain substituent, $CH_2N(CH_2CH_2)_2O$, which is shifted downfield from its corresponding peak in ligand **1**. The high-field



**Scheme 3.** Synthesis of the tri-dentate pyrrole-morpholine ligand and its metal complexes.