

New types of bi- and tri-dentate pyrrole-piperazine ligands and related zinc compounds: Synthesis, characterization, reaction study, and ring-opening polymerization of ϵ -caprolactone

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ABSTRACT

Reactions of one or two equivalents of formaldehyde and phenylpiperazine with pyrrole in methanol or ethanol generated substituted pyrrole ligands $C_4H_3NH-[2-CH_2N(CH_2CH_2)_2NPh]$ (**1**) and $C_4H_2NH-[2,5-[CH_2N(CH_2CH_2)_2NPh]_2]$ (**2**), respectively. Reacting **1** with one equivalent of $ZnMe_2$ in toluene generated a di-zinc compound **3**, $\{ZnMe\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}_2$, in moderate yield. Further reacting **3** with two equivalents of *p*-cresol in toluene overnight afforded phenoxy bridged di-zinc compound **4**, $\{Zn(\mu-O-C_6H_4-4-Me)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}_2$. Similarly, the reactions of one and two equivalents of tridentate substituted pyrrole ligand **2** with $ZnMe_2$ afforded Zn compounds $ZnMe\{C_4H_2N-[2,5-[CH_2N(CH_2CH_2)_2NPh]_2]\}$ (**5**) and $Zn\{C_4H_2N-[2,5-[CH_2N(CH_2CH_2)_2NPh]_2]\}_2$ (**6**), respectively, in moderate yield. All of these compounds were characterized using 1H and ^{13}C NMR spectroscopy. Compound **5** is relatively air and moisture sensitive and decomposes during the recrystallization process to yield a tri-Zn cluster, $\{Zn(\mu_2-OH)\{C_4H_2N-[2,5-[CH_2N(CH_2CH_2)_2NPh]_2]\}_3$ (**7**). The molecular geometries of compounds **1**, **3**, **4**, **6**, and **7** were also determined using single crystal X-ray diffractometric analysis. Compounds **3**, **4**, and **6** were used as initiators for the ring opening polymerization of ϵ -caprolactone, and all of the zinc compounds showed high conversion with broad or bimodal molecular weight distributions.

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Introduction

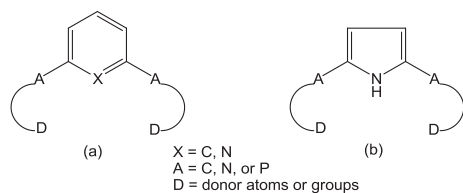
Tridentate pincer type ligands (Scheme 1(a)) are widely used in the synthesis of organometallic catalysts due to their versatile bonding modes and strong coordinating ability toward metal atoms [1–4]. Among of these pincer-type ligands, tridentate pyrrolyl-based pincer ligands, where the three nitrogen coordinating sites originated from pyrrole and two side arms, have been studied by several groups (Scheme 1(b)) [5–11]. Pyrrole, a component in porphyrins, such as heme and chlorophyll, can act as ligands and bind to metals in different bonding modes (Scheme 2). The pyrrole ring can bind to metal *via* different modes, such as η^1 -terminal

mode [12–16], μ_2 -bridge mode [17–22], and μ - η^1 : η^5 -bridge mode [23–27]. By combing the versatile pyrrole ring and pincer-type ligands [28,29], we developed a new type of pyrrolyl-based pincer ligand containing piperazine fragments, which may offer unique molecular geometries for metal complexes.

Ring-opening polymerization of the ϵ -caprolactone (CL) monomer is a general method for generating polycaprolactone [30–35] using catalysts, such as stannous octoate [36,37]. A wide range of catalysts for the ring opening polymerization of ϵ -caprolactone have been reviewed [38–42]. However, using stannous as a catalyst for ring opening polymerization has raised concern over health and safety. Therefore, more human health-friendly metal catalysts, such as Mg [43–46], Ca [47–50], and Zn [51–55], have been studied, and a variety of ligand systems have been adopted (Scheme 3). Therefore, we also studied the catalytic activity of these new metal complexes for the ring-opening polymerization of ϵ -caprolactone.

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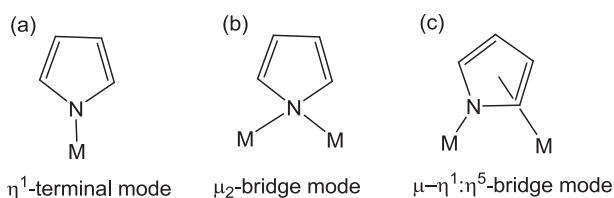
Scheme 1. Pincer-type ligands (a) aromatic or (b) pyrrole-based ligands.

Results and discussion

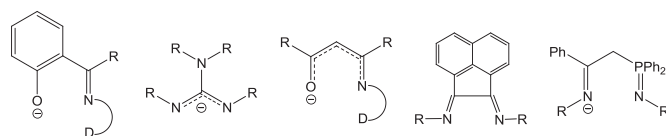
Synthesis and characterization

New types of bi- and tri-dentate pyrrole-piperazine ligands were synthesized using similar procedures as reported in the literature (Scheme 4) [56]. Using one or two equivalents of formaldehyde and phenylpiperazine with pyrrole in methanol or ethanol generated the substituted pyrrole ligands $C_4H_3NH-[2-CH_2N(CH_2CH_2)_2NPh]$ (**1**) and $C_4H_2NH-\{2,5-[CH_2N(CH_2CH_2)_2NPh]\}_2$ (**2**), respectively, via the Mannich reaction. These two substituted pyrrole ligands **1** and **2** have been characterized using 1H and ^{13}C NMR spectroscopy and X-ray single crystal diffractometry. A characteristic resonance for the methylene protons of side chain substituent $CH_2N(CH_2CH_2)_2NPh$ in the 1H NMR spectrum in $CDCl_3$ shows a singlet at δ 3.57 and 3.52 for **1** and **2**, respectively. In addition, the bidentate pyrrole ligand **1** shows an asymmetrical manner on the three CH protons of the pyrrole ring with three resonances δ at 6.08, 6.14, and 6.76. In contrast, the tri-dentate symmetrical substituted pyrrole ligand **2** shows only one resonance at δ 5.95 for the two CH protons of the pyrrole ring.

Reacting the bidentate pyrrole ligand **1** with one equivalent of $ZnMe_2$ in toluene generated a di-zinc compound **3**, $\{ZnMe\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}\}_2$, in moderate yield after work-up (Scheme 5). Colorless crystals of **3** were obtained from a saturated methylene chloride solution at $-20^\circ C$. The methylene protons of the side chain substituent, $CH_2N(CH_2CH_2)_2NPh$, of **3** show a singlet at δ 3.69 in the 1H NMR spectrum in $CDCl_3$, which is shifted downfield from its corresponded peak in ligand **1**. The high-field shift resonance for $Zn-Me$ is observed at δ -0.39 , which is comparable to the $Zn-Me$ resonances reported in the literature [57–59]. It is interesting to note that the methylene protons of the piperazine ring are split into three multiplets at δ 2.59, 3.12, and 3.54 with an integration ratio of 1:2:1. Presumably, the steric effect and the ring constraint on the molecular geometry give rise to the splitting. Variable temperature 1H NMR spectra of **3** in $CDCl_3$ did not resolve the splitting or reach the high temperature limit in the range of -45 to $20^\circ C$. Further reacting **3** with 2 equivalents of *p*-cresol in toluene overnight afforded phenoxide bridged di-zinc compound **4**, $\{Zn(\mu-O-C_6H_4-4-Me)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}\}_2$, in moderate yield. The 1H NMR spectrum of **4** in $CDCl_3$ shows a singlet at δ 2.22, indicating the methyl groups of the two phenoxide fragments. The methylene protons of the side chain substituent $CH_2N(CH_2CH_2)_2NPh$ has shifted to δ 3.83.



Scheme 2. Bonding modes of pyrrole to metals.



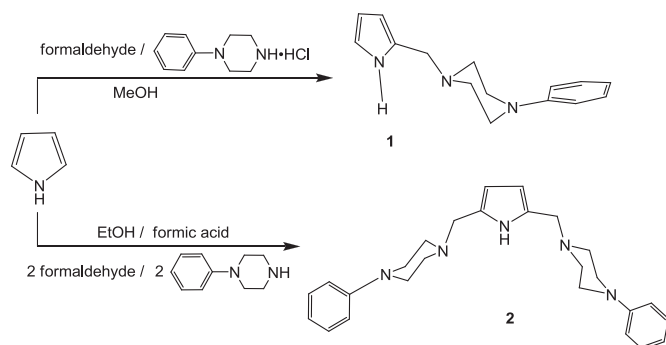
Scheme 3. Ligand systems involved in the catalysts for the ring-opening polymerization of ϵ -caprolactone.

Reacting one and two equivalents of tridentate substituted pyrrole ligand **2** with $ZnMe_2$ afforded Zn compounds, $ZnMe\{C_4H_2N-\{2,5-[CH_2N(CH_2CH_2)_2NPh]\}_2\}$ (**5**) and $Zn\{C_4H_2N-\{2,5-[CH_2N(CH_2CH_2)_2NPh]\}_2\}_2$ (**6**), respectively, in moderate yield (Scheme 6). The 1H NMR spectra of **5** and **6** both show characteristic resonances of methylene protons of the side chain substituent $CH_2N(CH_2CH_2)_2NPh$ at δ 3.60 and 3.61, respectively. Similar to compound **3**, the high-field shift resonance for the $Zn-Me$ of compound **5** is observed at δ -0.35 . Compound **5** is thermally unstable and is sensitive to air and moisture. Exposing **5** to air or increasing the reaction time both result in unidentified compounds. However, during the recrystallization process of compound **5**, a small amount of moisture leaked into the flask and caused the decomposition of compound **5**, generating a tri-Zn compound, $\{Zn(\mu_2-OH)\{C_4H_2N-\{2,5-[CH_2N(CH_2CH_2)_2NPh]\}_2\}\}_3$ (**7**).

Molecular geometries of **1**, **3**, **4**, **6** and **7**

A summary of the crystal data collection for compounds **1**, **3**, **4**, **6** and **7** and their selected bond lengths and angles are listed in Tables 1 and 2, respectively. All of the crystals of these compounds suitable for single crystal X-ray diffractometric analysis were obtained from saturated solutions at $-20^\circ C$, where **1**, **3**, and **4** used methylene chloride as the solvent and **6** and **7** used toluene.

The molecular structure of **1** is shown in Fig. 1 and bond lengths of pyrrole rings and side chain are comparable with similar pyrrole ligands reported in the literature [60–64]. The molecular geometry of **1** shows intramolecular hydrogen bonding with a bond length of $N(2)\dots H(1)$ ca. 2.95 Å, consistent with the values reported in the literature [65,66]. The molecular structures of **3** and **4** are shown in Figs. 2 and 3, respectively. Both compounds exist in dimeric geometries; however, the bonding modes of the pyrrolyl rings in **3** and **4** are quite different. The two pyrrolyl rings of compound **3** act as μ_2 -bridging ligands using the two pyrrole nitrogen atoms, and the two zinc atoms form a diamond plane with bond lengths of $Zn(1)-N(1)$ and $Zn(1)-N'(1)$ at 2.0478(17) and 2.2429(17) Å, and the bond angles of $Zn(1)-N(1)-Zn'(1)$ and $N(1)-Zn(1)-N'(1)$ are $89.04(6)^\circ$ and $108.21(6)^\circ$, respectively. The results are quite similar to those reported in the literature for a μ_2 -bridged pyrrole ring [17–22]. The bidentate ligands bind to the Zn atoms with an angle



Scheme 4. Synthesis of bi- and tri-dentate pyrrole-piperazine ligands **1** and **2**.

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