



# Tridentate pyrrolylzinc compounds: Synthesis, structures, reactivities and catalytic cyclotrimerization reaction of isocyanate



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## ABSTRACT

The reactions of ZnEt<sub>2</sub> with NNN-tridentate pincer type pyrrolyl ligands, 2,5-bis((dimethylamino)methylene)-1H-pyrrole (HL<sup>1</sup>), 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole (HL<sup>2</sup>) and 2,5-bis((piperidino)methylene)-1H-pyrrole (HL<sup>3</sup>), afford zinc ethyl compounds [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]ZnC<sub>2</sub>H<sub>5</sub> (**1**), [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>]ZnC<sub>2</sub>H<sub>5</sub> (**2**), and [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>]ZnC<sub>2</sub>H<sub>5</sub> (**3**) in high yield. Subjecting **1**, **2**, **3** with one equivalent of tert-butylphenol in THF generated {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**4**), {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**5**), {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**6**), respectively. Each has been characterized by satisfactory C, H and N microanalysis, NMR spectroscopy at ambient temperature, and single crystal X-ray structural analysis. The compounds Et<sub>6</sub>ZnO<sub>2</sub>[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>] (**7**) and Et<sub>6</sub>ZnO<sub>2</sub>[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>] (**8**) obtained accidentally from zinc ethyl compounds with traces of water. Each of compound **1–6** has been used as initiator for cyclotrimerization of isocyanate, and the organozinc compound **3** shows moderate reactivity toward the cyclotrimerization of isocyanate in Et<sub>2</sub>O solvent under mild conditions.

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## Introduction

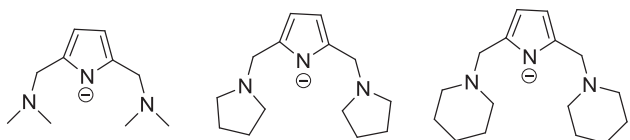
Over the past few years, the pincer ligands with three nitrogen donor functions {NNN} have played an increasingly important role in coordination chemistry. Due to their high thermal stability, unusual reactivity and high degree of flexibility concerning steric and electronic properties, they have been synthesized for making metal complexes to study catalysis of organic transformation reactions and used in inorganic coordination chemistry [1]. However, the monoanionic tridentate pyrrolyl ligands containing saturated methylene moieties (as depicted in Scheme 1) have been largely neglected. Although they were first synthesized in the late 1940s [2], few examples of organometallic complexes containing these tridentate ligands have been reported. In these studies, Huang's group employed the tridentate, substituted pyrrolyl ligands [C<sub>4</sub>H<sub>3</sub>N{2,5-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>}] as auxiliary ligands with aluminum [3a–3g] and zinc [3h] or transition metals including Zr [4a,4d,4g], Hf [4d], Ga [4b,4e], In [4b], Y [4c] and Mo [4f] to form organometallic

compounds, and evaluated their reactivity toward small organic molecules such as PhNCO, CO<sub>2</sub>, H<sub>2</sub>O, alcohols, phenol, ketone, amine, phenylethyne, triphenylsilanol and so on. Cui's group reported that the tridentate pyrrolyl ligands, 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole and 2,5-bis((piperidino)methylene)-1H-pyrrole, display κ<sup>1</sup>:κ<sup>2</sup> and mixed η<sup>5</sup>/κ<sup>1</sup> coordination modes owing to the different rare-earth metal ions (Sc, Y, Lu). These rare-earth metal complexes can generate binary cationic systems with an organoborate, which can initiate the precisely controlled or even living polymerization of isoprene [5]. In addition, titanium pyrrolyl complex, [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]Ti(NMe<sub>2</sub>)<sub>3</sub> was synthesized and characterized by Odom's group and found to be effective catalyst for the iminohydrazination of alkynes [6]. And Stalke reported the effects of group 14 metal (Ge, Sn, Pb) coordination on the π-system of the 2, 5-bis((pyrrolidino)-methyl)-1H-pyrrole pincer ligand [7].

Recently, we have reported alkali metal compounds containing substituted pyrrolyl ligands and their application in amidation of aldehydes with amines [8a] and cyclotrimerization of isocyanates [8b]. In our continuing interest in developing substituted pyrrolyl ligand systems, this paper focuses on the monoanionic tridentate pyrrolyl ligands, 2,5-bis((dimethylamino)methylene)-1H-pyrrole, 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole and 2,5-bis((piperidino)methylene)-1H-pyrrole, the corresponding alkyl zinc complexes and their reactivity.

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**Scheme 1.** Monoanionic tridentate pyrrolyl ligands containing saturated methylene moieties.

## Results and discussion

### Synthesis and characterization of zinc compounds (1–8)

Zinc compounds containing NNN-tridentate pincer type pyrrolyl ligands, 2,5-bis((dimethylamino)methylene)-1H-pyrrole (**HL<sup>1</sup>**), 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole (**HL<sup>2</sup>**) and 2,5-bis((piperidino)methylene)-1H-pyrrole (**HL<sup>3</sup>**), were synthesized and characterized by satisfactory C, H and N microanalysis, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} spectra in d<sub>8</sub>-THF or C<sub>6</sub>D<sub>6</sub> at ambient temperature, and single crystal X-ray structural data. As shown in **Scheme 2**, the reaction of ZnEt<sub>2</sub> with **HL<sup>1</sup>**, **HL<sup>2</sup>** and **HL<sup>3</sup>** in hexane afforded zinc ethyl complexes [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]ZnEt<sub>2</sub> (**1**), [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>]ZnEt<sub>2</sub> (**2**), and [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>]ZnEt<sub>2</sub> (**3**) in high yield along with the elimination of equivalent of ethane, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the results of X-ray structure.

Reacting **1**, **2**, **3** with one equivalent of tert-butylphenol in THF generated {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**4**), {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**5**), {[C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>]Zn(O-C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)}<sub>2</sub> (**6**), respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are also coincided to the corresponding structure. The complexes **7** and **8** were obtained accidentally from long storage of the resultant solution of ZnEt<sub>2</sub> with **HL<sup>2</sup>** and **HL<sup>3</sup>** in freezer. Despite repeated attempts according to the relevant report

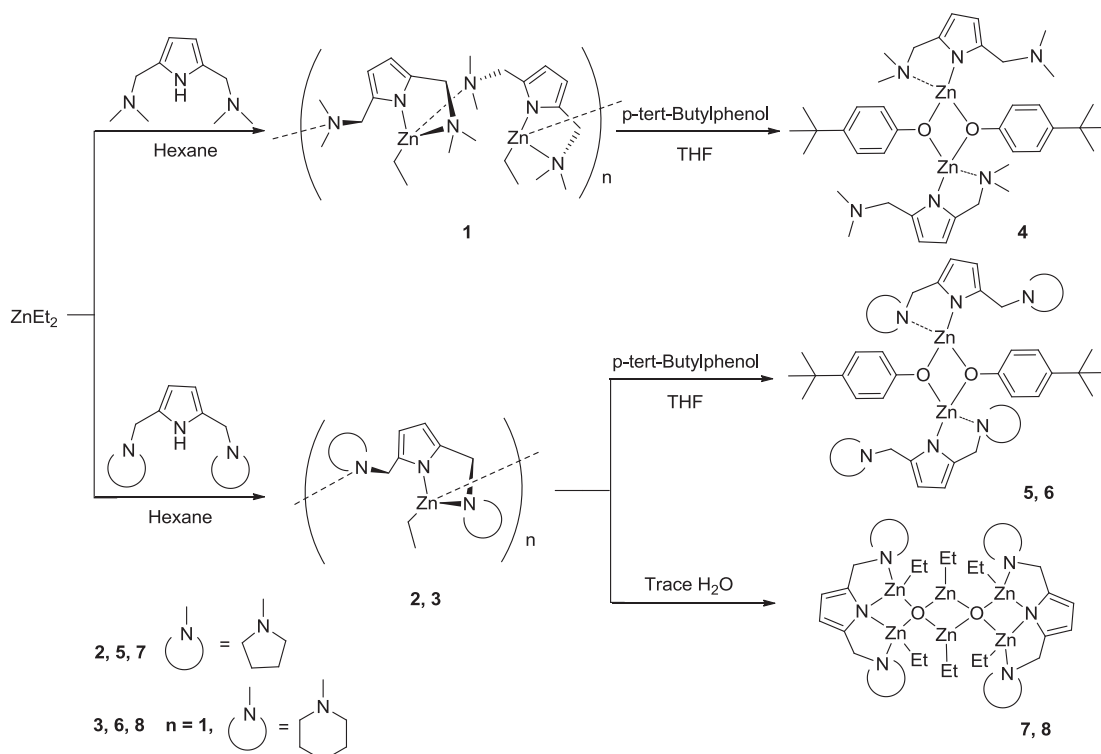
with traces of water [9], using a variety of different crystallization solvents, no expected products were isolated, but which is common phenomenon for such reactions. Unfortunately, due to the lack of 'pure' material, full analysis of these complexes were not possible. It is not discussed in detail but the crystallographic data are included in the **Supporting information**.

### X-ray single crystal structures of 1, 2, 3, 4, 6, 7 and 8

The molecular structure of a monomeric unit for the crystalline complex **1** is shown in **Fig. 1a**. Each asymmetric unit of **1** has two molecules of [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]ZnEt<sub>2</sub>. The tridentate pyrrolyl ligand only coordinates to the zinc center through pyrrolyl nitrogen and one NMe<sub>2</sub> fragment leaving another NMe<sub>2</sub> fragment binding to the zinc atom of another unit. This coordination mode leads to form polymeric structures (**Fig. 1b**). The geometry of the Zn atom can be described as a distorted tetrahedral. And the bond lengths of Zn2–N3, Zn2–N4 and Zn2–N5 are 2.196(7), 1.989(6) and 2.249(7) Å, respectively. The bite angle N4–Zn2–N5 of the pyrrolyl nitrogen and the NMe<sub>2</sub> amido nitrogen to the zinc atom is N4–Zn2–N5 80.5(3)°.

The crystalline polymeric complex **2** is built up of [C<sub>4</sub>H<sub>2</sub>N(2,5-CH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>]ZnEt<sub>2</sub> units having essentially similar geometric parameters to those in **1**, linked Zn atom via the uncoordinated NMe<sub>2</sub> fragment of another unit. As illustrated in **Fig. 2**, unlike **1**, each asymmetric unit of **2** has one molecule. The monomeric unit of **2** belongs to the monoclinic crystal system, space group P2(1)/n. The bond lengths of Zn1–N1 and Zn1–N2 are 1.994(6) and 2.168(7) Å, and the bite angle N1–Zn1–N2 is 81.7(3)°. These data are comparable with those in compound **1**.

Compound **3** was crystallized from a saturated hexane solution. As illustrated in **Fig. 3**, unlike **1** and **2**, it is not a polymeric complex. The Zn atom is three coordinate by ethyl carbon and nitrogen atoms of pyrrole ring and the N(CH<sub>2</sub>)<sub>5</sub> fragment. The bond lengths of



**Scheme 2.** Synthetic routes to the compounds 1–8.

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