

Lithium, magnesium, zinc complexes supported by tridentate pincer type pyrrolyl ligands: Synthesis, crystal structures and catalytic activities for the cyclotrimerization of isocyanates



Qiao Liu^a, Zhiqiang Guo^b, Hongfei Han^a, Hongbo Tong^b, Xuehong Wei^{a,*}

^aThe School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China

^bInstitute of Applied Chemistry, Shanxi University, Taiyuan 030006, PR China

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ABSTRACT

Lithium, magnesium, zinc complexes incorporating substituted symmetrical tridentate pyrrolyl ligands were synthesized conveniently and their application for the cyclotrimerization of isocyanate to corresponding isocyanurate has been investigated. The reaction of 1 equivalent of 2,5-bis(pyrrolidinomethyl)pyrrole {C₄H₂NH(2,5-CH₂NC₄H₈)₂} with n-BuLi generated [Li{C₄H₂N(2,5-CH₂NC₄H₈)₂}₂] (1) in diethyl ether. Treatment of 2 equivalents of C₄H₂NH(2,5-CH₂NC₄H₈)₂ with MgBu₂ or ZnEt₂ in THF afforded [Mg(THF){C₄H₂N(2,5-CH₂NC₄H₈)₂}₂] (2) or [Zn{C₄H₂N(2,5-CH₂NC₄H₈)₂}₂] (3) in high yield, respectively. Compounds 1, 2 and 3 were characterized by ¹H and ¹³C NMR spectra and their molecular structures were determined by single crystal X-ray diffraction. Furthermore, compounds 1, 2 and 3 were proved to be moderate to good initiators for cyclotrimerization of isocyanate to the corresponding isocyanurate in diethyl ether.

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1. Introduction

The heterocyclic compound pyrrole, which has the capability to bond metals in various bonding modes, has played a significant role in organometallic chemistry [1]. During the past few years, there is much information available in literature about the transition-metal and rare earth metal complexes bearing pyrrole and pyrrolyl ligands [2,3]. Until recently, main group elements-based pyrrolyl complexes have attracted increasing attention [4]. However, to the best of our knowledge, the chemistry of numerous main group elements-based pyrrolyl complexes has been much investigated, but, pyrrolyl-linked symmetrical tridentate pincer type complexes have been largely neglected. Only a few papers have been published by Huang's group [5]. In our continuing interest in developing main group metal compounds containing substituted pyrrolyl ligands as catalysts [6,7]. Aromatic isocyanurates, manufactured by cyclotrimerizing corresponding isocyanates, have been shown to enhance the uses of polyurethanes as coating materials and copolymer resins to enhance their water-resistance, transparency, and impact resistance [8,9]. Here we report the synthesis and structural features of lithium, magnesium, zinc complexes incorporating substituted symmetrical tridentate pyrrolyl

ligands and their catalytic activity for cyclotrimerization of isocyanate to the corresponding isocyanurate.

2. Experimental

2.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were purchased from commercial sources and dried prior to use. Deuterated solvents C₆D₆ were dried over activated molecular sieves (4 Å) and vacuum transferred before use. Hexane was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Metal-alkyls solutions {n-BuLi (hexane solution, 2.2 M), ZnEt₂ (hexane solution, 1.0 M), and MgBu₂ (heptane solution, 0.5 M)} were purchased from Aldrich and used as received. Glassware was oven-dried at 105 °C overnight. 2,5-Bis-((pyrrolidino)methyl)-pyrrole was prepared according to the literature [10].

2.2. Synthesis of [Li{C₄H₂N(2,5-CH₂NC₄H₈)₂}₂] (1)

n-BuLi (0.87 mL, 2.0 mmol) was added to a solution of C₄H₂NH(2,5-CH₂NC₄H₈)₂ (0.466 g, 2.0 mmol) in diethyl ether (20 mL) at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for 2 h. This resultant solution was con-

* Corresponding author. Tel.: +86 351 7018390; fax: +86 351 7011688.

E-mail address: xhwei@sxu.edu.cn (X. Wei).

centrated in *vacuo* to ca. 15 mL and stored at $-10\text{ }^{\circ}\text{C}$ for 4 days yielding compound **1** as colorless crystals in 87.2%. *Anal. Calc.* for $\text{C}_{28}\text{H}_{44}\text{N}_6\text{Li}_2$: C, 70.27; H, 9.27; N, 17.56. Found: C, 70.03; H, 9.41; N, 17.30%. $^1\text{H NMR}$ (C_6D_6): 6.38(s, 4H, $\text{C}_4\text{H}_3\text{N}$), 3.69(s, 8H, CH_2N), 2.44(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$), 1.32(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$). $^{13}\text{C NMR}$ (C_6D_6): δ (ppm) 138.4($\text{C}_4\text{H}_3\text{N}$), 105.2($\text{C}_4\text{H}_3\text{N}$), 59.08(CH_2), 54.0($\text{N}(\text{CH}_2)_4$), 23.36($\text{N}(\text{CH}_2)_4$).

2.3. Synthesis of $[\text{Mg}(\text{THF})\{\text{C}_4\text{H}_2\text{N}(2,5\text{-CH}_2\text{NC}_4\text{H}_8)_2\}_2]$ (**2**)

MgBu_2 (1.0 mL, 1.0 mmol) was added to a solution of $\text{C}_4\text{H}_2\text{N}(2,5\text{-CH}_2\text{NC}_4\text{H}_8)_2$ (0.466 g, 2.0 mmol) in tetrahydrofuran (20 mL) at $0\text{ }^{\circ}\text{C}$. The solution changed from colorless to pale yellow. The resulting mixture was warmed to room temperature and stirred for 3 h, then filtered. The pale yellow precipitate was dissolved in tetrahydrofuran. The solution was concentrated in *vacuo* to ca. 10 mL and stored at $-5\text{ }^{\circ}\text{C}$ yielding colorless crystals of **2** (86.5%). *Anal. Calc.* for $\text{C}_{32}\text{H}_{52}\text{N}_6\text{OMg}$: C, 69.31; H, 9.58; N, 14.26. Found: C, 69.07; H, 9.54; N, 14.11%. $^1\text{H NMR}$ (C_6D_6): 6.45(s, 4H, $\text{C}_4\text{H}_3\text{N}$), 3.62(t, 4H, THF), 3.60(s, 8H, CH_2N), 2.68(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$), 1.49(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$), 1.46(t, 4H, THF). $^{13}\text{C NMR}$ (C_6D_6): δ (ppm) 135.43($\text{C}_4\text{H}_3\text{N}$), 106.08($\text{C}_4\text{H}_3\text{N}$), 67.73(THF), 57.32(CH_2), 53.6($\text{N}(\text{CH}_2)_4$), 25.64(THF), 22.85($\text{N}(\text{CH}_2)_4$).

2.4. Synthesis of $[\text{Zn}\{\text{C}_4\text{H}_2\text{N}(2,5\text{-CH}_2\text{NC}_4\text{H}_8)_2\}_2]$ (**3**)

ZnEt_2 (1.0 mL, 1.0 mmol) was added to a solution of $\text{C}_4\text{H}_2\text{N}(2,5\text{-CH}_2\text{NC}_4\text{H}_8)_2$ (0.466 g, 2.0 mmol) in tetrahydrofuran (20 mL) at $0\text{ }^{\circ}\text{C}$. The solution changed from colorless to pale yellow. The resulting mixture was warmed to room temperature and stirred for 3 h, then filtered. The filtrate was concentrated in *vacuo* to ca. 10 mL and stored at $-5\text{ }^{\circ}\text{C}$ yielding colorless crystals of **3** (86.9%). *Anal. Calc.* for $\text{C}_{28}\text{H}_{44}\text{N}_6\text{Zn}$: C, 64.56; H, 8.67; N, 15.06. Found: C, 64.37; H, 8.46; N, 14.91%. $^1\text{H NMR}$ (C_6D_6): 6.14(s, 4H, $\text{C}_4\text{H}_3\text{N}$), 3.29(s, 8H, CH_2N), 2.22(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$), 1.18(s_{br} , 16H, $\text{N}(\text{CH}_2)_4$). $^{13}\text{C NMR}$ (C_6D_6): δ (ppm) 135.05($\text{C}_4\text{H}_3\text{N}$), 106.08($\text{C}_4\text{H}_3\text{N}$), 57.32(CH_2), 55.04($\text{N}(\text{CH}_2)_4$), 23.27($\text{N}(\text{CH}_2)_4$).

2.5. Typical procedure of cyclotrimerization of isocyanates

All the reactions were carried out under a nitrogen-filled Schlenk line. Considering a typical method, the catalyst was first dissolved in 15 mL Et_2O , followed by the addition of isocyanate. The mixture was immediately stirred at the room temperature for 24 h to produce isocyanurate. The resulting solid was isolated

by filtration and washed with Et_2O , then dried under vacuum to form a satisfactory yield.

3. Results and discussion

3.1. Synthesis and characterization

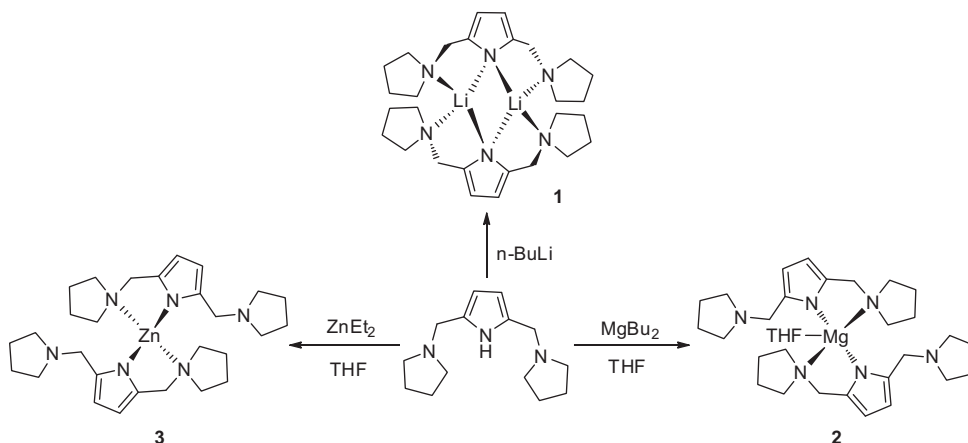
Compounds **1–3** were readily prepared in good yield from the reaction of substituted pyrrole precursor $[\text{C}_4\text{H}_2\text{N}(2,5\text{-CH}_2\text{NC}_4\text{H}_8)_2]$ with *n*-BuLi, ZnEt_2 and MgBu_2 , respectively (Scheme 1). Each of **1**, **2**, and **3** was easily purified by crystallization from a mixed solution of hexane and THF, and was characterized by ^1H and ^{13}C NMR spectra in C_6D_6 at ambient temperature, microanalyses and single crystal X-ray structural data. The ^1H and ^{13}C NMR spectra of compounds **1–3** exhibit a symmetrical geometry with only one set of signals for the substituted pyrrolyl and dipyrrolydinyl ligands being observed. All of complexes are highly air and moisture sensitive, which readily decompose upon exposure to the atmosphere.

3.2. Molecular structures of compounds **1**, **2** and **3**

The crystals of compounds **1**, **2** and **3** suitable for single crystal X-ray diffraction analysis were recrystallized from a saturated hexane solution or a mixed solution of hexane and THF. Data collection was performed with Mo $K\alpha$ radiation ($k = 0.71073\text{ \AA}$) on a Bruker Smart Apex CCD diffractometer at 223(2) K.

The ORTEP drawing of the molecular structure of the lithiated pyrrolyl compound (**1**) is shown in Fig. 1. The data collection and selected bond distances and angles are summarized in Table 1. The substituted pyrrolyl ligands act as tridentate ligands, lithium atoms are four-coordinate environment with a distorted tetrahedral geometry, linked through nitrogen atoms of pyrrole ring and the pyrrolidyl fragment. Two nitrogen atoms of pyrrolyl and two lithium atoms form a four-membered slightly folded ring with the nitrogen atom above the plane of the other nitrogen atom and the two lithium atoms 0.257 \AA . The angle between the planes of Li1N1Li2 and Li1N4Li2 is 9.17° . The bite angles of $\text{N}(\text{dipyrrolyl})\text{-Li-N}(\text{pyrrolyl})$ are $89.55^\circ(18)$ (N2Li1N1), $88.06^\circ(19)$ (N5Li1N4), $87.98^\circ(19)$ (N3Li2N1), and $89.44^\circ(19)$ (N6Li2N4), respectively. The bite angle of N4Li1N1 [$102.8^\circ(2)$] is similarly to that of N4Li2N1 [$102.9^\circ(2)$]. The Li–N bond distances are in the range of 2.034(5)–2.157(5) \AA which are close to the reported tridentate substituted pyrrolyllithium compound [5].

One of the most important magnesium compounds bearing pyrrolyl units (porphyrin) is chlorophyll which plays a key role in photosynthesis. A range of magnesium porphyrins and their



Scheme 1. Synthesis routes to compounds **1–3**.

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