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

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ABSTRACT

The reactions of $ZnEt_2$ with NNN-tridentate pincer type pyrrolyl ligands, 2,5-bis((dimethylamino)methylene)-1H-pyrrole (H**L^1**), 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole (H**L^2**) and 2,5-bis((piperidino)methylene)-1H-pyrrole (H**L^3**), afford zinc ethyl compounds $[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]ZnC_2H_5$ (**1**), $[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]ZnC_2H_5$ (**2**), and $[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]ZnC_2H_5$ (**3**) in high yield. Subjecting **1**, **2**, **3** with one equivalent of tert-butylphenol in THF generated $\{[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]Zn(O{-}C_6H_4\text{-}4\text{-}{}^tBu)\}_2$ (**4**), $\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]Zn(O{-}C_6H_4\text{-}4\text{-}{}^tBu)\}_2$ (**5**), $\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]Zn(O{-}C_6H_4\text{-}4\text{-}{}^tBu)\}_2$ (**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 $Et_6Zn_6O_2[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]_2$ (**7**) and $Et_6Zn_6O_2[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]_2$ (**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_2O solvent under mild conditions.

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 $[C_4H_3N\{2,5\text{-}(CH_2NMe_2)_2\}]$ 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_2, H_2O, 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 $\kappa^1{:}\kappa^2$ and mixed η^5/κ^1 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, $[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]Ti(NMe_2)_3$ 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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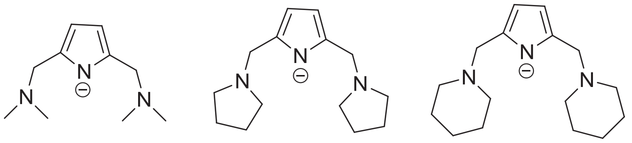


Scheme 1. Monoanionic tridentate pyrrolyl ligands containing saturated methylene moieties.

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 (H**L^1**), 2,5-bis((pyrrolidin-1-yl)methylene)-1H-pyrrole (H**L^2**) and 2,5-bis((piperidino)methylene)-1H-pyrrole (H**L^3**), were synthesized and characterized by satisfactory C, H and N microanalysis, ^{1}H, ^{13}C{^{1}H} spectra in d_8-THF or C_6D_6 at ambient temperature, and single crystal X-ray structural data. As shown in Scheme 2, the reaction of $ZnEt_2$ with H**L^1**, H**L^2** and H**L^3** in hexane afforded zinc ethyl complexes $[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]ZnC_2H_5$ (**1**), $[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]ZnC_2H_5$ (**2**), and $[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]ZnC_2H_5$ (**3**) in high yield along with the elimination of equivalent of ethane, respectively. The ^{1}H and ^{13}C NMR spectra are consistent with the results of X-ray structure.

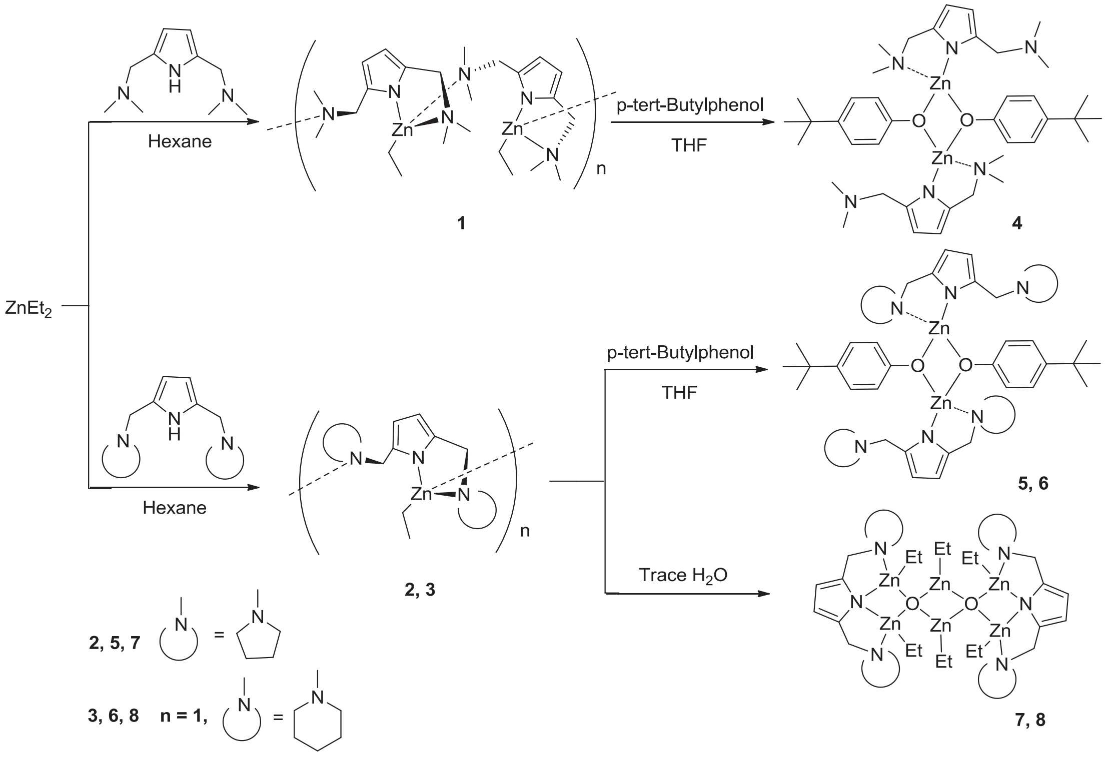
Reacting **1**, **2**, **3** with one equivalent of tert-butylphenol in THF generated $\{[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]Zn(O\text{–}C_6H_4\text{-}4\text{-}^t Bu)\}_2$ (**4**), $\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]Zn(O\text{–}C_6H_4\text{-}4\text{-}^t Bu)\}_2$ (**5**), $\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]Zn(O\text{–}C_6H_4\text{-}4\text{-}^t Bu)\}_2$ (**6**), respectively. The ^{1}H and ^{13}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 $ZnEt_2$ with H**L^2** and H**L^3** 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 $[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]ZnC_2H_5$. The tridentate pyrrolyl ligand only coordinates to the zinc center through pyrrolyl nitrogen and one NMe_2 fragment leaving another NMe_2 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_2 amido nitrogen to the zinc atom is N4–Zn2–N5 80.5(3)°.

The crystalline polymeric complex **2** is built up of $[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]ZnC_2H_5$ units having essentially similar geometric parameters to those in **1**, linked Zn atom via the uncoordinated NMe_2 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 *P*2(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 $N(CH_2)_5$ fragment. The bond lengths of



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

Zn–N1 and Zn1–N3 are 1.897(18) and 2.260(3) Å, respectively. The Zn–N(pyrrolyl) bond is shorter than the corrsponding bond lengths of **1** and **2**, and the bite angle N1–Zn1–N3 is 81.15(7)°.

The molecular structures of the dimeric compounds **4** and **6** are very similar and are illustrated in Figs. 4 and 5, respectively. The Zn atom is four coordinate with a distorted tetrahedral geometry, bonded to two nitrogen atoms of the pyrrole ring and the NMe_2 fragment and two oxygen atoms of tert-butylphenolate. In compound **4**, the bond lengths of Zn–O1 and Zn–O1′ are 1.948(3) and 1.980(3) Å, and the distance of Zn–N1 and Zn1–N2 are 1.891(3) and 2.129(4) Å, respectively. The bite angles of N1–Zn–N2 and O1–Zn–O1′ are 84.01(14) and 80.94(12)°. And for compound **6**, the bond lengths of Zn–N1, Zn–N3, Zn–O and Zn–O′ are 1.932(4), 2.142(4), 1.993(3) and 1.993(3) Å, respectively.

The molecular structures of compounds **7** and **8** are also very similar and are illustrated in Figs. 6 and 7, respectively. Four of the six zinc atoms are four coordinate with a distorted tetrahedral geometry, bonded to one carbon, one oxygen and two nitrogen atoms whereas the other two are three coordinate attached to one carbon and two oxygen atoms. The nitrogen and oxygen atoms are four coordinate in both structures. The bond lengths of Zn–O are in the range of 1.955–2.045(3) Å and the Zn–N bond distances are between 2.086 and 2.248(3) Å in compounds **7** and **8**.

The cyclotrimerization of isocyanate catalyzed by zinc compounds

Isocyanurates, the typical isocyanate cyclotrimerized products, could enhance the physical properties of polyurethanes, copolymer resins and coating materials [10], such as increased thermal and chemical resistance, water-resistance, transparency, and impact resistance [11]. Based on the commercial significance of isocyanurates, the cyclotrimerization of isocyanate has been studied thoroughly and many new types of catalysts have been developed to obtain the isocyanurates in high yields. For example, traditional Lewis-basic catalysts including N-heterocyclic carbenes [12], phosphines [13], amines [14], fluoride anions [15], p-toluenesulfinate [16] carbamate anions [17] and alkoxyalkenes [18], metal catalysts including organozinc amines and alkoxides [19], alkoxy niobium [20] and zirconium compounds [21], organotin (II) and (IV) compounds [22] and $Ti(bipyridyl)_3$ [23], copper and nickel halides [24], rare earth metal amides [25] and palladium (0) systems [26]. Recently, our group reported the alkali metal amides and bidentate pyrrolyl lithium complexes exhibiting excellent catalytic activities for the cyclotrimerization of isocyanates under mild conditions [8b,27]. For developing zinc compounds containing substituted pyrrolyl ligands, compounds **1**–**6** as initiators for isocyanate trimerization were carried out. Comparing pyrrolyl lithium complexes, the reactivity is relative low, only occurring at extended reaction time. The results are shown in Table 1.

Initially, phenyl isocyanate was selected as a model substrate, and the organozinc compounds **1**–**6** were screened as potential catalysts for cyclotrimerization of isocyanate. Good to excellent yields (71.6–92.4%) were obtained when each of **1**–**6** was used to promote the isocyanate to isocyanurates conversion in 12 h in Et_2O solvent at room temperature (Table 1, entries 1–6). Among the zinc ethyl compounds **1**–**3**, compound **3** gave the highest yield. In view of the solution states of **1** and **2** should be monomeric, the ^{13}C NMR results are consistent with the monomeric solution structure, the steric effect plays a key role in this reaction system. The activity of the compounds **4**–**6** was lower than that of the compounds **1**–**3**. This maybe the trigonal planar environment of monomeric zinc ethyl compounds offer an available coordination site or the

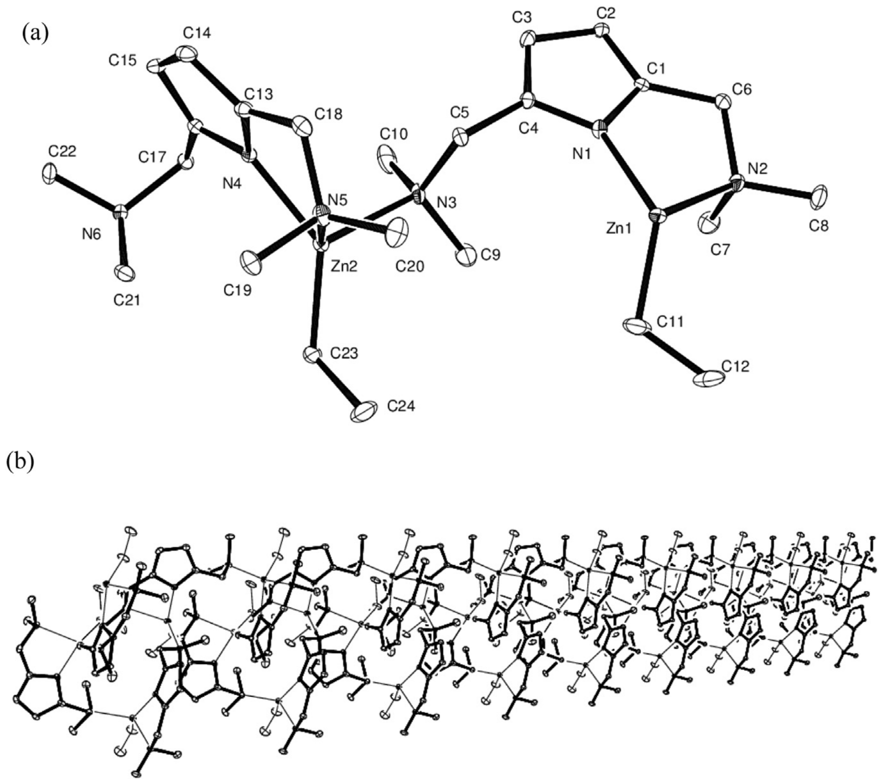


Fig. 1. (a) Molecular structure and (b) extended structures of **1**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn1–N1 1.994(6), Zn1–N2 2.168(7), Zn1–C11 1.958(15), Zn2–N4 1.989(6), Zn2–N5 2.249(7), Zn2–N3 2.196(7), Zn2–C23 1.973(9), C1–C6 1.499(11), C4–C5 1.532(11), N2–C6 1.498(11), N3–C5 1.487(10); N1–Zn1–N2 81.7(3), C1–C6–N2 109.5(6), C1–N1–C4 105.7(6), C4–C5–N3 116.6(7), N4–Zn2–N5 80.5(3), N3–Zn2–N4 100.7(3), N3–Zn2–N5 111.4(3).

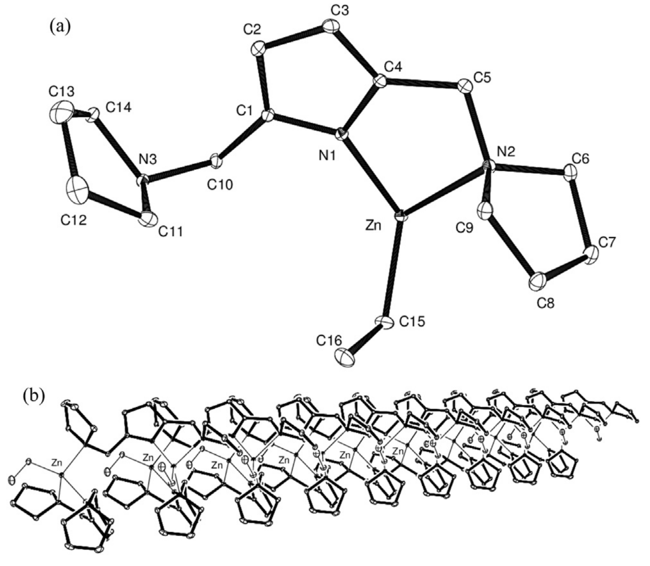


Fig. 2. (a) Molecular structure and (b) extended structures of **2**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn–N1 1.976(3), Zn–N2 2.244(3), Zn–C15 1.987(3), C4–C5 1.494(4), C1–C10 1.507(4), N2–C5 1.481(4), N3–C10 1.493(4); N1–Zn–N2 81.81(11), C4–C5–N2 110.6(3), C1–N1–C4 107.3(2), C1–C10–N3 117.8(3), C5–N2–Zn 103.76(18).

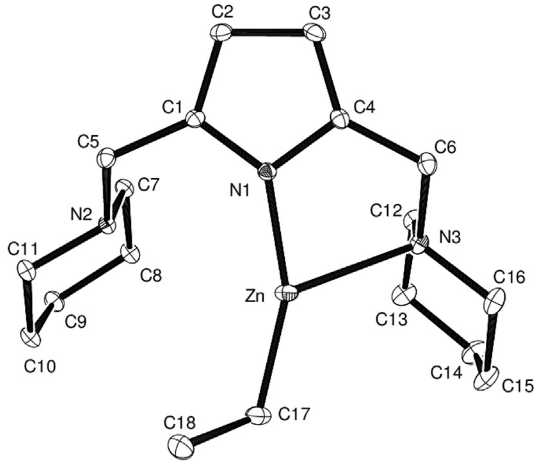


Fig. 3. ORTEP diagram of compound **3**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn–N1 1.897(18), Zn–N3 2.260(3), Zn–C17 1.937(3), C17–C18 1.485(5), C4–C6, 1.496(3), C1–C5 1.492(3), N3–C6 1.482(3), N2–C5 1.470(3), N1–C1 1.364(3); C1–N1–C4 107.45(18), N1–Zn–N3 81.15(7), C4–C6–N3 108.71(19), C1–C5–N2 111.46(18), N1–C4–C6 116.3(2), Zn–N3–C6 100.66(13).

difference of electronic features between the ethyl compounds and phenoxides. And compound **3** at 2.5 mol % or 1 mol % loading gave 82.4% or 54.5% yield of isocyanurates under the same conditions (Table 1, entries 7, 8), respectively. Using the optimized reaction conditions, the representative isocyanates, 4-chloro, 4-methyl and 4-methoxyphenyl isocyanate, were also examined using compound **3** as a catalyst at 5 mol % loading (Table 1, entries 9–11). Based on the experimental results and related literature [19], a proposed mechanism for the cyclotrimerization of isocyanates catalyzed by those zinc complexes follows a route similar to that for a variety of Lewis base catalyzed reaction is suggested: The zinc complex through a coordination template-effect, forces a defined number of monomer molecules into a specific configuration. Covalent bonds between the activated monomeric species are established upon breaking the initial coordinative bonds with the catalyst.

Conclusions

Six new zinc complexes containing monoanionic tridentate pyrrolyl ligands have been prepared in good yield. Each of **1**, **2**, **3**, **4** and **6** was easily purified by crystallization from hexane or mixed solution of hexane and THF, and was characterized by microanalysis, multinuclear NMR ambient temperature solution spectra and X-ray molecular structures. The isolations of both **7** and **8** were unexpected. These compounds **1**–**6** formed part of a screening programme aimed at identifying new catalysts for cyclotrimerization of isocyanates. The tests revealed, although the reactivity is relatively low comparing pyrrolyl lithium complexes [8b], compound **3** has proved to be a viable catalyst.

Experimental

General remarks

Unless otherwise noted, all syntheses and manipulations of air-sensitive materials were performed under a purified nitrogen atmosphere using the standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone under nitrogen. Hexane is dried using sodium potassium alloy and distilled under nitrogen prior to use. tert-butylphenol was recrystallized before use. $ZnEt_2$ (1.0 M solution in hexane; Alfa Aesar) were obtained commercially and used as received. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of the compounds were recorded on a Bruker DRX 300 instrument in C_6D_6 or d_8-THF at 298 K and referenced internally to the residual solvent resonances (^1H, ^{13}C). Elemental analyses were performed on a Vario EL-III instrument. Melting points were determined on a STUART SMP10 melting point apparatus and uncorrected. All tridentate pyrrolyl ligands were synthesized according to the literature procedure [2a,28].

Preparation

$[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]ZnC_2H_5$ (**1**)

To a stirred solution of $C_4H_2NH(2,5\text{-}CH_2NMe_2)_2$ (0.362 g, 2 mmol) in hexane (20 ml) was added $ZnEt_2$ (2.0 mL, 1.0 M) dropwise via a syringe at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The white solid was isolated by filtration and recrystallized from a saturated tetrahydrofuran and hexane solution to yield colorless crystals of **1** (0.447 g, 1.63 mmol, 81%). ^1H NMR (d_8-THF): 6.02 (s, 2H, C_4H_2N), 3.63 (s, 4H, $-CH_2-$), 2.49 (s, 12H, $-N(CH_3)_2$), 1.48 (t, $J = 7.8$, 3H, $ZnCH_2CH_3$), 0.45 (q, $J = 8.1$, 2H, $ZnCH_2CH_3$). ^{13}C NMR (d_8-THF): 133.9 (C_4H_2N), 105.3 (C_4H_2N), 60.5 ($-CH_2-$), 45.3 ($-N(CH_3)_2$), 13.3 ($ZnCH_2CH_3$), −3.2 ($ZnCH_2CH_3$). Anal. Calc. for $C_{12}H_{23}N_3Zn$: C, 52.47; H, 8.44; N, 15.30. Found: C, 52.39; H, 8.21; N, 14.93.

$[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]ZnC_2H_5$ (**2**)

The synthesis of compound **2** was carried out following the procedures similar to those used for the preparation of **1**. The white solid was recrystallized from a saturated diethyl ether and hexane solution to yield colorless crystals of **2** (0.503 g, 1.54 mmol, 77%). ^1H NMR (C_6D_6): 6.35 (s, 2H, C_4H_2N), 3.53 (s, 4H, $-CH_2-$), 2.58 (s, 8H, $-N(CH_2)_4$), 1.67 (t, $J = 8.1$, 3H, $ZnCH_2CH_3$), 1.57 (s,8H, $-N(CH_2)_4$), 0.59 (q, $J = 7.8$, 2H, $ZnCH_2CH_3$). ^{13}C NMR (C_6D_6): 135.5 (C_4H_2N), 104.5 (C_4H_2N), 57.1 ($-CH_2-$), 54.9 ($-N(CH_2)_4$), 23.4 ($-N(CH_2)_4$), 13.3 ($ZnCH_2CH_3$), 0.4 ($ZnCH_2CH_3$). Anal. Calc. for $C_{16}H_{27}N_3Zn$: C, 58.81; H, 8.33; N, 12.86. Found: C, 58.58; H, 8.49; N, 12.71.

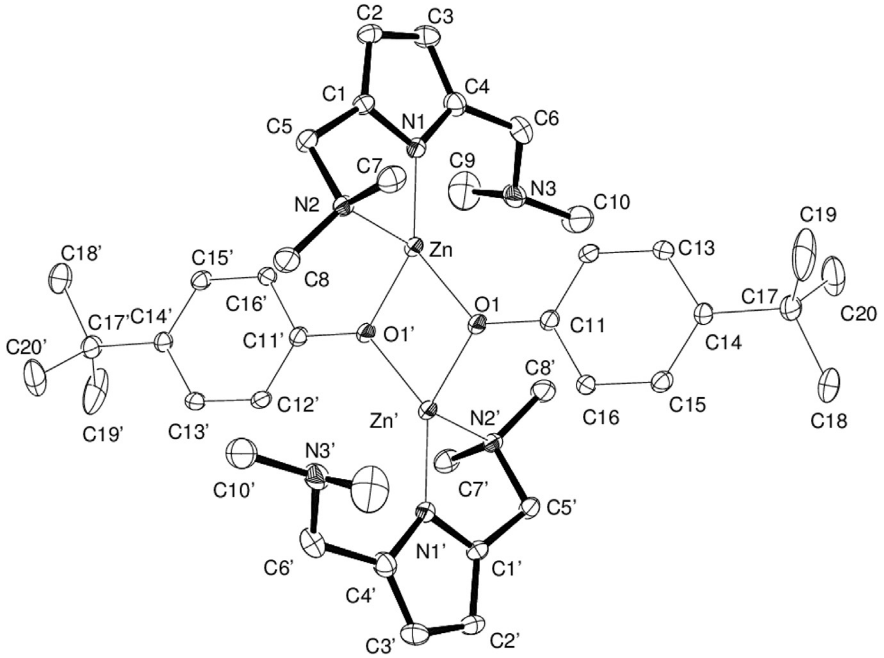


Fig. 4. ORTEP diagram of compound **4**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn–N1 1.891(3), Zn–N2 2.129(4), Zn–O1 1.948(3), Zn–O1′ 1.980(3), O1–C11 1.363(4), C1–C5 1.482(6), N2–C5 1.499(5), C4–C6 1.473(8), N3–C6 1.423(7); N1–Zn–N2 84.01(14), O1–Zn–O1′ 80.94(12), Zn–O1–Zn′ 99.06(12), N1–Zn–O1 141.04(13), N2–Zn–O1 107.17(13), C1–N1–C4 105.6(4), C1–C5–N2 108.4(3), N1–C1–C5 117.4(4).

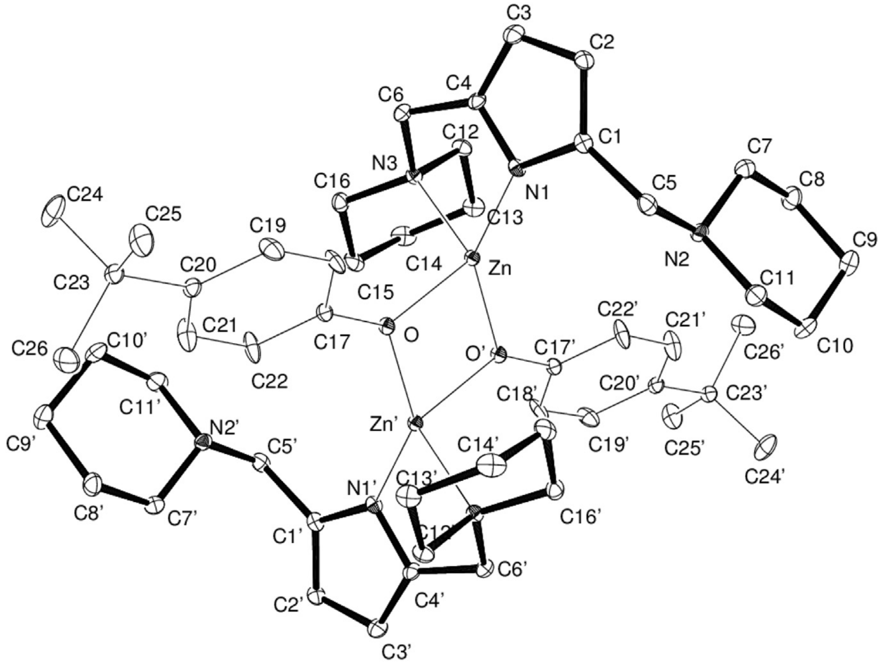


Fig. 5. ORTEP diagram of compound **6**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn–N1 1.932(4), Zn–N3 2.142(4), Zn–O 1.993(3), Zn–O′ 1.993(3), O–C17 1.376(6), C1–C5 1.532(8), N2–C5 1.438(8), C4–C6 1.504(8), N3–C6 1.491(6); N1–Zn–N3 86.24(17), C1–N1–C4 106.6(4), C4–C6–N3 109.8(4), N1–C4–C6 117.1(5), O–Zn–O′ 79.68(14), Zn–O–Zn′ 100.32(14), O–Zn–N1 142.77(17), O–Zn–N3 118.02(15).

*$[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]ZnC_2H_5$ (**3**)*

The synthesis of compound **3** was carried out following the procedures similar to those used for the preparation of **1**. The white solid was recrystallized from a saturated hexane solution to yield colorless crystals of **3** (0.589 g, 1.66 mmol, 83%). ^1H NMR (C_6D_6): 6.43 (s, 2H, C_4H_2N), 3.44 (s, 4H, $-CH_2-$), 2.29 (s, 8H, $-N(CH_2)_5$), 1.69 (t, J = 8.1, 3H, $ZnCH_2CH_3$), 1.49 (s, 8H, $-N(CH_2)_5$), 1.30 (s, 4H, $-N(CH_2)_5$), 0.82 (q, J = 8.1, 2H, $ZnCH_2CH_3$). ^{13}C NMR (C_6D_6): 134.4 (C_4H_2N), 106.3 (C_4H_2N), 59.5 ($-CH_2-$), 54.8 ($-N(CH_2)_5$), 25.9 ($-N(CH_2)_5$), 24.4 ($-N(CH_2)_5$), 12.2 ($ZnCH_2CH_3$), 3.4 ($ZnCH_2CH_3$). Anal. Calc. for $C_{18}H_{31}N_3Zn$: C, 60.93; H, 8.81; N, 11.84. Found: C, 60.71; H, 8.54; N, 11.66.

*$\{[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]Zn(O-C_6H_4\text{-}4\text{-}^tBu)\}_2$ (**4**)*

To a solution of $[C_4H_2N(2,5\text{-}CH_2NMe_2)_2]ZnC_2H_5$ (0.274 g, 1.0 mmol) in tetrahydrofuran (20 mL) was added tert-butylphenol

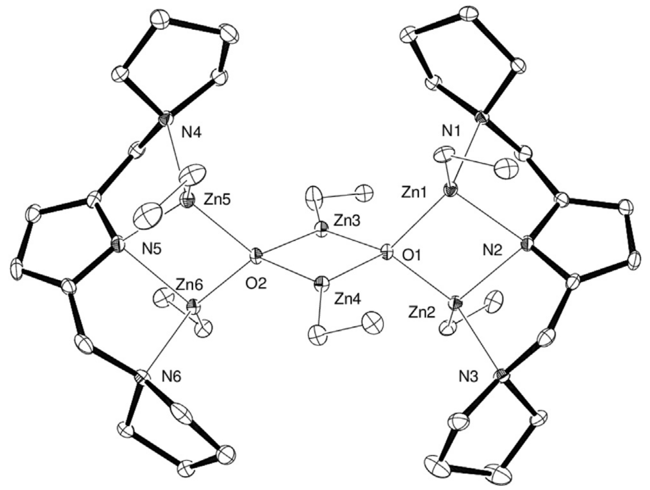


Fig. 6. ORTEP diagram of compound **7**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn1–N1 2.217(3), Zn1–N2 2.139(3), Zn2–N2 2.112(3), Zn2–N3 2.231(3), Zn1–O1 2.005(2), Zn2–O1 2.008(2), Zn3–O1 1.955(2), Zn4–O1 1.965(2), Zn3–O2 1.964(2), Zn4–O2 1.955(2), Zn5–O2 2.018(2), Zn6–O2 1.994(2), Zn5–N5 2.086(3), Zn5–N4 2.216(3), Zn6–N5 2.179(3), Zn6–N6 2.191(3); N1–Zn1–N2 82.35(11), N2–Zn2–N3 81.93(12), Zn1–N2–Zn2 86.45(10), N4–Zn5–N5 81.87(12), N5–Zn6–N6 82.87(12), Zn5–N5–Zn6 86.34(11), O1–Zn3–O2 88.39(9), O1–Zn4–O2 88.34(9), Zn3–O1–Zn4 91.57(9), Zn3–O2–Zn4 91.59(9).

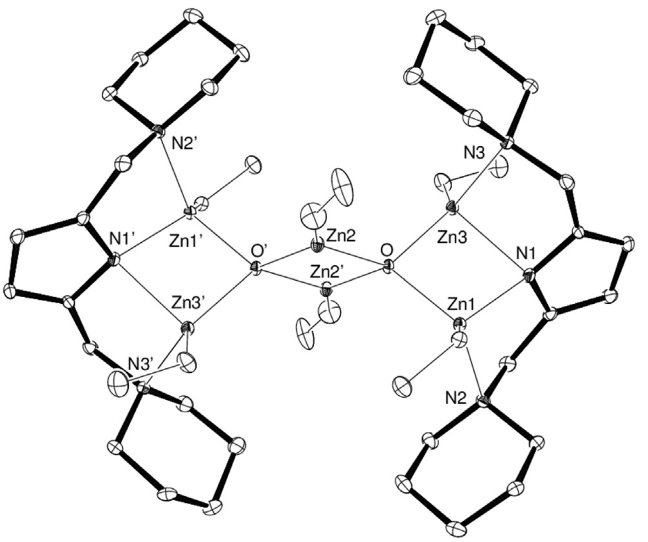
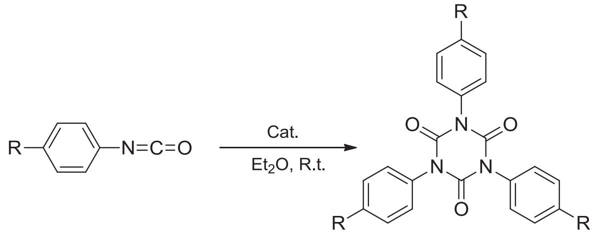


Fig. 7. ORTEP diagram of compound **8**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zn1–N1 2.095(3), Zn1–N2 2.198(3), Zn3–N1 2.198(3), Zn3–N3 2.248(4), Zn1–O 2.045(3), Zn3–O 2.010(3), Zn2–O 1.975(3), Zn2′-O 1.982(3); N1–Zn3–N3 82.53(11), N1–Zn1–N2 81.91(13), Zn1–N1–Zn3 85.80(13), O–Zn2–O′ 88.39(11), Zn2–O–Zn2′ 91.61(11), Zn1–O–Zn3 92.25(11).

(0.150 g, 1.0 mmol) in tetrahydrofuran (15 mL) at −78 °C. The resulting solution was stirred at room temperature for 1 h and dried in vacuo to remove all the volatiles. The orange residue was recrystallized from a saturated hexane solution to yield yellow crystals of **4** (0.233 g, 0.59 mmol, 59%). ^{1}H NMR (C_6D_6): 6.99 (d, $J = 0.6$, 4H, C_6H_4), 6.84 (d, $J = 0.9$, 4H, C_6H_4), 6.69 (s, 4H, C_4H_2N), 3.67 (s, 8H, $-CH_2-$), 2.18 (s, 24H, $-N(CH_3)_2$), 1.23 (t, 18H, $-C(CH_3)_3$). ^{13}C NMR (C_6D_6): 159.1 (C_6H_4), 141.4 (C_6H_4), 133.4 (C_6H_4), 126.8 (C_6H_4), 116.7 (C_4H_2N), 106.7 (C_4H_2N), 60.5 ($-CH_2-$), 45.9 ($-N(CH_3)_2$), 33.8 ($-C(CH_3)_3$), 31.6 ($-C(CH_3)_3$). Anal. Calc. for $C_{40}H_{62}N_6O_2Zn_2$: C, 60.84; H, 7.91; N, 10.64. Found: C, 60.52; H, 7.67; N, 10.39.

Table 1
The cyclotrimerization of isocyanate catalyzed by zinc compounds **1**–**6**.



Entry	Catalyst	Loading (mol %)	Substrate	Yield (%)
1	**1**	5	Phenyl isocyanate	84.9
2	**2**	5	Phenyl isocyanate	87.3
3	**3**	5	Phenyl isocyanate	92.4
4	**4**	5	Phenyl isocyanate	71.6
5	**5**	5	Phenyl isocyanate	74.3
6	**6**	5	Phenyl isocyanate	83.1
7	**3**	2.5	Phenyl isocyanate	82.4
8	**3**	1	Phenyl isocyanate	54.5
9	**3**	5	4-Chlorophenyl isocyanate	93.6
10	**3**	5	4-Methylphenyl isocyanate	90.7
11	**3**	5	4-Methoxyphenyl isocyanate	88.4

Reaction conditions: room temperature, 12 h.

$\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_4)_2]Zn(O{-}C_6H_4\text{-}4\text{-}^tBu)\}_2$ (**5**)

The synthesis of compound **5** was carried out following the procedures similar to those used for the preparation of **4**. The white solid was recrystallized from a saturated hexane solution to yield colorless crystals of **5** (0.232 g, 0.52 mmol, 52%). ^{1}H NMR (C_6D_6): 7.08 (d, $J = 6.9$, 4H, C_6H_4), 6.71 (d, $J = 6.9$, 4H, C_6H_4), 6.52 (s, 4H, C_4H_2N), 3.68 (s, 8H, $-CH_2-$), 2.59 (s, 16H, $-N(CH_2)_4$), 1.56 (s, 16H, $-N(CH_2)_4$), 1.29 (t, 18H, $-C(CH_3)_3$). ^{13}C NMR (C_6D_6): 160.3 (C_6H_4), 145.4 (C_6H_4), 129.6 (C_6H_4), 125.4 (C_6H_4), 123.2 (C_4H_2N), 113.8 (C_4H_2N), 62.3 ($-CH_2-$), 49.1 ($-N(CH_2)_4$), 34.9 ($-C(CH_3)_3$), 32.6 ($-C(CH_3)_3$), 27.9 ($-N(CH_2)_4$). Anal. Calc. for $C_{48}H_{70}N_6O_2Zn_2$: C, 64.50; H, 7.89; N, 9.40. Found: C, 64.21; H, 7.93; N, 9.23.

$\{[C_4H_2N(2,5\text{-}CH_2N(CH_2)_5)_2]Zn(O{-}C_6H_4\text{-}4\text{-}^tBu)\}_2$ (**6**)

The synthesis of compound **6** was carried out following the procedures similar to those used for the preparation of **4**. The white solid was recrystallized from a saturated hexane solution to yield colorless crystals of **6** (0.289 g, 0.61 mmol, 61%). ^{1}H NMR (C_6D_6): 7.09 (d, $J = 8.7$, 4H, C_6H_4), 7.01 (d, $J = 8.4$, 4H, C_6H_4), 6.79 (s, 4H, C_4H_2N), 3.80 (s, 8H, $-CH_2-$), 2.55 (s, 16H, $-N(CH_2)_5$), 1.51 (s, 16H, $-N(CH_2)_5$), 1.34 (s, 8H, $-N(CH_2)_5$), 1.25 (t, 18H, $-C(CH_3)_3$). ^{13}C NMR (C_6D_6): 158.5 (C_6H_4), 142.1 (C_6H_4), 133.8 (C_6H_4), 127.0 (C_6H_4), 117.4 (C_4H_2N), 107.9 (C_4H_2N), 60.5 ($-CH_2-$), 55.1 ($N(CH_2)_5$), 33.9 ($-C(CH_3)_3$), 31.6 ($-C(CH_3)_3$), 25.6 ($N(CH_2)_5$), 24.2 ($N(CH_2)_5$). Anal. Calc. for $C_{52}H_{78}N_6O_2Zn_2$: C, 65.74; H, 8.28; N, 8.85. Found: C, 65.91; H, 7.96; N, 8.68.

Typical procedure employed for cyclotrimerization of isocyanate

A 25 mL Schlenk flask was charged with zinc compounds (1.0 mmol) and 30 mL of diethyl ether was added, then phenyl isocyanate (20 mmol) was added dropwise through a syringe with stirring. The solution became cloudy gradually and the white suspension was stirred at room temperature for 12 h after the addition was completed. The resulting precipitate was isolated via filtration, washed with diethyl ether (3 × 10 mL) and dried under vacuum to give the corresponding isocyanurate.

X-ray crystallography

All crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Single X-ray diffraction data of the compounds were collected on a Bruker Smart Apex CCD diffractometer using monochromated MoKα radiation, $\lambda = 0.71073$ Å. A total of N reflections were collected by using ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [29]. Each structure was solved by direct method and refined on F^2 by full matrix least squares (SHELX97) using all unique data [30]. Then the remaining non-hydrogen atoms were obtained from the successive difference fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL) [31]. Details of the modeling of disorder in the crystals can be found in their CIF files.

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Appendix A. Supplementary material

CCDC 1019679–1019685 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.11.009.

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