



# Zinc and aluminum complexes derived from 2, 4-*N, N'*-disubstituted 1, 3, 5-triazapentadienyl ligands: Synthesis, characterization and catalysis of the ring-opening polymerization of *rac*-lactide



Dan Tian, Qianwen Xie, Lei Yan, Hongbo Tong, Meisu Zhou \*

Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, People's Republic of China

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## ABSTRACT

Bis(1,3,5-triazapentadienate)zinc complexes  $[N(Ph)C(R)NC(R)N(SiMe_3)]_2Zn$  ( $R = NMe_2$ , **1**; 1-piperidino, **2**) and (1,3,5-triazapentadienate)aluminum dichloride  $[N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)]AlCl_2 \cdot C_9H_{18}N_6$  (**3**) were synthesized and structurally characterized by X-ray crystallography and spectroscopic techniques. The X-ray structures of **1–3** showed that they crystallize in the triclinic system and prefer coordination to the zinc and aluminum centers via the terminal N atoms of the NCNCN ligand backbone, affording tetrahedral geometry. The catalytic properties of **1** and **2** were evaluated.

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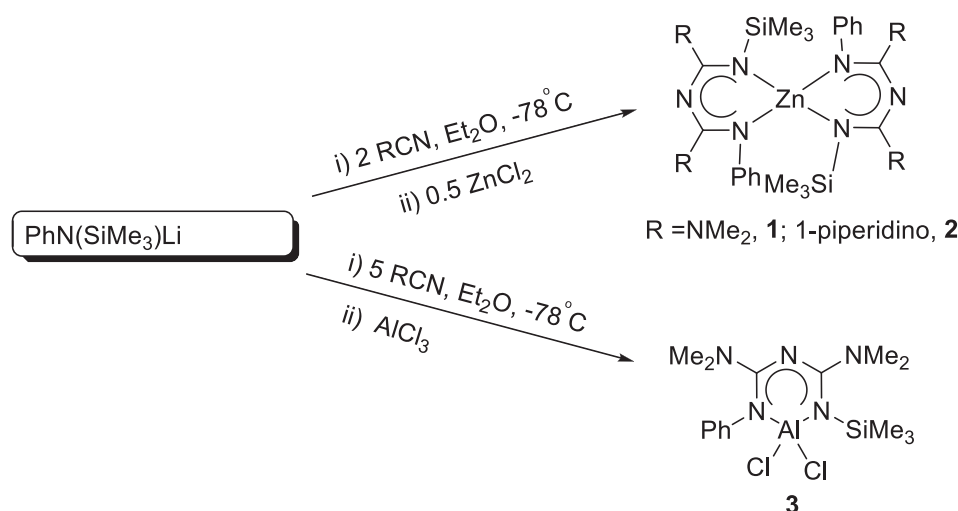
Noncyclic (hetero)pentadienyls have played important roles in the development of organometallic chemistry and extensively investigated in searching for the alternatives to cyclopentadienyls. Conjugated 5-membered  $\pi$  systems especially the nitrogen-containing ligands such as 1,5-diazapentadienyls [ $\beta$ -diketiminates] [**1**] and its nitrogen analogs 1,3,5-triazapentadienyls [**2,3**] not only provide a unique steric and electronic environment for stabilizing a vast array of main-group and transition metals, but allow facile tuning through substitution at the N atoms of the ligand backbone. The related 1,2,5-triazapentadienyls [**4**] and 1,2,4,5-tetraaza (known as “formazans”) ligands have also been studied [**5**]. Their zinc and aluminum compounds and some other main group metal complexes have been used as catalysts in the polymerization reactions [**6–11**]. In our previous publication, we described the synthesis and coordination chemistry of a series of 1,3,5-triazapentadienyl transition metal complexes [**12,13**] and main group metal such as magnesium complexes [**14**]. In continuing this research we report herein the synthesis and characterization of bis(1,3,5-triazapentadienate)zinc and (1,3,5-triazapentadienate)aluminum complexes and discuss their structures.

The starting ligand  $PhN(SiMe_3)Li$  was synthesized according to the literature procedures [**12**]. The formation of the 1,3,5-triazapentadienyl ligands involves insertion reactions of  $PhN(SiMe_3)Li$  into the  $C\equiv N$  functionality, followed by 1,3-silyl migrations. Treatment of  $PhN(SiMe_3)Li$  with two molar equivalents of dimethylcyanamide or

1-piperidinecarbonitrile and then 0.5 equivalents of zinc chloride yields **1** and **2**, respectively [**15,16**]. Treatment of  $PhN(SiMe_3)Li$  with five equivalents of dimethylcyanamide, followed by addition of equal equivalent of aluminum chloride gave **3** as colorless crystals in reasonable yield [**17**] (Scheme 1) with the formation of triazine. Both compounds **1** and **2** are very soluble in diethyl ether and dichloromethane, and less soluble in aliphatic hydrocarbon solvents and are conveniently crystallized as colorless crystals from  $Et_2O$ . Multi-nuclear NMR and elemental data indicated the formation of the complexes, and this indication was confirmed by X-ray diffraction studies on single crystals of **1–3** (Fig. 1–3) [**18–20**]. IR spectra exhibit strong absorptions at  $1529\text{ cm}^{-1}$  for **1** and  $1517\text{ cm}^{-1}$  for **2** which are assigned to  $C=N$  stretching due to coordination of nitrogen atoms. The strong bands around  $1440\text{ cm}^{-1}$  can be assigned to the  $C-N$  single bond stretching. The strong bands in the range of  $1294\text{--}1529\text{ cm}^{-1}$  can be assigned to the skeleton vibration of the 1,3,5-triazapentadienyl ligands.

The molecular structure of **1** (Fig. 1) crystallizes in the triclinic  $P\bar{1}$  space group. The structure contains a four-coordinate zinc atom with tetrahedral geometry consisting of four nitrogen atoms of two 1,3,5-triazapentadienyl anions with  $Zn1-N$  bond distances of 2.021 (2) [ $Zn1-N1$ ], 2.005 (2) [ $Zn1-N5$ ], 2.030 (2) [ $Zn1-N6$ ] and 1.991 (2) Å [ $Zn1-N10$ ], respectively. They are comparable to the mean values of  $Zn-N$  [1.9769 (18)–2.0234 (16) Å] in tetrahedral bis(formazanate)zinc compound [**5**] and 1,2,4-triphenyl-1,3,5-triazapentadiene zinc complex [ $Zn-N1$ , 2.0615 (12);  $Zn-N5$ , 1.9818 (12) Å] [**8**], but longer than those in three-coordinate  $\beta$ -diketimate zinc hydride complex [ $Zn-N1$ , 1.950 (1);  $Zn-N2$ , 1.952 (1) Å] [**21**].

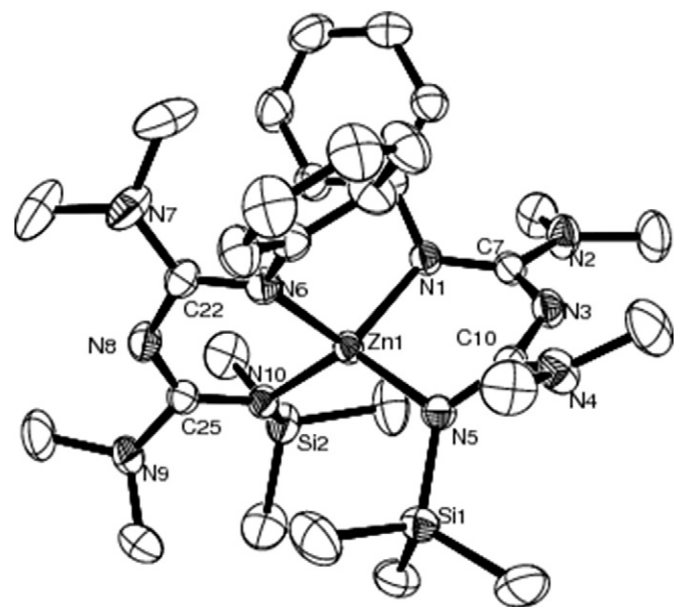
\* Corresponding author.  
E-mail address: [mszhou@sxu.edu.cn](mailto:mszhou@sxu.edu.cn) (M. Zhou).



**Scheme 1.** Synthetic routes to complexes **1–3**.

The bond angles N1–Zn1–N5 and N6–Zn1–N10 are 97.02 (7) and 97.03 (7)°, respectively, comparable to that in the three-coordinate β-diketiminato zinc hydride complex [N1–Zn–N2, 97.33 (4)°] [21], but larger than those in four-coordinate β-diketiminato zinc complex with NNCNN backbone [N–Zn–N, 87.98 (4)–93.18 (7)°] [5] and 1,3,5-triazapentadiene zinc dichloride complex [N1–Zn1–N5, 90.48 (5)°] [8].

The dihedral angle between planes N1Zn1N5 and N6Zn1N10 is 90.5°. Within the 1,3,5-triazapentadieno ligands, the N–C bond distances are in the range of 1.315 (3)–1.361 (3) Å. Bond angles N1–C7–N3, C7–N3–C10 and N3–C10–N5 are 123.69 (18), 127.56 (17) and 126.20 (18)°,



**Fig. 1.** Molecular structure of **1**. Thermal ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)–N(1) 2.021 (2), Zn(1)–N(5) 2.005 (2), Zn(1)–N(6) 2.030 (2), Zn(1)–N(10) 1.991 (2), N(1)–C(7) 1.360 (3), N(2)–C(7) 1.366 (3), N(3)–C(7) 1.339 (3), N(3)–C(10) 1.349 (3), N(4)–C(10) 1.383 (3), N(5)–C(10) 1.342 (3), N(6)–C(22) 1.330 (3), N(7)–C(22) 1.371 (3), N(8)–C(22) 1.361 (3), N(8)–C(25) 1.315 (3), N(9)–C(25) 1.434 (3), N(10)–C(25) 1.346 (3); N(1)–Zn(1)–N(5) 97.02 (7), N(6)–Zn(1)–N(10) 97.03 (7), C(7)–N(3)–C(10) 127.56 (17), C(22)–N(8)–C(25) 127.67 (18), Zn(1)–N(1)–C(7) 117.27 (13), Zn(1)–N(5)–C(10) 112.70 (13), Zn(1)–N(6)–C(22) 116.39 (13), Zn(1)–N(10)–C(25) 115.38 (13).

respectively. Each bidentate 1,3,5-triazapentadieno ligand forms a six-membered metallocycle ZnNCNCN, where the N1C7N3C10N5 five-membered ring is not planar. The dihedral angle between the N1C7N3 and the N3C10N5 is 40.1°.

The crystalline **2** (Fig. 2) has a similar structure to complex **1** except for the replacement of NMe<sub>2</sub> by 1-piperidino. In complex **2**, there are two chemically similar, crystallographically independent molecules in the crystal lattice and the bond distances and angles have no significant differences. The metal center is in a distorted tetrahedral environment consisting of the four nitrogen atoms of two bidentate 1,3,5-triazapentadieno anions with 93.1 and 92.4° of dihedral angles between planes N1Zn1N5 and N6Zn1N10, N11Zn2N15 and N16Zn2N20, respectively. The Zn1–N bond distances are in the range of 1.972 (2)–2.002 (2) Å, comparable to those of Zn2–N [1.974 (2)–2.006 (2) Å]. In the ligand moiety NCNCN, the C–N bond distances are in the range of 1.305 (3)–1.373 (4) Å, indicating π-electron delocalization in the NCNCN fragment. In **2**, the bond angles N–Zn1–N [N1–Zn1–N5, 96.95 (9); N6–Zn1–N10, 96.43 (9)°] are comparable to those of N–Zn2–N [N11–Zn2–N15, 96.02 (9); N16–Zn2–N20, 97.31 (9)°] and those of **1**.

The molecular structure of **3** is illustrated in Fig. 3, which contains two different independent molecules in the asymmetric unit, one is the 1,3,5-triazapentadienate aluminum complex and the other is a triazine molecule. The bond distances and angles in the triazine molecule are normal. The metal center is bound to two nitrogen atoms from the 1,3,5-triazapentadienyl ligand and two chlorine atoms, giving rise to a slightly distorted tetrahedral coordination environment. The dihedral angle between Cl1Al1Cl2 and N1Al1N5 is 87.8°. The bond distances of Al1–Cl1 and Al1–Cl2 are 2.129 (1) and 2.142 (1) Å, respectively, and those of Al1–N1 and Al1–N5 are 1.858 (2) and 1.855 (2) Å, respectively, similar to the Al–N distances [1.850 (2) Å] in β-diketiminato aluminum compound (TTP)AlCl<sub>2</sub> (TTPH = 2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentene) [22], but shorter than those in dimethyl aluminum diketiminato complex *R,R*-nacnac<sup>CH(Me)Ph</sup>AlMe<sub>2</sub> [Al1–N1, 1.9223 (15); Al1–N2, 1.9165 (15) Å] [7]. Bond distances N1–C7, C7–N3, N3–C10 and C10–N5 are 1.371 (3), 1.318 (3), 1.336 (3) and 1.374 (3) Å, respectively, indicating an obvious long–short–short–long pattern of C–N bond lengths in the NCNCN backbone. This is consistent with localized C=N and C–N bonding in previously reported monomeric U-shaped lithium 1,3,5-triazapentadienyl adducts of fluorinated ligands [{N}((C<sub>3</sub>F<sub>7</sub>)C(Dipp)N)<sub>2</sub>Li(THF)] and [{N}((C<sub>3</sub>F<sub>7</sub>)C(Mes)N)<sub>2</sub>Li(THF)<sub>2</sub>] [23]. Bond angle Cl1–Al1–Cl2 is 106.45 (4)°, narrower than that in (TTP)AlCl<sub>2</sub> (Cl1–Al1–Cl1A: 109.95 (6)°). Bond angle N1–Al1–N5 [100.06 (8)°] is comparable to that in (TTP)AlCl<sub>2</sub> [N1–Al1–N1A: 99.41

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