

# Salen-type zirconium complexes with a labile coordination site and a robust skeleton: crystal structure of $[(t\text{-Bu}_4\text{-salen})\text{ZrCl}_2(\text{H}_2\text{O})]$

Mei Wang<sup>a,\*</sup>, Hongjun Zhu<sup>a</sup>, Deguang Huang<sup>b</sup>, Kun Jin<sup>a</sup>,  
Changneng Chen<sup>b</sup>, Licheng Sun<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology,  
Zhongshan Road 158-46, Dalian 116012, PR China

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, PR China

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## Abstract

Treatment of  $\text{LZrCl}_2$  ( $\text{L} = N, N'$ -ethylenebis(3,5-di-*tert*-butylsalicylideneiminato) (**1**),  $N, N'$ -*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneiminato) (**2**)), which is an effective catalyst precursor for ethylene oligomerization, with 1.5 equiv of water in toluene afforded  $\text{H}_2\text{O}$ -coordinating salen-type zirconium complexes  $[\text{LZrCl}_2(\text{H}_2\text{O})]$ . The effects of the content of  $\text{H}_2\text{O}$  and the temperature on the equilibrium of association and disassociation of  $\text{H}_2\text{O}$  molecule in  $[\text{LZrCl}_2(\text{H}_2\text{O})_n]$  ( $n = 0, 1$ ) were studied in solution ( $\text{CDCl}_3$ ) by  $^1\text{H}$  NMR spectroscopy. The crystal and molecular structure of  $[\mathbf{1}(\text{H}_2\text{O})]$  was determined by X-ray diffraction analysis, which revealed that a herringbone supramolecular assembly was constructed in the crystalline state of  $[\mathbf{1}(\text{H}_2\text{O})]$ , stacked by the intermolecular hydrogen bonds between the OH group of the coordinating  $\text{H}_2\text{O}$  and one of the chloride ligands.

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## 1. Introduction

The chemistry of transition metal complexes with salen-type tetradentate Schiff base ligands has been one of the highlights in organometallic chemistry and homogeneous catalysis since Jacobsen and Katsuki found highly enantioselective epoxidation of olefins by salen-type manganese complexes. Hitherto numerous salen-type metal complexes have been prepared for almost all transition metals and even for non-transition metals, such as aluminum as a metal center [1]. Although salen-type complexes of middle and late d-block transition metals have been extensively investigated and used as catalysts in diverse organic reactions, very few reports have appeared describing the synthesis [1–5], crystal

structures [6–8] and catalytic properties of group 4 metal complexes with such ligands [9–11].

Recently, we have found that salen-type zirconium complexes gave rise to very efficient catalyst systems for the conversion of ethylene monomer into low-carbon linear  $\alpha$ -olefins when activated by an appropriate alkylaluminum co-catalyst [12]. To gain a better understanding of the coordinative property of the Zr center and the stability of the catalyst precursors, the behavior of the complexes  $\text{LZrCl}_2$  ( $\text{L} = N, N'$ -ethylenebis(3,5-di-*tert*-butylsalicylideneiminato) (**1**),  $N, N'$ -*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneiminato) (**2**)) with water was studied. It was found that there was a labile coordination site in the relatively stable framework of  $\text{LZrCl}_2$  and that the coordination and the substitution of O-donor solvents occurred readily at this site. Here, we describe the preparation of  $[\mathbf{1}(\text{H}_2\text{O})]$  and  $[\mathbf{2}(\text{H}_2\text{O})]$ , the reversible association and disassociation of  $\text{H}_2\text{O}$  molecules in the complexes  $[\mathbf{1}(\text{H}_2\text{O})]$  and  $[\mathbf{2}(\text{H}_2\text{O})]$ , and the crystal structure of  $[\mathbf{1}(\text{H}_2\text{O})]$ . To the best of our

\* Corresponding authors. Tel.: +0086-411-3702186; fax: +0086-411-3702185.

E-mail address: [symbuono@vip.sina.com](mailto:symbuono@vip.sina.com) (M. Wang).

knowledge, the structurally well-characterized neutral zirconium complexes coordinated with H<sub>2</sub>O are very sparse [13–15], due to the instability of most organo-zirconium complexes towards water.

## 2. Results and discussion

### 2.1. Preparation and spectroscopic characterization of [1(H<sub>2</sub>O)] and [2(H<sub>2</sub>O)]

Treatment of ZrCl<sub>4</sub> and the sodium salt of a substituted salen-type ligand in THF generated a mixture of THF-solvated and unsolvated species [LZrCl<sub>2</sub>(THF)<sub>*n*</sub>] (*n* = 0,1), which turned to pure unsolvated complexes **1** and **2** when refluxed in toluene. The analogous salen and salphen zirconium complexes in THF-solvated form were previously prepared and structurally characterized by Floriani and co-workers [16] and Repo et al. [17]. The H<sub>2</sub>O-solvated complexes [1(H<sub>2</sub>O)] and [2(H<sub>2</sub>O)] were obtained, using either the unsolvated species LZrCl<sub>2</sub> or the mixture obtained from a THF solution, with 1.5 equiv of H<sub>2</sub>O in toluene (Scheme 1). In the reactions, the molecules of H<sub>2</sub>O readily coordinated to the Zr center of LZrCl<sub>2</sub> as the seventh ligating member or replaced the coordinate-THF molecules in [LZrCl<sub>2</sub>(THF)<sub>*n*</sub>], without wrecking the framework of complexes **1** and **2**, which are greatly stabilized by the tetradentate salen-type ligand. As catalyst precursors used for oligomerization and polymerization of ethylene, salen-type zirconium complexes are facily approached and easily handled compared with the conventional metallocene catalysts and their derivatives. In contrast to the huge number of organozirconium complexes reported over the past several decades, the number of well-known neutral

zirconium complexes incorporating water as ligand is rather limited [13–15,18,19].

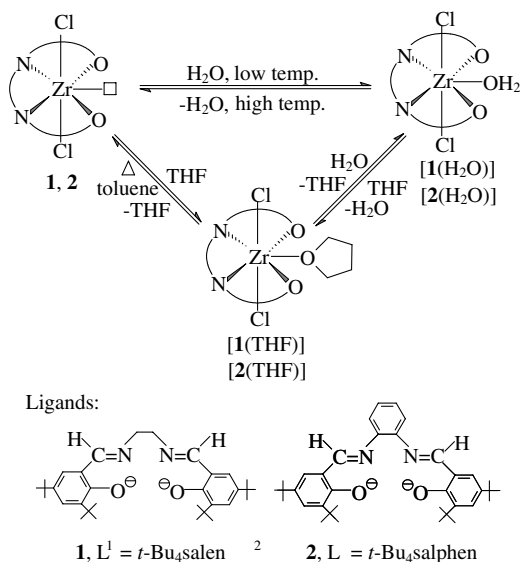
Complexes [1(H<sub>2</sub>O)] and [2(H<sub>2</sub>O)] were characterized by IR, <sup>1</sup>H NMR and elemental analysis. The characteristic bands of ν(C=N), at 1622 cm<sup>-1</sup> for [1(H<sub>2</sub>O)] and 1610 cm<sup>-1</sup> for [2(H<sub>2</sub>O)] in IR spectra, appeared almost in the same wavenumbers as unsolvated starting complexes **1** and **2**. Products [1(H<sub>2</sub>O)] and [2(H<sub>2</sub>O)] each displayed a broad band in the region of 3300–3500 cm<sup>-1</sup>, assigned to the O–H stretching frequency of the ligating H<sub>2</sub>O. As the coordination environment of the Zr center changed in unsolvated and solvated complexes, the resonance of the imino hydrogen in <sup>1</sup>H NMR spectra shifted accordingly. The signals of the imino hydrogens appeared at δ 8.40 for [1(H<sub>2</sub>O)] and 8.68 for [2(H<sub>2</sub>O)] in CDCl<sub>3</sub>, while the <sup>1</sup>H NMR spectra of complexes **1** and **2** each manifested a singlet signal of the imino hydrogen at δ 8.29 and 8.88, respectively. The evident shift of the resonance of the imino hydrogen in <sup>1</sup>H NMR spectra can be considered as a sort of useful spectroscopic indicator in the inference of solvent coordination to the zirconium salen-type complexes. The crystal structure of [1(H<sub>2</sub>O)] was determined by X-ray crystallography.

For comparison, the reactions of analogous complexes (salen)ZrCl<sub>2</sub> and (salphen)ZrCl<sub>2</sub> with H<sub>2</sub>O were also made. It was observed that the reactions occurred instantly, but due to the poor solubility of the resulting yellow solid we were unsuccessful in purifying and clearly identifying the structures of the products.

### 2.2. Reversible association and disassociation of [LZrCl<sub>2</sub>(H<sub>2</sub>O)<sub>*n*</sub>] (*n* = 0, 1)

The <sup>1</sup>H NMR spectra of [1(H<sub>2</sub>O)] and [2(H<sub>2</sub>O)] indicated the presence of an equilibrium between H<sub>2</sub>O-solvated and unsolvated forms in solution (CDCl<sub>3</sub>). The equilibrium was obviously affected by the concentration of H<sub>2</sub>O and the measuring temperature. The movement of the equilibrium between **2** and [2(H<sub>2</sub>O)] was explored by <sup>1</sup>H NMR spectra. The relative intensities of the two singlet signals in the region of δ 8.0–10.0 gave a token of the change in the ratio of **2** to [2(H<sub>2</sub>O)] in solution.

Fig. 1 gives the selected sections of <sup>1</sup>H NMR spectra of **2** in CDCl<sub>3</sub> with different contents of H<sub>2</sub>O. The molar ratios of complex **2** to H<sub>2</sub>O are 1:0.5, 1:1 and 1:2 in parts (a), (b) and (c) of Fig. 1, respectively, which show that the proportions of unsolvated and H<sub>2</sub>O-solvated forms change from 1:0.72 (Fig. 1(a)) to 1:1.19 (Fig. 1(b)) and then to 1:2.25 (Fig. 1(c)). Even in the presence of 2 equiv of H<sub>2</sub>O, the H<sub>2</sub>O-solvated form only accounted for 69% in solution. The steric congestion around the metal center, induced by the two *ortho tert*-butyl groups, might block the solvation of the complexes **1** and **2** to a certain extent. When a large excess of H<sub>2</sub>O was added to the solution, not only the relative intensities but also the



Scheme 1.

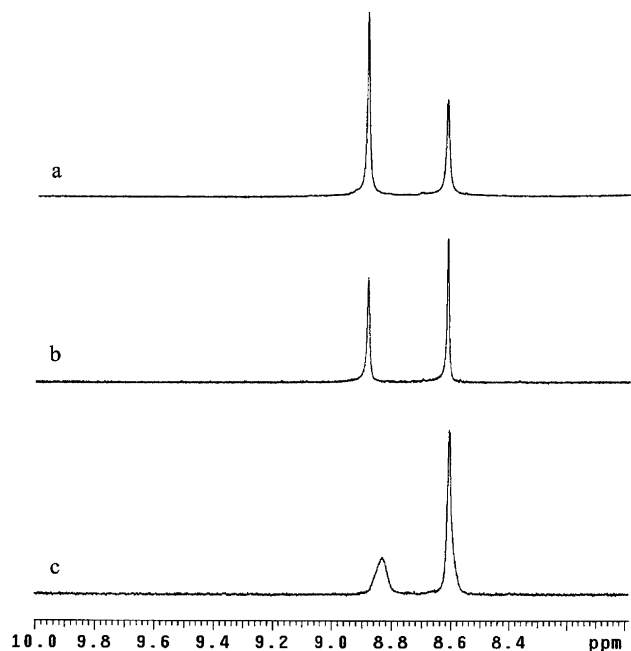


Fig. 1. The imino hydrogen region of  $^1\text{H}$  NMR spectra of **2** in  $\text{CDCl}_3$  with different contents of  $\text{H}_2\text{O}$  recorded at  $20^\circ\text{C}$ : (a) with 0.5 equiv of  $\text{H}_2\text{O}$ ; (b) with 1.0 equiv of  $\text{H}_2\text{O}$ ; (c) with 2.0 equiv of  $\text{H}_2\text{O}$ .

chemical shifts of the signals altered evidently. The signals attributed to the unsolvated form of **2** ( $\delta$  8.88) and the  $\text{H}_2\text{O}$ -solvated form ( $\delta$  8.68) shifted to  $\delta$  8.55 and 8.41, being very broad resonances. The evident shifts of the resonances suggest that the original coordination structures of **2** and  $[\mathbf{2}(\text{H}_2\text{O})]$  might change in the presence of a large excess of  $\text{H}_2\text{O}$ .

The  $^1\text{H}$  NMR spectra of **2** and  $[\mathbf{2}(\text{H}_2\text{O})]$  at different temperatures indicated that the association and dissociation of  $\text{H}_2\text{O}$  was a reversible process in solution. The selected sections of  $^1\text{H}$  NMR spectra in the range of  $\delta$  8.0–10.0 are shown in Fig. 2. The sample used for  $^1\text{H}$  NMR measurement was a mixture of **2** and  $[\mathbf{2}(\text{H}_2\text{O})]$  obtained from the reaction of **2** with 1.5 equiv of  $\text{H}_2\text{O}$  in toluene. The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  at  $20^\circ\text{C}$  (Fig. 2(a)) indicated that the proportion of unsolvated and  $\text{H}_2\text{O}$ -solvated forms was 1:1.93. The proportion changed to 1:1.09 (Fig. 2(b)) as the measuring temperature was quickly raised to  $60^\circ\text{C}$ , suggesting a fast dissociation of  $\text{H}_2\text{O}$  from the Zr center at higher temperature. The same integral ratio of the two singlet signals was observed when the  $^1\text{H}$  NMR spectrum was measured at  $60^\circ\text{C}$  after the sample was pre-heated in an oil bath to the identical temperature for 16 h. The experimental results showed that the dissociation of  $\text{H}_2\text{O}$  molecules reached its equilibrium at  $60^\circ\text{C}$  in several minutes. Despite the high affinity of zirconium to oxygen, the coordinated molecules of O-donor solvents in the salen-type zirconium complexes are apt to dissociate, leaving a vacant coordination site on the Zr center, which is significant in view of the

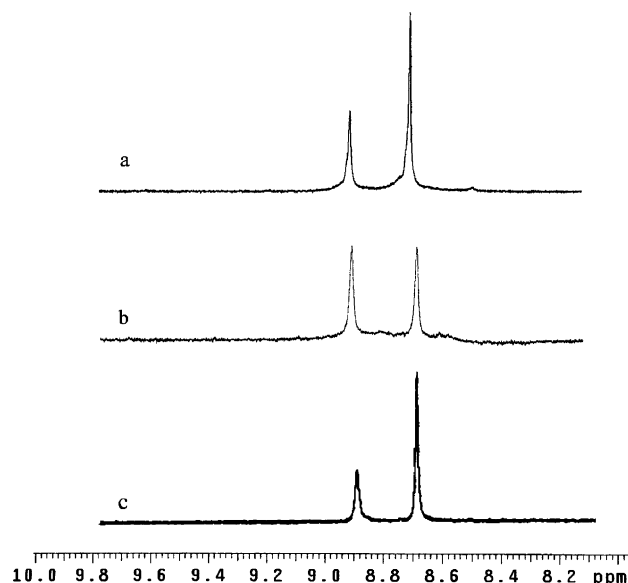


Fig. 2. The imino hydrogen region of  $^1\text{H}$  NMR spectra of the mixture of **2** and  $[\mathbf{2}(\text{H}_2\text{O})]$  in  $\text{CDCl}_3$  recorded at different temperatures: (a) at  $20^\circ\text{C}$ ; (b) at  $60^\circ\text{C}$ ; (c) at  $15^\circ\text{C}$ .

possible availability of these zirconium complexes as catalyst precursors in oligomerization and polymerization of ethylene. The bottom  $^1\text{H}$  NMR spectrum in part (c) of Fig. 2 was measured at  $15^\circ\text{C}$  after the same sample used for parts (a) and (b) stood overnight in a refrigerator. The proportion of **2** and  $[\mathbf{2}(\text{H}_2\text{O})]$  was 1:2.08 in this case (Fig. 2(c)), indicating that the free molecules of  $\text{H}_2\text{O}$  in solution coordinated again to the Zr center as the temperature decreased. The coordination equilibrium of  $\text{H}_2\text{O}$  with a metal center of the neutral zirconium complexes has been scarcely studied so far [13–15,19].

### 2.3. Crystal structure of $[\mathbf{1}(\text{H}_2\text{O})]$

The X-ray crystal structure of  $[\mathbf{1}(\text{H}_2\text{O})]$  with the atom-numbering scheme is depicted in Fig. 3. The important bond distances and angles are listed in Table 1 and crystallographic details and structure refinements are summarized in Table 2. The complex adopts a pseudopentagonal bipyramidal geometry with a seven-

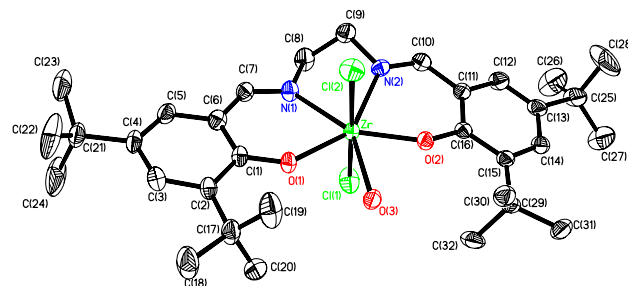


Fig. 3. Molecular structure of  $[\mathbf{1}(\text{H}_2\text{O})]$ . Hydrogen atoms are not included for clarity.

Table 1  
Selected bond lengths (Å) and angles (°) for **[1(H<sub>2</sub>O)]**

Bond lengths			
Zr–O2	2.056(3)	Zr–N2	2.335(4)
Zr–O1	2.069(3)	Zr–Cl2	2.4473(15)
Zr–O3	2.326(4)	Zr–Cl1	2.4661(15)
Zr–N1	2.317(4)		
Bond angles			
O2–Zr–O1	140.33(14)	O1–Zr–Cl2	89.04(10)
O2–Zr–O3	70.55(13)	O3–Zr–Cl2	95.52(11)
O1–Zr–O3	69.78(13)	N1–Zr–Cl2	90.32(12)
O2–Zr–N1	143.79(15)	N2–Zr–Cl2	83.33(11)
O1–Zr–N1	75.40(14)	O2–Zr–Cl1	86.92(10)
O3–Zr–N1	144.53(15)	O1–Zr–Cl1	93.00(10)
O2–Zr–N2	75.15(14)	O3–Zr–Cl1	90.33(12)
O1–Zr–N2	144.40(14)	N1–Zr–Cl1	84.90(12)
O3–Zr–N2	145.45(14)	N2–Zr–Cl1	91.85(11)
N1–Zr–N2	69.95(15)	Cl2–Zr–Cl1	174.15(6)
O2–Zr–Cl2	95.01(10)		

Table 2  
Crystallographic data for **[1(H<sub>2</sub>O)]**

Empirical formula	C <sub>32</sub> H <sub>48</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> Zr
Formula weight	670.84
Crystal size (mm)	0.70 × 0.54 × 0.22
<i>T</i> (K)	293(2)
$\lambda$ (Å)	0.71073
Crystal system	monoclinic
Space group	<i>P</i> <sub>2</sub> (1)/ <i>c</i>
<i>a</i> (Å)	11.6921(5)
<i>b</i> (Å)	9.3869(4)
<i>c</i> (Å)	31.7615(14)
$\beta$ (°)	99.6430(10)
<i>V</i> (Å <sup>3</sup> )	3436.7(3)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.297
$\mu$ (mm <sup>-1</sup> )	0.508
$\theta_{\text{min/max}}$ (°)	1.77/25.08
Reflections collected	10880
Reflections observed [ $> 2\sigma(I)$ ]	4392
Parameters refined	361
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.103
Final <i>R</i> <sub>1</sub> [ <i>I</i> $> \sigma(I)$ ]	0.0614
Final <i>wR</i> <sub>2</sub> [ <i>I</i> $> \sigma(I)$ ]	0.1384
<i>R</i> <sub>1</sub> (all data)	0.0975
<i>wR</i> <sub>2</sub> (all data)	0.1629

coordinate Zr center. The four donor atoms (N<sub>2</sub>O<sub>2</sub>) of the substituted salen ligand are approximately coplanar. The axial sites are occupied by two chlorine atoms in a considerably large angle of Cl(1)–Zr–Cl(2) (174.15(6)°) in **[1(H<sub>2</sub>O)]**, compared with its analogues, e.g. [(acen)ZrCl<sub>2</sub>(THF)] (169.1(1)°), [(salen)ZrCl<sub>2</sub>(THF)] (160.24(6)°) and [(salphen)ZrCl<sub>2</sub>(THF)] (165.2(1)°) [14,15]. The Zr atom of **[1(H<sub>2</sub>O)]** is nearly coplanar with the mean plane through the N<sub>2</sub>O<sub>2</sub> core, deviating from the plane by 0.0184 Å. The O(3) atom of the ligating H<sub>2</sub>O molecule in **[1(H<sub>2</sub>O)]** is only 0.0125 Å below the equatorial plane towards Cl(1). The difference (5.19°) between the Cl(2)–Zr–O(3) (95.52(11)°) and Cl(1)–Zr–O(3) angle (90.33(12)°) in **[1(H<sub>2</sub>O)]** is much smaller than

those found in [(acen)ZrCl<sub>2</sub>(THF)] (32.6°), [(salen)ZrCl<sub>2</sub>(THF)] (39.33°) and [(salphen)ZrCl<sub>2</sub>(THF)] (23.4°) [16,17]. The coplanarity of Zr, N(1), N(2), O(1), O(2) and O(3) atoms in **[1(H<sub>2</sub>O)]** is much better than in other seven-coordinate zirconium analogues. The coordination shape of the *t*-Bu<sub>4</sub> salen ligand in **[1(H<sub>2</sub>O)]** can be described as a stepped conformation (Fig. 3) [16,20]. The five-membered chelate ring in **[1(H<sub>2</sub>O)]** is in a *gauche* conformation with the ethylene carbon atoms below (C(8), 0.4249(2) Å) and above (C(9), 0.4626(2) Å) the N<sub>2</sub>O<sub>2</sub> coordination plane. The Zr–O(1, 2), Zr–N and Zr–Cl distances in **[1(H<sub>2</sub>O)]** are in agreement with the average bond lengths seen for the corresponding bonds in the zirconium complexes bearing tetradentate salen- and acen-type ligands in a planar fashion [16,17,21]. The Zr–O(3) bond distance (2.326(4) Å) is slightly shorter and the bite angle O(1)–Zr–O(2) (140.33(14)°) is significantly larger for **[1(H<sub>2</sub>O)]** than those in analogous complexes [(acen)ZrCl<sub>2</sub>(THF)] (2.376(1) Å, 132.4(1)°), [(salen)ZrCl<sub>2</sub>(THF)] (2.34(1) Å, 133.9(1)°) and [(salphen)ZrCl<sub>2</sub>(THF)] (2.338(2) Å, 137.6(1)°) [16,17]. The enlarged bite angle of O(1)–Zr–O(2) in **[1(H<sub>2</sub>O)]** allows a water molecule to enter the coordination sphere of the Zr center along the N<sub>2</sub>O<sub>2</sub> plane.

The complex **[1(H<sub>2</sub>O)]** crystallizes with four molecules in a monoclinic unit cell (Fig. 4). The special interest of complex **[1(H<sub>2</sub>O)]** is its self-assembling herringbone array stacked by intermolecular hydrogen bonds (O(3)⋯Cl(1) 3.235(5) Å; symmetry code:  $-x + 1, y + 1/2, -z + 3/2$ ), the distance of which falls well in the range of the corresponding values (3.03–3.35 Å) of previously reported supramolecular structures possessing O–H⋯Cl interactions [22–26]. The hydrogen bonding interactions of interlayers are shown in the

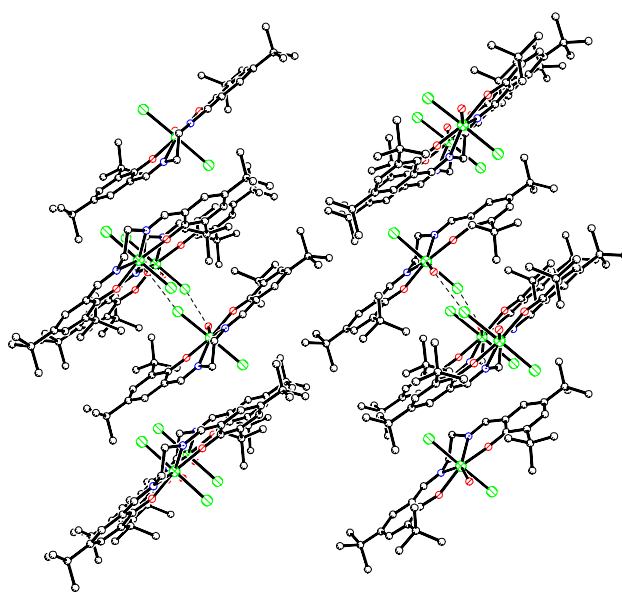


Fig. 4. Stereoplot of the unit cell of **[1(H<sub>2</sub>O)]**. The dotted lines represent the hydrogen bonds between O(3) and Cl(1) atom.

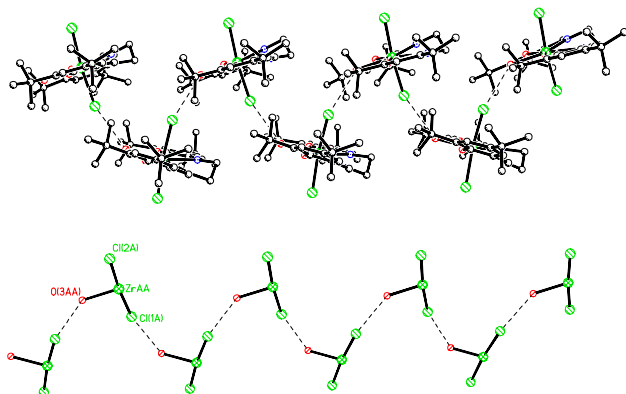


Fig. 5. (a) A projection of the chain structure of hydrogen-bonded  $[1(H_2O)]$  monomers, showing the interconnection of two paired layers. (b) A view of the zigzag proton channel in the crystal structure of  $[1(H_2O)]$ , with  $t\text{-Bu}_4\text{-salen}$  ligand omitted for clarity.

top of Fig. 5, which illustrates that the salen zirconium complex units stand in opposite orientation in two layers, the Cl(1) atom pointing down in one layer and up in the paired layer. In this way, of the two chlorine atoms only Cl(1) interacts with the OH group of  $H_2O$  molecule, forming a self-assembling one-dimensional supramolecular structure. The zigzag hydrogen bond chain (Fig. 5, bottom), constructed with the coverage of hydrophobic layer comprising *tert*-butyl groups in the crystal structure of  $[1(H_2O)]$ , resembles a proton transfer channel in biological systems [27,28]. In a broad sense, the coordination of  $H_2O$  to a transition metal center of organometallic complexes and the proton-coupled electron transfer are attracting topics in bioorganic chemistry.

### 3. Conclusions

As good candidates of post-metallocene catalyst precursors for oligomerization and polymerization of ethylene, the salen-type zirconium complexes  $LZrCl_2$  are easy of approach compared with conventional zirconocene complexes. The seventh coordination site in the salen-type zirconium complexes is quite labile towards various O-donors of small molecules, while the coordination framework of  $LZrCl_2$  is relatively robust. NMR Spectra show there exists a quick coordination equilibrium between  $LZrCl_2$  and  $H_2O$  in the solution of oxygen- and nitrogen-free solvents. The equilibrium shifts apparently as the content of  $H_2O$  and the measuring temperature varies. The X-ray studies indicate that  $[1(H_2O)]$  possesses the largest angles of O(1)–Zr–O(2) and Cl(1)–Zr–Cl(2) among the corresponding angles of previously reported analogous salen- and acen-type zirconium complexes. A herringbone supramolecular assembly is constructed in the crystalline state of  $[1(H_2O)]$ , stacked by intermolecular hydrogen bonds

between the OH group of the coordinating  $H_2O$  molecule and one of the chloride ligands (O–H $\cdots$ Cl). We have found that a very active catalyst system was generated in situ for ethylene oligomerization to low-carbon linear  $\alpha$ -olefins by treatment of the salen-type zirconium complexes with an appropriate alkylaluminum co-catalyst. Details of the catalytic performance of the complexes will be published elsewhere [12]. The further investigation on mechanistic information about the possible structures of the active species is in progress.

## 4. Experimental

### 4.1. General procedures

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Toluene and THF were distilled prior to use from sodium/benzophenone ketyl under a nitrogen atmosphere. Zirconium tetrachloride was purchased from Sigma-Aldrich Chemie GmbH. Other commercially available chemical reagents were used without further purification. Infrared spectra were recorded from KBr pellets using a JASCO FT/IR 430 spectrophotometer and  $^1H$  NMR spectra on a Varian INOVA 400NMR apparatus. Elemental analyses were performed on a CARLO ERBA MOD-1106 elemental analyzer.

### 4.2. Preparation of $[(t\text{-Bu}_4\text{-salen})ZrCl_2(H_2O)] [1(H_2O)]$ and $[(t\text{-Bu}_4\text{-salphen})ZrCl_2(H_2O)] [2(H_2O)]$

Starting complexes **1** and **2** were prepared according to literature procedures [16,29]. To the solution of complex **1** (280 mg, 0.43 mmol) in toluene (12 mL), 1.5 equiv of  $H_2O$  was dropped. The greenish yellow solution quickly turned to light yellow. The mixture was stirred for 10 min. After filtration with a cannula, the yellow crystalline solid was washed twice with pentane and dried in vacuo. Recrystallization of the obtained solid in  $CH_2Cl_2$ /pentane gave pure  $[1(H_2O)]$  as flake crystals. Yield: 130 mg (45%). Anal. calc. for  $C_{32}H_{48}N_2O_3Cl_2Zr$ : C, 57.29; H, 7.21; N, 4.18. Found: C, 57.11; H, 7.17; N, 4.16%. IR (KBr):  $\nu$  3425 (m, br, OH), 1622 (s, C=N)  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ , 293 K):  $\delta$  8.40 (s, 2H, N=CH), 7.59 and 7.21 (2s, each for 2H, CH of Ph), 4.14 (s, 4H,  $CH_2$  of ethylene group), 4.03 (br, 2H,  $H_2O$ ), 1.50 and 1.31 (2s, each for 18H,  $CH_3$  of *tert*-Bu) ppm.

Complex  $[2(H_2O)]$  was prepared by a procedure similar to that for  $[1(H_2O)]$ . Coordination reaction was made with **2** (280 mg, 0.40 mmol) and 1.5 equiv of  $H_2O$ . The orange solution turned to yellow. The light yellow crystalline solid was obtained after workup, which was recrystallized for purification. Yield: 103 mg (36%). Anal. calc. for  $C_{36}H_{48}N_2O_3Cl_2Zr$ : C, 60.15; H, 6.73; N,

3.90. Found: C, 60.36; H, 6.68; N, 3.87%. IR (KBr):  $\nu$  3414 (m, br, OH), 1610 (s, C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  8.68 (s, 2H, N=CH), 7.64–7.34 (8H, CH of Ph), 4.20 (br, 2H,  $\text{H}_2\text{O}$ ), 1.49 and 1.33 (2s, each for 18H,  $\text{CH}_3$  of *tert*-Bu) ppm.

#### 4.3. Structure determination of $[\text{I}(\text{H}_2\text{O})]$

The data were measured on a Siemens SMART System CCD diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation. A total of 10,880 reflections was collected, of which 6028 were unique and intensities of 4392 unique reflections were larger than  $2\sigma(I)$ . Data processing was accomplished with the SAINT processing program [30]. Intensity data were corrected for absorption by the SADABS program [31]. The structure was solved by direct methods and refined on  $F^2$  against full-matrix least-squares methods by using the SHELXTL97 program [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically except those of water molecules. The positions and thermal parameters of hydrogen atoms from water molecules were fixed during the structure refinement. The maximum and minimum peaks on the final difference Fourier map were 0.421 and  $-0.407 \text{ e } \text{\AA}^{-3}$  for  $[\text{I}(\text{H}_2\text{O})]$ .

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC-205635 for  $[\text{I}(\text{H}_2\text{O})]$ . These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +441223/336-033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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