Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 3929–3936
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Preparation and structures of 6- and 7-coordinate salen-type zirconium complexes and their catalytic properties for oligomerization of ethylene

Hongjun Zhu [a], Mei Wang [a,*], Chengbing Ma [b], Bo Li [a], Changneng Chen [b], Licheng Sun [a,c,*]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Zhongshan Road 158-46, Dalian 116012, PR China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, PR China
[c] KTH Chemistry, Organic Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden

Received 8 April 2005; received in revised form 16 May 2005; accepted 24 May 2005
Available online 29 June 2005

Abstract

A series of salen-type zirconium complexes of the general formula $LZrCl_2$ (L = *N*,*N*′-ethylenebis(salicylideneiminate), **3a**; *N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylideneiminate), **3b**; *N*,*N*′-ethylenebis(5-methoxysalicylideneiminate), **3c**; *N*,*N*′-ethylenebis(5-chlorosalicylideneiminate), **3d**; *N*,*N*′-ethylenebis(5-nitrosalicylideneiminate), **3e**; *N*,*N*′-*o*-phenylenebis(salicylideneiminate), **4a**; *N*,*N*′-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneiminate), **4b**; *N*,*N*′-*o*-phenylenebis(5-methoxysalicylideneiminate), **4c**; *N*,*N*′-*o*-phenylenebis(5-chloro-salicylideneiminate), **4d**) were prepared. The crystal structures of 6- and 7-coordinate zirconium complexes **4b** and [**4b** · $OCMe_2$] were determined by X-ray crystallography, which reveals that a salen-type zirconium complex possesses a labile coordination site on the Zr center with a relatively stable framework and that the coordination and the dissociation of O-donor molecules occur readily at this site. The catalytic properties of **3(a–e)** and **4(a–d)** were studied for ethylene oligomerization in combination with Et_2AlCl as co-catalyst. Complex **3c** featuring a methoxy-substituted salen ligand displayed higher activity than its analogous precursors having chloro and nitro groups as substituents. The catalytic reactions by **3(a–e)** and **4(a–d)** gave C_4–C_{10} olefins and low-carbon linear α-olefins in good selectivity.

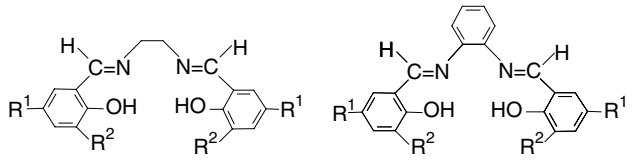
Keywords: Zirconium complexes; Shiff bases; Salen ligands; Ethylene oligomerization; Low-carbon α-olefins; Crystal structures

1. Introduction

The number of reported Group 4 metal complexes with N,O mixed donor chelating ligands, mostly salen [1–6], acen [7], β-aminoketone [8,9], pyridine–phenolate [10–12], amine–phenolate [13,14], imine–phenolate [15–20] and aminodiolate ligands [21,22], has grown quickly in the recent years. Investigations on the preparation and reactivity of these complexes generally aim at development of a new generation of effective non-metallocene single-site catalysts for polymerization and oligomerization of ethylene and α-olefins, as well as for other catalytic reactions [23,24]. Some zirconium and titanium complexes containing the N,O chelating ligands, either bi- or tetradentate, have been found to be high performance catalysts for polymerizations of ethylene, propylene [16–20] and 1-hexene [13,14]. It is of interest to understand the effects of the electronic and steric properties and the coordination geometry of N,O

* Corresponding authors. Tel.: +86 411 88993886; fax: +86 411 83702185 (M. Wang).
E-mail addresses: symbueno@dlut.edu.cn, symbueno@vip.sina.com (M. Wang).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.05.027



1a: $R^1 = R^2 = H$
1b: $R^1 = R^2 = t$-Bu
1c: $R^1 = OMe$, $R^2 = H$
1d: $R^1 = Cl$, $R^2 = H$
1e: $R^1 = NO_2$, $R^2 = H$

2a: $R^1 = R^2 = H$
2b: $R^1 = R^2 = t$-Bu
2c: $R^1 = OMe$, $R^2 = H$
2d: $R^1 = Cl$, $R^2 = H$

Scheme 1. The ligands used in the preparation of non-metallocene precatalysts.

ligands on polymerization and oligomerization of ethylene.

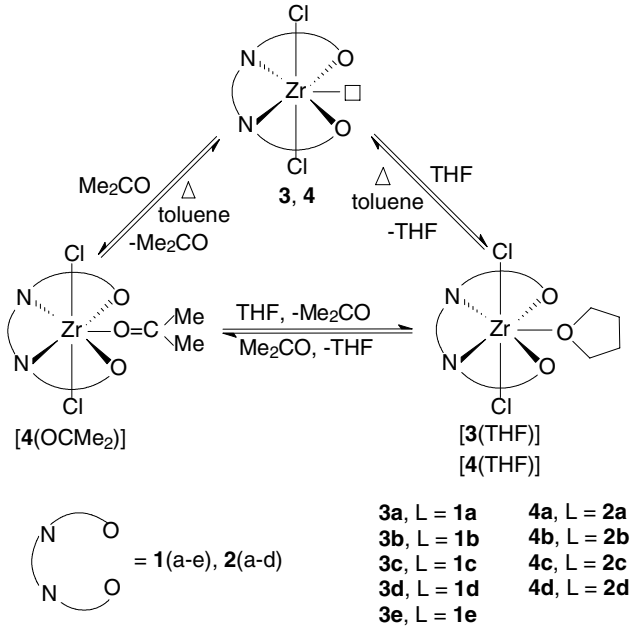
Although salen-type zirconium and titanium complexes have been known for decades [25–33], studies on the catalytic properties of these complexes are very limited for polymerization and oligomerization of ethylene or α-olefins [2–4]. Recently, we have found that salen-type zirconium complexes gave rise to efficient catalyst systems for the conversion of ethylene monomer into low-carbon linear α-olefins when activated by an appropriate alkylaluminum co-catalyst [5]. To gain an insight into the electronic and geometrical influence of salen and salphen ligands, we have prepared a series of salen-type zirconium complexes of the general formula $LZrCl_2$ (L = *N*,*N*′-ethylenebis(salicylideneiminate), **3a**; *N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylideneiminate), **3b**; *N*,*N*′-ethylenebis(5-methoxysalicylideneiminate), **3c**; *N*,*N*′-ethylenebis(5-chlorosalicylidene iminate), **3d**; *N*,*N*′-ethylenebis(5-nitrosalicylideneiminate), **3e**; *N*,*N*′-*o*-phenylenebis(salicylideneiminate), **4a**; *N*,*N*′-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneiminate), **4b**; *N*,*N*′-*o*-phenylenebis(5-methoxysalicylideneiminate), **4c**; *N*,*N*′-*o*-phenylenebis(5-chloro-salicylideneiminate), **4d**, Scheme 1). Here, we report the crystal structures of 6- and 7-coordinate salen-type zirconium complexes **4b** and [**4b** · $OCMe_2$] and the influence of the substituents of ancillary ligands on the catalytic activity and selectivity for ethylene oligomerization.

2. Results and discussion

2.1. Preparation and spectroscopic characterization of 3(a–e) and 4(a–d)

Complexes **3a**, **3b** and **4a**, **4b** were previously prepared [2,5,32] and the molecular structures of the THF-solvated species [**3a** · THF] and [**4a** · THF] were reported by Repo and Floriani [2,32]. The salen and salphen zirconium complexes **3**(**c**–**e**) and **4**(**c**,**d**) bearing methoxy-, chloro- and nitro-substituents were prepared with a similar protocol to that for unsubstituted **3a** and **4a**. Instead of $ZrCl_4 \cdot 2THF$ used in the literature, $ZrCl_4$ was directly reacted with a freshly prepared THF solution of the sodium salt of a substituted salen or salphen ligand at low temperature. The THF-solvated products were obtained in moderate yields (ca. 50%) for the complexes with chloro- and methoxy-substituents and in an acceptable yield (ca. 30%) for the one with a nitro group. The dissociation of the solvent molecule took place by refluxing of [**3** · THF] and [**4** · THF] in toluene to give the corresponding unsolvated complexes **3**(**c**–**e**) and **4**(**c**,**d**). Compared with the conventional metallocene catalyst precursors and their derivatives, the salen and salphen ligands are easily functionalized and the salen-type zirconium complexes are prepared conveniently. Complex [**4b** · $OCMe_2$] was simply generated by dissolving either the unsolvated species **4b** or [**4b** · THF] in acetone. The molecule of acetone was subjected to coordination to the 6-coordinate Zr center as the seventh ligating member, and to displacement of the THF molecule in [**4** · THF] (Scheme 2). It was found that there was a labile coordination site in the relatively stable framework of $LZrCl_2$ [**3**(**a**–**e**), **4**(**a**–**d**)] and that the association and the dissociation of O-donor solvents occurred readily at this site [2,32,34].

Complexes **3**(**a**–**e**) and **4**(**a**–**d**) were identified by IR, ^1H NMR and elemental analysis. The characteristic data of the C=N bands in IR spectra and the resonance of the imino hydrogen in ^1H NMR spectra for **3**(**a**–**e**) and **4**(**a**–**d**) are given in Table 1. Acetone-coordinate complex [**4b** · $OCMe_2$] displayed two strong bands at 1608 and 1699 cm^{-1}, attributed to the stretching vibrations of the C=N bond and the C=O bond of the acetone molecule, respectively. The signal of the imino hydrogen



Scheme 2. Equilibria between 6- and 7-coordinate salen-type zirconium complexes.

Table 1
The C=N bands in IR and the chemical shifts of imino hydrogen in ^{1}H NMR for **3(a–e)** and **4(a–d)**

Complex	IR (KBr) ν (C=N), cm^{-1}	^{1}H NMR δ (N=CH)
3a	1623	8.27 (DMSO)
3b	1624	8.29 ($CDCl_3$)
[**3c** · (THF)]	1629	8.67 (DMSO)
[**3d** · (THF)]	1622	8.45 (DMSO)
[**3e** · (THF)]	1636	8.78 (DMSO)
4a	1610	8.72 (DMSO)
4b	1610	8.88 ($CDCl_3$)
[**4c** · (THF)]	1620	9.28 (DMSO)
[**4d** · (THF)]	1612	8.82 (DMSO)

for the 7-coordinate complex [**4b** · $OCMe_2$] (8.63 ppm) shifted upfield by 0.25 ppm compared with that for the corresponding 6-coordinate complex **4b**.

2.2. Crystal structures of *4b* and [*4b* · ($OCMe_2$)]

To confirm the existence and the position of the labile coordination site in Group 4 metal salphen complexes, the molecular structures of **4b** and [**4b** · $OCMe_2$] were determined by X-ray crystallography. Although a few of crystal structures of salen-type Group 4 metal d^0 complexes with the coordination number 7 have been reported [2,32], so far only two salen-type Group 4 metal d^0 complexes with the coordination number 6 were structurally characterized, one with a common salen ligand [Ti(salen)Me_2] [27] and another featuring a salen-like ligand with a ferrocene group as the backbone [Zr(*t*-Bu-salfen)(CH_2Ph)$_2$] [6]. To the best of our knowledge, the crystal structure of **4b** is the first one of the 6-coordinate salphen complexes of Group 4 metals.

The molecular structures of **4b** and [**4b** · $OCMe_2$] are shown in Figs. 1 and 2, respectively. The important bond lengths and angles are listed in Table 2. Complex [**4b** · $OCMe_2$] consists of discrete molecules and acetone solvent molecules of crystallization in a molar ratio of 1:2 for the complex [**4b** · $OCMe_2$]/lattice acetone molecules. The Zr center of complex **4b** is 6-coordinate in a

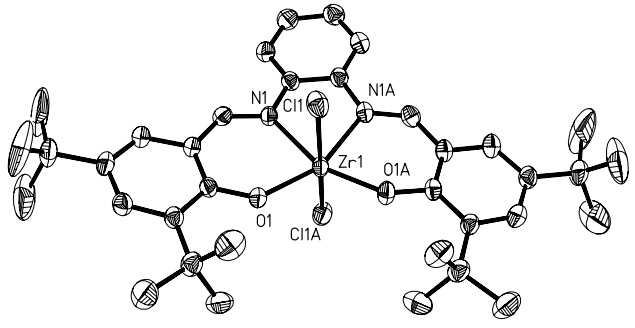


Fig. 1. Molecular structure of **4b** (thermal ellipsoids at 30% probability), with hydrogen atoms and the lattice THF molecule omitted for clarity.

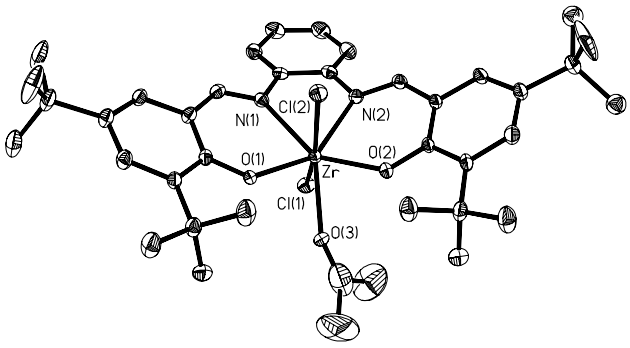


Fig. 2. Molecular structure of [**4b** · $OCMe_2$] (thermal ellipsoids at 30% probability), with hydrogen atoms and lattice acetone molecules omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **4b** and [**4b** · ($OCMe_2$)]

4b	
Zr–O(1)	1.976(3)
Zr–N(1)	2.275(4)
Zr–Cl(1)	2.4735(15)
O(1)–Zr–O(1A)	121.8(2)
O(1A)–Zr–N(1)	155.28(16)
O(1)–Zr–N(1)	82.89(15)
N(1A)–Zr–N(1)	72.4(2)
O(1A)–Zr–Cl(1)	93.60(12)
O(1)–Zr–Cl(1)	90.11(12)
N(1)–Zr–Cl(1)	85.95(12)
N(1A)–Zr–Cl(1)	87.89(12)
Cl(1)–Zr–Cl(1A)	172.36(9)
[4b · $OCMe_2$]	
Zr–O(1)	2.020(4)
Zr–O(2)	2.033(4)
Zr–O(3)	2.286(4)
Zr–N(1)	2.336(5)
Zr–N(2)	2.313(5)
Zr–Cl(1)	2.4994(16)
Zr–Cl(2)	2.4884(16)
O(1)–Zr–O(2)	130.54(15)
O(2)–Zr–O(3)	72.58(15)
O(1)–Zr–O(3)	73.90(15)
O(2)–Zr–N(1)	145.93(16)
O(1)–Zr–N(1)	78.29(15)
O(3)–0Zr–N(1)	140.53(16)
O(2)–Zr–N(2)	77.70(16)
O(1)–Zr–N(2)	146.55(15)
O(3)–0Zr–N(2)	138.74(16)
N(2)–Zr–N(1)	69.80(16)
O(2)–Zr–Cl(2)	83.98(12)
O(1)–Zr–Cl(2)	84.02(12)
O(3)–0Zr–Cl(2)	121.95(13)
N(1)–Zr–Cl(2)	81.55(12)
N(2)–Zr–Cl(2)	81.69(13)
O(2)–Zr–Cl(1)	106.17(11)
O(1)–Zr–Cl(1)	102.59(12)
O(3)–0Zr–Cl(1)	80.04(13)
N(1)–Zr–Cl(1)	79.33(12)
N(2)–Zr–Cl(1)	81.52(13)
Cl(2)–Zr–Cl(1)	157.97(6)

distorted octahedral geometry, and complex [**4b** · $OCMe_2$] adopts a pseudo-pentagonal bipyramidal geometry with a 7-coordinate Zr center. In both complexes, the four donor atoms (NNOO) of the substituted salphen ligand are approximately coplanar and the axial sites are occupied by two chloride ions. The coordination shape of the *t*-Bu_4–salphen ligand in **4b** is nearly in a plane, while it is in an umbrella conformation in [**4b** · $OCMe_2$] [32,35]. This is indicative of a better integral conjugate effect in 6-coordinate salphen complexes of Group 4 metals. The Zr atom of **4b** almost lies on the plane of the NNOO core, while the Zr atom of [**4b** · $OCMe_2$] deviates from the NNOO mean plane by 0.25 Å towards Cl(1). The O(3) atom from the coordinating acetone molecule in [**4b** · $OCMe_2$] is 1.37 Å above the NNOO mean plane towards Cl(1). The difference (41.9°) between the O(3)–Zr–Cl(2) (121.95(13)°) and O(3)–Zr–Cl(1) angle (80.04(13)°) in [**4b** · $OCMe_2$] is much larger than that found in its analogue [{(salphen)$ZrCl_2$} · THF] (23.4°) [32]. Presumably the spatial congestion between the methyl groups of the acetone molecule and the two *ortho tert*-butyl groups of the salphen ligand renders the O(3) atom away from the NNOO mean plane. The Zr–O(1,2), Zr–N and Zr–Cl distances in **4b** and [**4b** · $OCMe_2$] are in good agreement with those previously observed in the zirconium complexes bearing tetradentate salen- and acen-type ligands in a planar fashion [2,7,32]. The Cl(2)–Zr–Cl(1) angle is larger in **4b** (172.36(9)°) and somewhat smaller in [**4b** · $OCMe_2$] (157.97(6)°) compared with the angles in [{(salen)$ZrCl_2$} · THF] (160.24(6)°) and [{(salphen)-$ZrCl_2$} · THF] (165.2(1)°) [2,32]. The 6-coordinate complex **4b** possesses a small bite angle O(1)–Zr–O(2) (121.8(2)°), which is enlarged by 9° as the acetone molecule coordinates to the labile coordination site locating in the middle of the bite angle O(1)–Zr–O(2). A even larger bite angle O(1)–Zr–O(2) (137.6(1)°) was found in the THF-solvated analogue [32].

*2.3. Influence of the substituents of salen and salphen ligands on the catalytic properties of **3**(**a**–**e**) and **4**(**a**–**d**) for ethylene oligomerization*

We have reported the oligomerization of ethylene catalyzed by **3a**, **3b** and **4a**, **4b** [5]. To explore the electronic and geometrical influence of the ancillary ligands, further studies were made on the catalytic performance of a series of substituted-salen and -salphen zirconium complexes in combination with Et_2AlCl as co-catalyst. The catalytic reactions were carried out in a 100-mL autoclave under a constant ethylene pressure of 1.4 MPa at 150 °C with magnetic stirring. The same procedures as previously described were used for oligomerization reaction and product analysis [5]. The catalytic results of **3**(**c**–**e**) and **4d** are summarized in Table 3, and the catalytic data of **3a**, **3b** and **4a**, **4b** are also included for a comparison. In all cases, there is no solid polymer observed in the resulting solution. The olefins with more than 16 carbons were found in a trace amount by GC analysis, and the branched olefins were not detected by GC/MS spectra. Without the zirconium complex, Et_2AlCl did not exhibit activity for ethylene oligomerization under the present conditions.

All data obtained show that the salen complexes **3**(**a**–**d**) possess higher catalytic activity than their corresponding salphen complexes **4**(**a**–**d**). Presumably, the different activities of salen and salphen complexes are caused by both the distinct flexibility of the ligand frameworks and the shorter catalyst life-time of the salphen complexes. The preliminary results on the lifetimes of [**3a** · THF] and [**4a** · THF] catalysts generated by activation with Et_2AlCl showed that the activity of salphen complex [**4a** · THF] declined by 35% as the reaction period was prolonged from 30 to 60 min, while the activity of salen complex [**3a** · THF] went down by 25%. The salen-type ligand with an ethylene (–CH_2CH_2–) backbone is by far more flexible compared with the

Table 3
Results of ethylene oligomerization by **3**(**a**–**e**) and **4**(**a**–**d**)/Et_2AlCl catalyst systems

Entry[a]	Pre-cat.	Substituents	TOF[c] mol (mol h)$^{-1}$	$C^{=}_{4-10}$ Olefins[d]	$C^{=}_{4-10}/\Sigma C^{=}$	α-Linear olefins[d]	$\alpha - C^{=}_{4-10}/\Sigma C^{=}_{4-10}$
1	[**3a** · THF]	–	9300	85.0		78.6	
2	**3b**	4 *t*-Bu	7600	91.5		76.8	
3	[**3c** · THF]	2 OCH_3	12400	85.6		74.9	
4	[**3e** · THF]	2 NO_2	6400	87.0		83.0	
5[b]	[**3c** · THF]	2 OCH_3	34700	86.2		91.5	
6[b]	[**3d** · THF]	2 Cl	24800	86.7		88.7	
7	[**4a** · THF]	–	8000	88.9		81.0	
8	**4b**	4 *t*-Bu	2400	92.0		91.6	
9	[**4d** · THF]	2 Cl	5700	85.5		86.9	

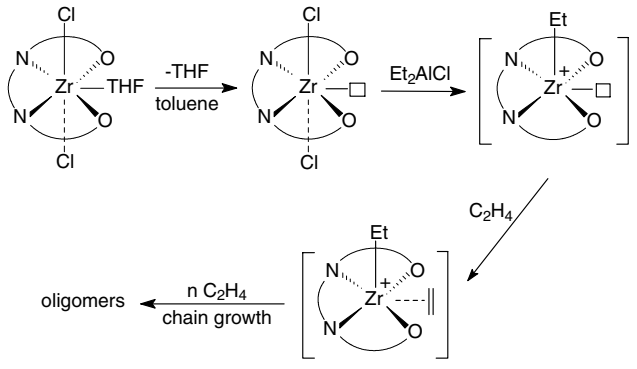
[a] Reaction conditions for all entries except entries 5 and 6: pre-catalyst 0.05 mmol (1.4 mmol/L), Al/Zr 100:1, 150°C, 1 h, $P(C_2H_4)$ 1.4 MPa, toluene 30 mL.

[b] Reaction conditions for entries 5 and 6: pre-catalyst 0.01 mmol (0.3 mmol/L), Al/Zr 300:1, 0.5 h. Other conditions are the same as those mentioned in footnote 'a'.

[c] TOF = mol C_2H_4 converted (mol Zr h)$^{-1}$.

[d] Determined by GC analysis with *n*-heptane as an internal standard and by GC/MS spectra.

salphen-type ligand with an *o*-phenylene (–C_6H_4–) as a backbone. As 7-coordinate zirconium complexes were desolvated in toluene, it is possible for zirconium salen complexes to form 6-coordinate species in a nonplanar coordination geometry of the salen ligand with a *cis*-Cl arrangement, in analogy to the known 6-coordinate zirconium acen complex [32], while the coordination geometry of the rigid salphen ligand maintains a planar fashion with a *trans*-Cl arrangement in both 7- and 6-coordinate species, the structures of which have been determined by X-ray crystallography. According to the prevalent argument, a *cis*-arrangement of the two chlorides in a zirconium complex precursor is a prerequisite for efficient catalysis of oligomerization and polymerization of ethylene or α-olefins. Some previous experimental results supported that the integral conjugation of a salphen ligand in an N,O-chelating zirconium complex keeps intact in the active species [5,17]. In this case, it is impossible for zirconium salphen complexes to form a species with a *cis*-arrangement of two chloride ions. The experimental results show that zirconium salphen complexes are catalytically active for ethylene oligomerization, although in a lower TOF than analogous salen complexes, to afford products with a high selectivity to low-carbon linear α-olefins. A plausible mechanism is suggested in Scheme 3. When a zirconium salphen complex is treated with an organo-aluminum co-catalyst, one of the axial chlorides is replaced by an alkyl group and the other chloride is abstracted by the Al of co-catalyst to generate a positive charge on the Zr center, as described by Keim et al. [9] and Fujita et al. [17,19] for the analogous zirconium catalysts in combination with the alkylaluminum co-catalysts. Although the coordination of ethylene at the apical position, i.e. the position *trans* to the alkyl group, appears to be favorable, the resulting species is inactive for chain growth by consecutive insertion. Taken into account that the association and dissociation of O-donor molecules readily occur on the equatorial coordination site between two oxygen atoms, the ligation of ethylene monomer to the labile coordination site on the Zr center of the active cationic salphen catalyst might take place, giving a species with *cis*-arrangement of an alkyl group and a coordinating ethylene monomer on the Zr center, which can readily undergo consecutive insertion reaction. There should be an equilibrium among the species generated by *trans*- and *cis*-coordination of ethylene and the disassociated 5-coordinate species. Chain growth is attained by the *cis*-coordination of monomers and consecutive insertion. This scenario is presented as one of the possible explanations for the catalytic activity of zirconium salphen complexes. Attempts to prepare the salen-type zirconium complex precursor with an ethylene monomer ligating to the labile coordination site was unsuccessful, and the further effort to introduce an alkenyl group as a pendant arm to salen and salphen ligands is in progress.



Scheme 3. The possible use of the labile coordination site in the mechanism of ethylene oligomerization.

The variation of the substituents on the ancillary ligands is capable of tuning the coordination micro-environment on the metal center, so as to adjust the catalytic activity and selectivity of the homogeneous single-site catalysts. In general, the electron releasing substituents benefit the catalyst system with a cationic transition metal center in an active species, and the electron withdrawing groups destabilize the active cationic species, resulting in the decrease of the catalyst activity. Although the mechanism of ethylene oligomerization by salen-type zirconium complex precursors remains uncertain, the catalytic data in Table 3 show that the electron releasing character of methoxy group on the phenolate moiety of the salen ligand has a positive influence on the activity of the present catalyst systems (entries 3 vs. 1 and 5 vs. 6). In contrast, the strong electron withdrawing character of nitro group has a marked negative influence on the activity (entries 4 vs. 1 and 3). Compared with the TOF of 9.3×10^3 h^{-1} for unsubstituted zirconium salen complex **3a**, the activity of **3c** featuring a methoxy-substituted salen ligand is up to a TOF of 1.24×10^4 h^{-1}, which is twice as that of **3e** featuring a nitro-substituted salen ligand. The experimental results suggest that a cationic alkyl zirconium species might be involved in the catalytic process. In an Al/Zr ratio of 300:1, **3c** displayed a higher TOF (3.47×10^4 h^{-1}), with good selectivities to C_4–C_{10} olefins and to low-carbon linear α-olefins, than that of **3d** with a chloro-substituted salen ligand. The effects of different substituents of the salphen ligand are in the same trend on the catalyst activities of zirconium salphen precursors **4(a–d)** in the oligomerization of ethylene. The catalytic data in Table 3 also indicate that the bulky substituent on the *ortho* position of the coordinate oxygen apparently benefits the selectivity of ethylene oligomerization to C_{4-10} olefins (entries 2 and 8), while the group on the *para* position does not display an obvious influence on the selectivity to low carbon olefins (entries 3–6).

3. Experimental

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. Ethylene (polymer grade) passed through molecular sieves (4 Å). Diethyl aluminum chloride and $ZrCl_4$ were purchased from Sigma–Aldrich Chemie GmbH. Other commercially available chemical reagents were used without further purification. Salen and salphen ligands and their sodium salts were prepared according to literature procedures [36]. Infrared spectra were recorded from KBr disks using a JASCO FT/IR 430 spectrophotometer. ^{1}H NMR spectra were recorded with a Varian INOVA 400NMR apparatus. Elemental analyses were performed on a THERMOQUEST-FLASH EA 1112 elemental analyzer. GC/MS analyses of oligomers were made using an HP6890GC/5973MS instrument.

3.1. Preparation of *3(a–e)* and *4(a–d)*

The preparation of complexes **3a**, **3b** and **4a**, **4b** was reported previously [5]. Salen and salphen zirconium complexes with methoxy-, chloro- and nitro-substituents on the benzene ring, [**3(c–e)** · THF] and [**4(c,d)** · THF], were prepared referring to literature procedures [32]. Instead of $ZrCl_4 \cdot 2THF$ used in the literature, $ZrCl_4$ (1.08 g, 4.61 mmol) was slowly raked into a freshly prepared THF solution (70 mL) of Na_2L (4.61 mmol, L = **1(c–e)**, **2(c,d)**) at −20 °C. After 1 h, the mixture was allowed to room temperature and then refluxed for 2 h. Afterwards the reaction condition and work-up were made as described in the literature [32]. The desolvated complexes **3(c–e)** and **4(c,d)** were prepared by refluxing the above-obtained complexes in toluene for 1 h. After filtration with a cannula, the crystalline product was washed two times with hexane and dried in vacuo.

Complex [3c · THF]. Yield: 1.51 g (55%). IR (KBr): *v* (C=N) 1629 (s) cm^{-1}. ^{1}H NMR (DMSO): *δ* 8.67 (s, 2H, N=C**H**), 7.14–6.77 (m, 6H, C**H** of Ph), 4.06 (s, 4H, C**H**$_2$ of ethylene group), 3.75 (s, 6H, OC**H**$_3$), 3.60 (t, 4H, OC**H**$_2$ of THF), 1.76 (m, 4H, C**H**$_2$ of THF). *Anal*. calc. for $C_{18}H_{18}N_2O_4Cl_2Zr \cdot 1.5THF$ (M_r = 596.64): C, 48.31; H, 5.07; N, 4.70. Found: C, 48.48; H, 4.98; N, 4.60%.

Complex [3d · THF]. Yield: 1.31 g (47%). IR (KBr): *v* (C=N) 1622 (s) cm^{-1}. ^{1}H NMR (DMSO): *δ* 8.45 (s, 2H, N=C**H**), 7.29–6.36 (m, 6H, C**H** of Ph), 4.28 (s, 4H, C**H**$_2$ of ethylene group), 3.60 (t, 4H, OC**H**$_2$ of THF), 1.76 (m, 4H, C**H**$_2$ of THF). *Anal*. calc. for $C_{16}H_{12}N_2O_2Cl_4Zr \cdot 1.5THF$ (M_r = 605.48): C, 43.64; H, 4.00; N, 4.63. Found: C, 43.77; H, 3.91; N, 4.60%.

Complex [3e · THF]. Yield: 0.92 g (32%). IR (KBr): *v* (C=N) 1636 (s) cm^{-1}. ^{1}H NMR (DMSO): *δ* 8.78 (s, 2H, N=C**H**), 8.33–6.60 (m, 6H, C**H** of Ph), 4.42 (s, 4H, C**H**$_2$ of ethylene group), 3.60 (t, 4H, OC**H**$_2$ of THF), 1.76 (m, 4H, C**H**$_2$ of THF). *Anal*. calc. for $C_{16}H_{12}N_4O_6Cl_2Zr \cdot 1.5THF$ (M_r = 626.58): C, 42.17; H, 3.86; N, 8.94. Found: C, 41.97; H, 3.73; N, 8.86%.

Complex [4c · THF]. Yield: 1.43 g (51%). IR (KBr): *v* (C=N) 1620 (s) cm^{-1}. ^{1}H NMR (DMSO): *δ* 9.28 (s, 2H, N=C**H**), 7.99–6.92 (m, 10H, C**H** of Ph), 3.80 (s, 6H, OC**H**$_3$), 3.60 (t, 4H, OC**H**$_2$ of THF), 1.76 (m, 4H, C**H**$_2$ of THF) ppm. *Anal*. calc. for $C_{22}H_{18}N_2O_4Cl_2Zr \cdot THF$ (M_r = 608.63): C, 51.31; H, 4.31; N, 4.60. Found: C, 51.19; H, 4.37; N, 4.56%.

Complex [4d · THF]. Yield: 1.48 g (52%). IR (KBr): *v* (C=N) 1612 (s) cm^{-1}. ^{1}H NMR (DMSO): *δ* 8.92 (s, 2H, N=C**H**), 7.71–6.74 (m, 10H, C**H** of Ph), 3.60 (t, 4H, OC**H**$_2$ of THF), 1.76 (m, 4H, C**H**$_2$ of THF). *Anal*. calc. for $C_{20}H_{12}N_2O_2Cl_4Zr \cdot THF$ (M_r = 617.47): C, 46.68; H, 3.26; N, 4.54. Found: C, 46.49; H, 3.22; N, 4.47%.

3.2. Preparation of *[4b · OCMe$_2$]*

Complex [**4b** · $OCMe_2$] was obtained by dissolving **4b** (320 mg, 0.46 mmol) or [**4b** · THF] (335 mg, 0.46 mmol) in acetone (6 mL) and the solution was stirred for a few minutes. After filtration, Et_2O was diffused into the acetone solution. Light yellow flake crystals were formed and isolated by removing all solution with a cannula. Compound [**4b** · $OCMe_2$] was isolated in 29% yield (101 mg). IR (KBr): *v* (C=O) 1699 s, *v* (C=N) 1608 s cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 8.63 (s, 2H, N=C**H**), 7.61–7.31 (m, 8H, C**H** of Ph), 2.18 (s, 18H, C**H**$_3$ of acetone), 1.47 and 1.33 (2s, each for 18H, C**H**$_3$ of *tert*-Bu). *Anal*. calc. for $C_{36}H_{46}N_2O_2Cl_2Zr \cdot 3Me_2CO$ (M_r = 875.13): C, 61.76; H, 7.37; N, 3.20. Found: C, 61.58; H, 7.36; N, 3.17%.

3.3. Structure determination

Crystallographic details and structure refinements are summarized in Table 4. The data were measured on a Siemens SMART System CCD diffractometer using graphite monochromated Mo Kα radiation (*λ* = 0.71073 Å). Data processing was accomplished with the SAINT processing program [37]. Intensity dada were corrected for absorption by the SADABS program [38]. The structure was solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELXTL97 program [39]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrically calculation.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC Nos. 232205 and 207350 contain the supplementary crystallographic data for **4b** and [**4b** · $OCMe_2$]. These data can be obtained free of charge

Table 4
Crystallographic data for **4b** and [**4b** · $OCMe_2$]

	[**4b**](THF)	[**4b** · $OCMe_2$]($2Me_2CO$)
Empirical formula	$C_{40}H_{54}Cl_2N_2O_3Zr$	$C_{45}H_{64}Cl_2N_2O_5Zr$
Formula weight	772.97	875.10
T (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	19.0974(7)	15.9526(7)
b (Å)	19.5025(6)	11.4939(5)
c (Å)	11.7734(3)	25.5186(12)
α (°)	90.00	
β (°)	109.7820(10)	100.6880(10)
γ (°)	90.00	
V (Å^3)	4126.2(2)	4597.9(4)
Z	4	4
D_{calc} (g cm^{-3})	1.244	1.264
μ(mm^{-1})	0.432	0.399
F(000)	1624	1848
Crystal size (mm)	$0.36 \times 0.28 \times 0.20$	$0.88 \times 0.32 \times 0.24$
$\theta_{min/max}$ (°)	2.08–25.04	1.40–25.06
Unique reflections	2622 (total: 3618)	5811 (total: 8073)
Parameters refined	218	516
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0697$	$R_1 = 0.0678$
	$wR_2 = 0.1616$	$wR_2 = 0.1738$
R indices (all data)	$R_1 = 0.1055$	$R_1 = 0.1052$
	$wR_2 = 0.1909$	$wR_2 = 0.2138$
Goodness-of-fit on F^2	1.093	1.002
Residual electron density (e Å^{-3})	0.575, −0.479	0.744, −0.881

at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax (internat.): +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3.4. Oligomerization of ethylene

The ethylene oligomerization reactions catalyzed by complexes **3(a–e)** and **4(a–d)** were performed as previously reported [5]. A toluene solution of the co-catalyst Et_2AlCl (1.0 mmol) in a preset Al/Zr ratio was added to either the toluene solution or suspension of the precursor complexes **3(a–e)** or **4(a–d)**. The suspension turned clear after the mixture was stirred for several minutes. No aging time was needed for these catalytic systems. The oligomerization reaction was carried out in a 100 mL autoclave under a constant ethylene pressure (1.4 MPa). The autoclave was heated in an oil bath to 150 °C and the contents were stirred magnetically with a constant speed for 1 h. After reaction, the valve of the autoclave to the ethylene pipeline was closed. The autoclave was cooled to room temperature and the tail gas was collected with a gasometer. The catalytic reactivity of a catalyst was calculated based on the weight difference of the autoclave before and after reaction. After the reaction was quenched by an alcoholic solution saturated with NaOH, the distribution of the oligomers was determined by GC analysis and GC/MS spectra of the collected gas and the obtained solution. The gas was analyzed at room temperature with an SE 30 column (30 m × 0.25 mm) and an FID detector and the solution was analyzed using a temperature program: 50–220 °C (9 °C/min, hold 8 min) with *n*-heptane as an internal standard.

Acknowledgments

We gratefully acknowledge the Chinese National Natural Science Foundation (Grant Nos. 20173006 and 20128005), the Swedish Energy Agency and the Swedish Research Council for financial supports.

References

[1] W. Leung, E.Y.Y. Chan, E.K.F. Chow, I.D. Williams, S. Peng, J. Chem. Soc., Dalton Trans. (1996) 1229.
[2] T. Repo, M. Klinga, P. Pietikäinen, M. Leskelä, A. Uusitalo, T. Pakkanen, K. Hakala, P. Aaltonen, B. Löfgren, Macromolecules 30 (1997) 171.
[3] B. Schweder, D. Walther, T. Dohler, O. Klobes, H. Gorls, J. Prakt. Chem. 341 (1999) 736.
[4] J. Huang, B. Lian, L. Yong, Y. Qian, Inorg. Chem. Commun. 4 (2001) 392.
[5] M. Wang, H. Zhu, K. Jin, D. Dai, L. Sun, J. Catal. 220 (2003) 392.
[6] A. Shafir, D. Fiedler, J. Arnold, J. Chem. Soc., Dalton Trans. (2002) 555.
[7] E.B. Tjaden, D.C. Swenson, R.F. Jordan, J.L. Petersen, Organometallics 14 (1995) 371.
[8] D. Jones, A. Robers, K. Cavell, W. Keim, U. Englert, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 255.
[9] D. Jones, K. Cavell, W. Keim, J. Mol. Catal. 138 (1999) 37.
[10] X. Bei, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 3282.
[11] T. Tsukahara, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 3303.
[12] T. Toupance, S.R. Dubberley, N.H. Rees, B.R. Tyrrell, P. Mountford, Organometallics 21 (2002) 1367.
[13] E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 122 (2000) 10706.
[14] S. Groysman, I. Goldberg, M. Kol, Organometallics 22 (2003) 3013.
[15] J. Strauch, T.H. Warren, G. Erker, R. Fröhlich, P. Saarenketo, Inorg. Chim. Acta 300–302 (2000) 810.
[16] S. Matsui, M. Mitani, J. Saito, N. Matsukawa, H. Tanaka, T. Nakano, T. Fujita, Chem. Lett. (2000) 554.
[17] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.
[18] Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 7888.
[19] H. Makio, N. Kashiwa, T. Fujita, Adv. Synth. Catal. 344 (2002) 477.
[20] Y. Tohi, H. Makio, S. Matsui, M. Onda, T. Fujita, Macromolecules 36 (2003) 523.
[21] P. Shao, R.A.L. Gendron, D.J. Berg, G.W. Bushnell, Organometallics 19 (2000) 509.
[22] M.E.G. Skinner, D.A. Cowhig, P. Mountford, Chem. Commun. (2000) 1167.
[23] P. Shao, R.A.L. Gendron, D.J. Berg, Can. J. Chem. 78 (2000) 255.

[24] A. Watanabe, T. Uchida, K. Ito, T. Katsuki, Tetrahedron Lett. 43 (2002) 4481.
[25] M.D. Hobday, T.D. Smith, Coord. Chem. Rev. 9 (1973) 311.
[26] C. Floriani, Polyhedron 8 (1989) 1717.
[27] C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa, C. Guastini, Angew. Chem. 101 (1989) 93;
C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa, C. Guastini, Angew. Chem., Int. Ed. Engl. 28 (1989) 64.
[28] M. Pasquali, F. Marchetti, A. Landi, C. Floriani, J. Chem. Soc., Dalton Trans. (1978) 545.
[29] G. Dell'Amico, F. Marchetti, C. Floriani, J. Chem. Soc., Dalton Trans. (1982) 2197.
[30] E. Solari, F. Corazza, C. Floriani, J. Chem. Soc., Dalton Trans. (1990) 1345.
[31] J. Rosset, C. Floriani, M. Mazzanti, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 29 (1990) 3991.
[32] F. Corazza, E. Solari, C. Floriani, J. Chem. Soc., Dalton Trans. (1990) 1335.
[33] E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Chem. Soc., Dalton Trans. (1992) 367.
[34] M. Wang, H. Zhu, D. Huang, K. Jin, C. Chen, L. Sun, J. Organomet. Chem. 689 (2004) 1212.
[35] M. Calligaris, G. Nardin, L. Randaccio, Coord. Chem. Rev. 7 (1972) 385.
[36] C.S. Marvel, S.A. Aspey, E.A. Dudley, J. Am. Chem. Soc. 78 (1956) 4905.
[37] Software packages SMART and SAINT, Siemens Energy & Automation Inc., Madison, Wisconsin, 1996.
[38] G.M. Sheldrick, SADABS Absorption Correction Program, University of Göttingen, Germany, 1996.
[39] G.M. Sheldrick, SHELXTL97 Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.