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Ethylene oligomerization by salen-type zirconium complexes to low-carbon linear α-olefins

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Abstract

A series of zirconium salen-type complexes were prepared by using $ZrCl_4$ and sodium salts of the tetradentate Schiff base ligands. In combination with Et_2AlCl, they displayed moderate to high catalytic activities in ethylene oligomerization under a pressure of 1.0–1.8 MPa at 150 °C in toluene. The main products are C_4–C_{10} olefins with good selectivity to linear α-olefins. The turnover frequency (TOF) of catalyst system $Zr(salen)Cl_2 \cdot THF/Et_2AlCl$, under a pressure of 1.8 MPa and in an Al/Zr molar ratio of 300, was $4.93 \times 10^4\ h^{-1}$ with a satisfactory selectivity to C_4–C_{10} olefins (89%), and linear α-olefins accounted for 95%. The steric and conjugate effects of the ligands on ethylene oligomerization, as well as the effects of cocatalysts, the Al/Zr molar ratios, the reaction temperature, the ethylene pressure, and the lifetime of the catalysts were studied.

Keywords: Zirconium complexes; Salen-type ligands; Schiff bases; Ethylene oligomerization; Low-carbon linear α-olefins

1. Introduction

Investigations of catalytic oligomerization of ethylene have been mainly focused on the complexes of titanium, zirconium, chromium, and nickel for decades [1–3]. In addition to the extensively studied complexes of group 4 metallocenes, the catalytic properties of related catalyst systems, such as half-sandwich titanium and boratabenzene zirconium complexes, were also reported for ethylene oligomerization by Bazan [4,5], Teuben and their co-workers [6]. Chromium compounds possessing nitrogen or oxygen ligands and tantalum(V) chloride were found to be effective catalyst precursors for the selective trimerization of ethylene to 1-hexene [7,8]. A variety of nickel complexes with P,O- (analogous to the Ni precursors used in the SHOP process) [2], P,N-, S,S-, or O,O-chelating ligands were widely studied, predominantly affording linear α-olefins in different selectivities to the chain length of the oligomers. In recent years, the discoveries of a new family of Fe(II)- and Co(II)-based bis(imino)pyridyl catalysts and a series of Ni(II)- and Pd(II)-based α-diimine catalysts, by Gibson [9,10], Brookhart and their co-workers [11–13], for ethylene polymerization and oligomerization have triggered an upsurge in preparation and catalysis of postmetallocene precatalysts, particularly the complexes incorporating diverse chelating Schiff base ligands.

The precatalysts formed by the combination of group 4 metals with various N,O-bidentate or N_2O_2-tetradentate salen-type ligands possess many advantages, such as facile approach, relative tolerance, readily adjusted ancillary ligands, and tunable steric and electronic coordination environments on the metal center. All these merits have drawn our attention to the catalytic performance of tetradentate zirconium salen-type complexes. Some salen-type complexes of late transition metals have proved to be good catalyst precursors for ethylene oligomerization to low-carbon olefins [14]. In contrast to transition metals of middle and late d-block, literature references are limited in the synthesis, crystal structures, and chemical behaviors of salen-type complexes of group 4 metals [15–26]. The two reactive M–Cl bonds in a zirconium salen-type complex are appropriate for alkylation of the metal center, which is one of the essential properties of precatalysts available for catalysis studies of ethylene oligomerization and polymerization. So far very few reports concerning ethylene polymerization by this class of Ti and Zr complexes have been found in the literature [27–31], and none is related to ethylene oligomer-

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ization. Here we report the results on the synthesis and catalytic properties of zirconium salen-type complexes $LZrCl_2$ (**1**–**4**) (**1**, H_2L^1, N, N'-*o*-ethylenebis(salicylideneiminate); **2**, H_2L^2, N, N'-*o*-phenylenebis(salicylideneiminate); **3**, H_2L^3, N, N'-*o*-ethylenebis(3,5-di-*tert*-butylsalicylideneiminate); **4**, H_2L^4, N, N'-*o*-phenylenebis(3,5-di-*tert*-butylsalicylidene iminate)) in combination with Et_2AlCl or EAO (ethylaluminoxane) as cocatalyst for ethylene oligomerization. Moderate to high catalytic activities for catalyst systems of zirconium complexes **1**–**4**/Et_2AlCl were observed with high selectivities to low-carbon α-olefins under high temperature (150 °C) and moderate pressure (1.0–1.8 MPa).

2. Experimental

2.1. 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. Ethylene (polymer grade) passed through molecular sieves (4 Å). Ethylaluminoxane was prepared by partial hydrolysis of Et_3Al with $Al_2(SO_4)_3 \cdot 18H_2O$ as a water source ($AlEt_3:H_2O$ = 1:1, mol/mol) in toluene at 0–5 °C [32]. Diethyl aluminum chloride, triethyl aluminum, and $ZrCl_4$ were 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 ^{1}H NMR spectra on a Varian INOVA 400NMR apparatus. Elemental analyses were performed on a CARLO ERBA MOD-1106 elemental analyzer. GC/MS analyses of oligomers were made using an HP6890GC/5973MS instrument.

2.2. Preparation of complexes **1**–**4**

All ligands and their sodium salts were prepared according to literature procedures [33].

Complexes **1**–**4** in the THF-solvated form were prepared by a modified method referring to the literature [15]. Instead of $ZrCl_4 \cdot 2THF$ used in the literature, the compound $ZrCl_4$ (1.08 g, 4.61 mmol) was slowly raked into a freshly prepared THF solution (70 ml) of Na_2L (4.61 mmol) at −20 °C. After half an hour the mixture was allowed to reach room temperature and stirred for another hour. Afterward the reaction conditions and work-up were as described in the literature [15].

The desolvated complexes **1**–**4** were prepared by refluxing the above-obtained complexes in toluene for 2 h. After being filtrated with a cannula, the crystalline solid was washed two times with pentane and dried in vacuo.

1, IR (KBr): ν(C=N) 1623 cm^{-1}. ^{1}H NMR (CD_3CN): δ 8.27 (s, 2H, N=C**H**), 7.50–6.86 (m, 8H, C**H** of Ph), 4.13 (s, 4H, C$\mathbf{H}_2$ of ethylene group). Anal. Calcd. for $C_{16}H_{14}N_2O_2Cl_2Zr$: C, 44.86; H, 3.29; N, 6.54. Found: C, 44.47; H, 3.32; N, 6.60.

2, IR (KBr): ν(C=N) 1610 cm^{-1}. ^{1}H NMR (CD_3CN): δ 8.72 (s, 2H, N=C**H**), 7.58–6.85 (m, 12H, C**H** of Ph). Anal. Calcd. for $C_{20}H_{14}N_2O_2Cl_2Zr$: C, 50.42; H, 2.96; N, 5.88. Found: C, 49.97; H, 2.93; N, 5.79.

3. THF, IR (KBr): ν(C=N) 1616 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.50 (s, 2H, N=C**H**), 7.64 and 7.28 (2s, each for 2H, C**H** of Ph), 4.14 (s, 4H, C$\mathbf{H}_2$ of ethylene group), 3.82 (m, 4H, C$\mathbf{H}_2$ of THF), 1.82 (m, 4H, C$\mathbf{H}_2$ of THF), 1.50 and 1.32 (2s, each for 9H, C$\mathbf{H}_3$ of *tert*-Bu).

3, IR (KBr): ν(C=N) 1624 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 2H, N=C**H**), 7.48 and 7.20 (2s, each for 2H, C**H** of Ph), 4.15 (s, 4H, C$\mathbf{H}_2$ of ethylene group), 1.50 and 1.31 (2s, each for 9H, C$\mathbf{H}_3$ of *tert*-Bu). Anal. Calcd. for $C_{32}H_{46}N_2O_2Cl_2Zr$: C, 58.86; H, 7.12; N, 4.29. Found: C, 58.61; H, 7.01; N, 4.34.

4. THF, IR (KBr): ν(C=N) 1603 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 2H, N=C**H**), 7.74–7.34 (m, 8H, C**H** of Ph), 3.76 (m, 4H, C$\mathbf{H}_2$ of THF), 1.83 (m, 4H, C$\mathbf{H}_2$ of THF), 1.48 and 1.32 (2s, each for 9H, C$\mathbf{H}_3$ of *tert*-Bu).

4, IR (KBr): ν(C=N) 1610 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 2H, N=C**H**), 7.73–7.33 (m, 8H, C**H** of Ph), 1.60 and 1.34 (2s, each for 9H, C$\mathbf{H}_3$ of *tert*-Bu). Anal. Calcd. for $C_{36}H_{46}N_2O_2Cl_2Zr$: C, 61.68; H, 6.63; N, 4.00. Found: C, 61.82; H, 6.60; N, 3.94.

2.3. Oligomerization of ethylene

The ethylene oligomerization reactions catalyzed by complexes **1**–**4** were performed as previously reported [34]. A toluene solution of the cocatalyst in a needed Al/Zr ratio was added to either the toluene solution or suspension of the precursor complexes **1**–**4**. 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 (1.0–1.8 MPa). The autoclave was heated in an oil bath to the preset temperature and the contents were stirred magnetically for a certain period. After reaction, the valve of the autoclave to the ethylene pipeline was closed. The autoclave was cooled, vented and weighed. The catalytic reactivity of a catalyst was calculated based on the weight difference of the autoclave before and after the 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 obtained solution with *n*-heptane as an internal standard.

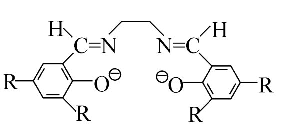
3. Results and discussion

3.1. Preparation and characteristics of zirconium salen-type complexes **1–4**

Zirconium salen-type complexes **1** · THF and **2** · THF were prepared by Repo and Floriani from $ZrCl_4 \cdot 2THF$. Both complexes were identified by X-ray crystallography [15,29]. In our experiment, $ZrCl_4$ was used directly as starting compound in the preparation of **1–4** to combine two synthetic steps into one.

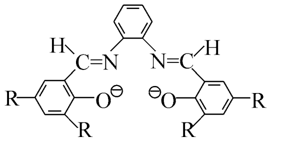
$$\mathrm{ZrCl_4 + Na_2L \xrightarrow[-20\text{–}80\,^\circ C,\,thf]{-2NaCl} ZrLCl_2 \cdot (THF)_{\mathit{n}}} \tag{1}$$

$$n = 0, 1$$



1, L^1 = salen, R = H

3, L^3 = ^{t}Bu$_4$salen, R = ^{t}Bu



2, L^2 = salphen, R = H

4, L^4 = ^{t}Bu$_4$salphen, R = ^{t}Bu

Except complex **1**, which was isolated in a yield of ca. 35%, good yields of **2–4** were obtained (60–75%). Complexes **3** and **4**, each incorporating four *tert*-butyl groups on the salen or salphen ligand, had much better solubility in toluene and other polar organic solvents than their analogues **1** and **2**.

The ^{1}H NMR spectra showed that when Na$_2$salen and Na$_2$salphen were used in the reactions, complexes **1** and **2** were isolated in THF-solvated form with a seven-coordinated metal center [Eq. (1)]. While using the sodium salts of the ligands having *tert*-butyl groups, Na_2L^3 and Na_2L^4, the reactions gave complexes **3** and **4** not only in a solvated form, but also in an unsolvated form with a six-coordinated metal center. According to the signals in the ^{1}H NMR spectra in $CDCl_3$ at 20 °C, the ratio of the THF-solvated to the unsolvated form is 0.78–0.79:1 for **3** and **4**. The steric congestion around the metal center, induced by the two *ortho tert*-butyl groups, may block the solvation of complexes **3** and **4** to a certain extent. When refluxed in toluene, all solvated zirconium complexes turned to the unsolvated form with an observable color change, from light yellow to yellow for **1** and **3** and from orange to reddish orange for **2** and **4**.

Complexes **1–4** in both solvated and unsolvated forms were characterized by IR, ^{1}H NMR, and elemental analysis. The characteristic bands (1619 cm^{-1} for **1** · THF and 1606 cm^{-1} for **2** · THF) of ν(C=N) in IR spectra and the signals in ^{1}H NMR spectra of **1** · THF and **2** · THF were identical with the spectroscopic data of $Zr(salen)Cl_2(THF)$ and $Zr(salphen)Cl_2(THF)$ reported in the literature [15,29]. The C=N-stretching vibrations of the unsolvated complexes **1–4** in IR spectra displayed minor blue shifts compared with the ν(C=N) bands of their corresponding THF-solvated forms. As the coordination environment of the metal center changed, resulting from the association and disassociation of a molecule of solvent, the resonance of the imino hydrogen in ^{1}H NMR spectra of metal salen complexes shifted apparently. The signals of the imino hydrogen in $CDCl_3$ appeared at δ 8.50 for **3** · THF and 8.70 for **4** · THF, while the ^{1}H NMR spectra of unsolvated complexes **3** and **4** showed singlet signals of the imino hydrogen at δ 8.29 and 8.88, respectively. The poor solubility of unsolvated complexes **1** and **2** thwarted us from acquiring clear ^{1}H NMR spectra. When the ^{1}H NMR spectra of **1** and **2** were measured in CD_3CN, two singlet signals for each complex appeared in the range of 8–10 ppm, at δ 9.92 and 8.27 in an integration ratio of 0.28:1 for **1** and at δ 9.93 and 8.72 in a ratio of 0.37:1 for **2**, which can be attributed to the resonance of the imino hydrogen in two coordination situations. The signals at δ 8.27 and 8.72 can be assigned to the imino hydrogen of unsolvated complexes **1** and **2**, respectively, and it is assumed that the signals with considerable downfield shifts at δ 9.92 and 9.93 result from the coordination of CD_3CN to the Zr center of complexes **1** and **2**. The elemental analyses of complexes **1–4** are consistent with the composition of supposed zirconium salen-type complexes. Crystal structures of solvated and unsolvated complexes **3** and **4** have been determined by X-ray studies. The structural results will be discussed in a forthcoming publication elsewhere.

3.2. Catalysis of ethylene oligomerization

The aim of this research is to gain a preliminary insight into the effects of the ligands, the Al/Zr molar ratios, and the reaction temperature and pressure, as well as the lifetime of the catalyst on ethylene oligomerization. The catalytic reactions were carried out in a stainless autoclave under a constant pressure of ethylene in toluene.

3.2.1. Effect of the ligands on the catalytic activity and oligomer distribution

With Et_2AlCl as cocatalyst at 150 °C, the effect of different salen-type ligands on the catalytic activity and oligomer distribution of the precatalysts **1**–**4** was explored. The results are summarized in Table 1. Among the zirconium complexes adopted, complex **4** exhibited a relatively low catalytic activity and the activity of **1** was calculated to be about four times higher than that of **4**. The order of catalytic activities for complexes **1**–**4** under the same condition might be brought about by the combination of three factors of the ligand structures: the steric congestion of bulky *tert*-butyl groups on the ligands, the electronic properties of the ligands differing in conjugate systems, and the flexibility of the ligands in coordination structures. The results of entries 3–6 in Table 1 showed that the complexes **3** and **4** displayed lower catalytic activities in comparison with their analogues **1** and **2**. The steric hindrance on the metal center, caused by the *tert*-butyl groups attached to the *ortho* positions of salicylidene, abated the interaction between the zirconium atom and the π-electron of the ethylene monomer and hence

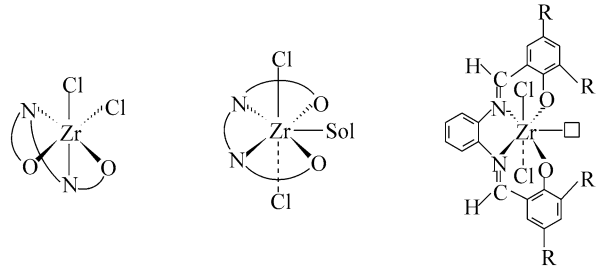
Table 1
Results of ethylene oligomerization by $LZrCl_2$ (**1**–**4**)/Et_2AlCl catalyst systems

Entry[a]	Precatalyst	TOF ($\times 10^{-3}$, h^{-1})	Products distribution[f] $C_4^{=}$	$C_6^{=}$	$C_8^{=}$	$C_{10}^{=}$	Linear olefins[f] α-$C_{4-10}^{=}/\sum C_{4-10}^{=}$	α
1	**1** · THF	9.32	24.0	28.7	20.6	11.8	78.6	0.58
2	**2** · THF	7.96	25.4	32.7	21.8	9.0	81.0	0.46
3	**1**	10.78	16.5	28.7	25.7	13.8	75.6	0.56
4	**2**	7.54	17.8	33.3	24.0	12.6	78.8	0.53
5	**3**	7.57	22.4	33.9	23.1	12.1	76.8	0.50
6	**4**	2.36	23.5	35.1	25.0	8.4	91.6	0.39
7	**1** · THF[b]	34.00	10.1	35.9	31.0	12.1	91.5	0.48
8	$(Ox)_2ZrCl_2$[c]	4.00	$C_{4-10}^{=}/\sum C^{=}$ 94.6				93.5	
9	$(acac)_2ZrCl_2$[d]	3.21	$C_{4-8}^{=}$ ca. 50					
10	$(fod)_2ZrCl_2$[d]	41.78	Linear C_{4-22} α-olefins					0.67
11	$(Pr^i\text{-Nacac})_2ZrCl_2$[e]	29.50	$C_{4-10}^{=}/\sum C^{=}$ 60.1				99.4	0.81

[a] Reaction conditions: precatalyst 0.05 mmol (1.4 mmol/L), Al/Zr 100, 150 °C, 60 min, $P(C_2H_4)$ 1.4 MPa, toluene 30 ml.
[b] Reaction conditions: precatalyst 0.01 mmol (0.3 mmol/L), 30 min. Other conditions are the same as above.
[c] Ref. [36]. Reaction conditions: $(Ox)_2ZrCl_2$ 0.025 mmol (0.8 mmol/L), cocatalyst Et_2AlCl, Al/Zr 60, 90 °C, 60 min, $P(C_2H_4)$ 1.8 MPa, toluene 30 ml.
[d] Ref. [37]. Reaction conditions: $(acac)_2ZrCl_2$ or $(fod)_2ZrCl_2$ 0.8 mmol/L, cocatalyst Me_2AlCl, Al/Zr 10, 60 °C, 10 min, $P(C_2H_4)$ 5.0 MPa, toluene 50 ml.
[e] Ref. [39]. Reaction conditions: $(Pr^i\text{-Nacac})_2ZrCl_2$ 0.02 mmol (1.0 mmol/L), cocatalyst $Et_3Al_2Cl_3$, Al/Zr 10, 100 °C, 60 min, $P(C_2H_4)$ 3.5 MPa, toluene 20 ml.
[f] Determined by GC analysis with n-heptane as an internal standard and by GC/MS spectra.

led to the deceleration of chain propagation in ethylene oligomerization, being disadvantageous for catalytic activity but advantageous for selectivity to low-carbon olefins. The α-value, which represents the probability of chain propagation, changed from 0.56 to 0.50 for the zirconium salen complexes **1** and **3** (entries 3 and 5 in Table 1) and from 0.53 to 0.39 for the salphen complexes **2** and **4** (entries 4 and 6 in Table 1).

It was observed that the salen complexes **1** and **3** manifested higher catalytic activities than their analogous salphen complexes **2** and **4**, respectively, and the activity of **4** having an N,N'-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneiminato) ligand dropped considerably compared with three other complexes. In order to give a plausible explanation for the experimental data, the reaction of **4** with Et_2AlCl was preliminarily explored by UV–vis and NMR spectra. Treatment of complex **4** with 30 eq of Et_2AlCl in toluene in reflux for 1 h, followed by hydrolysis, gave the starting salphen ligand, evidenced by the characteristic signal of the imino hydrogen (CH=N) in the ^1H NMR spectrum. Compared with the UV–vis spectrum of the toluene solution of **4**, which displayed two absorption bands in the 300–450 nm region centered at 315 and 383 nm, the spectrum of the mixture of **4** with 30 eq of Et_2AlCl in toluene showed only very slight blue-shifts of the two bands with increasing intensity and no novel band was observed. The experimental results suggested that the integral conjugate system in the salphen ligand is kept in the active species derived from zirconium salphen complexes. Although it was reported that monoalkylation of the salen ligand took place when $Ti(salen)Cl_2$ reacted with Grignard reagent in toluene [23], the reactions of L_2ZrCl_2 (L = N-(3-*tert*-butylsalicylidene)anilinato) with 30 eq of i-Bu_3Al and MAO, reported by Fujita and his coworkers, indicated that no alkylation occurred at the C=N group of the Schiff base ligands [27]. It is assumed that the conjugate effect and the flexibility of the ligands in coordination structures are important factors affecting the catalytic activity of the salen-type zirconium complexes. Two conjugate parts (–N=CHAr) are separated by a CH_2CH_2 bridge in a salen ligand, while the two parts are combined into an integral conjugate system in a salphen ligand by bonding the two parts to the *ortho* positions of a benzene ring. Accordingly, the desolvation of the zirconium salen complexes in toluene leads to six-coordinated complexes, which might rearrange to a nonplanar coordination geometry of the four donor atoms in a salen ligand with a *cis*-N, *cis*-O, and *cis*-Cl arrangement (structure A) (Fig. 1), just like the zirconium acen complex $(acen)ZrCl_2$, which was structurally characterized [15]. In contrast, the coordination geometry of a tetradentate salphen ligand is in a planar fashion with a *trans*-Cl arrangement (structure B) (Fig. 1) in both solvated and unsolvated forms, which has been proved by X-ray crystallography [35]. In the light of the results from the relevant



structure A structure B structure C

Fig. 1.

reactions, it is tentatively premised that the rigid planarity of the salphen ligand is kept intact in an active species. As an efficient catalyst precursor for the oligomerization and polymerization of ethylene, a *cis*-arrangement of the chlorides in zirconium complexes is appropriate for coordination and consecutive insertion of the monomer after a precatalyst is activated by an alkylaluminum compound. The higher catalytic activities were thus observed for the zirconium salen precatalysts **1** and **3**. With desolvation of the zirconium salphen complexes, a vacant coordination site between two oxygen atoms (structure C) (Fig. 1) is left, which proved to be a labile coordination site by the ^{1}H NMR spectra in $CDCl_3$. The catalytic activity of the zirconium salphen complexes **2** and **4** is presumably attributed to the probability of the monomer ligation to this vacant coordination site in the activated cationic zirconium salphen catalyst. In view of two bulky *tert*-butyl groups existing on the *ortho* position of each salicylidene of the salphen ligand, the large spatial block can shelter the vacant coordination site to some extent, leading to a great drop in the catalytic activity of complex **4**, while the product distribution tends to shift to low-carbon olefins.

The solvated complexes **1** · THF and **2** · THF were directly activated with Et_2AlCl and used in situ as a homogeneous catalyst in ethylene oligomerization (entries 1 and 2 in Table 1). High activities, with a TOF of 9.32×10^3 h^{-1} for **1** · THF and 7.96×10^3 h^{-1} for **2** · THF, were obtained. The solvation of the precatalysts did not obviously affect the catalytic activity and the selectivity in ethylene oligomerization. Under the pressure of 1.4 MPa and at the Al/Zr molar ratio of 100, the activity of **1** · THF came to a TOF of 3.40×10^4 h^{-1} with a satisfactory selectivity of 89% to C_4–C_{10} olefins, and among them C_4–C_{10} linear α-olefins accounted for 91%.

The previously reported results of ethylene oligomerization with other convenient postmetallocene catalysts, $(Ox)_2ZrCl_2$ (HOx = 8-hydroxyquinoline), $(acac)_2ZrCl_2$, and $(Pr^i\text{-Nacac})_2ZrCl_2$ (Pr^i-HNacac = 4-(*N*-isopropylamino)-3-penten-2-one) [36–39], the former two activated by Et_2AlCl and the latter by $Et_3Al_2Cl_3$ in toluene, were also listed in Table 1 to have a preliminary comparison of the activity and selectivity of the catalyst precursors with different bi- or tetradentate ligands. Although the catalytic reactions were not carried out under the same condition, the tendency was shown by the initial results that the zirconium salen complexes had higher activity than $(Ox)_2ZrCl_2$ and $(acac)_2ZrCl_2$. The propensities of catalyst systems **1**–**4**/Et_2AlCl to low-carbon linear α-olefins were similar with that of $(Ox)_2ZrCl_2/Et_2AlCl$ and much higher than those of $(acac)_2ZrCl_2/Me_2AlCl$ and $(Pr^i\text{-Nacac})_2ZrCl_2/Et_3Al_2Cl_3$.

3.2.2. Effects of the property of cocatalysts and the Al/Zr molar ratios

The property of alkylaluminum cocatalysts has an apparent effect on the catalytic activity and product distribution. The results of ethylene oligomerization catalyzed by **1** · THF and **2** · THF with EAO or Et_2AlCl as cocatalyst are listed in Table 2. In the case of employing EAO, both precatalysts **1** · THF and **2** · THF displayed low catalytic activities (entries 1 and 3 in Table 2) and the selectivity of C_4–C_{10} olefins was rather low, 29% for **1** · THF and 35% for **2** · THF. A noticeable amount of jelly-like polymer was formed in entries 1 and 3. When Et_2AlCl was used as a cocatalyst (entries 2 and 4 in Table 2), the selectivity of C_4–C_{10} olefins was calculated to be 85–89% and the catalytic activity was about six times higher than that of the catalyst system with EAO as cocatalyst. Although Et_2AlCl is an ineffective cocatalyst with conventional metallocene complexes, it is indeed an effective cocatalyst in combination with zirconium salen-type complexes in ethylene oligomerization to low-carbon olefins.

Table 3 gives the results of ethylene oligomerization in different molar ratios of Al/Zr catalyzed by **1** · THF. The activity went up obviously as the molar ratio of Al/Zr was increased from 50 to 100 (entries 3 and 4 in Table 3). When the molar ratio of Al/Zr was further increased from the threshold value of 100 to 200, and then to 300 (entries 1–3 in Table 3), the catalytic activity of **1** · THF smoothly rose to a TOF of 3.74×10^4 h^{-1}, which is comparable to the activity of catalyst system $(fod)_2ZrCl_2/Me_2AlCl$ (Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) in ethylene oligomerization [37]. The catalyst kept high selectivity to C_4–C_{10} olefins (86%) and to linear α-olefins (91%) as the molar ratio of Al/Zr was enhanced in the present experiments.

3.2.3. Influence of the reaction temperature and the ethylene pressure

A series of experiments were carried out in order to determine the optimal reaction temperature for the present catalyst system. The selected data are given in Table 4. Either

Table 2
Effect of the property of cocatalysts on ethylene oligomerization by **1** · THF and **2** · THF

Entry[a]	Precatalyst	Cocatalyst	TOF ($\times 10^{-3}$, h^{-1})	Olefins $C^{=}_{4-10}/\sum C^{=}$	Linear olefins α-$C^{=}_{4-10}/\sum C^{=}_{4-10}$	Note
1	**1** · THF	EAO	1.36	28.5	90.7	Polymer was observed
2	**1** · THF	Et_2AlCl	9.32	85.0	78.6	$\alpha = 0.58$
3	**2** · THF	EAO	1.32	35.0	92.5	Polymer was observed
4	**2** · THF	Et_2AlCl	7.96	88.9	81.0	$\alpha = 0.46$

[a] The reaction conditions are the same as those in footnote a of Table 1.

Table 3
Effect of different Al/Zr molar ratios on ethylene oligomerization by **1** · THF/Et_2AlCl

Entry[a]	Al/Zr (molar ratio)	TOF ($\times 10^{-3}$, h^{-1})	Olefins $C^{=}_{4-10}/\sum C^{=}$	Linear olefins α-$C^{=}_{4-10}/\sum C^{=}_{4-10}$	α
1	300	37.39	86.3	91.0	0.50
2	200	34.71	87.9	89.2	0.52
3	100	34.00	89.1	91.5	0.48
4	50	7.32	100	> 99	–

[a] Except for the Al/Zr molar ratios, the reaction conditions are the same as those in footnote b of Table 1.

increasing or decreasing the temperature from 150 °C led to an evident drop in catalytic activity for both **1** · THF and **2** · THF with Et_2AlCl as cocatalyst. The decrease in overall catalytic activity may be associated with gradual degradation of the active cation catalyst at temperatures above 150 °C. The selectivities to C_4–C_{10} olefins and linear α-olefins did not show significant changes as the temperature varied from 135 to 180 °C. Raising the ethylene pressure from 1.0 to 1.8 MPa greatly increased the catalytic activity of **1** · THF (entries 9–11 in Table 4), while the selectivities of low-carbon olefins and linear α-olefins did not evidence apparent changes. Under a pressure of 1.8 MPa in an Al/Zr molar ratio of 300 at 150 °C, the TOF of **1** · THF went up to 4.93×10^4 h^{-1} with the selectivity of 89% to $C_{4–10}$ olefins and 95% to linear α-olefins, which is comparable to the best results ever reported for Zr/Al catalyst systems in ethylene oligomerization considering both the activity and the selectivity to low-carbon linear α-olefins [1,36–39]. Recently, two novel catalyst systems of $Ni(naph)_2$ (naph = α-nitro-acetophenonato) and $Ni(sal)_2$ (sal = salicylaldiminato) complexes in combination of MAO or Et_2AlCl as cocatalyst were reported as highly active catalysts for ethylene oligomerization to low-carbon olefins (C_4–C_{10}) [14,40,41]. The TOFs of $Ni(sal)_2$ catalysts are up to 10^5–10^7 h^{-1}, but the selectivity to linear α-olefins is relatively low. In comparison, other catalyst systems based on late transition metals such as Fe, Co, Ni, and Pd featuring Schiff base ligands with MAO or MMAO as cocatalyst generally afford long-chain oligomers in high activities with perfect selectivities to linear α-olefins [9–13].

The preliminary results on the lifetimes of **1** · THF and **2** · THF catalysts generated by activation with Et_2AlCl in ethylene oligomerization are shown in Table 5. The zirconium salen-type complexes required no aging time to initiate the oligomerization reaction. The activities of **1** · THF and **2** · THF declined by half as the reaction time was prolonged from 30 to 120 min, accompanied with gradual decreases in the selectivities to C_4–C_{10} olefins and linear α-olefins.

4. Conclusions

In summary, the zirconium salen-type complexes in combination with Et_2AlCl are highly active at moderate pressure (1.0–1.8 MPa) and high temperature (150 °C) for ethylene oligomerization to low-carbon olefins with satisfactory selectivity of linear α-olefins. While with EAO as cocatalyst, dominant products are high-carbon oligomer as well as polymer and the catalytic activity is an order of magnitude lower than that obtained in the case of Et_2AlCl as cocatalyst. The present experimental results show that N_2O_2-tetradentate zirconium complexes, which are conveniently prepared and easily handled, activated by a proper cocatalyst, are promising homogeneous postmetallocene catalysts for ethylene oligomerization to low-carbon linear α-olefins. Further investigation on the electronic effect of the substituents attached to salen-type ligands and on mechanistic details is underway.

Table 4
Influence of the reaction temperature and the pressure on ethylene oligomerization

Entry[a]	Precatalyst	Temperature (°C), pressure (MPa)	TOF ($\times 10^{-3}$, h^{-1})	Olefins $C^{=}_{4-10}/\sum C^{=}$	Linear olefins α-$C^{=}_{4-10}/\sum C^{=}_{4-10}$	α
1	**1** · THF	180, 1.4	12.09	90.6	94.4	0.43
2	**1** · THF	165, 1.4	18.46	89.9	96.6	0.44
3	**1** · THF	150, 1.4	34.00	89.1	91.5	0.48
4	**1** · THF	135, 1.4	16.36	94.5	97.7	0.45
5	**2** · THF	180, 1.4	2.61	89.7	85.7	0.42
6	**2** · THF	165, 1.4	3.89	88.1	85.8	0.46
7	**2** · THF	150, 1.4	7.96	88.9	81.0	0.46
8	**2** · THF	135, 1.4	5.75	93.7	91.1	0.40
9[b]	**1** · THF	150, 1.8	49.32	89.3	94.9	0.48
10[b]	**1** · THF	150, 1.4	37.39	86.3	91.0	0.50
11[b]	**1** · THF	150, 1.0	26.91	87.8	90.0	0.49

[a] Except for reaction temperature, the reaction conditions of entries 1–4 are the same as those in footnote b and the conditions of entries 5–8 are the same as those in footnote a of Table 1.

[b] The reactions were carried out under the given pressure and with an Al/Zr molar ratio of 300, and the other conditions of entries 9–11 are the same as those in footnote b of Table 1.

Table 5
Effect of reaction time on ethylene oligomerization with Et_2AlCl as cocatalyst

Entry[a]	Precatalyst	Time (min)	TOF ($\times 10^{-3}$, h^{-1})	Olefins $C^{=}_{4-10}/\sum C^{=}$	Linear olefins α-$C^{=}_{4-10}/\sum C^{=}_{4-10}$
1	**1** · THF	30	12.36	88.0	84.5
2	**1** · THF	60	9.32	85.0	78.6
3	**1** · THF	120	6.29	78.6	73.3
4	**2** · THF	30	12.32	89.8	87.5
5	**2** · THF	60	7.96	88.9	81.0
6	**2** · THF	120	5.43	81.5	79.7

[a] Except for reaction time, the reaction conditions are the same as those in footnote a of Table 1.

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