



## Zirconadihydrophosphetes as highly active species for ethylene polymerization

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### ABSTRACT

The zirconadihydrophosphetes showed high activities for ethylene polymerization as well as copolymerization with  $\alpha$ -olefins or norbornene in the presence of methylaluminoxane (MAO) as cocatalyst. The alkylated intermediates as the active species were confirmed by NMR measurement. The cause for their high catalytic activities is assumed to be the disassociation and coordination of the ethylene-bridged phosphine to the zirconium species. A plausible mechanism for the polymerization is proposed.

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### 1. Introduction

Polyolefins now account for more than half the volume of all synthesized plastics and have a production of at least 110 million tons [1]. Driven by economic strategies and applications, industrial processes have been developed which have better performances, by both academic and industrial workers. The current processes employ catalysts such as Ziegler-Natta catalysts, Phillips catalysts, and single-site catalysts such as metallocenes. Since the discovery of cocatalyst of methylaluminoxane (MAO) by Kaminsky and Sinn [2–4], metallocene and other single-site catalysts have undergone a rapid development for olefin polymerization in the use of transition metal complexes as catalysts for the polymerizations of olefins, dienes, and styrene [5–8]. However, polyolefins produced by metallocene catalysts are sometime too high molecular weights and narrow molecular weight distributions to be directly used, so it is common to use their blends by blending with other polyolefins. Therefore, it is necessary to modify metallocene catalysts in order to produce polyolefins with wider molecular weight distributions and avoid blending polyolefins for better performance or modeling.

The metallocene active species for olefin polymerization are assumed to be their alkyl cations, 14-electron  $\text{Cp}_2\text{M}(\text{R})^+$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) [9–12], and as such are very sensitive to air and mois-

ture. An auxiliary ligand can enhance the stabilities of cationic 16-electron metallocene species  $\text{Cp}_2\text{Zr}(\text{R})(\text{L})^+$  ( $\text{L} = \text{THF}, \alpha$ -picoline,  $\text{PMe}_3$ , etc.) [13–18], as reported by the Jordan group. Such adducts demonstrated very low catalytic activities because of the stronger Zr–L bond which obstruct the coordination of ethylene on the Zr-site for further insertion reaction [13]. The auxiliary ligand interacts with the active center and readily provides a vacancy for olefin coordination. In case the auxiliary ligand maintains short distance for reversibly coordinating with active site during the olefin coordination, certain coordinative model could potentially stabilize active species and accelerate olefin polymerization. The zirconadihydrophosphetes chlorides recently reported by Xi et al. are stable in various organic solvents and in acidic aqueous solution [19]. The four-membered stable zirconophosphine ring is idealized to be model catalyst because of phosphete disassociation to provide a vacancy for olefin coordination at the Zr-site and the tendency of phosphete association forming the zirconadihydrophosphetes species resulting quickly insertion in polymerization. In our study, the enhanced ethylene pressure is necessary for the zirconadihydrophosphetes chlorides to show high catalytic activities in ethylene polymerization and copolymerization with  $\alpha$ -olefins or norbornene in the presence of MAO as co-catalyst. The methylated zirconadihydrophosphetes is assumed to be the active species, and such hypothesis is confirmed from the high performance in olefin polymerization by using alkylated zirconadihydrophosphetes instead of their chlorides. Herein, we report on our understanding of the active species of the stable zirconadihydrophosphetes and their performance in olefin polymerization.

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## 2. Experimental

### 2.1. General considerations

All manipulations of air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO-3A, a 1.93 M solution in heptane) were purchased from Akzo Nobel Corp. Other reagents were purchased from Aldrich or Acros Chemicals.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra of complexes were recorded on a JOEL 300 MHz instrument at ambient temperatures. NMR spectra of the polymer samples were recorded on a Bruker DMX 300 MHz instrument at 130 °C in 1,2-dichlorobenzene-*d*<sub>4</sub> using TMS as the internal standard. Molecular weights and polydispersity index (PDI) of polymers were determined by a PL-GPC220 instrument at 150 °C, using 1,2,4-trichlorobenzene as the solvent.

### 2.2. Synthesis of the complexes

#### 2.2.1. Preparation of (Z)-2-(biscyclopentadienylchlorozircono)-1,2-diphenylvinylidiphenyl phosphine (**1**)

Complexes **1** was prepared in 85% yield using the same procedure as in the literature [19].  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  5.81 (s, 10H), 6.80 (m, 2H), 7.09 (m, 14H), 8.04 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  111.2, 124.9, 125.0, 126.3, 127.8, 128.5, 128.7, 129.1, 129.7, 132.8, 133.2, 137.8, 138.0, 150.4, 215.0;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -39.4.

#### 2.2.2. Preparation of (Z)-2-(biscyclopentadienylmethylzircono)-1,2-diphenylvinylidiphenyl phosphine (**1a**)

To a solution of complex **1** (0.16 mmol, 100 mg) in 5 mL toluene, MeLi (0.48 mmol, 3 M in diethoxymethane) was added at -78 °C and the mixture was stirred for 1 h at the same temperature. The resulting mixture was warmed to room temperature and stirred for 12 h. The mixture was then filtered through a Celite Column, and the combined filtrate was evaporated under reduced pressure to give complex **1a** in 99% NMR yield, which was obtained as a yellow solid after washed with pentane and dried in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.14 (d, 3H), 5.54 (s, 10H), 6.76 (m, 2H), 7.08 (m, 14H), 7.78 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz, THF)  $\delta$  13.8, 107.4, 123.7, 124.8, 125.4, 127.3, 127.9, 128.2, 128.4, 129.0, 132.5, 134.2, 138.6, 140.4, 149.7, 215.1;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -28.9.

#### 2.2.3. Preparation of (Z)-2-(biscyclopentadienylbutylzircono)-1,2-diphenylvinylidiphenyl phosphine (**1b**)

To a solution of complex **1** (0.16 mmol, 100 mg) in 5 mL toluene,  $n\text{BuLi}$  (0.48 mmol, 1.6 M in hexane) was added at -78 °C and the mixture was stirred for 1 h at the same temperature. The resulting mixture was warmed to room temperature and stirred for 12 h. The mixture was then filtered through a Celite Column, and the combined filtrate was evaporated under reduced pressure to give complex **1b** in 99% NMR yield, which was obtained as a yellow solid after washed with pentane and dried in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.86–1.47 (m, 9H), 5.60 (s, 10H), 6.77 (m, 2H), 7.10 (m, 14H), 7.78 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  13.8, 30.5, 33.9, 37.4, 107.2, 123.8, 124.6, 125.5, 127.1, 127.4, 127.7, 128.1, 128.7, 132.1, 134.1, 138.1, 139.7, 151.8, 218.3;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -29.3.

#### 2.2.4. Preparation of (Z)-2-(biscyclopentadienylchlorozircono)-1,2-di(4-methylphenyl)vinylidiphenyl phosphine (**2**)

Complex **2** was prepared in 70% yield using the same procedure as in the literature [19].  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.86 (s, 3H), 2.14 (s, 3H), 5.84 (s, 10H), 6.64 (d, 2H), 7.10 (m, 12H), 8.08 (m, 4H);  $^{13}\text{C}$

NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 111.1, 124.9, 128.6, 128.7, 129.0, 129.2, 129.6, 132.7, 133.3, 134.4, 135.1, 135.8, 137.3, 147.6, 214.5;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -39.7.

#### 2.2.5. Preparation of (Z)-2-(biscyclopentadienylmethylzircono)-1,2-di(4-methylphenyl)vinylidiphenyl phosphine (**2a**)

To a solution of complex **2** (0.15 mmol, 100 mg) in 5 mL toluene, MeLi (0.45 mmol, 3 M in diethoxymethane) was added at -78 °C and the mixture was stirred for 1 h at the same temperature. The resulting mixture was warmed to room temperature and stirred for 12 h. The mixture was then filtered through a Celite Column, and the combined filtrate was evaporated to dryness under reduced pressure to give complex **2a** in 99% NMR yield, which was obtained as a yellow solid after washed with pentane and dried in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.12 (d, 3H), 1.84 (s, 3H), 2.17 (s, 3H), 5.58 (s, 10H), 6.63 (m, 2H), 7.05 (m, 12H), 7.82 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz, THF)  $\delta$  14.2, 20.9, 107.9, 125.4, 128.6, 128.8, 128.9, 129.0, 129.1, 129.5, 133.1, 135.1, 142.9, 145.0, 150.4, 214.2;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -29.5.

#### 2.2.6. Preparation of (Z)-2-(biscyclopentadienylchlorozircono)-1,2-di(*n*-butyl)vinylidiphenyl phosphine (**3**)

Complex **3** was prepared in 65% yield using the same procedure as in the literature [19].  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.72 (t, 3H), 1.20 (m, 7H), 1.42 (m, 2H), 1.68 (m, 2H), 2.32 (m, 4H), 5.84 (s, 10H), 7.07 (m, 6H), 7.83 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 14.1, 23.0, 24.2, 31.1, 31.4, 32.8, 39.6, 110.1, 128.4, 129.4, 133.3, 135.0, 138.8, 214.1;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -43.2.

#### 2.2.7. Preparation of (Z)-2-(biscyclopentadienylmethylzircono)-1,2-di(*n*-butyl)vinylidiphenyl phosphine (**3a**)

To a solution of complex **3** (0.17 mmol, 100 mg) in 5 mL toluene, MeLi (0.51 mmol, 3 M in diethoxymethane) was added at -78 °C and the mixture was stirred for 1 h at the same temperature. The resulting mixture was warmed to room temperature and stirred for 12 h. The mixture was then filtered through a Celite Column, and the combined filtrate was evaporated to dryness under reduced pressure to give complex **3a** in 98% NMR yield, which was obtained as a yellow solid after washed with pentane and dried in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.09 (d, 3H), 0.69 (t, 3H), 0.93 (t, 3H), 1.04 (m, 2H), 1.35 (m, 2H), 1.42 (m, 2H), 1.72 (m, 2H), 2.32 (m, 4H), 5.58 (s, 10H), 7.08 (m, 6H), 7.60 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz, THF)  $\delta$  12.4, 13.8, 14.2, 23.4, 24.8, 31.8, 33.3, 40.0, 107.0, 128.7, 129.3, 133.5, 134.0, 136.9, 217.0;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -32.2.

#### 2.2.8. Preparation of (Z)-2-(biscyclopentadienylchlorozircono)-1,2-diphenylvinylidiphenyl phosphine (**4**)

Complex **4** was prepared in 70% yield using the same procedure as in the literature [19].  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.16 (dd, 6H), 1.36 (dd, 6H), 2.23 (m, 2H), 5.93 (s, 10H), 6.82 (m, 6H), 7.00 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  20.0, 20.8, 26.8, 110.6, 124.3, 125.2, 125.9, 128.0, 128.4, 140.8, 141.1, 150.6, 209.7;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  -23.8.

#### 2.2.9. Preparation of (Z)-2-(biscyclopentadienylmethylzircono)-1,2-diphenylvinylidiphenyl phosphine (**4a**)

To a solution of complex **4** (0.18 mmol, 100 mg) in 5 mL toluene, MeLi (0.54 mmol, 3 M in diethoxymethane) was added at -78 °C and the mixture was stirred for 1 h at the same temperature. The resulting mixture was warmed to room temperature and stirred for 12 h. The mixture was then filtered through a Celite Column, and the combined filtrate was evaporated to dryness under reduced pressure to give complex **4a** in 99% NMR yield, which was obtained as a red solid after washed with pentane and dried in vacuo.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.01 (d, 3H), 0.98 (dd, 6H), 1.18 (dd, 6H), 2.10 (m,

2H), 5.67 (s, 10H), 6.87 (m, 6H), 7.05 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz, THF)  $\delta$  16.4, 20.1, 20.9, 26.9, 107.6, 123.5, 125.7, 127.9, 128.7, 129.0, 142.0, 143.4, 152.5, 213.0;  $^{31}\text{P}$  NMR (81 MHz, toluene, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  –19.1.

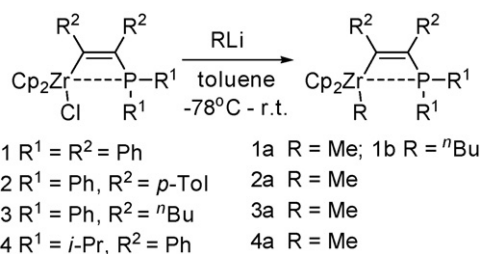
### 2.3. Polymerization procedure

A 500-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller was heated in vacuum for at least 2 h and at a temperature over 80 °C, allowed to cool to the required reaction temperature under an ethylene atmosphere, and then charged with the solvent, the desired amount of cocatalyst, and a solution of the catalytic precursor. The total volume was 100 mL. At the polymerization temperature, the reactor was sealed and pressurized to the desired ethylene pressure. The ethylene pressure was kept constant during the polymerization time by feeding the reactor with ethylene. At the end of the polymerization, the polymerization was quenched by addition 30 mL 10% HCl–EtOH. The precipitated polymer was washed with ethanol several times and dried under vacuum. In the case of copolymerization, the monomer solution was added prior to the catalyst solution.

## 3. Results and discussion

### 3.1. Synthesis and characterization of zirconadihydrophosphetes complexes

Complexes **1–4** were prepared in high yields according to the literature [19]. These complexes were alkylated in quantitative yields via the reaction of the monohalide precursors with 3 equiv RLi (R = Me,  $^n\text{Bu}$ ) in toluene (Scheme 1) [20,21]. However, it was necessary for the reaction time to be 12 h or longer at room temperature to complete the alkylation reaction, and this indicated the high stability of zirconadihydrophosphetes chlorides. Monitored by  $^{31}\text{P}$  NMR, in contrast to zirconadihydrophosphetes chlorides in toluene, the absorptions of the  $^{31}\text{P}$  nucleus of alkylated products were shifted downfield with net difference of 4.7–11.0 ppm (**1a**: 10.5 ppm; **1b**: 10.1 ppm; **2a**: 10.2 ppm; **3a**: 11.0 ppm; **4a**: 4.7 ppm). This indicated that the Zr–P bonds in these complexes become a little weaker. Meanwhile the phosphine group is still coordinated to the Zr center. Other spectroscopic data such as  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were all consistent with alkylation. In  $^1\text{H}$  NMR, 0.2–0.3 ppm



Scheme 1. Synthesis of complexes **1a–4a** and **2b**.

net shift to a higher field for the Cp ring was found (**1a**: 0.27 ppm; **1b**: 0.21 ppm; **2a**: 0.26 ppm; **3a**: 0.26 ppm; **4a**: 0.26 ppm); while the same phenomena were observed in  $^{13}\text{C}$  NMR measurements with peaks shifted to a higher field from 3.0 ppm to 4.0 ppm (**1a**: 3.8 ppm; **1b**: 4.0 ppm; **2a**: 3.3 ppm; **3a**: 3.1 ppm; **4a**: 3.0 ppm).

### 3.2. Ethylene polymerization and copolymerization

Complexes **1–4** were investigated for ethylene polymerization, and complex **1** was typically studied under various reaction conditions including changing the ethylene pressure, the reaction temperature, the amount of catalyst used, and the molar ratios of cocatalyst to Zr. The results are collected in Table 1.

Complexes **1–4** were inactive with various organoaluminums at ambient pressure of ethylene. Activated by MAO at 10 atmospheric pressures of ethylene, complex **1** showed a high activity for ethylene polymerization. With Al/Zr molar ratio fixed at 3000, the catalytic activity was sharply enhanced with higher concentrations of catalyst (see entries 1–3 in Table 1). If the concentration of catalyst was constant, the activity would be notably improved at high Al/Zr molar ratios (see entries 1 and 4 in Table 1). It is necessary to use excessive amounts of cocatalyst probably due to the high stability of the zirconadihydrophosphetes chlorides and the greater difficulty in their alkylation.

It is common for catalysts to show better catalytic activity at higher ethylene pressure, and this phenomenon was also observed with the catalytic system of **1**/MAO. A higher activity was observed at 30 atm than that at 10 atm when using both 2.5  $\mu\text{mol}$  complex **1** with 3000 Al/Zr molar ratio and 1.0  $\mu\text{mol}$  complex **1** with 15,000 Al/Zr molar ratio (see entries 3 and 5 or entries 4 and 9 in Table 1).

Table 1  
Ethylene polymerization catalyzed by complexes **1–4**/MAO.

Entry	Cat.	Cat. ( $\mu\text{mol}$ )	P (atm)	T (°C)	Al/Zr	Polymer (g)	Activity	$M_w^a$ ( $\times 10^{-5}$ )	PDI <sup>a</sup>
1	<b>1</b>	1.0	10	25	3,000	0.11	0.02	–	–
2	<b>1</b>	1.5	10	25	3,000	0.39	0.05	–	–
3	<b>1</b>	2.5	10	25	3,000	2.31	0.18	–	–
4	<b>1</b>	1.0	10	25	15,000	3.20	0.64	–	–
5	<b>1</b>	2.5	30	25	3,000	7.81	0.62	–	–
6	<b>1</b>	2.5	30	25	5,000	30.3	2.42	–	–
7	<b>1</b>	2.5	30	25	10,000	60.1	4.81	–	–
8	<b>1</b>	1.0	30	25	10,000	22.1	4.42	–	–
9	<b>1</b>	1.0	30	25	15,000	72.8	14.6	1.47	5.11
10	<b>1</b>	1.0	30	25	20,000	16.7	3.34	–	–
11	<b>2</b>	1.0	30	25	15,000	78.8	15.8	1.36	3.76
12	<b>3</b>	1.0	30	25	15,000	78.1	15.6	1.26	4.36
13	<b>4</b>	1.0	30	25	15,000	87.1	17.4	1.41	5.72
14	<b>1</b>	0.5	30	25	15,000	52.1	20.8	1.69	3.83
15	<b>2</b>	0.5	30	25	15,000	52.3	20.9	2.80	4.10
16	<b>3</b>	0.5	30	25	15,000	59.2	23.7	1.61	4.45
17	<b>4</b>	0.5	30	25	15,000	57.9	23.2	1.84	4.56
18	<b>1</b>	0.5	30	50	15,000	39.8	15.9	1.13	3.84
19	<b>1</b>	0.5	30	80	15,000	31.8	12.7	1.47	3.08
20	$\text{Cp}_2\text{ZrCl}_2$	1.0	30	25	15,000	50.6	10.1	1.14	1.87

Conditions: 30 min; 100 mL toluene; unit of activity:  $10^7 \text{ g mol(Zr)}^{-1} \text{ h}^{-1}$ .

<sup>a</sup> Determined by GPC.

**Table 2**  
Ethylene polymerization catalyzed by complexes **1–4**/MMAO.

Entry	Cat.	Cat. ( $\mu\text{mol}$ )	Polymer (g)	Activity	$M_w^a$ ( $\times 10^{-5}$ )	PDI <sup>a</sup>
1	<b>1</b>	0.5	20.5	8.20	–	–
2	<b>2</b>	0.5	32.7	13.1	–	–
3	<b>3</b>	0.5	22.9	9.16	–	–
4	<b>4</b>	0.5	31.9	12.8	–	–
5	<b>1</b>	1.0	62.0	12.4	0.85	4.36
6	<b>2</b>	1.0	68.5	13.7	1.04	4.65
7	<b>3</b>	1.0	58.7	11.7	0.88	4.56
8	<b>4</b>	1.0	64.3	12.9	1.14	5.46
9 <sup>b</sup>	<b>4</b>	1.0	52.0	10.4	0.50	3.86
10 <sup>c</sup>	<b>4</b>	1.0	6.0	1.20	4.75	2.41
11 <sup>d</sup>	<b>4</b>	1.0	12.8	2.56	1.42	10.73

Conditions: 30 min; 100 mL toluene; 25 °C; 30 atm; Al/Zr = 15,000; unit of activity:  $10^7 \text{ g mol(Zr)}^{-1} \text{ h}^{-1}$ .

<sup>a</sup> Determined by GPC.

<sup>b</sup> 100 mL chlorobenzene as the solvent.

<sup>c</sup> 100 mL n-heptane as the solvent.

<sup>d</sup> 100 mL dichloromethane as the solvent.

The amount of cocatalyst also exerted a strong influence on the catalytic behavior. The activities increased sharply with higher Al/Zr molar ratio (see entries 5–7 and 8–9 in Table 1), but decreased when adding too much cocatalyst which could be attributed that the remaining trimethylaluminum in MAO may deactivate the active species (see entry 10 in Table 1). If the Al/Zr molar ratio was fixed at 15,000, a higher activity was observed at a lower catalyst concentration (see entries 9, 11–17). However, there was no correlation between the substituents and the activities, all of which showed excellent catalytic behaviors (see entries 9, 11–17 in Table 1). These catalytic activities were maintained in the temperature range from 25 °C to 80 °C without any significant deleterious effects (see entries 14, 18–19 in Table 1), which indicated the very good stability of the active species. All polyethylenes produced showed high molecular weights with broad unimodal molecular weight distributions. The broad molecular weight distribution could be explained in terms of the resonance of the coordinated phosphine ligand during the course of ethylene coordination and insertion. In comparison, traditional zirconocene dichloride was also investigated under the same conditions (see entry 20 in Table 1), and higher activities were observed when using zirconadihydrophosphates chlorides (see entries 9, 11–13 in Table 1).

When activated by MMAO, the high activities for complex **1–4** with different amounts of catalyst were also observed (see entries 1–8 in Table 2). However the use of MMAO produced lower molecular weight polymers in contrast to those obtained by complex **1–4**/MAO. With a fixed Al/Zr molar ratio at 15,000, the activity with 0.5  $\mu\text{mol}$  catalyst was lower than that of 1  $\mu\text{mol}$  catalyst, which was

**Table 4**  
Copolymerization with different comonomers catalyzed by complex **1** at 30 atm.

Entry	Comonomer	C (mol/L)	T (°C)	Polymer/g	Activity	$M_w^a$ ( $\times 10^{-4}$ )	PDI <sup>a</sup>
1	1-Hexene	1.0	25	2.10	0.42	–	–
2	1-Hexene	1.0	50	56.9	11.4	–	–
3	1-Hexene	1.0	80	57.6	11.5	1.89	4.00
4	1-Hexene	1.5	80	56.0	11.2	–	–
5	1-Hexene	0.5	80	57.9	11.6	–	–
6	1-Hexene	0.3	80	56.6	11.3	4.83	3.02
7	1-Hexene	0.1	80	52.3	10.5	4.87	3.22
8	1-Octene	1.0	80	58.8	11.8	2.42	4.60
9	1-Octene	0.3	80	64.3	12.9	5.36	3.32
10	1-Octene	0.1	80	59.3	11.9	5.09	2.76
11	Norbornene	1.0	80	63.4	12.7	4.34	3.27
12	Norbornene	0.5	80	66.2	13.2	–	–
13	Norbornene	0.3	80	75.0	15.0	6.35	2.99
14	Norbornene	0.1	80	62.7	12.5	5.80	2.88

Conditions: 30 min; 100 mL toluene; 30 atm; cat.: 1.0  $\mu\text{mol}$ ; MAO/Zr = 15,000; unit of activity:  $10^7 \text{ g mol(Zr)}^{-1} \text{ h}^{-1}$ .

<sup>a</sup> Determined by GPC.

**Table 3**  
Copolymerization with different comonomers catalyzed by complex **1** at 10 atm.

Entry	Comonomer	C (mol/L)	T (°C)	Polymer (g)	Activity
1	Norbornene	1.0	25	0.04	0.003
2	Norbornene	1.0	80	2.48	0.20
3	Norbornene	0.5	80	8.40	0.67
4	Norbornene	1.5	80	0.25	0.02
5 <sup>a</sup>	1-Hexene	1.0	25	3.70	0.30
6 <sup>b</sup>	1-Hexene	1.0	80	15.8	1.26
7	1-Octene	1.0	25	2.01	0.16
8 <sup>c</sup>	1-Octene	1.0	80	21.5	1.72

Conditions: 30 min; 100 mL toluene; 10 atm; cat.: 2.5  $\mu\text{mol}$ ; MAO/Zr = 3000; unit of activity:  $10^7 \text{ g mol(Zr)}^{-1} \text{ h}^{-1}$ .

<sup>a</sup> 1-Hexene content: 2.3%, determined by  $^{13}\text{C}$  NMR spectra.

<sup>b</sup> 1-Hexene content: 8.7%, determined by  $^{13}\text{C}$  NMR spectra.

<sup>c</sup> 1-Octene content: 6.3%, determined by  $^{13}\text{C}$  NMR spectra.

opposite to the results using MAO as cocatalyst. In addition, the catalytic system with various solvents showed a remarkable difference in reactivity, probably due to the different solvent properties and the solubilities of the catalysts (see entries 8–11 in Table 2).

The copolymerization of ethylene with  $\alpha$ -olefins or cycloolefins is an important topic at the present time. Therefore complex **1** was investigated for its copolymerization at 10 atm (Table 3) and 30 atm (Table 4) of ethylene. In the copolymerization of ethylene and norbornene at 10 atm ethylene pressure, low catalytic activity was observed at room temperature (25 °C, see entry 1 in Table 3). However, this activity was dramatically improved at elevated polymerization temperatures and was nearly 60 times higher than that at room temperature (80 °C, see entry 2 in Table 3). This phenomenon can be explained by the nonbonding interactions between the growing polymer chain and the coordinated norbornene molecule [22]. As a result, high reaction temperature in the polymerization medium is required to accelerate the insertion of norbornene units. Similar phenomena were also observed for the copolymerization of ethylene with  $\alpha$ -olefins (see entries 5 and 6 for 1-hexene; entries 7 and 8 for 1-octene). According to NMR measurements, more 1-hexene was incorporated at elevated polymerization temperature (2.3 mol% for entry 5, while 8.7 mol% for entry 6). The high incorporation of 1-octene (6.3 mol%) was confirmed by the  $^{13}\text{C}$  NMR spectrum of polymer obtained at 80 °C (see entry 8 in Table 3). Upon changing the concentration of norbornene in the range of 0.5–1.5 mol/L, the catalytic activity was gradually decreased attributable to the steric hindrance of monomers (see entries 2–4 in Table 3).

At 30 atm ethylene pressure for copolymerization, all of the catalytic systems performed better than at 10 atm ethylene (Table 4). Similarly, the catalytic activity for the copolymerization of ethy-

**Table 5**  
Ethylene polymerization catalyzed by complexes **1a–4a** and **1b**.

Entry	Cat.	P (atm)	Al/Zr	Polymer (g)	Activity	$M_w^a$ ( $\times 10^{-5}$ )	PDI <sup>a</sup>
1 <sup>b</sup>	<b>1a</b>	1	500	0.04	0.16	–	–
2	<b>1a</b>	10	500	6.07	24.3	3.59	4.06
3	<b>1a</b>	10	200	4.52	18.1	3.48	3.02
4	<b>1a</b>	10	100	0.76	3.04	5.05	3.13
5	<b>1a</b>	30	500	20.2	80.8	2.30	6.60
6	<b>1a</b>	30	200	17.0	68.0	3.29	2.41
7	<b>1a</b>	30	100	6.40	25.6	2.53	2.39
8	<b>1b</b>	10	200	4.10	16.4	4.84	2.69
9	<b>1b</b>	10	100	0.86	3.44	3.11	2.73
10	<b>1b</b>	30	200	15.5	62.0	2.53	3.77
11	<b>2a</b>	10	200	2.57	10.3	–	–
12	<b>3a</b>	10	200	4.07	16.3	–	–
13	<b>4a</b>	10	200	3.65	14.6	–	–
14 <sup>c</sup>	<b>1b</b>	30	200	8.20	32.8	5.68	3.31
15 <sup>d</sup>	<b>1b</b>	30	200	20.4	81.6	0.68	4.32

Conditions: 30 min; 5  $\mu$ mol catalyst; cocat. MAO; 25 °C; 100 mL toluene; unit of activity:  $10^5$  g mol(Zr)<sup>-1</sup> h<sup>-1</sup>.

<sup>a</sup> Determined by GPC.

<sup>b</sup> 30 mL toluene.

<sup>c</sup> 0.5 mol/L hexene, 25 °C.

<sup>d</sup> 0.5 mol/L hexene, 80 °C.

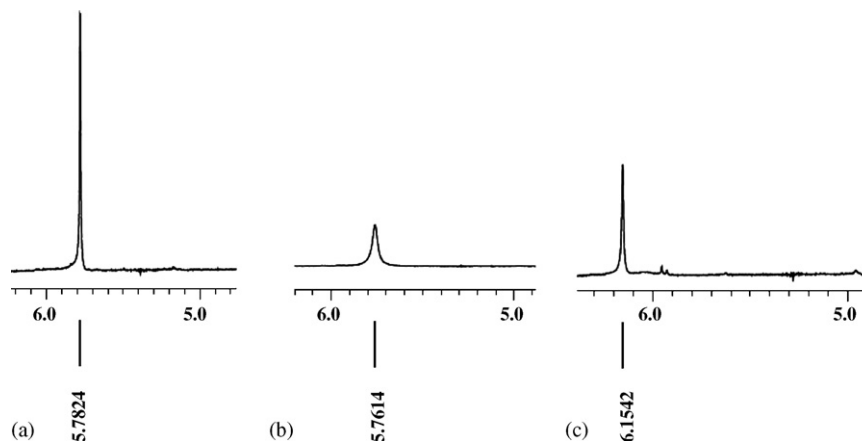
lene with 1-hexene was increased with increasing polymerization temperatures (see entries 1–3 in Table 4). With different 1-hexene concentration, the catalytic activity first increased and then slowly decreased to reach an optimum value at 0.5 mol/L of 1-hexene for the activity  $11.6 \times 10^7$  g mol<sup>-1</sup> h<sup>-1</sup>. The  $M_w$  values of the resultant copolymers decreased gradually with higher 1-hexene concentrations (see entries 3–7 in Table 4). The same trend was also observed for the ethylene – 1-octene and ethylene – norbornene copolymerization systems. Their activity peaked when the monomer concentration was 0.3 mol/L (see entries 8–14 in Table 4).

In order to investigate more fully the real active species alkylated zirconadihydrophosphetes, complexes **1a–4a** and **2b** were synthesized and used in ethylene polymerization. The complexes **1a** and **1b** were especially selected for detailed studies in order to understand the effects of different cocatalysts, different ethylene pressures and also the molar ratios of cocatalyst to Zr. Activated by MAO, these precursors showed good catalytic activities for ethylene polymerization and the results are summarized in Table 5. Under ambient pressure of ethylene, low catalytic activity was observed (see entry 1 in Table 5). High activity of  $2.43 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup> was achieved at 10 atm of ethylene (see entry 2 in Table 5) and further higher activity of  $8.08 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup> was obtained at 30 atm of ethylene (see entry 5 in Table 5), which was nearly 20 times

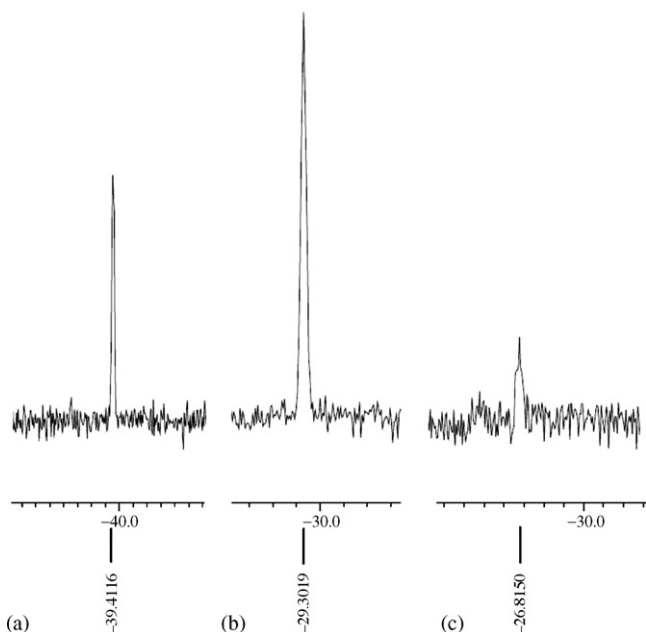
higher than that of Cp<sub>2</sub>Zr(R)(THF)<sup>+</sup> reported by the Jordan group [13]. As an explanation the Zr–P bond could be easily disassociated at high ethylene concentration (pressure) and replaced by a  $\pi$ -coordination bond. Noteworthy the molecular weights of the polyethylenes obtained were lower at higher ethylene pressures (see entries 2–7 in Table 5 and entries 8, 10 in Table 5). In addition, entries 2–7 in Table 5 indicated that the effects of varying the molar ratio of Al/Zr on the catalytic activity showed a large enhancement on the addition of more cocatalyst. The great advantage of using alkylated complexes instead of their chlorides is that the amount of cocatalyst is reduced to a molar ratio of Al/Zr equal to 200. For other complexes **2a–4a**, the results were similar to those of **1a** and **1b** (see entries 11–13 in Table 5). The copolymerization of ethylene with 1-hexene is also investigated and typical results when using complex **1b** are summarized in Table 5 (entries 14 and 15). Similarly, when used in copolymerization, complex **1b** showed lower activities at low temperatures (see entry 14 in Table 5), which increased dramatically at higher temperature (see entry 15 in Table 5). However, the  $M_w$  values of the resultant copolymers decreased at higher polymerization temperatures, because the higher incorporation of the hexene increased steric hindrance, and resulted the termination of the polymer chain in case the comonomer inserted as the last monomer [23].

### 3.3. Toward the active species and plausible mechanism

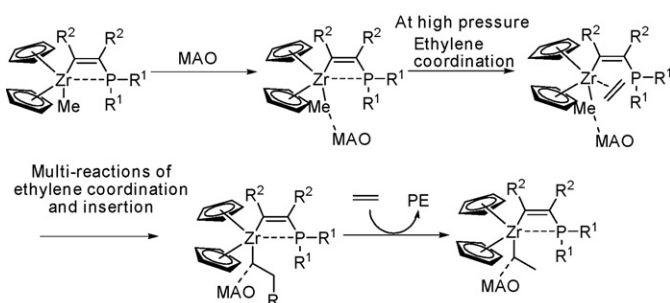
From the above results for complexes **1a–4a** and **1b**, it is very clear that MAO is indispensable in excess amounts in order to generate the active species. To understand the role of MAO, 50 equiv. and 200 equiv. MAO were mixed with the alkylated complexes, and <sup>1</sup>H NMR and <sup>31</sup>P NMR determinations were carried out. On adding 50 equiv. MAO, there was no obvious color change. The color of these systems containing 200 equiv. MAO would immediately change (from yellow to red for complexes **1a–3a** and **1b**, from red to yellow for complex **4a**). According to <sup>1</sup>H NMR, the peak for the Cp ring is shifted downfield (NMR Shift for **1a**: 0.49 ppm; **1b**: 0.37 ppm; **2a**: 0.45 ppm; **3a**: 0.45 ppm; **4a**: 0.49 ppm). This shift indicates that MAO can activate the Zr–Me (<sup>*n*</sup>Bu) bond and form a bimetallic active species which includes Zr···Me (<sup>*n*</sup>Bu)···Al bonds [24]. The influence of the sterically expanded structure around the Zr center is weakened, resulting in ethylene insertion. The <sup>31</sup>P NMR shift is also downfield and indicates the existence of a possible bimetallic active species (NMR shift for **1a**: 8.0 ppm; **1b**: 2.5 ppm; **2a**: 17.8 ppm; **3a**: 20.4 ppm; **4a**: 7.3 ppm), and provides strong and compelling evidence that the Zr–P bond becomes weaker when using excess MAO and so ethylene can coordinate to the active center and insertion.



**Fig. 1.** <sup>1</sup>H NMR spectra for Cp in toluene: (a) complex **1b** (b) the mixture of **1b** and 50 equiv. MAO (c) the mixture of **1b** and 200 equiv. MAO.



**Fig. 2.**  $^{31}\text{P}$  NMR spectra in toluene: (a) complex **1** (b) complex **1b** (c) the mixture of **1b** and 200 equiv. MAO.



**Scheme 2.** Plausible mechanism in ethylene coordinated polymerization.

However the four-membered ring still exists (all the  $^{31}\text{P}$  NMR value are negative). An obvious NMR shift for complex **1b** is shown in Figs. 1–2.

Based on the above ethylene polymerization results and the NMR evidence, a plausible mechanism can be proposed as follows (Scheme 2). First, an alkylated zirconadihydrophosphete is produced by alkylation with MAO, and the excess MAO then reacts with the alkylated complex to activate the Zr–Me ( $n\text{Bu}$ ) bond and to form a bimetallic active species. During these processes, the Zr–P bond becomes much weaker and the ancillary phosphine ligand easily dissociates, leaving a vacant position. The phosphine group protects “the active site”, but can allow ethylene monomer insertion due to the lower electronic density of zirconium under suitable conditions. At low ethylene pressures, the competition of the coordination reaction between the phosphine group and ethylene forms a favorable phosphine coordinated complex. At higher ethylene pressure, the ethylene coordinated complex will be favored and a fast transformation through the insertion reaction to form a phosphine coordinated intermediate again takes place.

## 4. Conclusions

A series of alkylated zirconadihydrophosphetes were synthesized and characterized. Upon activated by MAO, the stable zirconadihydrophosphetes chlorides and alkylated zirconadihydrophosphetes showed high catalytic activity for ethylene polymerization and copolymerization. MAO played an important role for activating the Zr–alkyl bond and generated possible bimetallic species to facilitate the ethylene coordination and insertion. The ancillary phosphine ligand in the catalysts could be easily associated and disassociated, protecting the active centers and also increased ethylene insertion for polymerization. A detailed plausible mechanism for polymerization is therefore proposed.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.11.023.

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